[Contribution from the Chemical Laboratories of Morehouse College of the Atlanta University System]

A COMPARATIVE STUDY OF SOME REACTIONS OF THE METHYL AND THE ETHOXY FREE RADICALS IN A GRADED SERIES OF SOLVENTS[1]

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Received May 5, 1953

In an earlier paper (1) it has been reported that by a judicious choice of the solvent molecule subjected to attack by a free radical the relative percentages of cleavage[2] and of disproportionation experienced by an alkyl free radical or by an alkoxy free radical can be varied. When the solvent molecules in these reactions contained readily cleft hydrogen atoms the cleavage reaction predominated, while a solvent molecule with only difficultly cleft hydrogens caused these free radicals to react to a lesser extent by cleavage and to a greater extent by disproportionation. This evidence supports the theory of the existence of a so-called "energy-factor" (1) in these reactions involving free radicals.

The present paper is the preliminary report of a study the purpose of which is to determine the effect that the introduction of the carbomethoxy group[3] into a solvent molecule in positions of close proximity to the site of the cleavage attack by a free radical has upon the cleavage tendencies of the methyl and the ethoxy free radical with regard to that solvent molecule. The introduction of this group into said position has little or no effect on the percentage of cleavage exhibited by the *methyl* free radical, while the proximity of these groups to the preferred seat of attack seems to decrease the percentage of cleavage exhibited by the *ethoxy* free radical, to increase its percentage disproportionation, and in selected cases, even to reverse the seat of the cleavage attack. It is suggested that these carbomethoxy groups in the solvent molecule exert a possible repulsive effect upon the approaching free radical which repulsion is distinctly greater when this free radical is *ethoxy* than when it is *methyl*. This phenomenon involving the contribution of such repulsion to the over-all activation energy required for cleavage by a free radical at a given position in the solvent molecule has been termed the "repulsion factor" (1). In the preceding paper (1) the sol-

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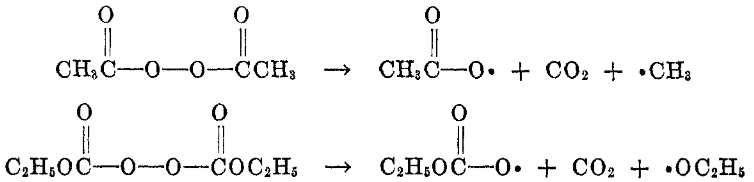
[1] This material has been presented as paper number 84 before the Organic Division of the American Chemical Society at the Spring meeting, Los Angeles, March 19, 1953.

[2] Some referees prefer the term hydrogen abstraction to cleavage. We have for this reason used this term elsewhere (1). Both of these terms apply to reactions involving the attack of the free radical (here $\cdot CH_3$ and $\cdot OC_2H_5$) upon an hydrogen-containing solvent molecule withdrawing therefrom a single hydrogen atom and imprisoning it as part of the resulting molecule (CH_4 and C_2H_5OH). This leaves behind a "residual free radical" derived from the solvent molecule. Depending on the nature of this residual free radical, the temperature, the nature of the solvent, and the nature of the parent peroxide molecule, it may react in several ways. In most of the cases here reported the residual free radical dimerizes. In other cases it has apparently disproportionated.

[3] Other groups found to exhibit a similar effect are chlorine and carboxy. Studies involving these groups will be reported in a later publication. Fluorine is suspected but it has not yet been investigated.

vent molecule and the free radical involved in each reaction were chosen with the idea in mind of keeping this "repulsion factor" at a fairly constant minimum while allowing the "energy factor" to vary throughout a series of reactions. The equations which follow represent reactions reported in the present paper. For each of these reactions the solvent molecule and the free radical have been chosen so as to attempt to keep the "energy factor" at a fairly constant minimum while allowing the "repulsion factor" to vary throughout the series.

