Tetrahedron Vol. 26, pp. 4153 to 4166. Pergamon Press 1970. Printed in Great Britain

NUCLEOPHILIC CHARACTER OF ALKYL RADICALS GENERATED IN REDOX PROCESSES—III

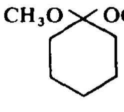
THE REACTIVITY OF ALKYL RADICALS TOWARDS CONJUGATED OLEFINS

F. Minisci, P. Zammori
Istituto di Chimica Organica della Facoltà di Scienze, Via M. D'Azeglio, 85 Parma, Italy
and
R. Bernardi, M. Cecere and R. Galli
Istituto di Chimica del Politecnico di Milano

(*Received in the UK* 10 *February* 1970; *Accepted for publication* 30 *April* 1970)

Abstract—New syntheses were carried out by alternating free radical additions of ethyl, n-propyl, n-butyl, sec-butyl, cyclohexyl, α-chloromethyl, α-chloroethyl, γ-chloropropyl and 5-(methoxycarbonyl) pentyl radicals to pairs of conjugated olefins. The sources of the alkyl radicals were the redox systems: acyl peroxides/cuprous ion and 1-methoxycyclohexylhydroperoxide/ferrous ion. The relative reactivities of the above mentioned radicals towards butadiene, acrylonitrile, 2,3-dimethylbutadiene, methyl acrylate, methyl methacrylate, acrylic acid and maleic anhydride are discussed in quantitative terms according to their nucleophilic character.

The nucleophilic character of alkyl radicals generated in redox processes appears evident in the addition to conjugated olefins[1] and in the alkylation of protonated heteroaromatic bases.[2] As we have previously shown, the 5-(methoxycarbonyl) pentyl radical (I) is more reactive with olefins conjugated to electronwithdrawing groups (acrylonitrile, acrylates, acrylic acid, maleic anhydride) than with α-methylstyrene.[1] This particular radical (I) was chosen mainly because of its potential synthetic interest: in fact it can be obtained easily and in high yields from cyclohexanone and hydrogen peroxide according to the following reaction:



$$+ Fe^{++} \rightarrow \underset{\text{I}}{CH_3OCO{-}(CH_2)_4{-}\dot{C}H_2} + FeOH^{++} \qquad \text{(a)}$$

Furthermore, in the past some authors have disagreed about the affinity of this radical towards conjugated olefins and about its polar character.[1, 3]

In this paper we will demonstrate that the radical (I) is more reactive with olefins conjugated with strongly electronwithdrawing groups than with butadiene. We also will give further support to the nucleophilic character of this radical and provide new syntheses and new compounds starting from products of industrial interest. We will also approach the problem on a more general basis by using a more versatile source of alkyl radicals, i.e. the acyl peroxides/cuprous ion redox system:

$$\begin{aligned} &RCOOOCOR + Cu^{+} \rightarrow RCOO\cdot + RCOOCu^{+} \\ &RCOO\cdot \rightarrow R\cdot + CO_2 \end{aligned} \qquad \text{(b)}$$

The acyl peroxides are readily obtained from the corresponding carboxylic acids, so that a large variety of alkyl radicals can be produced using very mild conditions. In this context we have examined the reactivity of methyl, ethyl, n-propyl, n-butyl, isopropyl, sec-butyl, cyclohexyl, chloromethyl, α-chloroethyl and γ-chloropropyl radicals with butadiene, 2,3-dimethylbutadiene, acrylonitrile, methyl acrylate, methyl methacrylate and acrylic acid.

RESULTS AND DISCUSSION

The method used is essentially the same with both sources of radicals (1-methoxycyclohexylhydroperoxide and acyl peroxides), although the experimental conditions and the products formed are different. This method is based on the fact that the alkyl radicals are produced in the presence of two olefins, one being a conjugated diene and the other an olefin conjugated with electronwithdrawing groups.

In each case the main products are formed according to the following theoretical suppositions: because of its nucleophilic character, the alkyl radical (II) mainly adds on to the olefins conjugated with electronwithdrawing groups:

$$\underset{\text{II}}{R\cdot} + CH_2{=}CHX \rightarrow \underset{\text{III}}{R{-}CH_2{-}\dot{C}HX} \qquad (X = CN, COOR) \qquad \text{(C)}$$

The new radical (III) formed, achieves a prevalent electrophilic character owing to the proximity of the electronwithdrawing group X. Subsequent addition occurs exclusively on the conjugated diene:

$$R{-}CH_2{-}\dot{C}HX + CH_2{=}CH{-}CH{=}CH_2 \rightarrow \underset{\text{IV}}{R{-}CH_2{-}CHX{-}CH_2{-}\overbrace{CH{\cdots}CH{\cdots}CH_2}^{\cdot}} \qquad \text{(d)}$$

This phenomenon is well known as an alternating effect in radical copolymerization. In fact, if the process were not interrupted at this point, the allyl radical (IV), because of its nucleophilic character, would add to the olefin conjugated with the electronwithdrawing group and the process would continue leading to an alternating copolymer.

The copolymerization can be completely prevented by the quantitative oxidation of the allyl radical IV:

$$R{-}CH_2{-}CHX{-}CH_2{-}\overbrace{CH{\cdots}CH{\cdots}CH_2}^{\cdot} + Cu^{++} \rightarrow \qquad \text{(e)}$$

$$\underset{\text{V}}{R{-}CH_2{-}CHX{-}CH_2{-}\overbrace{CH{\cdots}CH{\cdots}CH_2}^{+}} + Cu^{+}$$

The final products are produced either by the interaction of the allyl cation with the solvent or by the intramolecular interaction with the X group.

