Experimental Section

All reagents were commercial materials and redistilled before use.

Determination of the Rate of Decomposition of *t*-Butyl Peroxide in Solvents.—A master solution of a solvent and *t*-butyl peroxide (TBP) was carefully weighed out in a 5:1 molar ratio. About 1.5 ml of this solution was delivered to each of eight tubes prepared by sealing one end of a 27-cm length of 9-mm-o.d. Pyrex tube. The tubes were then sealed and immersed in an oil bath maintained at the required temperature ±0.03°. Tubes were removed from the bath at appropriate time intervals and immediately quenched in cold tap water. The time intervals were adjusted so that the final tube in a run was taken from the bath near the end of the first half-life of the peroxide.

Each of the samples was analyzed for its *t*-butyl peroxide content by the following gas chromatographic method. The solution from the tube was poured into a tared 2-dram vial and weighed. An amount of a suitable internal standard was added, and the vial was weighed again. This mixture was subjected to gas chromatographic analysis (F & M Model 700) to obtain the peak areas of peroxide and internal standard. Three gas chromatographic column systems were used: (1) a commercial 4-ft, 10% silicone rubber column (F & M Scientific Corp.) operating at a column temperature of 55° using chlorobenzene as the internal standard; (2) several 15-ft columns packed with 15–17% E-600 (Dow Chemical Co.) on Chromosorb W operating at a column temperature of 65° using ethyl acetate as the internal standard; and (3) a 12-ft column, packed with didecyl phthalate on Chromosorb W operating at a column temperature of 70° using 2-pentanone as the internal standard. Exit port flow rates were adjusted to 60 ml/min in each case. The last system was found to be the best from the standpoint of speed and reproducibility.

The amount of *t*-butyl peroxide remaining was calculated by

$$\text{mmol of peroxide/g of soln} = \frac{K \times \text{wt of I.S.} \times \text{peak area of peroxide} \times 1000}{\text{mol wt of peroxide} \times \text{sample wt} \times \text{peak area of I.S.}}$$

where K, the correction factor relating peak areas of peroxide to internal standard (I.S.), is obtained by chromatographing a known mixture of peroxide and internal standard.

Millimoles of peroxide remaining after the various time intervals were used to calculate the reaction rate constant shown in Table I.

Determination of Heats of Solution.—The equipment used for determining the heats of solution was an apparatus described by Tyson, McCurdy, and Bricker[14] for performing differential thermometric titrations. The design of this apparatus is similar in most respects to that described by Arnett, *et al.*[15] differing somewhat only in the calorimeter setup. The procedure employed for obtaining the heats of solution is essentially that described in detail by Arnett, *et al.* It consisted of first calibrating a chart recorder to an input of heat into the calorimeter containing to solvent. When calibrated, a small, but accurately measured, amount of *t*-butyl peroxide is introduced into the rapidly stirred solvent by means of 100-μl Hamilton syringe fitted with a Cheney adapter. The heat change in the mixture resulting from solution of the peroxide was recorded on the chart recorder, and the heat of solution is calculated from this recorded heat and the amount of peroxide added. These heats of solution are partial molal heats of solution at infinite dilution. Normally three injections of peroxide were made, and in no case did a definite trend in the magnitude of the measured values indicate that the solutions were no longer "infinitely dilute." The heats of solution determined by this method are given in Table III.

Registry No.—*t*-Butyl peroxide, 110-05-4.

Acknowledgment.—We wish to acknowledge the National Institutes of Health for support of part of this work. We also wish to express our gratitude to Professor C. E. Bricker for use of equipment for determining the heats of solution and to Dr. Harriet Benson for invaluable assistance in the calculations of the rate constants and activation parameters.

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[14] B. C. Tyson, W. H. McCurdy, Jr., and C. E. Bricker, *Anal. Chem.*, **33**, 1640 (1961).

[15] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

Reactions of Ester Free Radicals. The 2-Carbomethoxy-2-propyl Radical

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The reactions of the 2-carbomethoxy-2-propyl radical (VI) were investigated *via* the dehydrodimerization of methyl isobutyrate and the decomposition of dimethyl 2,2′-azobisisobutyrate. Products from both reactions were identified, and mechanistic pathways were formulated. In the dehydrodimerization process, efficiencies were found to decrease with increasing peroxide concentration. This was attributed to enhanced interaction of VI with the *t*-butoxy radical and subsequent telomerization. It was determined that coupling and disproportionation of 2-carbomethoxy-2-propyl radical proceeded with little difference in activation energies. Over the range 90–165°, $E_C - E_D = 0.21$ kcal mol^{-1}. The site of radical attack on a series of aliphatic esters was determined by the corresponding free-radical additions to norbornene.

The site of free-radical attack on carboxylic esters poses an interesting question of directive effects. Walling and Mintz[1] have recently shown that aliphatic esters are notably inert to attack by *t*-butoxy radicals. This they ascribed to the electron-withdrawing effect of the carboxy group and, in turn, the lowering of electron density of adjacent carbon–hydrogen bonds. This and related polar effects argue for strong polar contributions to the transition state of hydrogen abstraction.[1,2] Earlier workers[3] interpreted such effects as being partly electrostatic in nature, with an actual repulsion exerted between the incoming radical and the electronegative ester group.

Opposing this unfavorable polar effect is a counterbalancing resonance effect. The driving force for the formation of a carbonyl-adjacent radical is a resonance stabilization of the order of 4 kcal mol^{-1}.[4] Experimentally it has been shown that attack by methyl radicals occurs at a carbon–hydrogen bond adjacent to

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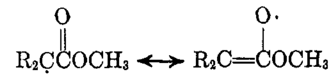
[1] C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967).

[2] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 356–369.

[3] H. C. McBay, O. Tucker, and A. Milligan, *J. Org. Chem.*, **19**, 1003 (1954).

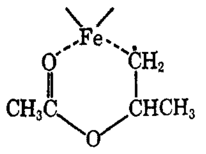
[4] S. W. Benson, K. W. Egger, and D. M. Golden, *J. Amer. Chem. Soc.*, **87**, 468 (1965).



$$R_2\overset{O}{\overset{\|}{C}}OCH_3 \longleftrightarrow R_2C{=}\overset{O\cdot}{\overset{|}{C}}OCH_3$$

the carbonyl group. Thus, methyl and ethyl isobutyrate,[5] methyl stearate,[6] dimethyl succinate,[7] dimethyl malonate,[3] methyl acetoacetate,[7] methyl phenylacetate,[8] methyl α-chloroacetate,[9] and methyl α-fluoroacetate[9] all gave rise to the α,α′-coupled dehydro dimers.

