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 Abstract approved:

A study of the effects of structural modification at the alpha position of ethyl 2-bromocarboxylates on their rates of addition to two alkene pairs was undertaken. In the competition between 3-propoxypropene and 1-octene at 70°, a 37% increase in selectivity was observed in going from carboxylates generating primary radicals to those generating tertiary radicals. These results yield good correlations with electronic and/or steric parameters. When the competition between 1-methylcyclohexene and 1-octene was examined, no simple systematic variation of selectivity with structure was observed. An explanation is offered, which is based on the greater persistence of hindered carboethoxyalkyl radicals and the resultant changes in transition state structure. Factors Influencing the Competitive Rates of Free-Radical Addition of Ethyl 2-Bromocarboxylates to Selected Alkene Pairs

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FACTORS INFLUENCING THE COMPETITIVE RATES OF FREE-RADICAL ADDITION OF ETHYL 2-BROMO-CARBOXYLATES TO SELECTED ALKENE PAIRS

INTRODUCTION

Aspects of Radical Addition to Alkenes

One of the first free radical reactions for which a firm mechanistic basis has been set forth is the anti-Markovnikoff addition of hydrogen bromide to alkenes. In the presence of suitable radical initiators a chain mechanism competes with the ionic mechanism for control of the addition of hydrogen bromide to the substrate. This mechanism is shown in Equations 1 - 3, where the final two steps constitute the chain process.

$$In \cdot + HBr \longrightarrow Br \cdot + InH$$
 (1)

$$Br \cdot + RCH = CH_2 \xrightarrow{rds} RCHCH_2 Br$$
 (2)

$$RCHCH_2Br + HBr \longrightarrow RCH_2CH_2Br + Br \cdot (3)$$

The regioselectivity of radical-chain hydrobromination of alkenes is opposite to that observed for ionic addition. The traditional explanation ascribes the addition of bromine atoms to the less substituted carbon atom of the double bond to generate the more highly substituted radical (1 - 3). The factors influencing the addition of hydrogen bromide to an alkene double bond were first studied by Kharasch and his co-workers (4 - 6). As may be inferred from the reaction sequence shown on the last page, the presence of a radical initiator is very important. Hydrogen bromide addition to 3-bromopropene can produce both 1,2-dibromopropane and 1,3-dibromopropane:

$$CH_2 = CHCH_2Br + HBr \longrightarrow CH_3CHCH_2Br + BrCH_2CH_2CH_2Br (4)$$

Br

When the addition is carried out in the presence of air or oxygen, high yields of 1,3-dibromopropane are obtained, while samples of peroxide-free 3-bromopropene give over 80% of 1,2-dibromopropane under a nitrogen atmosphere (4, 6). This behavior is due to the high sensitivity of 3-bromopropene to autoxidation by atmospheric oxygen. The resultant peroxidic species may initiate the radical reaction. The 1,3-dibromopropane was also the major product when the reaction was carried out in the presence of added peroxides. The major product was 1,2-dibromopropane when antioxidants were present. The effect of photoinitiation on the hydrogen bromide addition to 3-bromopropene was also examined by Kharasch (4, 5). The observations were that high yields of 1,3-dibromopropane were obtained under conditions of strong illumination, while high yields of 1,2-dibromopropane were found

if the reaction was carried out in the dark.

The dependence of hydrogen bromide addition on the structure of the alkene has also been extensively investigated. Results obtained by Abell (7) and Tedder and Walton (8), which are in general agreement, show that the reactivity of propene is approximately 15 times greater than that of ethene, and that the reactivity of 2-methylpropene is nearly 300 times greater than that of ethene. This marked increase in relative reactivity is usually attributed to the greater stability of tertiary and secondary radicals vs. the primary species. These results also agree with a formalism in which "electrophilic" bromine atoms prefer to attack at double bonds with greater electron density.

Despite the fact that specific stereochemistry may be associated with radical initiated addition of hydrogen bromide to certain alkenes (9), it has been demonstrated that the initial addition of a bromine atom to the double bond is a reversible process (10). Thus, the long known isomerization of <u>cis</u>- and <u>trans</u>-stilbene and dimethyl maleate to dimethyl fumarate by traces of bromine is a radical chain process, as illustrated in Scheme I on the next page. Since the intermediate radical easily undergoes rotation about the C-C bond, halogen atom loss can lead to the formation of either isomer.



The bromine catalyzed isomerization of <u>cis</u>-dibromoethene, investigated by Steinmetz and Noyes using radioactive bromine, illustrates that the bromine atoms, which are attached to the same carbon in the intermediate radical, are equivalent (11), as shown in Scheme II.



Scheme II

The addition of other electrophilic radicals to alkenes has also been extensively studied. The addition of thiols to alkenes (Equation 5) also gives rise to anti-Markovnikoff products and resembles hydrogen bromide addition (12).

$$RCH=CH_2 + HSR' \longrightarrow RCH_2-CH_2SR' (5)$$

It was shown by Ashworth and Burhardt that the rate of thiophenol addition to styrene is enhanced photolytically (13). The effect of peroxides was also to enhance the rate of anti-Markovnikoff addition product formation, thus suggesting the presence of radical intermediates (13). In the studies done by Sivertz and co-workers, it was found that the step involving thiyl radical addition to the double bond is also reversible (14). These results were supported by the fact that in some cases thiols catalyzed <u>cis</u> - <u>trans</u> isomerization of alkenes (15). There is, however, some dependence on temperature and the stability of the thiyl radical involved (16).

A fairly extensive literature is extant on the application of the Hammett equation for additions of various thiophenols to substituted styrenes (17 - 19). In most cases good correlations with moderate negative rho values are obtained. Much poorer correlations are found when the alkene contains an electron donating group such as methyl or methoxy.

Geers, Gleicher and Church obtained good Hammett correlations for a series of reactions of substituted thiophenols with α -methylstyrene and α -methylstyrenes containing electron withdrawing groups (20). This is shown in Table 1 below. The greatest selectivity was observed for addition to m-trifluoromethyl- α -methylstyrene. A strong electron withdrawing group in the aromatic portion of the alkene minimizes the electron density at the reactive double bond and, therefore, increases the selectivity of the system in competitive reaction with thiyl radicals.

Alkene Substituent	Rho ^a	Correlation Coefficient
m-CF ₃	-0.41 ± 0.02	-0.99
p-Cl	-0.27 ± 0.04	-0.96
Н	-0.18 ± 0.02	-0.98
р-СН ₃	-0.15 ± 0.07	-0.59
p-OCH ₃	-0.08 ± 0.05	-0.56

<u>TABLE 1</u>. Effects of Alkene Substituents on Rho Values for Substituted Thiyl Radical Addition to Various α -Methylstyrenes at 70°.

 All results are based on correlations using sigma plus parameters. For the reactions of α -methylstyrenes containing electron donating groups in the aromatic ring, poor correlation coefficients were observed in the attempted linear least square treatment of the data. This suggests that possibly non-linear functions were being observed. Gleicher and co-workers have suggested that this is due to differing electronic effects in the ground states and transition states which may vary independently.

The addition of carbon free radicals to alkenes has also been the subject of frequent investigation (21 - 24). The electronic nature of such radical species is variable. Thus, for example, trihalomethyl radicals, which have electron withdrawing groups attached to the radical center, resemble the bromine atom and most thiyl radicals by showing electrophilic character.

The negative rho values reported by Martin and Gleicher in Hammett correlations of trichloromethyl radical additions to 3-substituted-propenes, 4-substitutedl-butenes, and 5-substituted-l-pentenes indicate a moderate electronic demand at the reaction site (21). This implies that the addition of the trichloromethyl radical to the double bond of the series of compounds under study is governed by the inductive polar effect of the substituent.

Recently, much attention has been focused on the polar and steric effects in the free radical addition of

unsubstituted alkyl radicals to alkenes (25 - 28). The rates of addition of such free radicals to alkenes are in part controlled by the substituent X at the radical center on the one hand, and on the other hand, partly by the substituents Y and Z at the two unsaturated carbon atoms of the alkene. The general reaction is shown in Equation 6.

The effects of Y and Z have been observed to be very different (16). Giese showed that only polar effects are exerted on the rate of alkyl radical addition when the substituent Z is varied (16). Positive rho values, which Giese obtained from the relative reactivity plots, indicate nucleophilic character for unsubstituted alkyl radicals.

The nature of the α -substituent effect is totally different from that found for the variation of Z. The substituent Y at the vinylic carbon atom undergoing attack may sterically hinder the approach of free radicals. A marked decrease in reactivity was observed in the addition of the cyclohexyl radical when Y was changed from hydrogen atom to the <u>tert</u>-butyl group. Polar groups in the α position also modify reactivity by an electronic effect. These effects are somewhat smaller than those found when the same groups occupy a β position.

The rate of addition also depends on the substituents present in the attacking species. The papers of Minisci <u>et al</u>. (29) and Baban and Roberts (30) report that when X is an alkyl group, there is an increase in the reactivity of the radical toward electron-deficient alkenes. Minisci and co-workers showed that in alkyl radical addition to alkenes, selectivity is greater for secondary radicals than for either primary or methyl radicals. This is due to both steric and polar factors (29).