Further detailed examination of the interactions (c), (d) and (e) shows that (c) is not completely selective, because two side reactions take place; one reaction (f) is the oxidation of the alkyl radical (II) by the cupric ion,

$$\mathrm{R\cdot + Cu^{++} \rightarrow Products + Cu^{+}} \qquad \text{(f)}$$

(this oxidation can also be related to the nucleophilic character of the radical R·), and the other side reaction (g) is the addition of the radical II to the conjugated diene and the subsequent oxidation of the allyl radical:

$$\begin{gathered}\mathrm{R\cdot + CH_2{=}CH{-}CH{=}CH_2 \rightarrow R{-}CH_2{-}\overbrace{CH{\cdots}CH{\cdots}CH_2}^{\cdot}} \\ + \qquad \text{(g)} \\ \mathrm{R{-}CH_2{-}\overbrace{CH{\cdots}CH{\cdots}CH_2}^{\cdot} + Cu^{++} \rightarrow R{-}CH_2{-}\overbrace{CH{\cdots}CH{\cdots}CH_2}^{+} + Cu^{+}} \\ \mathrm{VI}\end{gathered}$$

On the basis of the reaction (g), it was possible to calculate the relative reaction rates of the two olefins towards the radical II. The reaction was carried out in a homogeneous medium with excess olefin in order to minimize the change in concentrations during the process. The ratios of the products formed from V and those from VI were used to determine quantitatively the relative reaction rates of the two reacting olefins. This is possible as the interaction (d) is completely selective, i.e. no other competitive process occurs in any example, except that of methyl methacrylate, which will be discussed later.

The interaction (e), which is the only process concerning the allyl radical, is also completely selective.

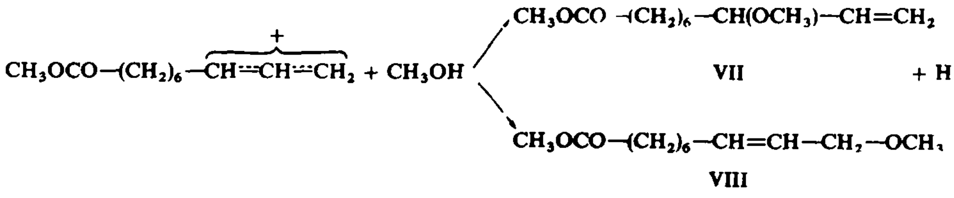
This method seems to be particularly useful for calculating the affinity of alkyl radicals towards several of the more important vinyl monomers, completely preventing the occurrence of homopolymerization and copolymerization.

The reaction with 1-methoxycyclohexylhydroperoxide is carried out in methanol with ferrous sulphate and cupric sulphate. The interaction (f) leads essentially to methyl 5-hexenoate:

$$\mathrm{CH_3OCO{-}(CH_2)_4{-}CH_2^{\cdot} + Cu^{++} \rightarrow CH_2OCO{-}(CH_2)_3{-}CH{=}CH_2 + Cu^{+} + H^{+}}$$

Quantitatively this side reaction is insignificant and does not affect the validity of the method.

The reaction (g) results in a mixture of two methoxy-derivatives VII and VIII:



$$\mathrm{CH_3OCO{-}(CH_2)_6{-}\overbrace{CH{\cdots}CH{\cdots}CH_2}^{+} + CH_3OH \rightarrow \begin{cases} \mathrm{CH_3OCO{-}(CH_2)_6{-}CH(OCH_3){-}CH{=}CH_2} \quad \text{VII} \\ \mathrm{CH_3OCO{-}(CH_2)_6{-}CH{=}CH{-}CH_2{-}OCH_3} \quad \text{VIII} \end{cases} + H^{+}}$$

Analogously the reaction (e) results in a mixture of the two methoxy derivatives IX and X:

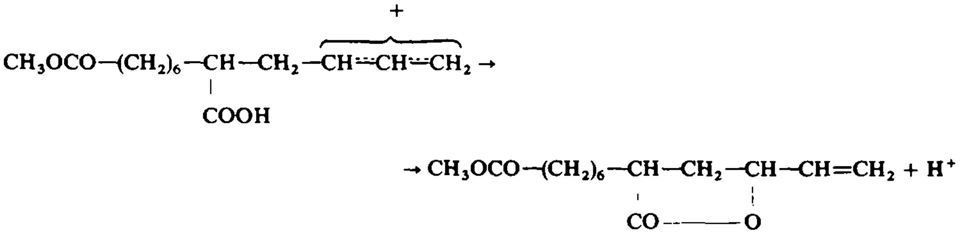
$$CH_3OCO{-}(CH_2)_6{-}CHX{-}CH_2{-}CH(OCH_3){-}CH{=}CH_2$$

IX

$$CH_3OCO{-}(CH_2)_6{-}CHX{-}CH_2{-}CH{=}CH{-}CH_2{-}OCH_3$$

X

Whenever the substituent is a carboxyl or a methoxycarbonyl group, an intramolecular reaction occurs forming the lactone XI:

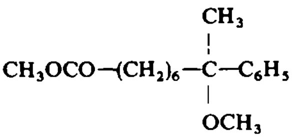


$$CH_3OCO{-}(CH_2)_6{-}\underset{\displaystyle COOH}{\underset{|}{CH}}{-}CH_2{-}\overset{+}{\overbrace{CH{\overset{\cdot\cdot}{-}}CH{\overset{\cdot\cdot}{-}}CH_2}} \rightarrow$$

$$\rightarrow CH_3OCO{-}(CH_2)_6{-}\underset{\displaystyle CO\text{———}}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle O}{\underset{|}{CH}}{-}CH{=}CH_2 + H^+$$

XI

Comparing these results with those obtained using α-methylstyrene[1] instead of butadiene, we can deduce indirectly that butadiene is more reactive than α-methylstyrene towards the 5-(methoxycarbonyl)pentyl radical. This conclusion has been directly confirmed in a competitive test with butadiene and α-methylstyrene. In this case, of course, no alternating radical addition takes place, but only the compound XIV is formed together with the compounds VII and VIII,



$$CH_3OCO{-}(CH_2)_6{-}\underset{\displaystyle OCH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}C_6H_5$$

XIV

The results are reported in Table 2; butadiene is shown to be 1·8 times more reactive than α-methylstyrene.