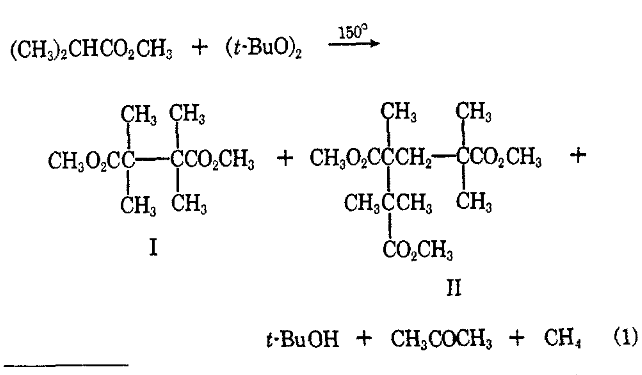
As the alcohol portion of the esters is lengthened and branching is increased, however, it becomes a competing site for radical attack. In vinyl acetate polymerization, chain transfer increased sharply (1:10:30) as the solvent was varied from methyl acetate to ethyl acetate to isopropyl acetate.[10] Autoxidation of alkyl acetates was also found to proceed, at least in part, by radical attack at the alcohol portion of the ester.[10] Similarly, oxidation with Fenton's reagent has been reported[8] to occur at the alcohol portion of acetates when the alcohol chain was at least two carbon atoms long. The major product from isopropyl acetate oxidation was the diacetate of hexane-2,5-diol,[8] apparently derived from an iron-stabilized radical intermediate.



As a probe into the synthetic response of ester free radicals, a systematic study of their reactions was undertaken. The results of this work are presented below.

Results

Dehydrodimerization.—In this study the 2-carbomethoxy-2-propyl radical was chosen as a model. It was generated under dehydrodimerization conditions by the treatment of methyl isobutyrate with di-*t*-butyl peroxide[11] at 150°. The resulting major products were identified as the dehydro dimer (I) and the dehydro trimer (II). The structure of I, previously reported by other workers,[5,12] was independently verified by spectral analyses and by transformation to tetramethylsuccinic anhydride (Experimental Section). The structure of II was elucidated by the following spectral analysis.



$$(CH_3)_2CHCO_2CH_3 + (t\text{-}BuO)_2 \xrightarrow{150^\circ}$$

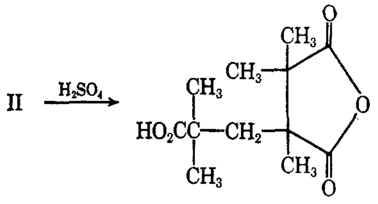
$$CH_3O_2C\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}CO_2CH_3 + CH_3O_2C\overset{CH_3}{\underset{CH_3\underset{CO_2CH_3}{C}CH_3}{C}}CH_2-\overset{CH_3}{\underset{CH_3}{C}}CO_2CH_3 +$$

I II

$$t\text{-}BuOH + CH_3COCH_3 + CH_4 \quad (1)$$

The nmr spectrum of II exhibited five sharp singlets (τ 9.01, 8.98, 8.86, 8.82, and 8.78) arising from five nonequivalent methyl groups. The AB pairs (centers at τ 7.90 and 7.50, J = 14 cps) arose from the magnetically nonequivalent methylene protons.[13,14] The low-field position of these resonances can be attributed to the diamagnetic anisotropic effects resulting from the proximity of the three ester carbonyl groups to the methylene protons.[15] Examination of molecular models indicates that one of the favored conformations places all three ester carbonyls close to the methylene protons. In chloroform-*d* the nine methoxy protons appeared as a single peak (τ 6.31). This peak resolved into two resonances (τ 6.33 and 6.31, 1:2 ratio) when pyridine was employed as the solvent.

Treatment of II with concentrated sulfuric acid and subsequent hydrolysis afforded III (infrared ν_{max} 1846 and 1777 cm^{-1}, 1702 cm^{-1}). The nmr spectrum of III showed five nonequivalent methyl groups (τ 8.78, 8.76, 8.74, 8.71, and 8.68), a methylene resonance (τ 8.03), and a hydroxyl proton (τ 2.64).



(2)

III

When *t*-butyl hydroperoxide was employed as the radical source, methyl 2-hydroxyisobutyrate (IV) was formed, in addition to I and II. Under both thermal (150°) and photolytic (2537 Å) conditions, IV became a significant coproduct (14–34% yield).[16]

The yield of I was found to vary as a function of peroxide concentration. As the initial *t*-butyl peroxide concentration was increased from 0.5 to 10 mol %, the yield of I diminished correspondingly. This effect, shown graphically in Figure 1, was also observed for II, but to a lesser degree. Increasing the peroxide concentration also resulted in an enhancement of telomeric residue. At 20 mol % of *t*-butyl peroxide, the nonvolatile telomer comprised 20 wt % of the products. An identical telomer composition (2.25 methyl methacrylate–methyl isobutyrate) was obtained independently from the controlled telomerization of methyl isobutyrate and methyl methacrylate.

Dimethyl 2,2′-Azobis(isobutyrate).—The 2-carbomethoxy-2-propyl radical was independently generated from the thermolysis of dimethyl 2,2′-azobis(iso-

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[5] G. A. Razuvaov and L. S. Boguslovskaya, *Zh. Obshch. Khim.*, **31**, 3440 (1961); *Chem. Abstr.*, **57**, 3284*d* (1962).

[6] S. A. Harrison, L. E. Peterson, and D. H. Wheeler, *J. Chem. Soc.*, 349 (1955).

[7] M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Org. Chem.*, **10**, 394 (1945).

[8] G. A. Razuvaov and L. S. Boguslovskaya, *Bul. Inst. Politeh Iasi*, **8**, 141 (1962); *Chem. Abstr.*, **60**, 7901*f* (1964).

[9] M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Org. Chem.*, **10**, 386 (1945).

[10] M. Lazar, J. Pavlinec, and Z. Movasek, *Collect. Czech. Chem. Commun.*, **26**, 1380 (1961); *Chem. Abstr.*, **55**, 2419*e* (1961).

[11] Sulfur, Fenton's reagent, oxygen, and *t*-butyl hydroperoxide in combination with various transition metal ions were found to be ineffective dehydrodimerization reactants.

[12] A. F. Bickel and W. A. Waters, *Rec. Trav. Chim.*, **69**, 312 (1950).

[13] F. Kaplan and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 4666 (1961).

[14] G. M. Whitesides, J. J. Brocki, D. Holtz, H. Steinberg, and J. D. Roberts, *ibid.*, **87**, 1058 (1965).

[15] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, pp 123–125.

[16] D. J. Trecker and R. S. Foote, *Chem. Commun.*, 841 (1967).