In contrast to traditional opinion which accentuates electronic factors, Tedder and Walton suggest that the rate and orientation of free-radical additions is mainly sterically controlled (31). In a series of studies, relative rates and orientation of perfluoroalkyl radical additions to alkenes were measured by the above workers (32 - 36). The data are presented in Table 2 on the next page. All of the radicals listed in Table 2 are clearly electrophilic in nature. The marked increase in positional selectivity that is observed for secondary and tertiary radicals is almost entirely due to a reduction in the rate of addition to the more substituted carbon atom of the double bond. The conclusion drawn by the above workers is that steric effects play a major role in determining the rate and orientation of radical additions. This tendency of free-radicals to attack at the less

TABLE 2.	The Relative Rates and Orientation of Addition of	
	Perfluoroalkyl Radicals to Fluoroalkenes at 164°C	•

Alkene	_	cf ₃ .ª	°₂ [₽] ₅· ^b	n-C ₃ F ₇ . ^c	(CF ₃) ₂ CF・ ^d	(CF ₃) ₃ C・ ^e
CH ₂ =CH ₂ (E)		1.00	1.00	1.00	1.00	1.00
$CF_2 = CH_2 \leftarrow \alpha$	k _α /k _E	0.15	0.17	0.22	0.24	0.33
$CH_2 = \underline{CF}_2 \leftarrow \underline{\beta}$	k _β /k _E	0.006	0.002	0.0025	0.00023	
	k _α /k _β	25	85	88	1043	" _∞ "
CF ₂ =CF ₂		0.12	0.067	0.045	0.008	0.00078
a Reference 32	b Ref	erence 33	c _{Referenc}	e 34 ^d Ref	erence 35 e	Reference 36

•

hindered end of alkenes need not be limited to electrophilic species. Table 3 combines the results of several investigations (32, 37 - 39). It is noted that the extremely electrophilic trifluoromethyl radical, the nucleophilic methyl radical, and species of intermediate electronic nature all prefer to attack at the less hindered end of l,l-difluoroethene.

Radical	k _α /k _β	^k C ₂ F ₄ ^{/k} C ₂ H ₄
CH ₃ ^a	25	9.5
CH2F ^b		3.4
CHF2 ^C	6.7	1.1
CF3 ^d	25	0.1
a Reference 37		C Reference 39
^b Reference 38		d _{Reference} 32

TABLE 3. Positional Selectivity of Fluorinated Methyl Radicals Toward 1,1-Difluoroethene at 164°C.

Unlike the situation encountered with the bromine atom and thiyl radicals, both electrophilic and nucleophilic carbon radicals apparently undergo irreversible additions to alkenes. This irreversibility has been

explained by Giese to be a result of the strong exothermicity of the addition reaction, since a strong sigma bond is formed at the expense of breaking a pi-bond (16).

Steric Effects in the Generation of Radicals by Reactions Other Than Addition

Evidence for the operation of steric effects have also been observed in hydrogen atom abstractions. In a series of studies Minisci and co-workers have examined the effect of varying the alkyl group in the reaction of dialkylamino radical cations to abstract hydrogen atoms from methyl decanoate and n-heptane (40). The chain portion of this process is shown in Equations 7 and 8.

$$R' + R'H \xrightarrow{rds} R_2^{+}NH_2 + \cdot R'$$

$$R' + R_2^{+}NHC1 \xrightarrow{rds} R'C1 + R_2^{+}NH$$

$$(8)$$

Table 4 on the next page presents the difference in positional selectivity of these two substrates with a pair of dialkylamino radical cations as the hydrogen abstracting agents. When N-chlorodiisobutylamine was used as the radical source, hydrogen abstraction from the methylene position adjacent to the terminal methyl group increased relative to the other positions as shown in Table 4. The conclusion drawn from the above data was that the

penultimate position was the least sterically hindered secondary site, and therefore least susceptible to unfavorable interactions with the large incoming radical. It is expected that the larger the radical, the greater the tendency to attack at this position.

TABLE 4. Effect on the Positional Selectivity of Hydrogen Atom Abstraction by Dialkylamino Radical Cations as a Result of Varying the Alkyl Group.

Alkyl Group		Substrate								
		сн ₃ -		—СН ₂ —	СН ₂	СН ₂ -	CH ₂	CH	3	
Methyl		1.1	55.6	29.0	14.3					
Isobutyl		1.3	64.4	22.9	11.3					
	сн ₃ -	-CH2-	— ^{СН} 2 ⁻	—СН ₂ -	CH ₂	СН ₂ -	—СН ₂ -	·CH2	-CH2CO2	CH ₃
Methyl	1.1	44.4	21.6	17.5	10.7	4.1	0.5			
Isobutyl	1.4	57.7	19.1	13.3	6.7	1.7	trace			

In several related investigations, Gleicher and coworkers have examined the steric effects of hydrogen atom abstraction from a series of toluene derivatives by the radical generated photolytically from bromotrichloromethane (41 - 43). For the reactions of bromotrichloromethane with α -alkyltoluenes, Eghdami, Gleicher, and Totherow observed that as the size of the alkyl group increased, the reactivity toward the radical generated from bromotrichloromethane decreased, relative to the reactivity of ethylbenzene (43). This trend was also observed for various α, α -dialkyltoluenes in their reactivity toward the radical generated from bromotrichloromethane. These results are listed in Table 5.

TABLE 5. Relative Rates of Disappearance of α -Alkyltoluenes in their Photolytic Reaction with Bromotrichloromethane per Benzylic Hydrogen Atom at 70°C.

Compound (x)	k _x /k _{cumene}
Cumene	1.00
sec-Butylbenzene	0.48 ± 0.04
3-Phenylpentane	0.17 ± 0.02
Ethylbenzene	0.15 ± 0.01
n-Propylbenzene	0.12 ± 0.01
Isobutylbenzene	0.042 ± 0.002
Toluene	0.017 ± 0.001
Neopentylbenzene	0.003 ± 0.0005

^a Statistically corrected.

The conclusion drawn from these findings is that the ease of hydrogen abstraction is reduced as the potential for unfavorable steric interactions between the abstracting radical and the groups at the benzylic position increase.

In free-radical allylic brominations utilizing N-bromosuccinimide (NBS), steric effects may also play a role. The chain portion of the mechanism for this reaction is shown in Equations 9 - 11.

$$RH + Br \cdot - R \cdot + HBr (9)$$

$$R \cdot + Br_2 - RBr + Br \cdot (10)$$

$$\bigvee_{O}^{O}$$
N-Br + HBr - \bigvee_{O}^{O} N-H + Br₂ (11)

Generally speaking, an allylic methylene group is normally a more preferred site for bromination with NBS than is a corresponding allylic methyl group (44). It has been observed, however, that 2,4,4-trimethyl-l-pentene reacts with NBS to give 2-bromomethyl-4,4-dimethyl-lpentene (45). This is shown in Equation 12.

$$CH_{3} - CH_{2} - C$$

This product arises from hydrogen abstraction at the

allylic methyl group rather than at the sterically hindered neopentyl methylene group.

Steric effects in radical reactions may also be of a slightly different type. The bulkiness of the groups attached to the radical center of an alkyl radical can enhance the stability of the system by preventing the approach of potentially reacting substrates. Systems possessing such characteristics have been referred to as "persistent radicals" (46). This idea was first set forward by Gomberg in 1900 to partially explain the stability of the triphenylmethyl radical (47). The fact that the triphenylmethyl dimer is a head to tail dimer, rather than a head to head hexaphenylethane, shows how strongly simple coupling is hindered (48, 49). It took over seventy years, however, before it was recognized that the persistence of radicals could be due solely to steric factors (46). Griller and Ingold have undertaken a systematic study of carbon-centered radicals, starting with the transient methyl radical and monitoring the effect of successive substitution of hydrogen by bulky groups such as tert-butyl and trimethylsilyl (46). While no persistent primary radicals were observed by the above workers, the di-tert-butylmethyl radical, 1, the 2,2,4,6,6-pentamethylcyclohexyl radical, 2, and the 2,2,4,4,6,6-hexamethylcyclohexyl radical, 3, were found

to be persistent secondary radicals.



The tertiary alkyl species comprise the largest class of persistent radicals.

The studies of Ballester et al. show extreme persistence for the perchlorobenzyl radical, 4 (50).



In this system the benzene ring has been rotated nearly ninety degrees out of the plane containing the two exocyclic chlorine atoms. While an estimated 13 Kcal/mole of stabilization energy is lost in this conformation of the radical, the radical has shown a relatively long life-time due to the large groups attached to the trigonal center.

STATEMENT OF PROBLEM

As discussed in the previous section, there exists a complex interplay of polar, steric, and bond strength effects which govern the rate and orientation of free radical addition to alkenes. In undertaking the present study, our desire was to examine the addition of a series of related radicals to selected alkene pairs. It should be possible to select a series in such a manner that two of the above three factors may be considered reasonably constant. We have chosen to thus evaluate the effect of varying the size of the attacking radical in a systematic fashion.

In 1948 Kharasch and associates reported that various esters of 2-bromocarboxylates add to the alkene double bond as shown in Equation 13 (51).

$$\operatorname{RCH=CH}_{2} + \operatorname{Br-}_{\operatorname{C}-CO_{2}R'''}^{\operatorname{R}'} \xrightarrow{\operatorname{ROOR}} \operatorname{RCHCH}_{2} - \operatorname{C-CO_{2}R'''}_{\operatorname{Br}} (13)$$

The free-radical mechanism for this reaction is shown in Scheme III on the next page. Termination of the chain mechanism occurs by the expected dimerization and disproportionation reactions. The chain length for these additions is fairly large. An extensive review of the

synthetic scope of these reactions may be found in a review article by Walling and Huyser (52). General addition of carboethoxyalkyl radicals to the less hindered carbon atom of the double bond is observed (52).





Since in all the systems herein studied a bond is being generated between two sp^3 -hybridized carbon atoms, we feel that our assumption of constant strength of the bond formed is justifiable. In the series of esters of secondary 2-bromocarboxylates, where R' = H and R" is

varied, it is safe to assume that electronic factors are also nearly constant. We have chosen for our study the traditional series of alkyl groups: methyl, ethyl, isopropyl, and t-butyl. Although a few people feel that electronically these alkyl groups are different (53), the majority believe that these groups and hence our secondary alkyl radicals are electronically equivalent (54). Therefore, any difference in the competitive reactivity of the secondary 2-bromocarboxylate esters toward alkene pairs should be due to steric factors alone. Furthermore, using the chosen alkene pairs we shall investigate the addition of ethyl 2-bromoethanoate, which generates a primary radical center; as well as ethyl 2-bromo-2-methylpropanoate and ethyl 2-bromo-2ethylbutanoate, two systems which generate tertiary radical centers.