It is now possible to confirm indirectly the results obtained with the two series of olefins dividing the data obtained with α-methylstyrene by the factor 1·8. The average experimental values for butadiene and the data calculated from the experimental of α-methylstyrene are reported in Table 3. The agreement between experimental and calculated values is quite satisfactory, since small variations in the quantitative analyses of the reaction products can cause large differences in the relative reactivities, particularly when the difference in the reactivity of the two olefins is high.

At this point we studied this new type of radical reaction with a more versatile

TABLE 1. RELATIVE REACTIVITIES OF THE OLEFINS TOWARDS I

Molar ratios	Mol %					Relative reactivities
Acrylonitrile : butadiene	VII	VIII	IX	X		
1 : 3	19·2	10·1	18·4	52·3		7·2
1 : 1	10·4	4·4	22·5	62·7		5·7
Acrylic acid : butadiene	VII	VIII	XI			
1 : 3	46·7	20·0	33·3			1·5
3 : 1	10·0	4·5	85·5			2·0
Methyl acrylate : butadiene	VII	VIII	IX	X	XI	
1 : 3	27·0	19·5	4·9	7·1	41·5	3·4
3 : 1	8·0	3·6	7·5	10·4	70·5	2·6
Maleic anhydride : butadiene	VII	VIII	XII	XIII		
1 : 1	5·4	2·5	25·4	66·7		11·4

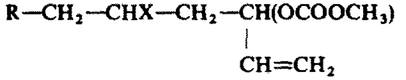
TABLE 2. RELATIVE REACTIVITIES OF BUTADIENE AND α-METHYLSTYRENE TOWARDS I

Molar ratio	Mol %			Relative reactivity
	VII	VIII	XIV	
1 : 1	40·0	21·5	35·5	1·8

TABLE 3. REACTIVITIES RELATIVE TO α-METHYLSTYRENE AND BUTADIENE

	Experimental		Experimental	Calculated
α-Methylstyrene	1·0			
Butadiene	1·8	Butadiene	1·0	1·0
Acrylic acid	2·2	Acrylic acid	1·7	1·2
Methyl acrylate	5·4	Methyl acrylate	3·0	3·0
Acrylonitrile	11·0	Acrylonitrile	6·4	6·1
Maleic anhydride	19·3	Maleic anhydride	11·4	10·8

source of alkyl radicals. The decomposition of the acyl peroxides with cuprous oxide and cupric acetate in acetonitrile and acetic acid, as was recently reported by other authors,[4] appears to be most suitable. The reaction is similar to the one described above. If the solvent is changed, and acetoxy rather than methoxy derivatives are formed. The main reaction products have the following general structures:

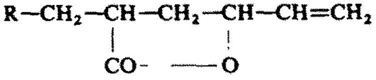


$$\underset{\displaystyle CH{=}CH_2}{R{-}CH_2{-}CHX{-}CH_2{-}\underset{|}{C}H(OCOOCH_3)}$$

XV

$R{-}CH_2{-}CHX{-}CH_2{-}CH{=}CH{-}CH_2{-}OCOCH_3$

XVI



$$R{-}CH_2{-}\underset{\displaystyle CO{-}}{\underset{|}{C}H}{-}CH_2{-}\underset{\displaystyle {-}O}{\underset{|}{C}H}{-}CH{=}CH_2$$

XVII

$R{-}CH_2{-}CH(OCOCH_3){-}CH{=}CH_2$

XVIII

$R{-}CH_2{-}CH{=}CH{-}CH_2{-}OCOCH_3$

XIX

R is the alkyl radical formed in reaction (b) and X is an electronwithdrawing group (CN, COOH, COOMe).

Acrylonitrile and butadiene reacted at different concentrations with methyl, ethyl, n-butyl, isopropyl, sec-butyl, cyclohexyl, chloromethyl, α-chloroethyl and γ-chloropropyl radicals and gave the results which are summarized in Table 4.

The results obtained with acrylonitrile, 2,3-dimethylbutadiene and n-butyl and cyclohexyl radicals are reported in Table 5. The behaviour is qualitatively the same as that observed with butadiene. Compounds XVa, XVIa, XVIIIa and XIXa are formed, which differ from the corresponding compounds obtained from butadiene only by the presence of two Me groups in the molecule of the diene. These results show clearly that 2,3-dimethylbutadiene is less reactive than butadiene. This conclusion was directly confirmed by a competitive test carried out with butadiene, 2,3-dimethylbutadiene and the cyclohexyl radical (Table 6).

There is good agreement between the experimental value (1·9) and the calculated value (1·8) obtained from the data reported in Tables 4 and 5, thus confirming the validity of the experimental method.

The results with methyl acrylate, butadiene and n-butyl and cyclohexyl radicals are reported in Table 7.

The data found using acrylic acid, butadiene and n-butyl radical are reported in Table 8. The actual relative reactivities are slightly higher, since an acid product, with the probable structure XVI (X = COOH) is formed in small amounts, although it was not quantitatively determined.

Finally the results found with methyl methacrylate, butadiene and n-propyl and n-butyl radicals are reported in Table 9. In this case the behaviour is anomalous, because in addition to the usual products (XVIb and XVIIb, which differ from the corresponding compounds obtained from methyl acrylate only by the presence of a