TABLE I

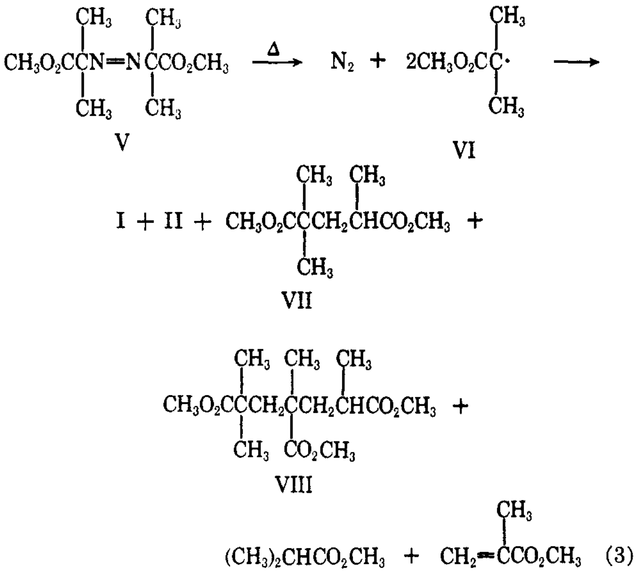
PRODUCTS FROM DECOMPOSITION OF METHYL 2,2'-AZOBIS(ISOBUTYRATE)[a]

Run	Solvent	Temp, °C	Time, hr	Dimer I[b]	Dimer VII[b]	Trimer II[b]	Trimer VIII[b]	MIB[b,c]	MMA[b,d]	IV
1	Chlorobenzene	102	2.0	45.2	2.9	16.4	3.4	32.8	0.4	...
2	Chlorobenzene	76	5.5	34.6	1.9	12.4	4.9	34.4	...	...
3	Chlorobenzene	60	52	35.2	2.4	5.2	0.9	26.0	1.4	...
4	Chlorobenzene[e]	90	4.0	11.4	...	...	...	6.3	6.2	...
5	*t*-BuOOH[f]	79	5.5	40.8	3.1	7.7	3.9	31.8	1.0	5.3
6	(*t*-BuO)$_2$[g]	81	5.5	40.3	1.7	12.8	5.7	28.1	0.4	...

[a] Concentration of V was 0.1 *M* throughout. [b] Yields are based on reacted V. [c] Methyl isobutyrate. [d] Methyl methacrylate. [e] Decomposed in the presence of a twofold molar excess of galvinoxyl. [f] Molar ratio of *t*-BuOOH/V was 2.1. [g] Molar ratio of (*t*-BuO)$_2$/V was 1:1.

butyrate).[12,17] The products obtained are shown in Chart I. The yields of the products, obtained under a variety of experimental conditions, are compiled in Table I.

CHART I



$$CH_3O_2CC(CH_3)_2N{=}NC(CH_3)_2CO_2CH_3 \ (\text{V}) \xrightarrow{\Delta} N_2 + 2CH_3O_2CC(CH_3)_2\cdot \ (\text{VI}) \longrightarrow$$

$$\text{I} + \text{II} + CH_3O_2CC(CH_3)_2CH_2CH(CH_3)CO_2CH_3 \ (\text{VII}) +$$

$$CH_3O_2CC(CH_3)_2CH_2C(CH_3)(CO_2CH_3)CH_2CH(CH_3)CO_2CH_3 \ (\text{VIII}) +$$

$$(CH_3)_2CHCO_2CH_3 + CH_2{=}C(CH_3)CO_2CH_3 \quad (3)$$

The extent of geminate reactions of the 2-carbomethoxy-2-propyl radical in the solvent cage was estimated by decomposing V (in chlorobenzene at 90°) in the presence of excess galvinoxyl.[18] Only I, methyl isobutyrate, and methyl methacrylate were formed; the yields were 11.4, 6.3, and 6.2%, respectively, indicating the extent of cage reaction at 90° to be *ca.* 23% (see Table I).

The response of the 2-carbomethoxy-2-propyl radical to changes in temperature was probed by decomposing V in *o*-dichlorobenzene at different temperatures, allowing sufficient reaction time to ensure complete decomposition of the azo compound at each temperature. The ratio of rate constants for coupling and disproportionation was determined from the ratio of I to methyl isobutyrate (*i.e.*, $k_C/k_D \sim$ yield of I/methyl isobutyrate). The product data obtained from reaction at the various temperatures are presented in Table II. The corresponding plot of log (I/methyl isobutyrate) was a linear function of $1/T$. The difference in activation energies, $E_C - E_D$, obtained from this Arrhenius plot, was found to be only 0.21 kcal mol^{-1}.

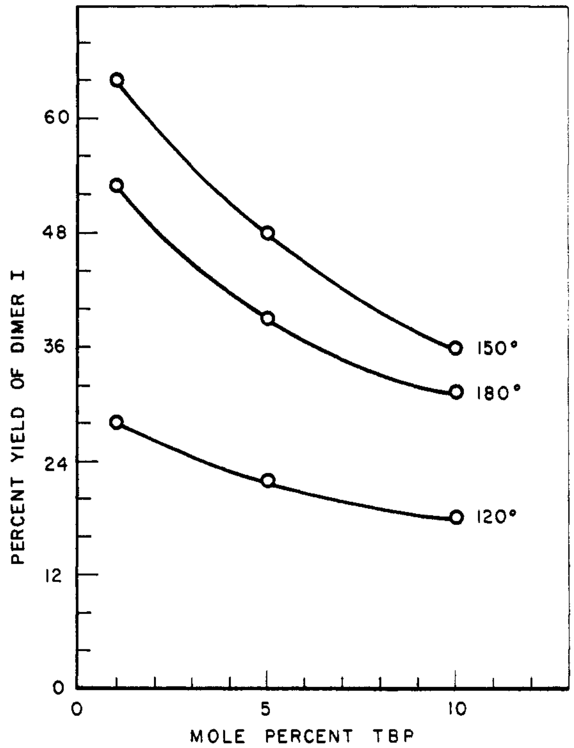


Figure 1.—The yield of I at 120, 150, and 180°, as a function of di-*t*-butyl peroxide concentration.

TABLE II

EFFECT OF TEMPERATURE ON THE RATIO OF COUPLING TO DISPROPORTIONATION[a]

Temp, °C	Yield,[b] % I	Yield,[b] % Me$_2$CHCO$_2$Me	Ratio of I/Me$_2$CHCO$_2$Me
90	48.2	30.0[c]	1.607
115	49.1	30.0[c]	1.637
140	49.8	30.0[c]	1.661
165	50.5	30.0[c]	1.686

[a] Concentration of V in *o*-dichlorobenzene was 0.65 *M* in each run. [b] Yields were based on reacted V and were normalized to 95% conversion. [c] Average yield (0.5% average deviation) was taken, owing to slight but consistent scatter in values.

To test the possibility that radical VI might be inducing the decomposition of *t*-butyl peroxide, mixtures of V and TBP were heated without solvent at 81° (Table I) and in *o*-dichlorobenzene at 150°. As indicated in Table I, the presence of peroxide had no noticeable effect on the product distribution of the reaction. Moreover, both a control thermolysis of *t*-butyl peroxide for 1 hr at 150° and a comparable reaction with added V resulted in an identical decomposition (52 ± 2%) of the peroxide.