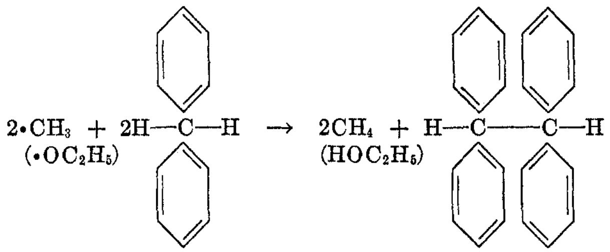
The free radicals used in this work have been generated by the thermal decomposition of the appropriate diacyl peroxide in a given solvent[4]



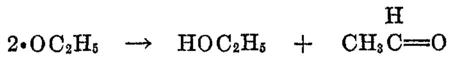
$$CH_3\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}CH_3 \rightarrow CH_3\overset{O}{\overset{\|}{C}}-O\cdot + CO_2 + \cdot CH_3$$

$$C_2H_5O\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}OC_2H_5 \rightarrow C_2H_5O\overset{O}{\overset{\|}{C}}-O\cdot + CO_2 + \cdot OC_2H_5$$

When the methyl free radical was generated in a solution of diphenylmethane 1,1,2,2-tetraphenylethane was obtained in 70% yield[5] and some higher polymers were formed.



The ethoxy free radical, $\cdot OC_2H_5$, was generated in a solution of diphenylmethane and it reacted by cleavage to the extent of 69% to produce 1,1,2,2-tetraphenylethane and ethanol. Some of these ethoxy free radicals underwent disproportionation (approximately 7%).



$$2\cdot OC_2H_5 \rightarrow HOC_2H_5 + CH_3\overset{H}{C}{=}O$$

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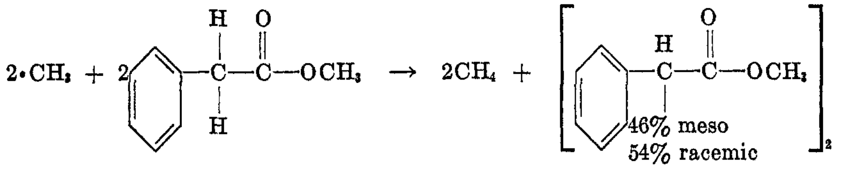
[4] For details concerning the mechanisms of these decompositions see references (1, 2, 6, 7 8).

[5] The percentage cleaved is calculated on the basis of the equation given above as follows:

$$\frac{2 \times \text{moles of dimer}}{\text{moles of methane (or } C_2H_5OH + CH_3CHO)} \times 100 = \text{percentage of the methyl (or ethoxy)}$$

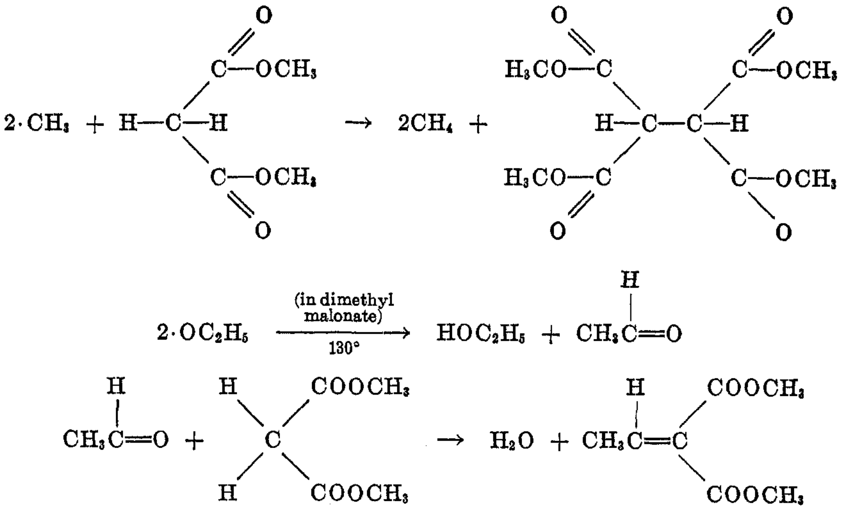
free radicals which react by cleavage to give a dimeric product. In some cases methyl (or ethoxy) radicals attack the dimer giving rise to trimers and tetramers. This occurrence in the solution reduces the apparent percentage cleavage as calculated by this equation. Hence all these data (See Tables I and II) on percentage cleavage represent at best the minimum percentage of cleavage which could possibly be occurring during each of these reactions.

When the methyl free radical is generated in a solution of methyl phenylacetate the dimer, dimethyl α,α'-diphenylsuccinate, was obtained in 68% yields (2).