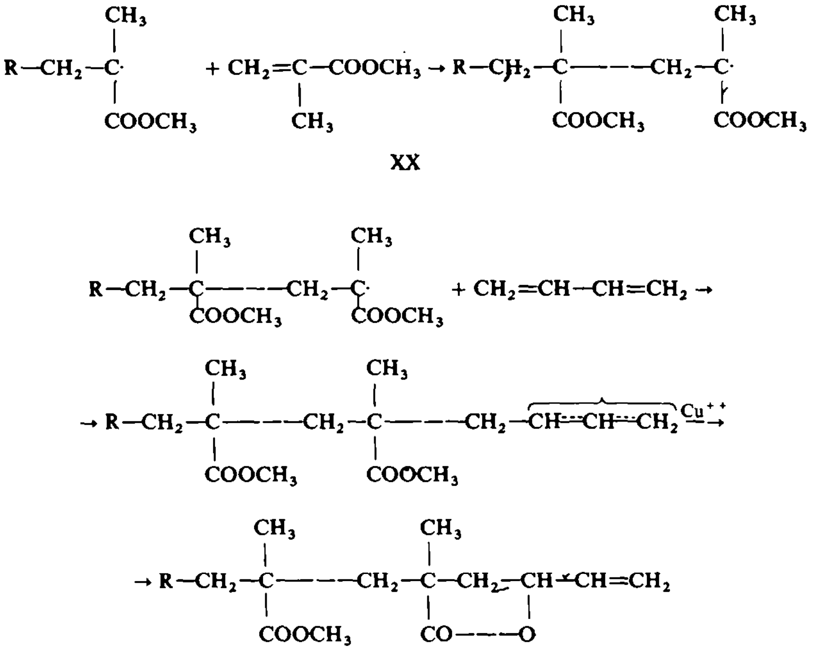
TABLE 4. RELATIVE REACTIVITIES OF ALKYL RADICALS TOWARDS ACRYLONITRILE AND BUTADIENE

Molar ratios Acrylonitrile : butadiene	Mol %				Relative reactivities
	XVIII	XIX	XV	XVI	
$ClCH_2$					
1:1	22·1	24·2	24·6	29·1	1·2
1:3	33·5	36·7	13·4	17·4	1·3
$\cdot CH_3$					
3:1	11·7	4·9	38·5	44·9	1·8
1:3	46·1	18·7	18·9	16·3	1·7
$CH_3—\dot{C}HCl$					
1:1	14·8	21·2	26·6	37·4	1·8
1:3	31·2	33·0	16·8	19·0	1·7
$ClCH_2—CH_2—\dot{C}H_2$					
1:1	13·2	8·1	30·5	48·2	3·7
1:3	35·5	19·3	18·8	26·4	2·5
$CH_3—\dot{C}H_2$					
1:1	8·4	5·6	32·5	53·5	6·2
1:3	18·8	13·8	27·8	39·6	6·2
$CH_3—CH_2—CH_2—\dot{C}H_2$					
3:1	2·1	1·4	30·6	65·9	9·1
1:3	15·0	10·3	27·1	47·6	8·8
C_6H_{11}					
3:1	2·3	1·4	38·6	57·7	8·9
1:1	4·9	4·6	35·2	55·3	9·5
1:3	13·6	10·4	33·4	42·6	9·5
$CH_3—\dot{C}H—CH_3$					
1:1	3·5	4·7	32·6	59·2	11·0
1:3	7·3	12·4	30·8	49·5	12·1
$CH_3—CH_2—\dot{C}H—CH_3$					
1:1	2·4	3·7	34·4	59·5	15·1
1:3	4·2	11·2	29·0	55·6	16·5

TABLE 5. RELATIVE REACTIVITIES OF N-BUTYL AND CYCLOHEXYL RADICALS TOWARDS ACRYLONITRILE AND 2,3-DIMETHYLBUTADIENE

Molar ratios Acrylonitrile : 2,3-dimethylbutadiene	Mol %				Relative reactivities
	XVIIIa	XIXa	XVa	XVIa	
$n\text{-}C_4H_9$					
1:1	3·5	2·7	74·8	19·0	14·9
1:3	10·2	7·8	69·5	12·5	13·6
C_6H_{11}					
1:1	1·5	3·6	69·0	25·9	17·8

Me group in the position α to the methoxy-carbonyl), the compound XXI is also formed according to the following sequence:



$$R-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\cdot + CH_2=\underset{CH_3}{C}-COOCH_3 \rightarrow R-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\cdot$$

XX

$$R-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}\cdot + CH_2=CH-CH=CH_2 \rightarrow$$

$$\rightarrow R-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\overbrace{CH \cdots CH \cdots CH_2}^{\cdot} \xrightarrow{Cu^{++}}$$

$$\rightarrow R-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2-\overset{CH_3}{\underset{CO-}{C}}-CH_2-\underset{-O}{CH}-CH=CH_2$$

XXI

All these results substantially confirm the theoretical suppositions on which these new syntheses have been based. The nucleophilic character of the alkyl radicals is a very important factor in determining the observed sequence of reactivities. In fact the resonance energy of α-cyano and α-carboxyalkyl radicals, produced by the addition of alkyl radicals to acrylic acid, ester, or nitrile, cannot be as high as that of the allyl radicals formed from conjugated dienes. The nucleophilic character of the alkyl radicals and the consequent selectivity towards olefins with opposite polar character increases according to the sequence: $\dot{C}H_2Cl < CH_3\dot{C}HCl < \dot{C}H_3 < ClCH_2-CH_2-\dot{C}H_2 < C_2H_5^{\cdot} < n-C_4H_9^{\cdot} < C_6H_{11}^{\cdot} < iso\text{-}C_3H_7^{\cdot} < sec\text{-}C_4H_9^{\cdot}$.

In agreement with the polar character of the groups bonded to the radical carbon, the secondary alkyl radicals are more nucleophilic and more selective than the primary ones or the Me radical; the introduction of a Cl atom into the alkyl radical reduces this nucleophilic character.

The difference in the reactivity between the n-butyl and ethyl radicals and the isopropyl and sec-butyl radicals is quite surprising. A very small difference of selectivity could be expected in these cases on the grounds of the different electronreleasing capacities between the Me and n-Pr groups and between the Me and Et groups. However the same sequence of selectivity was observed also in the homolytic alkylation of protonated heteroaromatic bases with the same radicals,[5] confirming the large influence of the nucleophilic character of the alkyl radicals on the addition to unsaturated systems.