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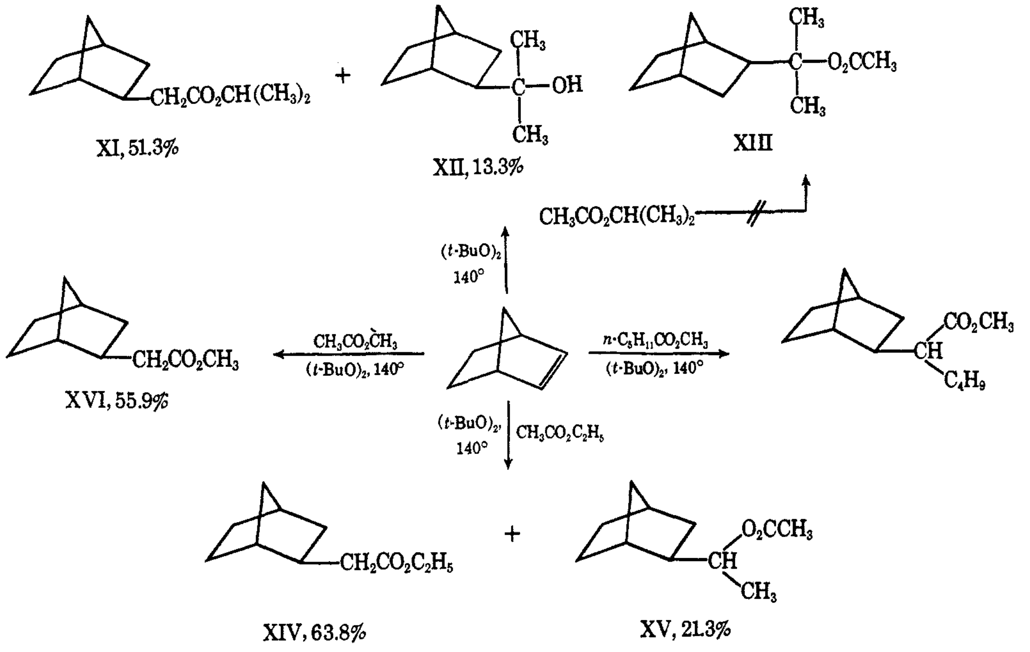
(17) J. Thiele and K. Hensen, *Ann.*, **290**, 1 (1896).

(18) P. D. Bartlett and T. Furahashi, *J. Amer. Chem. Soc.*, **84**, 2596 (1962).

Chart II



A similar series of experiments were conducted with V and *t*-butyl hydroperoxide. In addition to the normal products derived from the ester radical (Chart I), IV was formed in 5–10% yields. The reactions, carried out under deoxygenated conditions at 92°, are summarized in Table III. It should be noted that the presence of a hydrogen donor solvent enhanced the yield of IV, whereas added hydroquinone retarded its formation.

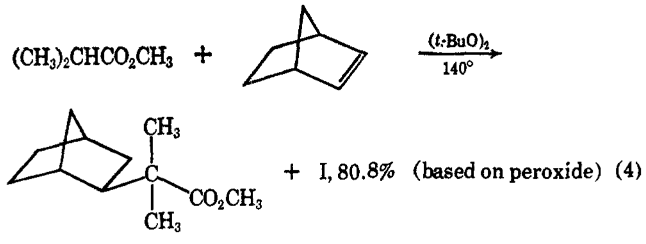
Table III

Yields of Methyl 2-Hydroxyisobutyrate from Decomposition of V[a]

		Yield of IV, %	
Solvent	Additive	Based on V	Based on reacted *t*-BuOOH
t-BuOH	None	0.0	0.0
t-BuOH	*t*-BuOOH, 1.3 *M*	4.9	49.5
Me_2CHCO_2Me	*t*-BuOOH, 1.3 *M*	10.5	. . .
Me_2CHCO_2Me	*t*-BuOOH, 1.3 *M*; HQ,[b] 0.06 *M*	0.8	8.1

[a] Concentration of V was 0.65 *M* in each instance. Reaction temperature was 92°. [b] Hydroquinone.

Addition to Olefins.—The ester radical was effectively scavenged by reaction with norbornene, a strained olefin[19] of high radical affinity.[20] The addition of methyl isobutyrate to norbornene is shown in eq 4.

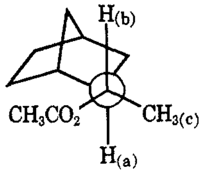


(4)

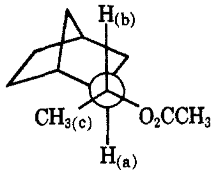
To establish the principal sites of radical attack on esters of differing chain length and branching, free-radical additions to norbornene were also conducted with methyl acetate, ethyl acetate, isopropyl acetate, and methyl hexanoate. The results are summarized in Chart II. It is significant that in every instance radical formation occurred predominantly on the carbonyl-adjacent site.

Structures of the adducts were elucidated from analytical and spectroscopic data. In the nmr spectrum of XIV, the methyl and methylene protons of the carboethoxy function appeared as the usual triplet and quartet (J = 8 cps) at τ 8.77 and 5.86. The magnetically nonequivalent[13,14] protons of the carbonyl-adjacent methylene group exhibited nearly identical chemical shifts (*ca.* τ 7.8) and were coupled to each other ($J \simeq$ 7 cps) and to the 2-*endo* proton ($J \simeq$ 6 cps). The bridgehead protons also appeared in this envelope. The spectrum of XI was quite similar to that of XIV. The heptet (J = 3 cps) at τ 5.0 and the doublet (J = 3 cps) at τ 8.80 established the presence of the isopropoxy group. The pattern and integration of the signals at τ 7.7–8.1 were identical with those in the spectrum of XIV and were assigned to the carbonyl-adjacent methylene protons and to the bridgehead protons.