Experimentally, our choice of alkene pairs was severely limited by factors of miscibility and separability via gas chromatography. It was finally decided to examine two alkene pairs. In one case we chose 1-octene and 3-propoxypropene, which are two sterically equivalent terminal alkenes. It has been shown by Martin and Gleicher that 1-octene is twice as reactive as alkoxypropenes in the addition of the trichloromethane radical to the double bond (55). This clearly demonstrates that electronically the double bonds of 1-octene and

3-propoxypropene are different. We feel that any selectivity due to an electronic difference in the double bonds of the two alkenes would be made more manifest as the size of the attacking radical is increased.

For the second case we have chosen to compare the relative reactivity of ethyl 2-bromocarboxylates toward alkenes having different spacial requirements. For this we will examine 1-octene in competition with 1-methylcyclohexene which has a trisubstituted double bond.

It should be noted that in the first set of experiments, 1-octene possesses the double bond of greater electron density relative to 3-propoxypropene. In the studies involving the second alkene pair, the double bond of 1-octene has the lower electron density as compared to 1-methylcyclohexene.

RESULTS AND DISCUSSION

Detail on equipment and compounds utilized will be found in the Experimental Section. All relative rate data reported in this thesis were directly obtained by standard competitive techniques. Approximately equal molar amounts of the two alkenes were allowed to competitively react with a four fold molar excess of the ethyl 2-bromocarboxylate. Dry benzene was utilized as the solvent and chlorobenzene was present as an internal GLC standard.

Reactions were thermally initiated by benzoyl peroxide at a constant temperature of 70.0° ± 0.1°C. Reaction times were kept constant at twenty-four hours with the total alkene consumption generally varying from fifteen to thirty percent.

For each reaction studied, the mixture of starting materials was divided among several tubes. The air in the tubes was replaced with nitrogen by subjecting the samples to a series of freezing and thawing cycles. The tubes were then sealed under a nitrogen atmosphere at reduced pressure. All but one (which was reserved as a starting material mixture) were immersed in a 70°C oil bath. After the prescribed time, the reactions were quenched. For each alkene the extent of the reaction was determined by measuring the amount of alkene which

disappeared relative to that present in the unreacted sample. This was accomplished by means of GLC analyses using a Varian 200 GLC chromatograph. Chlorobenzene was the internal standard.

The relative rates of disappearance obtained above would be equivalent to the relative rates of addition if all of the alkene which reacted was used only in this process. Other reactions of the alkene, however, could also be taking place. One such possible side reaction is allylic bromination taking place via a rate determining hydrogen atom abstraction as shown in Equation 14.



The competition between addition of a radical to a double bond and allylic hydrogen abstraction is very dependent on the nature of the radical involved. For a typical carbon radical such as trichloromethyl, Huyser has shown that the addition reaction is the favored process (56). A terminal alkene, such as 1-octene, will undergo addition about forty-four times more readily than allylic hydrogen atom abstraction. An internal alkene, such as 1-methylcyclohexene, will, however, undergo much more hydrogen abstraction. This is due both to an increase in the number of allylic positions and a decrease in the accessability of the double bond. The addition reaction is still preferred. Enhanced allylic reactivity might also be expected for 3-propoxypropene. This should be due to the fact that the allylic position is adjacent to an oxygen atom (57). The extent of allylic hydrogen abstraction can be ascertained by determining the amount of ethyl carboxylate formed in our reaction. None could be detected in any of our runs.

A second possible side reaction would be polymerization of the initial alkenes. The polymerization reaction is enhanced when the alkene used forms a very stable free radical (e.g., styrene), or if the alkene used is not sterically hindered (52).

In reactions where polymer formation is the preferred pathway, a very poor material balance between the consumption of starting materials should exist. Since in all cases studied here a reasonably good material balance was obtained (1 mole alkene for 0.9 - 1.1 moles carboxylate), we believe that polymerization products were produced only in small amounts, if any were formed at all.

Product Studies

Extensive studies have been performed on the addition of various ethyl 2-bromocarboxylates to 1-octene and other terminal alkenes (51). It was decided to

examine the product obtained in the reaction of the sterically hindered ethyl 2-bromo-3,3-dimethylbutanoate with 3-propoxypropene. Although good material balance was not observed, the major product was that expected for addition, with the apparent formation of diastereomeric pairs of ethyl 4-bromo- $2-\underline{t}$ -butyl-5-propoxy-pentanoate.

A product study for the reaction of ethyl bromoethanoate with 1-methylcyclohexene in the presence of benzoyl peroxide was carried out. The reaction products were mainly ethyl (2-methyl-1-cyclohexenyl)ethanoate and ethyl (2-methyl-2-cyclohexenyl)ethanoate. These products are formed through a dehydrohalogenation of the original addition product. Reasonably good material balance (78%) was obtained. One of the minor by-products observed was phenylbenzoate, most probably formed from the initiator within the solvent cage.

Initiation of the above system by AIBN did not lead to detectable amounts of adduct products. Instead, large yields (76%) of 2,3-dicyano-2,3-dimethylbutane, the dimer of l-cyano-l-methylethyl radical, were obtained. This is perhaps not surprising when the known reluctance of this radical to add to double bonds is considered (58). Fortunately, all kinetic runs utilized benzoyl peroxide as initiator.

Evaluation of the Reversibility of Carboethoxyalkyl Radical Addition to Double Bonds

To examine for possible reversibility of the addition of carboethyoxyalkyl radicals to alkenes, it was decided to study the reaction of ethyl 2-bromo-3,3-dimethylbutanoate with <u>cis</u>-2-heptene. Reversibility of the addition step should have resulted in the formation of some <u>trans</u>-2-heptene, since it is more stable than the <u>cis</u> isomer by approximately 1.0 Kcal/mole.

After two days of reaction, under conditions comparable to those for the systems previously studied, eighteen percent of the starting <u>cis</u>-2-heptene had disappeared forming addition products. However, no <u>trans</u>-2-heptene could be detected. It is estimated that no more than 0.2% of the reaction follows a reversible pathway. This result is completely analogous to those obtained for the additions of other carbon radicals to alkenes (16).

Kinetic Studies

The kinetic data obtained for the disappearance of 3-propoxypropene relative to 1-octene in their reaction with ethyl 2-bromocarboxylates are presented in Table 6. The data show only a 37% increase in selectivity in going from the least selective system to the most selective one. For the four ethyl 2-bromocarboxylates,
TABLE 6. Relative Rate Constants for the Disappearance of 3-Propoxypropene as Compared to 1-Octene in their Reaction with Ethyl 2-Bromocarboxylates (RR'C-CO₂Et) at 70°C.

Ester	krel	Number of Runs
R = R' = H	0.98 ± 0.03	6
$R = H;$ $R' = CH_3$	1.06 ± 0.03	5
$R = H;$ $R' = CH_3CH_2$	1.08 ± 0.02	6
$R = H; R' = (CH_3)_2CH$	1.14 ± 0.02	6
$R = H; R' = (CH_3)_3C$	1.24 ± 0.03	6
$R = R' = CH_3$	1.31 ± 0.03	5
$R = R' = CH_3CH_2$	1.36 ± 0.04	6

which form secondary radical intermediates, the relative selectivity increases by 17% in going from methyl to the bulky <u>t</u>-butyl group. This slight variation can be explained by electronic differences, steric variation, or both.

We have attempted to correlate the logarithms of the relative rate factors or selectivities with various electronic and steric parameters according to the linear free energy approach as shown in Equations 15 and 16.

$$\log(k/k_{o}) = \sigma \rho \tag{15}$$

$$\log(k/k_{o}) = sE_{s}$$
(16)

Here σ is the substituent's electronic constant, ρ is the sensitivity of the system to the electronic variation, \mathbf{E}_{s} is the substituent's steric constant, s is the corresponding sensitivity of the system to the steric variation, and k and k_o are the rate constants for the system under study and the reference system, respectively. Since in our case we are dealing with competitive kinetics whereby each substrate reacts with a pair of alkenes, the factors, ρ and s, which reflect the sensitivity of the system to substituent variation, are not defined the same as those of Taft; however, we still feel that there is a close resemblance. Therefore, we will use the symbols ρ and s as used in Taft's equations, keeping in mind that in our case these refer to the sensitivity of alkene pairs to the variation of the substituent(s) of the attacking radical.

1

Table 7 contains the parameters utilized and the logarithms of the relative selectivities. The slopes, and correlation coefficients obtained from the least square analyses of these data are shown in Table 8.

Since there is a wide range of possible sets of steric and electronic parameters available, we must first look at how these parameters were developed in order to choose the ones that will best correlate our system. The electronic constant for the substituent effect in aliphatic systems, σ^* , was first developed by Taft (59, 60). In his study, Taft suggested that since the electronic nature of the substituent has little effect on the rate of acid-catalyzed hydrolysis of metaor para-substituted benzoates (the ρ value is near zero), the electronic nature of the substituent will also have little effect on the acid-catalyzed hydrolysis of aliphatic esters. Taft further suggested that in the basecatalyzed hydrolysis, the electronic influence of a substituent cannot be neglected. This is seen from the large value of ρ for the base-catalyzed hydrolysis of meta- or para-substituted ethyl benzoates. The aliphatic

TABLE 7. Substituent Electronic and Steric Parameters for Ethyl 2-Bromocarboxylates (RR'C-CO₂Et) Br

Ester	log(k _{rel})	Σσ*	ΣσΙ	$\Sigma \sigma_p^+$	ΣEs	Σe° s
R = R' = H	-0.010	0.98	0	0	2.48	0
$R = H; R' = CH_3$	0.025	0.49	-0.046	-0.311	1.24	-1.24
$R = H; R' = CH_3CH_2$	0.033	0.39	-0.055	-0.295	1.17	-1.51
$R = H; R' = (CH_3)_2CH$	0.057	0.30	-0.064	-0.280	0.77	-2.09
$R = H; R' = (CH_3)_3C$	0.093	0.19	-0.074	-0.256	-0.30	-3.38
$R = R' = CH_3$	0.117	0	-0.092	-0.622	0	-2.48
$R = R' = CH_3CH_2$	0.134	-0.20	-0.110	-0.590	-0.14	-3.02

TABLE 8. The Slopes and Correlation Coefficients Obtained for the Correlations of the Logarithms of the 3-Propoxypropene to 1-Octene Relative Rate Constants with Various Electronic and Steric Substituent Parameters.