TABLE 6. RELATIVE REACTIVITIES OF CYCLOHEXYL RADICAL TOWARDS BUTADIENE AND 2,3-DIMETHYLBUTADIENE

Molar ratios Butadiene: 2,3-dimethylbutadiene	Mol %				Relative reactivities
	XVIII	XIX	XVIIIa	XIXa	
3:1	27·8	57·9	12·3	2·0	2·0
1:1	21·0	42·7	31·5	4·8	1·8

Relative reactivity: experimental (average value), 1·9; calculated from Tables 4 and 5, 1·9.

TABLE 7. RELATIVE REACTIVITIES OF N-BUTYL AND CYCLOHEXYL RADICALS TOWARDS METHYL ACRYLATE AND BUTADIENE

Molar ratios Methyl acrylate : butadiene	Mol %				Relative reactivities
	XVIII	XIX	XV–XVI	XVII	
		n-C_4H_9			
3:1	4·4	3·5	37·4	54·7	3·8
1:3	26·6	21·1	23·2	29·1	3·3
		C_6H_{11}			
3:1	3·3	3·6	14·2	78·9	4·6
1:1	7·7	9·4	8·4	74·5	4·9

TABLE 8. RELATIVE REACTIVITIES OF N-BUTYL RADICAL TOWARDS ACRYLIC ACID AND BUTADIENE

Molar ratios Acrylic acid : butadiene	Mol %			Relative reactivities
	XVIII	XIX	XVII	
3:1	3·9	3·1	93·0	4·3
1:1	8·3	8·3	83·4	4·9
1:3	19·5	19·8	60·7	4·6

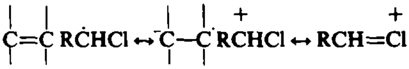
TABLE 9. RELATIVE REACTIVITIES OF N-BUTYL AND N-PROPYL RADICALS TOWARDS METHYL METHACRYLATE AND BUTADIENE

Molar ratios Methyl methacrylate : butadiene	Mol %					Relative reactivities
	XVIII	XIX	XVIb	XVIIb	XXI	
		n-C_3H_7				
3:1	4·6	4·4	10·5	51·5	29·0	3·2
1:1	20·5	11·4	4·9	60·0	3·2	2·2
		n-C_4H_9				
3:1	6·0	6·0	7·3	62·0	18·7	2·4
1:3	33·1	27·1	1·7	35·3	2·8	2·0

It is interesting to note that α and γ-chloroalkyl radicals react in the normal way, whereas the presumed β-chloroalkyl radicals formed from β-chloropropionyl and β-chlorobutyryl peroxides do not appreciably react with the conjugated olefins under the same experimental conditions. This could indicate that a Cl atom in the β position causes a particular instability in the alkyl radicals, probably due to a β scission:

$$\mathrm{R{-}CHCl{-}CH_2^{\cdot} \rightarrow R{-}CH{=}CH_2 + Cl\cdot}$$

The α-chloroalkyl radicals and the α-cyano and carboxyalkyl radicals behave in entirely different ways; the latter two add exclusively to the same conjugated diene, whereas the former adds to the butadiene and acrylonitrile at a comparable rate. This result indicates that a Cl atom in the α position could cause, in the addition of the alkyl radical to the double bond (effects well known in the ionic reactions), an inductive electronwithdrawing effect which would be partially balanced by a conjugated electronreleasing effect with a contribution to the transition state of the following polar forms:



$$\overset{|}{\underset{|}{\mathrm{C}}}{=}\overset{|}{\underset{|}{\mathrm{C}}}\ \mathrm{R\dot{C}HCl} \leftrightarrow {}^{-}\overset{|}{\underset{|}{\mathrm{C}}}{-}\overset{|}{\underset{|}{\mathrm{C}}}{}^{\cdot}\,\mathrm{R\overset{+}{C}HCl} \leftrightarrow \mathrm{RCH{=}\overset{+}{Cl}}$$

The results with 2,3-dimethylbutadiene further confirm the nucleophilic character of the alkyl radicals. Since, in our opinion, the steric effects do not affect the reactivity in the addition of n-butyl and cyclohexyl radicals to butadiene and 2,3-dimethylbutadiene, a higher reactivity of 2,3-dimethylbutadiene would be expected because of the resonance stabilization of the intermediate allyl radical. An opposite sequence of reactivities occurs, i.e. butadiene is more reactive than 2,3-dimethylbutadiene towards n-butyl and cyclohexyl radicals. This means that the electronreleasing effect of the Me groups in 2,3-dimethylbutadiene, increasing the electron availability of the diene, not only balances the positive effect that the presence of the Me groups causes on the resonance stabilization of the intermediate allyl radical, but also reduces the reactivity of the 2,3-dimethylbutadiene. Also in this case, therefore, the polar character of the n-butyl and cyclohexyl radicals prevails over the resonance stabilization in determining the reactivity sequence.

A similar argument explains the lower reactivity of methyl methacrylate towards n-butyl and n-propyl radicals compared to that of methyl acrylate. Furthermore this is the only case among those investigated, in which the alternating addition to the monomer couples is not completely selective. The radical XX does not attack butadiene exclusively, as occurs with all the other analogous radicals investigated, but to some extent also adds on to the methyl methacrylate forming the compound XXI.

The lack of selectivity of the radical XX can also be correlated with its polar character. The Me group reduces the electrophilic character of the radical (XX) in comparison with the corresponding radical obtained from methyl acrylate and, moreover, the electron availability is higher in methyl methacrylate than in methyl acrylate. Both these polar factors contribute to the increase in the reactivity of the radical (XX) towards methyl methacrylate when compared to the reactivity of the radical III (X = COOMe) towards methyl acrylate. In addition, the radical III (X = COOMe), because of its higher electrophilic character, is more reactive than the radical XX towards butadiene. In the addition of the radical XX steric factors should effect the reactivity of butadiene and methyl methacrylate to the same extent and there should not be, therefore, a discriminating factor between these two olefins. It follows that the radical III adds exclusively to butadiene, whereas the addition of the radical XX to butadiene is competitive with the addition to methyl methacrylate.