The nmr spectrum of XV was of interest, since it represented another example[13,14] of the magnetic nonequivalence of protons due to molecular asymmetry. The favorable conformers of the two diasterioisomers involved[21] are shown in XVa and XVb. Duplicate methyl resonances appeared at τ 7.96 and 8.00 (carbomethoxy protons) and at 8.80 and 9.90 (H_c



XVa



XVb

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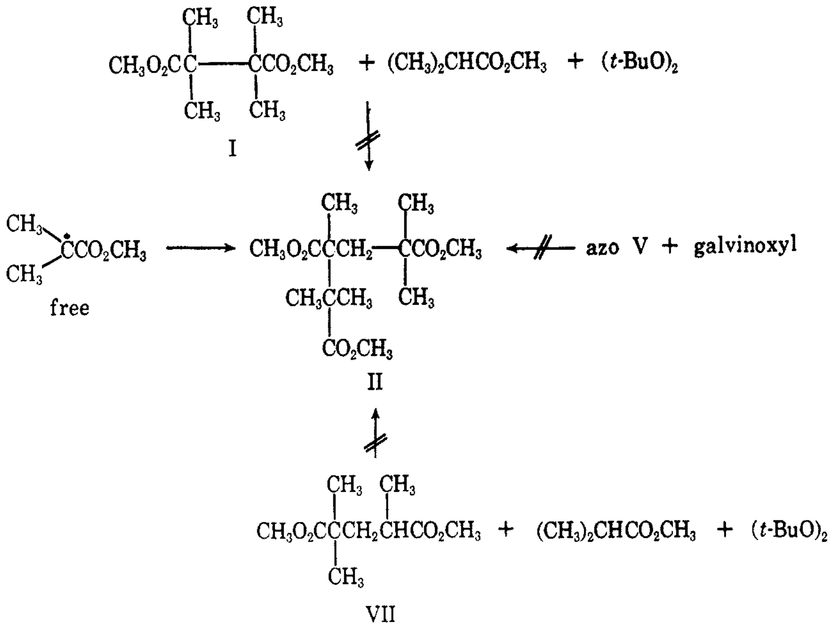
[19] R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957).

[20] J. Gresser, A. Rajbenbach, and M. Szwarc, *ibid.*, **83**, 3005 (1961).

[21] Each diasterioisomer comprises an enantiomeric pair.

CHART III



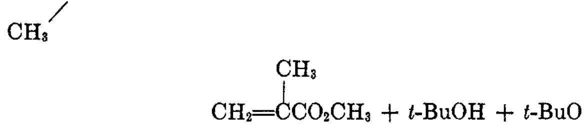
protons, J_{bc} = 6 cps). Proton b appeared as a multiplet (two ABX_3 patterns; J_{bc} = 6 cps, $J_{ab} \simeq$ 8 cps) centered at τ 5.36. The bridgehead protons appeared at τ 7.77 and 7.94. The nmr spectrum of X was quite similar to that of XV, with double carbomethoxy proton resonances (τ 6.34 and 7.38) also apparently derived from different diasterioisomers.

Discussion

The extent of cage reaction is pertinent to any discussion of "free" ester radicals formed from the decomposition of V. The galvinoxyl scavenging experiments indicate that only 23% of VI reacts as geminate pairs in the cage at 92° and that the cage reaction consists solely of coupling and disproportionation. The 23% cage participation is consistent with values reported for other azo decompositions at similar temperatures.[22,23] The fact that only coupling and disproportionation occur in the solvent cage indicates that free radical VI must be responsible for the formation of the secondary products. The possibility that trimer II might arise from secondary dehydrodimerization reactions was eliminated by the unsuccessful attempts to cross-dehydrodimerize methyl isobutyrate, VII, and I (Chart III). The best explanation for the formation of II is that VI adds to methyl methacrylate and that the resultant radical couples with a second VI moiety. The formation of VII and VIII may be rationalized in an analogous fashion. The over-all mechanistic scheme is presented in Chart IV. It should be noted that all of the secondary products are attributed to subsequent radical reactions with methyl methacrylate.

Perhaps the single most striking piece of data in the dehydrodimerization process is the inverse relationship of the yield of dimer I to peroxide concentration (Figure 1). Several possible explanations present themselves. One is that radical VI may be directly responsible for the induced decomposition of *t*-butyl peroxide. Internally induced decomposition of peroxides resulting from attack of a radical on the O–O bond of the peroxide is a well-characterized reaction.[24,25] Moreover, it has been shown that both alcohol radicals, $R_2\dot{C}\text{-}OH$,[26] and amine radicals, $R_2\dot{C}\text{-}NH\text{-}R$,[27] are effective in bringing about the induced decomposition of *t*-butyl peroxide in solution (eq 5). A similar process might be invoked in the reaction of VI with *t*-butyl peroxide (eq 6).

$$R_2\dot{C}OH + (t\text{-}BuO_2) \longrightarrow R_2CO + t\text{-}BuOH + t\text{-}BuO\cdot \quad (5)$$



$$(CH_3)_2\dot{C}CO_2CH_3 + (t\text{-}BuO)_2 \longrightarrow CH_2{=}C(CH_3)CO_2CH_3 + t\text{-}BuOH + t\text{-}BuO\cdot \quad (6)$$

The validity of eq 6 was tested by decomposing V in the presence of *t*-butyl peroxide at 81°, conditions where the average incidence of ester radicals was low, and at 150°, where the steady-state concentration of VI was high. The results, in Table I (compare runs 2 and 6), indicate no deleterious effect on the yield of I due to the presence of the peroxide. Moreover, rate measurements at 150°, *vide supra,* showed that the presence of V and/or VI did not alter either the initial rate or over-all degree of *t*-butyl peroxide decomposition. These results militate against an induced decomposition (eq 6) as the cause of diminishing yields of I.

An alternative explanation is summarized in Chart V. As indicated previously, the methyl isobutyrate–methyl methacrylate telomer content in the reaction mixture increased with increasing peroxide in much the same manner that the formation of I decreased (Figure 1). This suggests that the loss of efficiency may be attrib-

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(22) S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 143 (1966).

(23) See ref 2, p 76 ff.

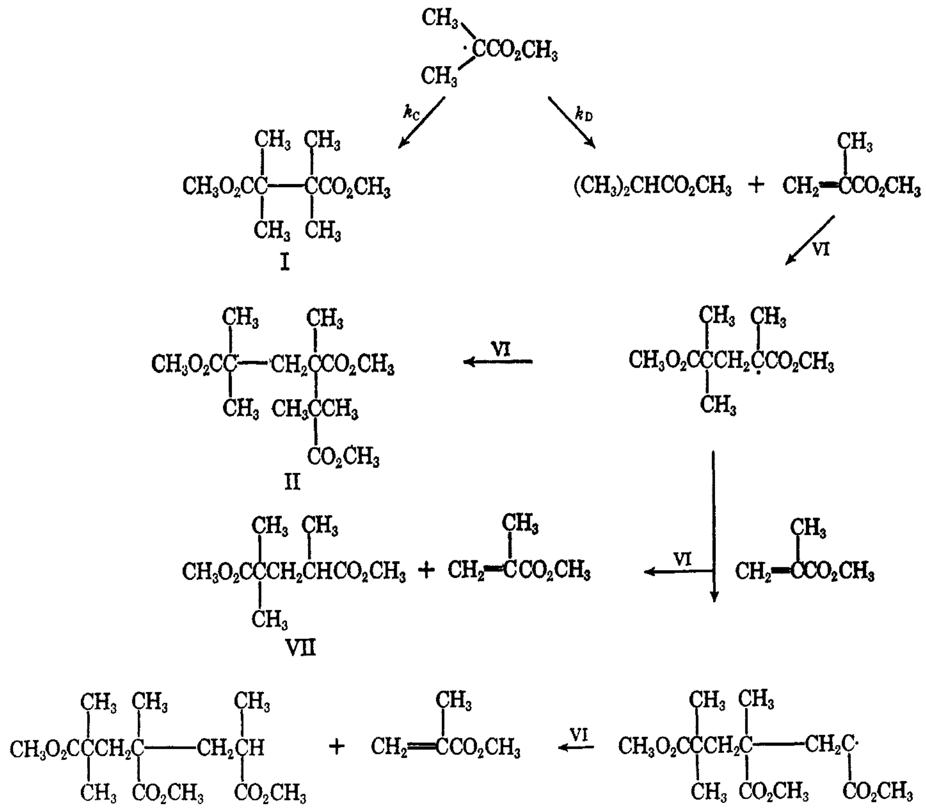
(24) E. R. Bell, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **72**, 337 (1950).