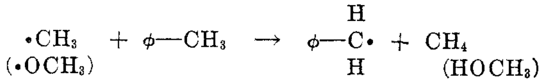


When the ethoxy free radical was generated in a solution of methyl phenylacetate the dimer (and ethanol) were obtained through cleavage and subsequent dimerization to the extent of 29%.

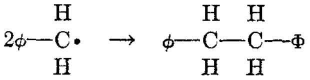
The *methyl* free radical was found to cleave an *alpha* hydrogen from dimethyl malonate to give 1,1,2,2-tetracarbomethoxyethane in 50% yields, while the *ethoxy* free radical when generated in this solvent does not cleave these doubly activated *alpha* hydrogens, but undergoes disproportionation exclusively (100%) to give ethanol and acetaldehyde. The acetaldehyde apparently condenses with some of the dimethyl malonate, for while none of the 1,1,2,2-tetracarbomethoxyethane was formed, a small quantity of ethylidine dimethyl malonate was obtained.



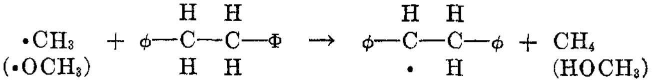
A graded series of solvents starting with the hydrocarbon 1,2-diphenylethane (bibenzyl) was also considered in this study. When the methoxy and the methyl free radicals are generated in separate experiments (3) in toluene as a solvent yields of the dimer, 1,2-diphenylethane, approaching 100% are obtained if the ratio of toluene to peroxide is large (20 to 1). At higher concentrations, however, one obtains some trimer and tetramer. This indicates that 1,2-diphenylethane succumbs to cleavage by both these free radicals even in the presence of excess toluene, and therefore that hydrogen from bibenzyl is more readily cleft than from toluene.



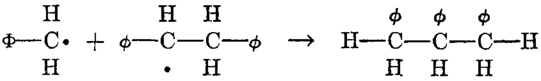
$$\underset{(\cdot OCH_3)}{\cdot CH_3} + \phi\text{—}CH_3 \rightarrow \phi\text{—}\overset{H}{\underset{H}{C}}\cdot + \underset{(HOCH_3)}{CH_4}$$



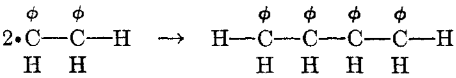
$$2\phi\text{—}\overset{H}{\underset{H}{C}}\cdot \rightarrow \phi\text{—}\overset{H}{\underset{H}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{—}\Phi$$



$$\underset{(\cdot OCH_3)}{\cdot CH_3} + \phi\text{—}\overset{H}{\underset{H}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{—}\Phi \rightarrow \phi\text{—}\overset{H}{\underset{\cdot}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{—}\phi + \underset{(HOCH_3)}{CH_4}$$



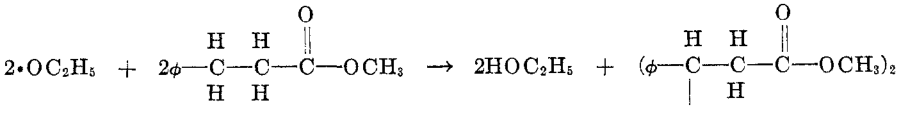
$$\Phi\text{—}\overset{H}{\underset{H}{C}}\cdot + \phi\text{—}\overset{H}{\underset{\cdot}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{—}\phi \rightarrow H\text{—}\overset{\phi}{\underset{H}{C}}\text{—}\overset{\phi}{\underset{H}{C}}\text{—}\overset{\phi}{\underset{H}{C}}\text{—}H$$



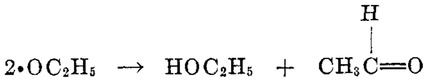
$$2\cdot\overset{\phi}{\underset{H}{C}}\text{—}\overset{\phi}{\underset{H}{C}}\text{—}H \rightarrow H\text{—}\overset{\phi}{\underset{H}{C}}\text{—}\overset{\phi}{\underset{H}{C}}\text{—}\overset{\phi}{\underset{H}{C}}\text{—}\overset{\phi}{\underset{H}{C}}\text{—}H$$

Styles (4) has generated the methyl free radical in methyl hydrocinnamaet and obtained a 17% yield of dimethyl β,γ-diphenyladipate accounting for cleavage by the methyl free radical at the *beta* position. Cleavage by the methyl free radical, however, is apparently not entirely selective in this solvent for he also reports an undetermined amount of glutarates which could conceivably be derived here only through cleavage by some of the methyl free radicals at the *alpha* position in methyl hydrocinnamate (barring rearrangement). These data of Styles are in good keeping with the already published data (2, 5) of Kharasch that both the phenyl group and the carbomethoxy group are extremely activating with respect to the hydrogen atoms attached to carbons adjacent to them.