The comparison of the results obtained with acrylic acid, methyl acrylate, n-butyl and 5-(methoxycarbonyl)pentyl radical shows a discrepancy. The n-butyl radical seems to be more reactive towards the acid than the ester, which is in contrast to the 5-(methoxycarbonyl)pentyl radical. This behaviour could be due to either the different experimental conditions (with the radical I the reaction is carried out in the presence of sulfuric acid, different metal salts and solvents) or due to the greater analytical problems found in the quantitative determination of the reaction products formed with acrylic acid; in this case in fact, besides the neutral products (lactones XI and XVIII), small amounts of acid products are formed and the quantitative analysis results are slightly doubtful. These discrepancies were also found in the comparison of the results obtained with α-methylstyrene and butadiene (Table 3); only in the case of acrylic acid is there poor agreement between the experimental and calculated values. However it is certain that both radicals, n-butyl and 5-(methoxycarbonyl)-pentyl, although under different experimental conditions, are more reactive towards acrylic acid than butadiene since the values for the acrylic acid reported in Tables 1 and 7 are slightly lower than the actual values.

EXPERIMENTAL

Reaction of cyclohexanone peroxide

General procedure. The procedure is the same as was described previously for α-methylstyrene.[1] All the reaction products were isolated by preparative GLC and the purified samples were used for checking the quantitative GLC determinations. The ratios of the pairs of olefins in each experiment are reported in Tables 1 and 2; in all cases the ratio between H_2O_2 and the olefins was 1/8. No polymers or telomers were formed. The yields of the crude products based on the H_2O_2 used were in the range of 60–85%.

Quantitative GLC. Instrument: Perkin–Elmer model 880 with a flame ionization detector and a 2 ft × $\frac{1}{8}$ in i.d. column, packed with silanized Gas-Chrom. P and 1% SE-30. 80–100 mesh. Carrier gas: N_2 at a flow rate of 20 ml/min. Temperature range programmed from 100° to 200° (increase of 4–10°/min).

Preparative GLC. Instrument: Aerograph A 750 with a flame ionization detector and a 5 ft × $\frac{1}{4}$ in i.d. column, packed with Chrom. P and 20% SE-30. 60–80 mesh. Carrier gas: N_2 at a flow rate 150 ml/min. Temperature: isotherm between 140° and 200°.

Products VII *and* VIII. These compounds were prepared by an experiment in which the only olefin was butadiene. The products, isolated by preparative GLC, were identified as VII and VIII by comparison (IR, NMR and MS) with known compounds.[3]

Reaction with acrylonitrile. The compounds IX and X (X = CN) were isolated by preparative GLC. They have the same elementary composition (IX, Found: C, 67·1; H, 9·4; N, 5·2. X, Found: C, 67·3; H, 9·2; N, 5·3. $C_{15}H_{25}NO_3$ requires: C, 67·4; H, 9·4; N, 5·2). MS X: m/e (%): 267 (0·1), 236 (4·5), 204 (15), 183 (4), 151 (19), 85 (87), 71 (100), 55 (50), 41 (42). The scarse molecular ion (267) loses Me (236) and MeOH (285). Loss of MeOH occurs from the 236 ion producing an 204 ion. Significant fragments are: 183 (NC—$(CH_2)_7$—COOMe), 151 (183—MeOH), 85 (CH_2—CH=CH—CH_2—OMe), 71 (CH_2—CH=CHOMe) due to a previous shift of the double bond position, 55 which is derived from 85 by a loss of CH_2O as proved by the appropriate metastable ion, and 41 derived from 71 by an analogous process. MS IX *m/e* (%): 267 (0·1), 236 (0·8), 235 (0·4), 204 (6), 183 (5), 151 (1·7), 85 (3), 55 (7·5), 51 (13). This differs structurally from X since IX does not yield much 85 fragment. NMR IX: MeO (s at 3·25 δ), MeOOC (s at 3·65 δ), 3 vinyl protons at 5·20–5·70 δ. NMR X: MeO (s at 3·25 δ), MeOOC (s at 3·65 δ), 2 vinyl protons centred at 5·63 δ. IR IX: 2250 cm^{-1} (CN), 1750 cm^{-1} (CO), 990 and 930 cm^{-1} (CH=CH_2). IR X: 2250 cm^{-1} (CN), 1750 cm^{-1} (CO), 975 cm^{-1} (CH=CH *trans*).

Reaction with acrylic acid. The compound XI was isolated by distillation (b.p. 172–173/0·5 mm, 98% at

GLC) and by preparative GLC. (Found: C, 66·0; H, 8·7. $C_{14}H_{22}O_4$ requires: C, 66·1; H, 8·7%; MS *m/e* (%): 223 (18), 22 (11), 112 (100), 74 (42), 59 (29). The molecular ion is missing and the fragments 223 (M—OCH_3), 222 (M—MeOH), 74 (the McLafferty rearrangement ion on the Me ester CO group) and 59 ($MeOCO^+$) are typical of Me esters. An abundant and significant ion is 112 due to the loss of $CH_2{=}CH{-}(CH_2)_4{-}COOMe$ as a result of a McLafferty rearrangement on the lactone CO group.

IR: 1780 cm^{-1} (CO lactone), 1750 cm^{-1} (CO ester), 990 and 930 cm^{-1} ($CH{=}CH_2$). Saponification of XI with NaOH in MeOH produces the corresponding carboxilic acid, m.p. 96–97. (Found: C, 64·9; H, 8·3. $C_{13}H_{20}O_4$ requires: C, 65·0; H, 8·4%); MS: fragmentation is very similar to that of XI. The highest mass fragment is 22 (M—H_2O). The abundant and significant ion 112 has the same structure as the corresponding fragment of XI.