	Nature	of Corr	relation	Slope	Correlation Coefficient
Σσ	* (all	points	included)	-0.13	-0.961
Σσ	* (all	points	except <u>t</u> -butyl)	-0.13	-0.966
Σσ	+ (all	points	included)	-0.21	-0.868
Σσ	+ (all p	points	except <u>t</u> -butyl)	-0.23	-0.949
Σσ	I (all	points	included)	-1.43	-0.962
Σσ	I (all	points	except <u>t</u> -butyl)	-1.41	-0.965
ΣE	s (all	points	included)	-0.05	-0.928
ΣE	s (all	points	except <u>t</u> -butyl)	-0.06	-0.955
Σe	° (all	points	included)	-0.04	-0.905
Σe	° (all	points	except <u>t</u> -butyl)	-0.05	-0.949

polar substituent, σ^* , is therefore defined as shown in Equation 17.

$$\sigma^{\star} = \frac{\log(k/k_{o})_{B} - \log(k/k_{o})_{A}}{2.48}$$
(17)

The difference between the data from base and acid catalyses is, in effect, a correction for steric effects. The factor 2.48 is introduced in order that the σ and σ^* constants of a substituent will have approximately the same value.

Taft also pointed out that any differences observed in the acid-catalyzed hydrolysis of ortho-substituted ehtyl benzoates must be due solely to steric effects. Taft defined E_s, a steric substituent constant, by Equation 18.

$$E_{g} = \log(k/k_{o})_{\Lambda}$$
(18)

Although Equation 18 was derived using a series of aromatic compounds, these E_s parameters have been also applied to aliphatic systems. It should also be noted that both σ^* and E_s are defined relative to the methyl substituent.

Another parameter, which might prove useful in

correlating substituent effects in aliphatic systems, is σ_p^+ (61). This parameter was originally developed for systems in which pronounced substituent mesomeric effects are transmitted through an aromatic ring. However, in a study of substituent effects on hydrogen atom abstraction from α -substituted toluenes, as shown in Equation 19, Fredrich, Fredrich, Andrews and Keefer obtained a much better correlation with σ_p^+ rather than the aliphatic substituent parameters (62).

$$\bigcirc$$
 -CH₂-X + Br· \longrightarrow \bigcirc -CH-X + HBr (19)

This has been explained as being the result of a direct mesomeric or hyperconjugative interaction between the substituent and the developing radical center. These interactions have also been observed before by our research group in related hydrogen atom abstraction studies (41, 43).

A third polar substituent constant for aliphatic systems, σ_{I} , has been also developed by Taft (63). This parameter, which uses hydrogen rather than the methyl group as the reference point, has a much smaller absolute magnitude than σ^* . Also, it has been claimed that σ_{I} takes into account any possible hyperconjugation. Based on this, Ritchie and Sager have suggested complete abandonment of σ^* in favor of σ_{τ} (64).

Also, the steric substituent constant, E_s , has been corrected for C-H and C-C hyperconjugation by Palm (65). The new steric substituent constant, E_s° , is related to E_s as shown in Equation 20, where N_H is the number of α -hydrogens and N_C is the number of α -carbons.

$$E_{g}^{\circ} = E_{g} + 0.33(N_{H} - 3) + 0.13 N_{C}$$
 (20)

The slopes and correlation coefficients obtained with the previously discussed parameters, utilizing Equations 15 and 16, are shown in Table 8. Some of these correlations show higher precision when the results for <u>t</u>-butyl substituted carboxylates are omitted. This may be a result of enhanced steric effects as we move from the isopropyl group to the <u>t</u>-butyl group.

In the cases where the σ^* or σ_I constants are used, the four correlation coefficients are virtually identical. Figure 1 represents a plot of the logarithms of the selectivities against a summation of σ^* values.

The replacement of the α -hydrogens in the radical generated from ethyl 2-bromoethanoate by alkyl groups also changes the electronic nature of the radical. The carboethoxymethyl radical is usually considered to be an electrophilic species. In attacks on substituted



Figure 1. Correlation of the logarithms of the 3-propoxypropene to 1-octene relative rate constants with the carboxylate electronic substituent parameters for the reaction of the alkene pair with ethyl 2-bromocarboxylates.

benzenes, it prefers to react with systems containing electron donating groups (66). In the present study, a preferential addition to the double bond of 1-octene is expected and observed. Introduction of any alkyl group(s) apparently gives the resulting radical an overall nucleophilic character.

It should be also noted that the introduction of electron withdrawing groups into the attacking radical can increase its electrophilic nature. The radical generated from diethyl 2-bromo-1,3-propanedicarboxylate (diethyl α -bromomalonate) shows a selectivity of 0.51 ± 0.01 in competitive addition to 3-propoxypropene and 1-octene.

Although they show approximately equal correlation coefficients, the slopes, ρ^* and ρ_I , are different by a factor slightly greater than ten. This is not unusual and coincides with the ratio of 10.6 cited by other groups (67). This is, of course, due to the smaller numerical values of σ_I . Since the slopes are negative, the selectivity increases when electron-donating groups are introduced into the attacking carboethoxyalkyl radical. This is very reasonable since addition of electrondonating substituents stabilizes the radical intermediate. The small magnitude of the slope is consistent with a modest electronic effect. Similar sensitivities to substituent changes have been observed in other radical additions to alkenes. For example, addition of the

trichloromethyl radical to 3-substituted propenes showed a ρ^* of 0.15 ± 0.01 (55).

Although the correlation with σ_p^+ improves significantly when the t-butyl substituent is omitted, the correlation coefficient is still not as good as those obtained with the previously discussed parameters. The cases wherein better correlations were obtained with σ_{p}^{+} rather than σ^* all involved hydrogen atom abstraction from α -substituted toluenes (41, 43, 62). In such reactions there is an appreciably large amount of charge separation developed in the transition state. The extent of charge separation might well be smaller for addition reactions. This would be particularly relevant if the addition reaction has an earlier transition state as is generally supposed (68).

Since steric parameters are on the average ten times greater than the corresponding electronic parameters, the slopes, s and s° should therefore be ten times smaller than the ρ^* values, if the sensitivities to steric and electronic factors are equal. Since the slopes obtained in our correlations with steric parameters are equal to only a third to a fourth of the ρ values, a much larger steric sensitivity is being observed.

Correlation of the results with the E_s and E_s° steric parameters improved upon the omission of the data for the <u>t</u>-butyl substituent. Between the two, E_s° shows the more significant change. One would expect that these steric parameters should already account for the bulkiness of the <u>t</u>-butyl group; however, these parameters were developed by Taft for the hydrolysis of orthosubstituted ethyl bezoates, which is an entirely different system from ours. The fact that E_s° improves more than E_s can be interpreted as being due to a large difference in the hyperconjugative and mesomeric effects between Taft's system and ours. A plot of the logarithms of the selectivities against a summation of E_s values for all points is given in Figure 2.

The observed selectivities can also be explained as being a result of a combination of steric and electronic effects. A four parameter linear free energy relationship similar to the one formulated by Taft can be employed (69). This is shown in Equation 21.

$$\log(k/k_{o}) = \rho\sigma + sE_{o} + C \qquad (21)$$

It is obvious that the combination of those parameters which showed good correlations individually will also show a good correlation when the four parameter equation is used. Indeed, certain electronic and steric parameters are directly proportional to each other; for



Figure 2. Correlation of the logarithms of the 3-propoxypropene to 1-octene relative rate constants with the carboxylate steric substituent parameters for the reaction of the alkene pair with ethyl 2-bromocarboxylates.

ω 9 example, σ^* or σ_I is proportional to either steric parameter employed. The relationship obtained employing σ_p^+ and E_s° , which are not proportional to each other, is shown in Equation 22.

$$\log k_{calc.} = -0.117\Sigma \sigma_{p}^{+} - 0.027\Sigma E_{s}^{\circ} - 0.027 \qquad (22)$$

The selectivities calculated using this relationship are shown in Table 9. A plot of the logarithms of the calculated selectivities versus the corresponding experimental values shows a slope of 0.991, an intercept of -0.0006, and a correlation coefficient of 0.970. The average deviation between the calculated and experimental selectivities is approximately 2.4 percent. A representation of this is found in Figure 3. It is worth mentioning that the calculated and experimental values for the <u>t</u>-butyl substituted system are in perfect agreement with each other.

The kinetic results obtained for the rate of disappearance of 1-methylcyclohexene relative to 1-octene in their reaction with ethyl 2-bromocarboxylates are presented in Table 10. One might expect that the majority of the carboethoxyalkyl radicals, which are nucleophilic species, would prefer to attack 1-octene, which is the alkene of lower electron density. Arguments based on

TABLE 9. Selectivities Calculated for Ethyl 2-Bromocarboxylates (RR'C-CO₂Et) Br Using a Four Parameter Equation.

System	Experimental Selectivity	Calculated Selectivity	
R = R' = H	0.98	0.94	
$R = H; R' = CH_3$	1.06	1.10	
$R = H; R' = CH_3CH_2$	1.08	1.12	
$R = H; R' = (CH_3)_2CH$	1.14	1.15	
$R = H; R' = (CH_3)_3C$	1.24	1.24	
$R = R' = CH_3$	1.31	1.30	
$R = R' = CH_3CH_2$	1.36	1.33	



Figure 3. The experimental 3-propoxypropene to 1-octene relative rate constants for the reaction with ethyl 2-bromocarboxylates versus those calculated by a four parameter equation.

TABLE 10. Relative Rate Constants for the Disappearance of 1-Methylcyclohexene as Compared to 1-Octene in their Reaction with Ethyl 2-Bromocarboxylates (RR'C-CO₂Et) at 70°C.