(25) L. B. Gortler and M. D. Sultzman, *J. Org. Chem.*, **31**, 3821 (1966).

(26) E. S. Huyser and C. J. Bredeweg, *J. Amer. Chem. Soc.*, **86**, 2401 (1964).

(27) E. S. Huyser, C. J. Bredeweg, and R. Van Scoy, *ibid.*, **86**, 148 (1964).

CHART IV



uted to a hydrogen exchange of VI with *t*-butoxy radicals in which methyl methacrylate is formed. In terms of kinetic differences, $k_2 > k_1$ and, at high *t*-butoxy radical concentrations, k_2 (VI) $\geqslant k_1$ (methyl isobutyrate). Conversely, at low *t*-butoxy radical concentrations, where the VI content is correspondingly low, k_1 (methyl isobutyrate) $> k_2$ (VI).

The fact that reaction 8 competes favorably with reaction 7 at high peroxide concentration is reasonable if one considers the thermochemistry involved. Reaction 7 is exothermic by about 13 kcal mol^{-1}, whereas reaction 8 is estimated to be exothermic by about 66 kcal mol^{-1} as a result of weakening of the methyl C–H bond by the β-radical site. The calculations follow.

$$\Delta H_f\,(\mathrm{H}\cdot) = 52.1\ \text{kcal mol}^{-1}\,{}^{28}$$
$$\Delta H_f\,(\cdot\mathrm{CMe_2CO_2Me}) = -67.3\ \text{kcal mol}^{-1}\,{}^{29}$$
$$-\Delta H_f\,(\mathrm{Me_2CHCO_2Me}) = 107.9\ \text{kcal mol}^{-1}\,{}^{30}$$

$$\Delta H_r\,(\mathrm{MeO_2CCMe_2{-}H}) = 92.7\ \text{kcal mol}^{-1}$$
$$\Delta H_f\,(\mathrm{H}\cdot) = 52.1\ \text{kcal mol}^{-1}\,{}^{28}$$
$$\Delta H_f\,(\mathrm{CH_2{=}CMeCO_2Me}) = -79.3\ \text{kcal mol}^{-1}\,{}^{30}$$
$$-\Delta H_f\,(\cdot\mathrm{CMe_2CO_2Me}) = 67.3\ \text{kcal mol}^{-1}\,{}^{29}$$

$$\Delta H_r\,(\mathrm{MeO_2C\dot{C}MeCH_2{-}H}) = 40.1\ \text{kcal mol}^{-1}$$

$$t\text{-BuO}\cdot + \mathrm{H}\cdot \longrightarrow t\text{-BuOH} \quad \Delta H = -106.0\ \text{kcal mol}^{-1}\,{}^{31}$$
$$\mathrm{Me_2CHCO_2Me} \longrightarrow \cdot\mathrm{CMe_2CO_2Me} + \mathrm{H}\cdot \quad \Delta H = 92.7\ \text{kcal mol}^{-1}$$

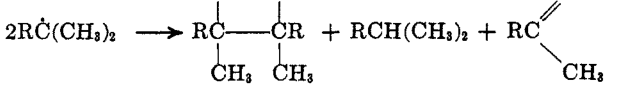
$$\mathrm{Me_2CHCO_2Me} + t\text{-BuO}\cdot \longrightarrow \cdot\mathrm{CMe_2CO_2Me} + t\text{-BuOH} \quad \Delta H = -13.3\ \text{kcal mol}^{-1}$$

$$t\text{-BuO}\cdot + \mathrm{H}\cdot \longrightarrow t\text{-BuOH} \quad \Delta H = -106.0\ \text{kcal mol}^{-1}\,{}^{31}$$
$$\cdot\mathrm{CMe_2CO_2Me} \longrightarrow \mathrm{CH_2{=}CMeCO_2Me} + \mathrm{H}\cdot \quad \Delta H = 40.1\ \text{kcal mol}^{-1}$$

$$\cdot\mathrm{CMe_2CO_2Me} + t\text{-BuO}\cdot \longrightarrow \mathrm{CH_2{=}CMeCO_2Me} + t\text{-BuOH} \quad \Delta H = -65.9\ \text{kcal mol}^{-1}$$

Although several assumptions were necessarily made to estimate these values,[29,30] the same free heat of formation of VI was used in each calculation. Therefore, while the absolute heats of reaction may be substantially in error, the difference in exothermicity of the two processes, 53 kcal mol^{-1}, should be reasonably accurate.

Still another probe of the reactivity of the ester radical concerns its relative propensity for coupling as opposed to disproportionation. Inspection of Table II indicates that coupling is favored by a factor of about 1.6, is essentially independent of temperature, and has a slight positive activation energy. It is of interest to compare the coupling/disproportionation ratio obtained in this study with that of related $\mathrm{R\dot{C}(CH_3)_2}$ radicals. All measurements made in the liquid phase showed[32–34] that activation energies for coupling and disproportionation were essentially equal



$$2\mathrm{R\dot{C}(CH_3)_2} \longrightarrow \mathrm{RC(CH_3)_2{-}C(CH_3)_2R} + \mathrm{RCH(CH_3)_2} + \mathrm{RC(=CH_2)CH_3}$$

R = C_6H_5[32]	95	5
CO_2CH_3	61	39
CH_3[33]	18	82

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[28] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, Inc., New York, N. Y., 1960, Appendix C.

[29] Average value calculated from group contributions.[30]

[30] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Hangen, H. E. O'Neal A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, in press.