Reaction with methyl acrylate. The compounds IX, X (X = COOMe) and XI were isolated by preparative GLC. XI was identified by comparison with product obtained with acrylic acid. IX and X have the same elementary composition (IX Found: C, 64·1; H, 9·1. X Found: C, 63·8; H, 9·3. $C_{16}H_{28}O_5$ requires: C, 64·0; H, 9·3%); MS of IX and X are very similar: molecular ion (300) and significant fragments are 268 (M—MeOH), 85 ($CH{-}CH{=}CH{-}CH_2OMe$) more abundant in X and 71 ($CH_2{-}CH{=}CHOMe$) more abundant in IX. IR: IX 990 and 930 cm^{-1} ($CH{=}CH_2$). X 975 cm^{-1} (CH=CH *trans*).

Reaction with maleic anhydride. The compounds XII and XIII, isolated by preparative GLC, were identified by elementary analysis, MS, IR, and NMR. (XII Found: C, 60·2; H, 8·4. XIII Found: C, 60·1; H, 8·5. $C_{18}H_{30}O_7$ requires: C, 60·3; H, 8·4%); MS of XII and XIII: The molecular ion is missing, but significant fragments are 326 (M—MeOH), 294 (326 —MeOH), 71 ($CH_2{-}CH{=}CHOMe$), 59 (MeOCO). IR: XII 990 and 930 cm^{-1} ($CH{=}CH_2$).

XIII 975 cm^{-1} (CH=CH *trans*). NMR: XII MeO (3H, s at 3·2 δ), MeOCO (9H, s at 3·6 δ), vinyl protons (3H at 5·2–5·7 δ). XIII MeO (3H, s at 3·2 δ), MeOCO (9H, s at 3·6 δ), vinyl protons (2H centred at 5·5 δ).

Reaction of acyl peroxides with olefins

General procedure. The acyl peroxide (0·04 moles) was added at 0° with stirring and N_2 flushing to a mixture of cuprous oxide (5·7 g), cupric acetate (8 g) and the two olefins (0·32 mol; the ratios used are reported in Tables 4–9). The mixture was stirred for an additional 50 min at 0°, then poured into water the aqueous soln was extracted with ether. The ethereal extract was washed with $NaHCO_3$ aq and dried over Na_2SO_4. After removal of the solvent and excess olefin, the residue was analysed directly by GLC. Yields of the products of the alternating addition (XV, XVI, XVII), based on the acyl peroxide, were in the range of 40–80%. This was dependent on the ratios of the two reacting olefins, the reactivity of the alkyl radical and the reactivity of the olefin conjugated to the electronwithdrawing groups (the highest yield, 80%, was obtained with acrylonitrile and sec-butyl radical). All the compounds were isolated by preparative GLC and the pure samples were identified and also used to check the response of the GLC in the quantitative determinations. The analyses were carried out as described for cyclohexanone peroxide but using the following programmed temp:

Alkyl radical	Olefins	Range of temp	Rate of temp increase
CH_3	acrylonitrile, butadiene	90–200°	10°/min
C_2H_5	acrylonitrile, butadiene	65–150°	8°/min
iso-C_3H_7	acrylonitrile, butadiene	100–130°	7°/min
n-C_4H_9	acrylonitrile, butadiene	100–130°	7°/min
sec-C_4H_9	acrylonitrile, butadiene	100–130°	7°/min
C_6H_{11}	acrylonitrile, butadiene	130–210°	6°/min
CH_2Cl	acrylonitrile, butadiene	100–195°	6°/min
CH_3CHCl	acrylonitrile, butadiene	100–210°	6°/min
$Cl(CH_2)_3$	acrylonitrile, butadiene	110–195°	6°/min
n-C_4H_9	methyl acrylate, butadiene	90–170°	7°/min
C_6H_{11}	methyl acrylate, butadiene	130–210°	6°/min
n-C_3H_7	methyl methacrylate, butadiene	100–180°	7°/min
n-C_4H_9	methyl methacrylate, butadiene	100–190°	7°/min
n-C_4H_9	acrylonitrile, 2,3-dimethylbutadiene	90–180°	7°/min
C_6H_{11}	acrylonitrile, 2,3-dimethylbutadiene	140–200°	6°/min
C_6H_{11}	Butadiene, 2,3-dimethylbutadiene	105–200°	6°/min

Products. XVII, XIX, XIIIa and XIXa, in which R = CH_3, C_2H_5, n-C_3H_7, sec-C_3H_7, n-C_4H_9, sec-C_4H_9, C_6H_{11}, CH_2Cl, CH_3CHCl, $ClCH_2—CH_2—CH_2$. These compounds were prepared by experiments in which the only olefin used was butadiene or 2,3-dimethylbutadiene. XVIII and XIX, when R is n-C_4H_9, were identified as 3-acetoxyoctene-1 and 1-acetoxyoctene-2 trans by comparison (IR, NMR, MS) with the known compounds.[6] All the other compounds, which differ only by the nature of their R group, were readily identified by MS and IR. Mass spectra revealed in every sample the molecular ion M and significant fragments M—MeCO and M—MeCOOH. IR analysis distinguishes between the isomers XVIII and XIX; in the compounds with the structure XVIII bands are present at 930 and 990 cm^{-1} ($CH=CH_2$); in compounds having the structure XIX there is a band at 975 cm^{-1} (CH=CH *trans*). The IR of XVIIIa differs from that of XIXa by a band at 895 cm^{-1} ($C=CH_2$).