	Ester	^k rel	Number of Runs
R	= R' = H	1.18 ± 0.04	6
R	= H; R' = CH ₃	1.25 ± 0.02	6
R	= H; $R' = CH_3CH_2$	1.31 ± 0.02	5
R	= H; R' = $(CH_3)_2CH$	1.48 ± 0.04	6
R	$= H; R' = (CH_3)_3C$	2.19 ± 0.04	6
R	= R' = CH ₃	1.18 ± 0.04	6
R	$= R' = CH_3CH_2$	1.24 ± 0.02	6

steric considerations would also lead one to expect that the terminal alkene should be the more reactive system. This expectation has not been met.

The primary radical generated from ethyl 2-bromoethanoate shows a selectivity of 1.18 ± 0.04 . This is a reasonable value for an electrophilic species. Similarly, preferred reaction with 1-methylcyclohexene is also shown by the related electrophilic radicals generated from diethyl 2-bromo-1,3-propanedicarboxylate (selectivity = 1.10 ± 0.02) and bromotricarboethoxymethane (selectivity = 2.13 ± 0.03). Although these two latter radicals should be much more electrophilic than the one generated from ethyl 2-bromoethanoate, the selectivities are not uniformly greater. This can be readily rationalized on the basis of the steric demands of these two larger radicals.

Surprisingly, the corresponding secondary and tertiary carboethoxyalkyl radicals, which are more nucleophilic in nature, also prefer to react with 1methylcyclohexene rather than 1-octene. None of the simple steric or electronic parameters discussed previously can correlate the data for all of the seven ethyl 2-bromocarboxylates investigated. Correlation of more limited data sets, however, is possible. The results obtained for the four secondary systems employed yield a rather good correlation with σ^* ($\rho^* = -0.77$; r = 0.94), σ_p^+ ($\rho^+ = 4.34$; r = 0.96), and E_s (s = -0.15; r = 0.99). Two points, however, must be made. First, inclusion of the data for the one primary radical significantly worsens the correlations, while further inclusion of data from the two tertiary systems leads to no correlation at all; i.e., $r \approx 0.0 - 0.2!!$ Secondly, the slopes of these correlations contradict the initial expectations. The positive ρ^+ value may well be an artifact of the similarity in the values of the four σ_p^+ constants used (inclusion of the other three points produces a negative ρ^+ value). However, why should the most bulky of the secondary radicals be the one with the greatest tendency to attack the relatively hindered double bond of 1-methylcyclohexene??

The ideas associated with the persistence of radicals may provide a possible explanation. Because of their size, persistent radical species are reluctant to undergo reaction. When reaction does occur, it will be less exothermic or more endothermic than that for some related, non-persistent species. In terms of Hammond's Postulate, the reaction of a persistent species involves a transition state which shows a greater resemblance to the product radical (70). In the present system this would favor addition to 1-methylcyclohexene, since the radical derived from that alkene is tertiary.

It is not being argued that we have progressed from reactions governed only by ground state considerations to reactions governed only by transition state effects. Both ground state and transition state factors are operative in all reactions, but in a variable ratio. The following summary is applicable to the results under discussion:

- A. <u>Primary carboethoxyalkyl radical</u>: This is the least persistent of the radicals investigated. Ground state factors based on the electrophilicity of this species favors attack at the more electron rich double bond. Product state effects coincidently favor the same system. A relatively early transition state, however, is probably present.
- B. <u>Secondary carboethoxyalkyl radicals</u>: These are more persistent than the primary radical both on electronic and steric grounds. The steric requirements of these four systems differ greatly among themselves in monotonic fashion with more product state control found for the largest alkyl substituent. The extent of nucleophilic character associated with these species may be too small to account for the lack of a ground state alkene electron density effect. This would mean that the effects of the single alkyl

group and the carboethoxy group at the radical center approximately neutralize each other.

C. <u>Tertiary carboethoxyalkyl radicals</u>: These must be nucleophilic in nature and moderately persistent. Based upon the E_s values, however, the two tertiary systems studied have smaller steric demands than the secondary system containing the <u>t</u>-butyl group. Based solely on persistence, a transition state comparable to that for a secondary system possessing an isopropyl group may be envisioned. The much greater nucleophilic character of the tertiary radicals, however, will result in more ground state control and in a partial decrease in the selectivity for these systems.

One might ask why similar effects were not observed in the competition between 3-propoxypropene and 1-octene. These reactions should also be governed by both ground state and transition state factors. The secondary radicals generated from the addition of the carboethoxyalkyl radicals to both 3-propoxypropene and 1-octene, however, should be species of similar electronic nature. Therefore, the greater transition state effects in the

reactions of the more persistent carboethoxyalkyl radicals should play a smaller role in determining the selectivities.

EXPERIMENTAL

General

All of the compounds utilized for this study were liquids, whose boiling points were determined by distillation during purification. All boiling points are uncorrected.

Both proton and carbon NMR spectra were taken on a Varian FT-80A spectrometer. Spectroquality deuterated chloroform was used as the solvent.

Gas-liquid chromatography (GLC) analyses were carried out utilizing a Varian Aerograph 200 gas chromatograph equipped with a linear temperature programmer and thermal conductivity dectectors. A $15' \times 1/4"$ column containing 5% SE-30 on Chromosorb W was used in this investigation. Helium was used as the carrier gas.

Purification of Ethyl 2-Bromoethanoate

Commercial ethyl 2-bromoethanoate (Aldrich) was distilled, and the fraction boiling between 158 - 159°C was collected. Gas-liquid chromatography showed the sample to be greater than 99% pure.

Purification of Ethyl 2-Bromopropanoate

Commercial ethyl 2-bromopropanoate (Aldrich) was distilled and the fraction boiling at 157 - 158° was collected. Gas-liquid chromatography showed the purity of the sample to be greater than 98%.

Purification of Ethyl 2-Bromobutanoate

Commercial ethyl 2-bromobutanoate (Aldrich) was distilled and the fraction boiling at 62° at 10 mm was collected. Gas-liquid chromatography showed the sample to be more than 98% pure.

Purification of Ethyl 2-Bromo-3-methylbutanoate

Ethyl 2-bromo-3-methylbutanoate, which had been prepared by D. Kravetz (a former member of our research group) applying the methods utilized in the preparation of ethyl 2-bromo-2-ethylbutanoate (see p. 54), was distilled and the fraction boiling at 72 - 73° at 10 mm was collected. Gas-liquid chromatography showed the sample to be more than 98% pure.

Purification of Ethyl 2-Bromo-3,3-dimethylbutanoate

Ethyl 2-bromo-3,3-dimethylbutanoate was also prepared by D. Kravetz in the same fashion as ethyl 2-bromo-2-ethylbutanoate. The compound was distilled and the fraction boiling at 61° at 2 mm was collected. Gasliquid chromatography showed the sample to be more than 98% pure.

Purification of Ethyl 2-Bromo-2-methylpropanoate

Commercial ethyl 2-bromo-2-methylpropanoate (Aldrich) was distilled and the fraction boiling at 64 - 65° at 10 mm was collected. Gas-liquid chromatography showed the sample to be more than 99% pure.

Purification of Diethylbromomalonate

Commercial diethylbromomalonate (Aldrich) was distilled and the fraction boiling at 123° at 20 mm was collected. Gas-liquid chromatography showed the sample to be more than 99% pure.

Purification of 1-Octene

Commercial 1-octene (Aldrich) was distilled and the fraction boiling at 120 - 121° was collected. Gas-liquid chromatography showed the sample to be more than 98% pure.

Purification of 1-Methylcyclohexene

Commercial 1-methylcyclohexene (Aldrich) was distilled and the fraction boiling at 109 - 110° was collected. Gas-liquid chromatography showed the sample to be more than 99% pure.

Purification of Cis-2-heptene

Commercial <u>cis</u>-2-heptene (Aldrich) was distilled and the fraction boiling between 97 - 98° was collected. Gas-liquid chromatography showed the sample to be more than 99% pure.

Purification of Chlorobenzene

Commercial chlorobenzene (Matheson, Coleman, and Bell) was distilled and the fraction boiling between 130 - 131° was collected. Gas-liquid chromatography proved the sample to be more than 98% pure.

Purification of AIBN

Commercial azo-bisisobutyronitrile (K and K Laboratories, Inc.) was recrystallized from ethanol.

Purification of Benzene

Reagent grade benzene (Aldrich) was distilled and the fraction boiling at 80° was collected. Gas-liquid chromatography showed the purity to be greater than 99%.

Preparation of 3-Propoxypropene

The Williamson Synthesis (71) was used for preparing 3-propoxypropene:

CH₃CH₂CH₂OH → CH₃CH₂CH₂ONa

CH₂=CHCH₂Br + CH₃CH₂CH₂ONa PrOH CH₂=CHCH₂OCH₂CH₂CH₂CH₃ + NaBr

The sodium propoxide was prepared by the addition of 12.5 g (0.55 moles) of sodium to 250 mL of freshly distilled 1-propanol under nitrogen. After all of the sodium had dissolved, 3-bromopropene (0.65 g, 0.55 moles) was added from an addition funnel over a period of two hours. The reaction mixture was then refluxed overnight. Next, the white precipitate of sodium bromide was filtered off, and the remaining material (which contained an excessive amount of propanol) was distilled using a spinning band column. The fraction boiling at 81° was then extracted with water to remove the remaining traces of 1-propanol. The propoxypropene was then dried over calcium chloride. The pure product weighed 7.4 grams. This corresponded to a yield of 13%. The boiling point was 90°C; $n_D^{20} = 1.3960$ (experimental); $n_D^{20} = 1.3919$ (literature). NMR analysis showed a purity of greater than 98%.