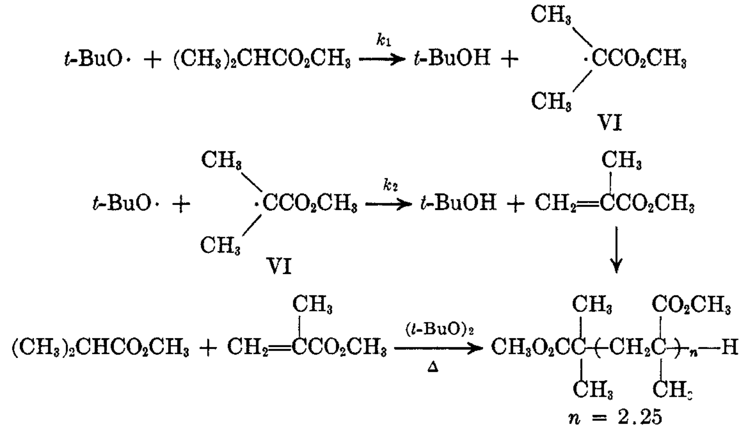
[31] C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p 136.

[32] S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966).

[33] J. Kraus and J. Calvert, *ibid.*, **79**, 5921 (1957).

[34] P. S. Dixon, A. P. Stefani, and M. Szwarc, *ibid.*, **85**, 2551 (1963).

CHART V



$$t\text{-BuO}\cdot + (CH_3)_2CHCO_2CH_3 \xrightarrow{k_1} t\text{-BuOH} + \cdot C(CH_3)_2CO_2CH_3\ (\text{VI}) \quad (7)$$

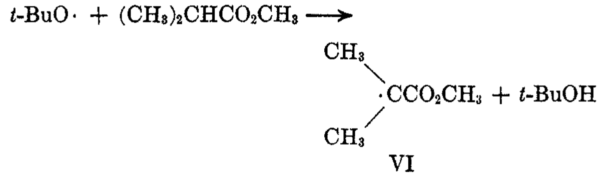
$$t\text{-BuO}\cdot + \cdot C(CH_3)_2CO_2CH_3\ (\text{VI}) \xrightarrow{k_2} t\text{-BuOH} + CH_2{=}C(CH_3)CO_2CH_3 \quad (8)$$

$$(CH_3)_2CHCO_2CH_3 + CH_2{=}C(CH_3)CO_2CH_3 \xrightarrow[\Delta]{(t\text{-BuO})_2} CH_3O_2CC(CH_3)_2\text{-}(CH_2C(CH_3)(CO_2CH_3))_n\text{-}H$$

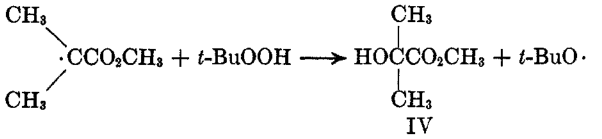
$n = 2.25$

in each case. It will be noted that there is a regular decrease in coupling as the reactivity of the radical increases. It is apparent that steric factors are not important in determining the course of the reaction.

Another point of interest is the formation of IV from reaction of VI with *t*-butyl hydroperoxide. The data in Table III are consistent with a homolytic displacement on the hydroperoxide O–O bond,[16,35] as depicted below. A similar sequence has been proposed[36,37] to account for the hydroxylation of hydrocarbons by per acids.



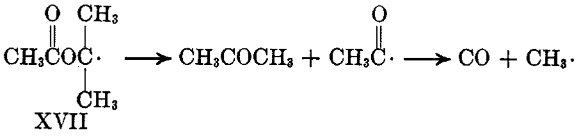
$$t\text{-BuO}\cdot + (CH_3)_2CHCO_2CH_3 \longrightarrow \cdot C(CH_3)_2CO_2CH_3\ (\text{VI}) + t\text{-BuOH} \quad (7)$$



$$\cdot C(CH_3)_2CO_2CH_3 + t\text{-BuOOH} \longrightarrow HOC(CH_3)_2CO_2CH_3\ (\text{IV}) + t\text{-BuO}\cdot \quad (9)$$

The results of the ester free-radical addition reactions merit some attention. Contrary to expectations of preference for attack on a tertiary or secondary rather than primary hydrogen and contrary to any notions of geminal oxygen stabilization, the carbonyl-adjacent site was clearly favored in all instances. In fact, only with ethyl acetate was a second product isolated. (Minor products were evident in the gas chromatograms of each reaction mixture.)

Remarkably, no XIII was isolated from the reaction of isopropyl acetate with norbornene.[38] No explanation is immediately apparent. Steric factors were no more severe than in the methyl isobutyrate addition. Some pyrolytic destruction of XIII may have occurred, but this could account for only a small percentage of the addition products. The best explanation is that radical XVII, if formed, readily underwent β scission at the elevated reaction temperatures. Regardless of the fate of XVII, adduct XI, resulting from abstraction of a primary, carbonyl-adjacent hydrogen, constituted over 50% of the theoretical yield. Hence, it appears that an unexpected degree of stabilization[4] is gained by interaction of the odd electron with the carbonyl group of the ester.



$$CH_3C(=O)OC(CH_3)_2\cdot\ (\text{XVII}) \longrightarrow CH_3COCH_3 + CH_3\dot{C}{=}O \longrightarrow CO + CH_3\cdot \quad (10)$$

Experimental Section

Dehydrodimerization of Methyl Isobutyrate.—In a typical run, methyl isobutyrate (1020 g, 10.0 mol) and di-*t*-butyl peroxide (146 g, 1.0 mol) were placed in a stainless steel, 3-l., rocking autoclave. The system was purged with nitrogen and heated at 140° for 11 hr. Fractionation on a 24-in. spinning-band column yielded I in several fractions (bp 69–70° at 4.0 mm) and II (bp 104° at 0.025 mm), as clear oils.

Several fractions of I crystallized upon standing and were washed with cold hexane, filtered, and dried. The resulting crystals had mp 32–33°; ir $\nu_{C=O}$ 1727 cm^{-1}; nmr τ 8.77 (singlet, CH_3, 12 H) and 6.31 (singlet, OCH_3, 6 H).

Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.36; H, 9.03.

A solution of I (5.0 g, 2.48×10^{-2} mol), sodium hydroxide (1.1 g, 2.73×10^{-2} mol), water (30 ml), and methanol (40 ml) was stirred under reflux for 118 hr. Acidification with hydrochloric acid and evaporation afforded a white solid, which was subsequently washed with water and hexane. The tetramethylsuccinic anhydride thus obtained had mp 180° (sealed tube; lit.[39] 180–182°); nmr τ 8.73 (singlet).

Anal. Calcd for $C_8H_{14}O_4$: C, 55.15; H, 8.10. Found: C, 54.89; H, 8.09.

Vpc analysis of II showed it to be of >95% purity (ir $\nu_{C=O}$ 1728 cm^{-1}).

Anal. Calcd for $C_{15}H_{26}O_6$: C, 59.58; H, 8.67. Found: C, 59.60; H, 8.71.

Treatment of II (10 g) with concentrated sulfuric acid (30 ml) and subsequent hydrolysis afforded a white solid. After several recrystallizations from hexane–acetone, the material (III) melted at 174–175°.

Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.47; H, 7.32.

Dehydrodimerization of methyl isobutyrate with 20 ml % of di-*t*-butyl peroxide gave rise to a clear, viscous residue (20 wt % yield), in addition to I and II. This material (mol wt 335; ir $\nu_{C=O}$ 1722 cm^{-1}) was equivalent to a 2.25:1 methyl methacrylate–methyl isobutyrate telomer prepared by treatment of methyl isobutyrate (1020 g, 10.0 mol) with methyl meth-

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(35) C. F. Cullis, A. Fisk, A. Saeed, and D. L. Trimm, *Proc. Roy. Soc.* (London), **A289**, 402 (1966).

(36) D. L. Heywood, B. Phillips, and H. A. Stansbury, Jr., *J. Org. Chem.*, **26**, 281 (1961).

(37) D. Lefort, C. Paquot, and J. Sorba, *Bull. Soc. Chim. Fr.*, 1385 (1959); D. Lefort and J. Sorba, *ibid.*, 2373 (1961); T. M. Luong and D. Lefort, *ibid.*, 827 (1962).

(38) Product XII may have resulted either from the *in situ* hydrolysis of XIII, which seems unlikely, or from the free-radical addition of isopropyl alcohol, present as an impurity in isopropyl acetate. The latter explanation is preferred.

(39) L. Eberson, *Acta Chem. Scand.*, **13**, 40 (1959).

TABLE IV

ANALYTICAL AND YIELD DATA FOR ESTER–NORBORNENE ADDUCTS

	Adducts				Calcd, %		Found,[a] %	
Ester	Compd	Yield, %	Bp, °C (mm)	$\nu_{C=O}$, cm^{-1}	C	H	C	H
Methyl isobutyrate	IX	54.6	84 (1.2)	1726	73.43	10.27	73.61	10.32
Methyl hexanoate	X	69.4	70 (0.02)	1728	74.94	10.78	74.85	11.13
Isopropyl acetate	XI	51.3	54 (0.15)	1736	73.43	10.27	73.43	10.34
Ethyl acetate	XIV	63.8	62 (8.5)	1736	72.49	9.95	72.55	10.03
	XV[b]	21.3	114 (9.5)	1734	72.49	9.95	72.52	9.95
Methyl acetate	XVI	55.9	114 (10)	1734	71.39	9.59	71.50	9.65

[a] The correct molecular weight was obtained by mass spectroscopy for each compound. [b] Analytical sample was collected by preparative-scale vpc (20-ft SE-30 column, 150°).

acrylate (10 g, 0.1 mol) in the presence of di-*t*-butyl peroxide (1.5 g, 0.01 mol) at 135° for 6 hr.

Anal. Calcd for $C_{16.25}H_{28}O_{6.5}$: C, 59.59; H, 8.58; mol wt, 329. Found: C, 59.91; H, 8.69; mol wt, 328.

Treatment of methyl isobutyrate with *t*-butyl hydroperoxide under both thermal (150°, 16 hr) and photochemical (2537 Å, 77 hr) conditions afforded, in addition to I and II, compound IV (14–34% yield). Compound IV was isolated by distillation (bp 69° at 30 mm): ir ν_{OH} 3250 cm^{-1}, $\nu_{C=O}$ 1728 cm^{-1}; nmr τ 8.60 (singlet, CH_3, 6 H), 6.24 (singlet, OCH_3, 3 H), and 5.64 (singlet, OH, 1 H).

Anal. Calcd for $C_5H_{10}O_3$: C, 50.83; H, 8.53; mol wt, 118. Found: C, 50.55; H, 8.41; mol wt, 118.

Quantitative studies of methyl isobutyrate dehydrodimerization were conducted at different temperatures and different di-*t*-butyl peroxide concentrations. The reactions were carried out in small, sealed Pyrex tubes which were placed in an autoclave, covered with methyl isobutyrate, and heated to the appropriate temperatures. The analysis was accomplished by vpc. The products determined, internal standards employed, and vpc conditions were as follows: I and II, *exo,trans,exo*-pentacyclo-[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradecane,[40] 10-ft 5% Carbowax 20M on Chromosorb G, 190°; di-*t*-butyl peroxide, chlorobenzene, 12-ft didecyl phthalate on Fluoropak 80, 80°; IV, cumene, 10-ft 10% Ucon 50HB2000 on Chromosorb W, 95°. The results are shown graphically in Figure 1.

Decomposition of V.—Products obtained from the thermal decomposition of V (Table I) were determined by vpc analysis. I, II, IV, VII, VIII, and di-*t*-butyl peroxide were analyzed as described above. Methyl isobutyrate and methyl methacrylate were analyzed on a 10-ft 10% Ucon 50HB2000 on Chromosorb W column at 95°, employing toluene as the internal standard. Unreacted V was determined by uv spectroscopy [λ_{max} 362 mμ (ϵ_{max} 18.5), Beers law followed in chlorobenzene]. The yields reported in Table I were based on reacted V.

VII was isolated from a synthesis run by fractional distillation: bp 29° (0.02 mm); ir $\nu_{C=O}$ 1726 cm^{-1}; nmr τ 8.87 (doublet J = 7 cps, CO-adjacent CH_3, 3 H), 8.85 and 8.82 (singlets, CO-adjacent *gem*-CH_3's 6 H), 8.42 (ABX quartet, J = 14 cps and J = 4 cps; CH_2, 1 H), 7.82 (AB doublet, J = 14 cps, CH_2, 1 H), 7.53 (multiplet, CO-adjacent CH, 1 H), and 6.37 (singlet, OCH_3, 6 H).

Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.41; H, 8.91. Found: C, C, 59.51; H, 8.86.

Free-Radical Additions to Norbornene.—In each run, a solution of the ester (15 mol), norbornene (14.1 g, 0.14 mol), and di-*t*-butyl peroxide (3.3 g, 2.25 × 10^{-2} mol) was placed in a stainless steel 3-l. autoclave. The autoclave was purged with nitrogen, and then rocked at 140° for 12 hr. After cooling, the contents of the autoclave were analyzed for unreacted norbornene. The unreacted ester and the peroxide decomposition products were removed under reduced pressure, leaving a residual liquid which constituted the reaction product. This material was carefully fractionated on a 24-in. spinning-band column. The product data for each ester are compiled in Table IV.

Registry No.—I, 17072-58-1; II, 17060-93-4; III, 17072-59-2; IV, 2110-78-3; V, 2589-57-3; VI, 2887-41-4; VII, 17072-61-6; IX, 17072-62-7; X, 17072-63-8; XI, 17072-64-9; XIV, 17072-65-0; XV, 17072-66-1; XVI, 4596-06-9.

Acknowledgment.—The authors are indebted to Professor A. Padwa for many helpful suggestions.

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[40] D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965).