In the course of the present study the ethoxy free radical was generated in methyl hydrocinnamate and the meso and racemic forms of dimethyl β,γ-diphenyl adipate were obtained (total yields of 27%) together with some acetaldehyde and ethanol. The fact that no glutarates and no succinates were isolated indicates that, unlike the methyl free radical (4), the ethoxy free radical attacks this solvent selectively at the position (*beta*) more remote from the carbomethoxy group.

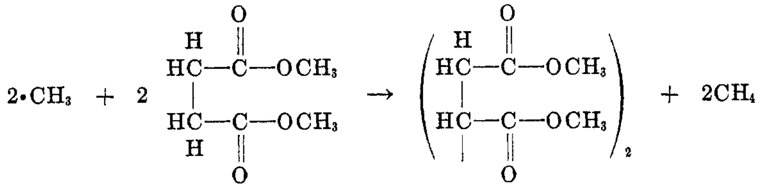


$$2\cdot OC_2H_5 + 2\phi\text{—}\overset{H}{\underset{H}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}OCH_3 \rightarrow 2HOC_2H_5 + (\phi\text{—}\overset{H}{\underset{|}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}OCH_3)_2$$



$$2\cdot OC_2H_5 \rightarrow HOC_2H_5 + CH_3\overset{H}{\overset{|}{C}}\text{=}O$$

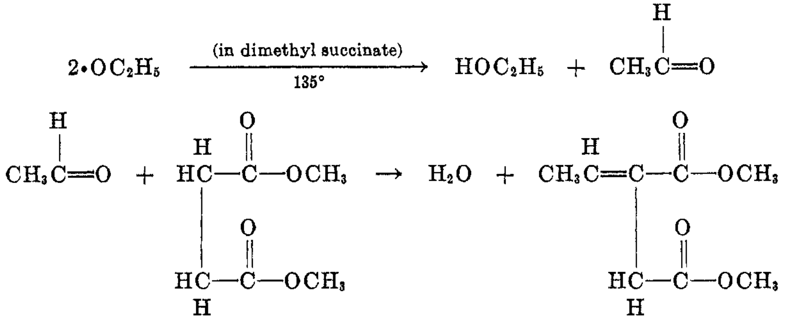
It has been demonstrated that the methyl free radical attacks dimethyl succinate by cleavage of one of its *alpha* hydrogens to give the dimer 1,2,3,4-tetracarbomethoxybutane (2) in 80% yields.



$$2\cdot CH_3 + 2\begin{array}{l}\overset{H}{HC}\text{—}\overset{\overset{O}{\|}}{C}\text{—}OCH_3\\ \;|\\ \underset{H}{HC}\text{—}\underset{\underset{O}{\|}}{C}\text{—}OCH_3\end{array} \rightarrow \left(\begin{array}{l}\overset{H}{HC}\text{—}\overset{\overset{O}{\|}}{C}\text{—}OCH_3\\ \;|\\ HC\text{—}\underset{\underset{O}{\|}}{C}\text{—}OCH_3\\ \;|\end{array}\right)_2 + 2CH_4$$

98% racemic
2% meso

The ethoxy free radical was generated in dimethyl succinate and no dimeric product was obtained. In this solvent the ethoxy free radical reacts exclusively by disproportionation. A small quantity of ethylidine dimethyl succinate was isolated.



$$2\cdot OC_2H_5 \xrightarrow[135^\circ]{\text{(in dimethyl succinate)}} HOC_2H_5 + CH_3\overset{\overset{H}{|}}{C}{=}O$$

$$CH_3\overset{\overset{H}{|}}{C}{=}O + \begin{array}{l}\overset{H}{HC}\text{—}\overset{\overset{O}{\|}}{C}\text{—}OCH_3\\ \;|\\ \underset{H}{HC}\text{—}\overset{\overset{O}{\|}}{C}\text{—}OCH_3\end{array} \rightarrow H_2O + \begin{array}{l}CH_3\overset{H}{C}{=}C\text{—}\overset{\overset{O}{\|}}{C}\text{—}OCH_3\\ \qquad\;\;|\\ \qquad\underset{H}{HC}\text{—}\overset{\overset{O}{\|}}{C}\text{—}OCH_3\end{array}$$