Preparation of Ethyl 2-Bromo-2-ethylbutanoate

The procedure described in Reference 72 was used.

$$(CH_{3}CH_{2})_{2}CH-CO_{2}H \xrightarrow{1) SOCl_{2}, Br_{2}} (CH_{3}CH_{2})_{2}C-CO_{2}Et$$

$$2) EtOH Br$$

A 250 mL three-neck flask equipped with an addition funnel and a reflux condensor capped with a calcium chloride drying tube was charged with 16.2 g (0.140 mol) 2-ethylbutanoic acid and 17.2 g (0.145 mol) of thionyl chloride. As the reaction mixture was being stirred, bromine was introduced slowly from the addition funnel until the reaction mixture retained a deep bromine coloration. The remainder of the bromine was then added at once. Α total of 45.4 g (0.284 mol) of bromine was used. The flask was then heated to 90 °C for 1.5 hours. An additional 11.2 g (0.0700 mol) of bromine was then added, and the reaction mixture was kept at 90 °C for 18 more hours. The reaction mixture was then cooled and poured into 60 mL of chilled ethanol. After gas evolution stopped, the reaction mixture was washed with water. Ether was added to the organic material, and the resultant solution was washed with aqueous sodium bicarbonate to remove any traces of acid. The organic layer was then dried over anhydrous magnesium sulfate. The ether was removed by means of rotary evaporation, and the product was

distilled at a temperature of 54°C and a pressure of 0.7 mm, yielding 31.2 g (78% yield) of pure ethyl-2-bromo-2-ethylbutanoate; n_D^{20} (experimental) = 1.4526

Preparation of Bromotricarboethoxymethane

The procedure described in Reference 73 was used.

$$HC(CO_2Et)_3 \xrightarrow{1) Br_2/CHCl_3} BrC(CO_2Et)_3$$

A 100 ml three-neck flask equipped with an addition funnel and a reflux condensor capped with a calcium chloride drying tube was charged with 12.5 g (0.0400 mol) of tricarboethoxymethane, 20 mL of chloroform, and two crystals of iodine. A solution of 11.1 g (0.0700 mol) of bromine in 12 mL of chloroform was then added dropwise from the addition funnel. After all the bromine was added, the reaction mixture was refluxed for two hours, and then it was distilled under reduced pressured. The fraction collected at 105 - 106°C and 2 mm was the desired product; n_D^{20} (experimental) = 1.4527. $CH_{3}CH_{2}CH_{2}OCH_{2}-CH=CH_{2} + (CH_{3})_{3}CCHCO_{2}Et \xrightarrow{AIBN, 70^{\circ}}_{N_{2}, 2 \text{ days}}$ $CH_{3}CH_{2}CH_{2}OCH_{2}-CH-CH_{2}-CHCO_{2}Et$ Br $CH_{3}CH_{2}CH_{2}OCH_{2}-CH-CH_{2}-CHCO_{2}Et$ Br $C(CH_{3})_{3}$

A solution of 2.45 g (0.0244 mol) of 3-propoxypropene in 15 q (0.0980 mol) of ethyl 2-bromo-3,3-dimethylbutanoate was treated with 0.41 g (0.0025 mol) of AIBN in accord with the methodology of Kharasch et al. (51). The reaction mixture was kept at 70 °C for two days. The addition product was isolated using the following The unreacted 3-propoxypropene (1.96 g) was approach. collected in a dry-ice trap at a pressure of 2 mm. The unreacted ethyl 2-bromo-3,3-dimethylbutanoate was removed by distillation at 61°C at a reduced pressure of 2 mm. An additional 1.4 g of material was collected by further distillation at a temperature of 112 - 114°C (2 mm). GLC analysis showed the presence of four compounds, including some unreacted starting bromoester. Separation was carried out by GLC. An NMR spectrum of the GLC fraction corresponding to the two major unequal and unseparable peaks showed the following signals: a multiplet at δ 0.9 (12 H), a triplet at δ 1.3 (3 H),

a multiplet at δ 1.6 (4 H), a multiplet at δ 3.25 - 3.65 (6 H), and a quartet at δ 4.2 (2 H).

The relative simplicity of the NMR spectrum described above, which was obtained for the two-compound mixture, suggests that these two compounds are similar in structure. It is very probable that these compounds are diastereomers of ethyl 4-bromo-2-<u>t</u>-butyl-5-propoxypentanoate. If similar GLC response factors are assumed, a yield of 0.95 g of these addition products may be claimed. This corresponds to a yield of 63%.

Product Study for the Reaction Between 1-Methylcyclohexene and Ethyl Bromoethanoate

A solution of 2.40 g (0.0250 mol) of 1-methylcyclohexene in 16.9 g (0.100 mol) of ethyl bromoethanoate was treated with 0.606 g (0.00250 mol) of benzoyl peroxide. The reaction mixture was kept at 70°C for two days under a nitrogen atmosphere. To isolate the addition product, the unreacted 1-methylcyclohexene was collected in a dryice trap at a pressure of 2 mm. The unreacted ethyl bromoethanoate was distilled at 2 mm pressure and 26°C. An additional 1.9 g of material was collected by further distillation at a temperature of 70 - 72°C (0.25 mm). Gas chromatographic analysis showed the presence of three compounds, including some unreacted starting material. Gas chromatographic separation was carried out and the NMR spectrum of the major GLC product peak was consistent with that of a mixture of Compounds 5 and 6, the dehydrohalogenation products derived from the original adduct.



The ratio of <u>5</u> to <u>6</u> may be evaluated from the statistically corrected relative areas of the methylene group in <u>5</u>, which is located between the carbon-carbon double bond and the carboethoxy group ($\delta = 2.95$), and the single alkene proton in <u>6</u> ($\delta = 5.41$). The value obtained was 1.8:1. The amounts of these alkenes correspond to a 78% yield based on 1-methylcyclohexene consumed.

Kinetics

The usual competitive procedures were used to calculate the relative rate constants, employing Equation 23 (74, 75).

$$k_{rel} = (k_1/k_2)_{dis} = \frac{Ln[(Alkene 1)_o/(Alkene 1)_f]}{Ln[(Alkene 2)_o/(Alkene 2)_f]}$$
(23)

Here $(k_1/k_2)_{dis}$ is the rate constant ratio for the disappearance of Alkene 1 (3-propoxypropene or 1-methylcyclohexene) relative to Alkene 2 (1-octene); (Alkene 1)_o and (Alkene 1)_f are the number of moles of 3-propoxypropene or 1-methylcyclohexene present initially and finally; and (Alkene 2)_o and (Alkene 2)_f are the number of moles of 1-octene present initially and finally. The ratio (Alkene)_o/(Alkene)_f of Equation 23 may be directly obtained from the chromatographic analysis results using the following relationship:

(Alkene)_o
(Alkene)_f =
$$\frac{\begin{bmatrix} Area under the alkene peak \\ Area under the chlorobenzene peak \end{bmatrix} initially}{\begin{bmatrix} Area under the alkene peak \\ Area under the chlorobenzene peak \end{bmatrix} finally}$$

Chlorobenzene was used as the internal standard in all of the runs. For detailed data on the kinetic studies see the Appendix.

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APPENDIX

Appendix Tables 11 - 27 indicate the actual relative reactivities of substituted ethyl 2-bromo-carboxylates toward alkene pairs.

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.032	0.468	31.4	0.997
_	Alkene 2	1.50	1.028	0.472	31.5	
	Bromocarboxylate	6.00	5.11	0.89	14.8	
2	Alkene l	1.50	1.03	0.47	31.3	0.978
	Alkene 2	1.50	1.02	0.48	31.9	
	Bromocarboxylate	6.00	5.06	0.94	15.7	
3	Alkene l	1.50	0.989	0.511	34.1	1.004
	Alkene 2	1.50	0.993	0.507	33.9	
	Bromocarboxylate	6.00	5.08	0.912	15.2	
4	Alkene l	1.50	1.05	0.45	29.7	0.973
	Alkene 2	1.50	1.04	0.46	30.4	
	Bromocarboxylate	6.00	5.12	0.88	14.8	
5	Alkene l	1.50	0.997	0.503	33.5	0.978
-	Alkene 2	1.50	0.988	0.510	34.1	••••
	Bromocarboxylate	6.00	5.09	0.91	15.2	
6	Alkene l	1.50	1.02	0.48	31.6	0.923
	Alkene 2	1.50	0.993	0.507	33.8	
	Bromocarboxylate	6.00	5.08	0.92	15.3	
	Average Material E	Balance = 0.9	94 ± 0.04	Avera	age $k_1/k_2 = 0$.98 ± 0.03

TABLE 11. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 3-Propoxypropene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl Bromoethanoate in Benzene at 70° (Reaction Time = 24 Hours).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k _l /k ₂
1	Alkene l	1.50	1.05	0.45	30.2	1 06
	Alkene 2	1.50	1.07	0.43	29.1	1.00
	Bromocarboxylate	6.00	5.13	0.87	14.5	
2	Alkene l	1.50	1.09	0.41	27.0	1.10
	Alkene 2	1.50	1.13	0.37	25.0	
	Bromocarboxylate	6.00	5.29	0.71	11.8	
3	Alkene l	1.50	1.08	0.42	28.3	1.03
	Alkene 2	1.50	1.09	0.41	27.6	
	Bromocarboxylate	6.00	5.22	0.78	13.0	
4	Alkene l	1.50	1.04	0.46	30.8	1.03
	Alkene 2	1.50	1.05	0.45	30.1	
	Bromocarboxylate	6.00	5.16	0.84	14.0	
5	Alkene l	1.50	1.13	0.37	24.8	1.09
	Alkene 2	1.50	1.16	0.34	22.9	
	Bromocarboxylate	6.00	5.36	0.64	10.7	

TABLE 12. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 3-Propoxypropene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromopropanoate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.11	0.39	25.8	1.09
	Alkene 2	1.50	1.13	0.37	24.7	
	Bromocarboxylate	6.00	5.35	0.65	10.8	
2	Alkene l	1.50	1.20	0.30	19.9	1.10
	Alkene 2	1.50	1.23	0.27	18.3	
	Bromocarboxylate	6.00	5.46	0.54	9.0	
3	Alkene l	1.50	1.17	0.33	21.5	1.08
	Alkene 2	1.50	1.20	0.30	20.1	
	Bromocarboxylate	6.00	5.42	0.58	9.7	
4	Alkene l	1.50	1.28	0.22	14.8	1.09
	Alkene 2	1.50	1.29	0.21	13.7	
	Bromocarboxylate	6.00	5.52	0.48	8.0	
5	Alkene l	1.50	1.16	0.34	22.5	1.04
	Alkene 2	1.50	1.17	0.33	21.9	
	Bromocarboxylate	6.00	5.29	0.71	11.7	
6	Alkene l	1.50	1.24	0.26	17.5	1.09
	Alkene 2	1.50	1.26	0.24	16.1	
	Bromocarboxylate	6.00	5.52	0.48	8.0	
	Average Material B	alance = 0.9	98 ± 0.09	Avera	age $k_1/k_2 = 1$.08 ± 0.02

TABLE 13. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 3-Propoxypropene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromobutanoate in Benzene at 70° (Reaction Time = 24 Hr.).