Reaction with acrylonitrile and butadiene (Table 4). XV and XVI, in which X = CN and R = CH_3, C_2H_5, sec-C_3H_7, n-C_4H_9, sec-C_4H_9, C_6H_{11}, CH_2Cl, CH_3CHCl, $ClCH_2—CH_2—CH_2$. A complete analysis was carried out only for R = n-C_4H_9. (XV Found: C, 69·9; H, 9·3; N, 6·3. XVI Found: C, 69·8; H, 9·4; N, 6·3. $C_{13}H_{21}NO_2$ requires: C, 70·0; H, 9·4; N, 6·3%); MS XV: The molecular ion is missing, but significant fragments are 180 (M—MeCO), 164 (M—MeCOOH), 99 ($CH_2—CH=CHOCOMe$) and 124 (M—99). MS XVI: Main fragments 180 (M—MeCO), 164 (M—MeCOOH) and 113 ($CH_2—CH=CH—CH_2—OCOMe$). NMR XV: MeCOO (s at 2·0 δ), 3 vinyl protons in the range 5–5·8 δ. NMR XVI: MeCOO (s at 1·97 δ) and 2 vinyl protons centred at 5·70 δ. IR XV: 2250 cm^{-1} (CN), 1740 cm^{-1} (CO), 990 and 930 cm^{-1} ($CH=CH_2$). IR XV: 2250 cm^{-1} (CN), 1740 cm^{-1} (CO), 975 cm^{-1} (CH=CH *trans*).

All the other compounds corresponding to the structure XV and XVI were readily identified by IR and MS. The spectra are very similar to those found for XV (R = n-C_4H_9) and XVI (R = C_4H_9), which are described above.

Reaction with acrylonitrile and 2,3-dimethylbutadiene (Table 5). XVa and XVIa, in which X = CN and R = C_4H_9, C_6H_{11}. For R = n-C_4H_9: (XVa Found: C, 71·6; H, 10·2; N, 5·5. XVIa Found: C, 71·7; H, 9·8; N, 5·6. $C_{15}H_{25}NO_2$ requires: C, 71·8; H, 10·0; N, 5·6%). The two isomers can be easily distinguished by NMR, since XVIa has no vinyl protons. The IR spectra of XVa has the typical band at 895 cm^{-1} ($C=CH_2$). MS of both isomers shows the molecular ion 251 and the fragments 208 (M—MeCO) and 191 (M—MeCOOH). The corresponding compounds in which R = C_6H_{11} were identified by IR and MS, and the spectra are quite similar to those described for R = n-C_4H_9.

Reaction with acrylic acid and butadiene (Table 8). XVII, in which R = n-C_4H_9. (Found: C, 72·4; H, 9·9. $C_{11}H_{18}O_2$ requires: C, 72·5; H, 9·9%). IR: 1780 cm^{-1} (CO lactone), 930 and 990 cm^{-1} ($CH=CH_2$). MS: molecular ion 182; and the abundant and significant fragment is 112, due to the loss of pentene-1 as a result of a McLafferty rearrangement of the lactone CO group.

Reaction with methyl acrylate and butadiene (Table 7). XV, XVI and XVII, in which X = COOMe and R = n-C_4H_9 and C_6H_{11}. A complete analysis was carried out for the molecule where R = n-C_4H_9. (XV Found: C, 65·5; H, 9·4. XVI Found: C, 65·7; H, 9·4. $C_{14}H_{24}O_4$ requires: C, 65·7; H, 9·4). MS of XV and XVI reveal significant fragments 213 (M—MeCO), 196 (M—MeCOOH), 153 (M—MeCO), 113 ($CH_2—CH=CH—C_2—OCOMe$), 99 ($CH_2—CH=CHOCOMe$). IR: XV 1740 cm^{-1} (CO), 990 and 930 cm^{-1} ($CH=CH_2$). XVI 1740 cm^{-1} (CO), 975 cm^{-1} (CH=CH *trans*). XVII was identified by comparison with the product obtained from acrylic acid. The products obtained from the cyclohexyl radical were identified by IR and MS.

Reaction with methyl methacrylate and butadiene (Table 9). XVIb, XVIIb and XXI, in which X = COOMe and R = n-C_3H_7 and n-C_4H_9. For R = n-C_3H_7: XVIb (Found: C, 65·4; H, 9·5. $C_{14}H_{24}O_4$ requires: C, 65·7; H, 9·4%). IR: 1740 cm^{-1} (CO ester), 975 cm^{-1} (CH=CH *trans*). MS: significant fragments 213 (M—MeCO), 196 (M—MeCOOH), 153 (196-MeCO), 113 ($CH_2—CH=CH—CH_2OMe$). XVIIb (Found: C, 72·7; H, 9·8. $C_{11}H_{18}O_2$ requires: C, 72·5; H, 9·9%). IR: 1770 cm^{-1} (CO lactone), 990 and 930 cm^{-1} ($CH=CH_2$). MS: Molecular ion (182) and an abundant and significant ion 126, due to the loss of butene-1 as a result of a McLafferty rearrangement on the lactone CO group are observed. XXI (Found: C, 68·0; 9·2. $C_{16}H_{26}O_4$ requires: C, 68·1; H, 9·2%). IR: 1730 cm^{-1} (CO ester), 1770 cm^{-1} (CO lactone), 990 and 930 cm^{-1} ($CH=CH_2$). MS: Molecular ion 282; the significant and abundant fragment is 126 which has the same structure as the corresponding fragment of XVIIb. NMR: MeOCO (3H, s at 3·65 δ), 3 vinyl protons at 5–6 δ, 1 allyl proton centred at 4·8 δ and 19 protons at 0·8–2·5 δ. The corresponding compounds with R = n-C_4H_9 were readily identified by comparison of the IR, NMR and MS.

REFERENCES

[1] F. Minisci, M. Cecere, R. Galli and R. Bernardi, *Tetrahedron* **25**, 2667 (1969)

[2] F. Minisci, R. Galli, M. Cecere, V. Malatesta and T. Caronna, *Tetrahedron Letters* 5609 (1968); F. Minisci, R. Galli, V. Malatesta and T. Caronna, *Tetrahedron* **26**, 4083 (1970).

[3] J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.* **84**, 3946 (1962); F. Minisci and R. Galli, *Chim. Industria* **45**, 448 (1963)

[4] J. K. Kochi, A. Bemis and C. L. Jenkins, *J. Am. Chem. Soc.* **90**, 416 (1968)

[5] Unpublished results from these laboratories

[6] J. K. Kochi and H. E. Mains, *J. Org. Chem.* **30**, 1862 (1965)