TABLE 14. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 3-Propoxypropene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromo-3-methylbutanoate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	^k 1 ^{/k} 2
1	Alkene l	1.50	1.15	0.35	23.4	1.14
	Alkene 2	1.50	1.19	0.31	20.9	
	Bromocarboxylate	6.00	5.27	0.73	12.2	
2	Alkene l	1.50	1.15	0.35	23.1	1.14
	Alkene 2	1.50	1.19	0.31	20.4	
	Bromocarboxylate	6.00	5.24	0.76	12.6	
3	Alkene l	1.50	1.16	0.34	22.9	1.15
	Alkene 2	1.50	1.19	0.31	20.4	
	Bromocarboxylate	6.00	5.30	0.70	11.9	
4	Alkene l	1.50	1.14	0.36	23.7	1.16
	Alkene 2	1.50	1.19	0.31	20.8	
	Bromocarboxylate	6.00	5.27	0.73	12.1	
5	Alkene l	1.50	1.16	0.34	22.8	1.10
	Alkene 2	1.50	1.19	0.31	20.9	
	Bromocarboxylate	6.00	5.29	0.71	12.0	
6	Alkene l	1.50	1.14	0.36	24.1	1.12
	Alkene 2	1.50	1.17	0.33	21.9	
	Bromocarboxylate	6.00	5.24	0.76	12.6	
	Average Material B	alance = 1.	10 ± 0.02	Avera	age $k_1/k_2 = 1$.14 ± 0.02

TABLE 15. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 3-Propoxypropene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromo-3,3-dimethylbutanoate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.20	0.30	20.0	1.30
	Alkene 2	1.50	1.26	0.24	16.0	2100
	Bromocarboxylate	6.00	5.44	0.56	9.3	
2	Alkene l	1.50	1.18	0.32	21.3	1.23
	Alkene 2	1.50	1.24	0.26	17.3	
	Bromocarboxylate	6.00	5.37	0.63	10.5	
3	Alkene l	1.50	1.21	0.29	19.3	1.21
	Alkene 2	1.50	1.26	0.24	16.0	_ •
	Bromocarboxylate	6.00	5.48	0.52	8.7	
4	Alkene l	1.50	1.18	0.32	21.3	1.24
	Alkene 2	1.50	1.24	0.26	17.3	
	Bromocarboxylate	6.00	5.38	0.62	10.3	
5	Alkene l	1.50	1.32	0.18	12.0	1.25
	Alkene 2	1.50	1.36	0.14	9.3	
	Bromocarboxylate	6.00	5.71	0.29	4.8	
6	Alkene l	1.50	1.19	0.31	20.7	1.22
	Alkene 2	1.50	1.24	0.26	17.3	
	Bromocarboxylate	6.00	5.43	0.57	9.5	
	Average Material B	alance = 1.0	01 ± 0.06	Avera	age $k_1/k_2 = 1$.24 ± 0.03

TABLE 16. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 3-Propoxypropene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromo-2-methylpropanoate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.30	0.20	13.6	1.33
_	Alkene 2	1.50	1.34	0.16	10.4	
	Bromocarboxylate	6.00	5.62	0.38	6.3	
2	Alkene l	1.50	1.28	0.22	14.4	1.29
	Alkene 2	1.50	1.33	0.17	11.3	
	Bromocarboxylate	6.00	5.55	0.45	7.5	
3	Alkene l	1.50	1.31	0.19	12.7	1.34
	Alkene 2	1.50	1.36	0.14	9.56	
	Bromocarboxylate	6.00	5.68	0.32	5.3	
4	Alkene l	1.50	1.28	0.22	14.7	1.29
	Alkene 2	1.50	1.32	0.28	11.7	
	Bromocarboxylate	6.00	5.58	0.42	6.98	
5	Alkene l	1.50	1.33	0.17	11.4	1.31
	Alkene 2	1.50	1.36	0.14	9.13	
	Bromocarboxylate	6.00	5.58	0.42	6.98	
	Average Material B	alance = 1.	1 ± 0.2	Avera	age $k_1/k_2 = 1$.31 ± 0.03

TABLE 17. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 3-Propoxypropene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromo-2-ethylbutanoate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.36	0.14	9.3	1.32
	Alkene 2	1.50	1.39	0.11	7.17	
	Bromocarboxylate	6.00	5.75	0.25	4.17	
2	Alkene l	1.50	1.42	0.08	5.50	1.31
	Alkene 2	1.50	1.44	0.06	4.23	
	Bromocarboxylate	6.00	5.76	0.24	4.00	
3	Alkene l	1.50	1.41	0.09	6.16	1.38
	Alkene 2	1.50	1.43	0.07	4.49	
	Bromocarboxylate	6.00	5.79	0.21	3.50	
4	Alkene l	1.50	1.39	0.11	7.57	1.39
	Alkene 2	1.50	1.42	0.08	5.44	,
	Bromocarboxylate	6.00	5.77	0.23	3.83	
5	Alkene l	1.50	1.42	0.08	5,19	1.34
	Alkene 2	1.50	1.44	0.06	3.89	2101
	Bromocarboxylate	6.00	5.81	0.19	3.17	
6	Alkene l	1.50	1.43	0.07	4.56	1.40
•	Alkene 2	1.50	1.45	0.05	3.28	1
	Bromocarboxylate	6.00	5.84	0.16	2.66	
	Average Material B	alance = 1.3	3 ± 0.2	Avera	age $k_1/k_2 = 1$.36 ± 0.04

TABLE 18. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 3-Propoxypropene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Diethyl 2-Bromo-1,3-propanedicarboxylate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	0.66	0.84	55.8	0.510
	Alkene 2	1.50	0.31	1.19	79.9	
	Bromocarboxylate	6.00	3.95	2.05	34.2	
2	Alkene l	1.50	0.62	0.88	58.6	0.518
	Alkene 2	1.50	0.27	1.23	81.8	
	Bromocarboxylate	6.00	3.90	2.10	35.2	
3	Alkene l	1.50	0.65	0.85	56.7	0.525
	Alkene 2	1.50	0.30	1.20	79.7	
	Bromocarboxylate	6.00	3.92	2.08	34.2	
4	Alkene l	1.50	0.644	0.86	57.0	0.512
	Alkene 2	1.50	0.290	1.21	80.8	
	Bromocarboxylate	6.00	3.93	2.07	34.5	
5	Alkene l	1.50	0.70	0.80	53.4	0.502
	Alkene 2	1.50	0.33	1.17	78.1	01002
	Bromocarboxylate	6.00	3.99	2.01	33.5	
6	Alkene l	1.50	0.64	0.86	57.2	0.528
	Alkene 2	1.50	0.30	1.20	79.9	0.0-0
	Bromocarboxylate	6.00	3.92	2.08	34.7	
	Average Material B	alance = 1.	01 ± 0.01	Avera	age $k_1/k_2 = 0$.52 ± 0.01

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.15	0.35	23.1	1.18
	Alkene 2	1.50	1.20	0.30	20.0	
	Bromocarboxylate	6.00	5.43	0.57	9.51	
2	Alkene l	1.50	1.13	0.37	24.8	1.22
	Alkene 2	1.50	1.19	0.31	20.7	
	Bromocarboxylate	6.00	5.35	0.65	10.9	
3	Alkene l	1.50	1.21	0.29	19.4	1.14
	Alkene 2	1.50	1.24	0.26	17.3	_ •
	Bromocarboxylate	6.00	5.31	0.69	11.5	
4	Alkene l	1.50	1.18	0.32	21.5	1.20
	Alkene 2	1.50	1.23	0.27	18.3	
	Bromocarboxylate	6.00	5.38	0.62	13.7	
5	Alkene l	1.50	1.16	0.34	22.6	1,13
	Alkene 2	1.50	1.20	0.31	20.3	1.10
	Bromocarboxylate	6.00	5.36	0.64	16.9	
6	Alkene l	1.50	1.15	0.35	23.0	1 23
	Alkene 2	1.50	1.21	0.29	19.1	1.20
	Bromocarboxylate	6.00	5.23	0.77	12.8	
	Average Material B	alance = 1.0	0 ± 0.1	Ave	rage $k_1/k_2 = 1$	1.18 ± 0.04

TABLE 19. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 1-Methylcyclohexene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl Bromoethanoate in Benzene at 70° (Reaction Time = 24 Hours).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.22	0.28	18.3	1.23
	Alkene 2	1.50	1.27	0.23	15.1	
	Bromocarboxylate	6.00	5.48	0.52	8.6	
2	Alkene l	1.50	1.22	0.28	18.3	1.27
	Alkene 2	1.50	1.28	0.22	14.5	/
	Bromocarboxylate	6.00	5.45	0.55	9.2	
3	Alkene l	1.50	1.20	0.30	19.7	1.22
	Alkene 2	1.50	1.25	0.25	16.4	
	Bromocarboxylate	6.00	5.42	0.58	10.7	
4	Alkene l	1.50	1.20	0.30	19.7	1.28
	Alkene 2	1.50	1.26	0.24	15.8	
	Bromocarboxylate	6.00	5.39	0.61	10.2	
5	Alkene l	1.50	1.16	0.34	22.5	1 26
	Alkene 2	1.50	1.22	0.28	18.4	1.20
	Bromocarboxylate	6.00	5.31	0.69	11.6	
6	Alkene l	1.50	1.19	0.31	20.4	1.27
	Alkene 2	1.50	1.25	0.25	16.4	
	Bromocarboxvlate	6.00	5.42	0.58	10.7	

TABLE 20. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 1-Methylcyclohexene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromopropanoate in Benzene at 70° (Reaction Time = 24 Hr.).

TABLE 21. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 1-Methylcyclohexene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromobutanoate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.34	0.16	10.5	1.28
	Alkene 2	1.50	1.38	0.12	8.30	
	Bromocarboxylate	6.00	5.69	0.31	5.20	
2	Alkene l	1.50	1.35	0.15	10.0	1.33
	Alkene 2	1.50	1.39	0.11	7.60	
	Bromocarboxylate	6.00	5.71	0.29	4.90	
3	Alkene l	1.50	1.33	0.17	11.7	1.29
	Alkene 2	1.50	1.37	0.13	9.00	
	Bromocarboxylate	6.00	5.67	0.33	5.50	
4	Alkene l	1.50	1.34	0.16	10.9	1.33
	Alkene 2	1.50	1.38	0.12	8.30	-
	Bromocarboxylate	6.00	5.70	0.30	5.00	
5	Alkene l	1.50	1.31	0.19	12.5	1.32
	Alkene 2	1.50	1.36	0.14	9.70	
	Bromocarboxylate	6.00	5.62	0.38	6.30	
	Average Material B	alance = 1.0	0 ± 0.2	Ave	rage $k_1/k_2 = 1$	1.31 ± 0.0

TABLE 22. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 1-Methylcyclohexene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromo-3-methylbutanoate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.20	0.30	20.0	1.48
	Alkene 2	1.50	1.29	0.21	13.8	
	Bromocarboxylate	6.00	5.39	0.61	10.2	
2	Alkene l	1.50	1.28	0.22	14.5	1.49
	Alkene 2	1.50	1.35	0.15	10.0	
	Bromocarboxylate	6.00	5.58	0.42	7.0	
3	Alkene l	1.50	1.20	0.30	20.1	1.55
	Alkene 2	1.50	1.30	0.20	13.5	
	Bromocarboxylate	6.00	5.42	0.58	9.67	
4	Alkene l	1.50	1.21	0.29	19.2	1.50
	Alkene 2	1.50	1.30	0.20	13.2	
	Bromocarboxylate	6.00	5.46	0.54	9.00	
5	Alkene l	1.50	1.30	0.20	13.1	1.44
	Alkene 2	1.50	1.36	0.14	9.3	
	Bromocarboxylate	6.00	5.59	0.41	6.8	
6	Alkene l	1.50	1.28	0.22	14.5	1.48
-	Alkene 2	1.50	1.35	0.15	10.1	
	Bromocarboxylate	6.00	5.61	0.39	6.5	
	Average Material B	alance = 1.	14 ± 0.06	Ave	rage $k_1/k_2 = 1$	1.48 ± 0.0

TABLE 23. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 1-Methylcyclohexene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromo-3,3-dimethylbutanoate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.30	0.20	13.1	2.25
	Alkene 2	1.50	1.40	0.10	6.7	
	Bromocarboxylate	6.00	5.68	0.32	5.3	
2	Alkene l	1.50	1.32	0.18	12.3	2.15
	Alkene 2	1.50	1.41	0.09	6.0	
	Bromocarboxylate	6.00	5.71	0.29	4.8	
3	Alkene l	1.50	1.29	0.21	13.8	2.16
	Alkene 2	1.50	1.40	0.10	6.7	
	Bromocarboxylate	6.00	5.68	0.32	5.3	
4	Alkene l	1.50	1.29	0.21	13.8	2.16
	Alkene 2	1.50	1.40	0.10	6.7	
	Bromocarboxylate	6.00	5.68	0.32	5.3	
5	Alkene l	1.50	1.25	0.25	16.9	2.22
	Alkene 2	1.50	1.38	0.12	8.0	
	Bromocarboxylate	6.00	5.62	0.38	6.3	
6	Alkene l	1.50	1.25	0.25	16.9	2.22
	Alkene 2	1.50	1.38	0.12	8.0	
	Bromocarboxylate	6.00	5.61	0.39	6.5	
	Average Material B	alance = 1.0	0.02 ± 0.02	Ave	cage $k_1/k_2 = 2$	2.19 ± 0.04

TABLE 24. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 1-Methylcyclohexene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromo-2-methylpropanoate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.30	0.20	13.1	1.19
	Alkene 2	1.50	1.33	0.17	11.1	
	Bromocarboxylate	6.00	5.52	0.48	7.96	
2	Alkene l	1.50	1.27	0.23	15.2	1.13
	Alkene 2	1.50	1.30	0.20	13.5	
	Bromocarboxylate	6.00	5.63	0.37	6.21	
3	Alkene l	1.50	1.24	0.26	17.6	1.18
	Alkene 2	1.50	1.27	0.23	15.1	
	Bromocarboxylate	6.00	5.48	0.52	8.71	
4	Alkene l	1.50	1.17	0.33	21.8	1.25
	Alkene 2	1.50	1.23	0.27	17.8	
	Bromocarboxylate	6.00	5.42	0.58	4.75	
5	Alkene l	1.50	1.27	0.23	15.1	1.16
	Alkene 2	1.50	1.30	0.20	13.1	
	Bromocarboxylate	6.00	5.62	0.38	5.47	
6	Alkene l	1.50	1.30	0.20	13.3	1.20
	Alkene 2	1.50	1.32	0.18	12.0	
	Bromocarboxylate	6.00	5.61	0.39	6.47	
	Average Material B	alance = 1.	0 ± 0.1	Ave	rage $k_1/k_2 = 1$	1.18 ± 0.0

TABLE 25. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 1-Methylcyclohexene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Ethyl 2-Bromo-2-ethylbutanoate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.35	0.15	10.0	1.24
	Alkene 2	1.50	1.35	0.15	10.0	
	Bromocarboxylate	6.00	5.63	0.37	6.2	
2	Alkene l	1.50	1.33	0.17	11.3	1.25
	Alkene 2	1.50	1.36	0.14	9.3	
	Bromocarboxylate	6.00	5.62	0.38	6.3	
3	Alkene l	1.50	1.33	0.17	11.3	1.22
	Alkene 2	1.50	1.36	0.14	9.3	
	Bromocarboxylate	6.00	5.65	0.35	5.8	
4	Alkene l	1.50	1.33	0.17	11.3	1.28
	Alkene 2	1.50	1.36	0.14	9.3	
	Bromocarboxylate	6.00	5.66	0.34	5.7	
5	Alkene l	1.50	1.33	0.17	11.3	1.23
-	Alkene 2	1.50	1.36	0.14	9.3	
	Bromocarboxylate	6.00	5.67	0.33	5.5	
6	Alkene l	1.50	1.35	0.15	10.0	1.23
-	Alkene 2	1.50	1.38	0.12	8.0	
	Bromocarboxylate	6.00	5.64	0.36	6.0	
	Average Material B	alance = 1.	1 ± 0.1	Ave	rage $k_1/k_2 = 1$	1.24 ± 0.02

TABLE 26. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 1-Methylcyclohexene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Diethyl 2-Bromo-1,3-propanedicarboxylate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	k ₁ /k ₂
1	Alkene l	1.50	1.08	0.42	28.0	1.08
	Alkene 2	1.50	1.10	0.40	26.7	
	Bromocarboxylate	6.00	5.21	0.79	13.2	
2	Alkene l	1.50	1.04	0.46	30.7	1.13
	Alkene 2	1.50	1.09	0.41	27.3	
	Bromocarboxylate	6.00	5.18	0.82	13.7	
3	Alkene l	1.50	1.08	0.42	28.0	1.08
	Alkene 2	1.50	1.10	0.40	26.7	
	Bromocarboxylate	6.00	5.24	0.76	12.7	
4	Alkene l	1.50	1.10	0.40	26.7	1.07
	Alkene 2	1.50	1.12	0.38	25.3	-
	Bromocarboxylate	6.00	5.25	0.75	12.5	
5	Alkene l	1.50	1.13	0.37	24.7	1.10
-	Alkene 2	1.50	1.17	0.33	22.0	
	Bromocarboxylate	6.00	5.33	0.67	11.2	
6	Alkene l	1.50	1.09	0.41	27.3	1.12
-	Alkene 2	1.50	1.13	0.37	24.7	
	Bromocarboxylate	6.00	5.27	0.73	12.2	
	Average Material B	alance = 0.	95 ± 0.01	Ave	rage $k_1/k_2 =$	1.10 ± 0.02

TABLE 27. Rate Constant Ratio, k_1/k_2 , for the Disappearance of 1-Methylcyclohexene (Alkene 1) Relative to 1-Octene (Alkene 2) in their Addition Reaction with Triethyl Bromomethanetricarboxylate in Benzene at 70° (Reaction Time = 24 Hr.).

Run	Compound	Mmoles Initial	Mmoles Final	Mmoles Used	Percent Reaction	^k 1 ^{/k} 2
1	Alkene l	1.50	0.90	0.60	40.0	2.12
	Alkene 2	1.50	1.18	0.32	21.3	
	Bromocarboxylate	6.00	5.03	0.97	16.2	
2	Alkene l	1.50	0.95	0.55	36.7	2.04
	Alkene 2	1.50	1.20	0.30	20.0	
	Bromocarboxylate	6.00	5.08	0.92	15.3	
3	Alkene l	1.50	1.10	0.40	26.7	2.09
	Alkene 2	1.50	1.30	0.20	13.3	_ • • •
	Bromocarboxylate	6.00	5.35	0.65	10.8	
4	Alkene l	1.50	1.13	0.37	24.7	2.11
	Alkene 2	1.50	1.31	0.19	12.7	
	Bromocarboxylate	6.00	5.42	0.58	9.7	
5	Alkene l	1.50	1.10	0.40	26.7	2.07
	Alkene 2	1.50	1.29	0.21	14.0	
	Bromocarboxylate	6.00	5.38	0.62	10.3	
6	Alkene l	1.50	0.96	0.54	36.0	2.01
	Alkene 2	1.50	1.20	0.30	20.0	
	Bromocarboxvlate	6.00	5.31	0.69	11.5	