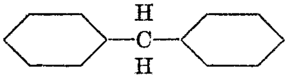
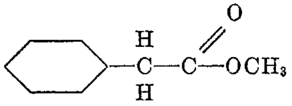
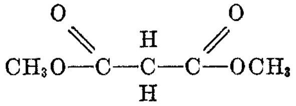
All these data appear in summarized form in Tables I and II.

The evidence presented here supports the postulate of this so-called "repulsion factor" operative in these reactions. It is here suggested that the existence of an oxygen atom in the ethoxy free radical at that end of the radical at which the odd electron predominantly resides and hence at that end of the radical primarily involved in the cleavage mechanism causes this radical to experience repulsion by the neighboring carbomethoxy groups to a greater extent than does the purely hydrocarbon alkyl free radical, the methyl free radical. The apparent reduction in the extent to which a given hydrogen atom succumbs to cleavage by an *ethoxy* free radical due to the proximity of carbomethoxy groups is more remarkable when viewed in the light of the fact that such proximity of carbomethoxy groups *increases* the extent to which the analagous hydrogen atom succumbs to cleavage by the *methyl* free radical (2).

It is well known that the carbomethoxy group has an activating effect for Claisen-type condensations on hydrogen atoms in positions adjacent to it. It is thus consistent with the proposed theory that from just those reactions in which cleavage by the ethoxy free radical is at the minimum and disproportionation leading to formation of acetaldehyde is at the maximum, presumably because of the presence of these carbomethoxy groups in the solvent molecule, the corresponding ethylidine derivative of the solvent molecule has been isolated. When

TABLE I

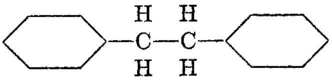
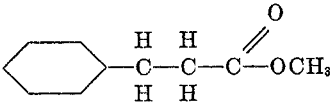
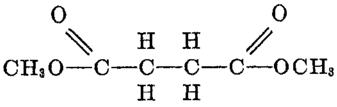
Reactions of Free Radicals with Solvents

SOLVENT	RADICAL	TEMP., °C.	CLEAVAGE, %
 I	$\cdot CH_3$ $\cdot OCH_3$ $\cdot OC_2H_5$	140 118 120	70 70 69
 II	$\cdot CH_3$[a] $\cdot OC_2H_5$	110 140	68 29
 III	$\cdot CH_3$ $\cdot OC_2H_5$	130 130	50 0

[a] Kharasch, McBay, and Urry, *J. Org. Chem.*, **10,** 394 (1945).

TABLE II

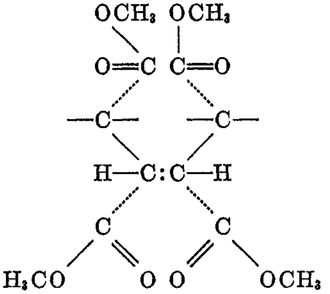
Reactions of Free Radicals with Substituted Ethanes

SOLVENT	RADICAL	TEMP., °C.	POSITION ATTACKED	CLEAVAGE, %
 IV	$\cdot CH_3$[a] $\cdot OCH_3$[a]	125 115	*Alpha* *Alpha*	>80 >80
 V	$\cdot CH_3$[b]	95	*Alpha*[d] *Beta*[d]	( ) 17
	$\cdot OC_2H_5$	125	*Alpha*[d] *Beta*[d]	0 27
 VI	$\cdot CH_3$[c] $\cdot OC_2H_5$	110 135	*Alpha* —	80 0

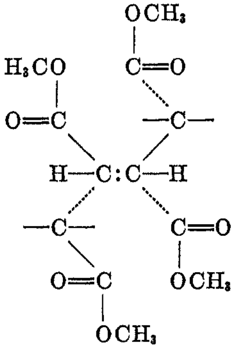
[a] 1,2-Diphenylethane is readily attacked by both methyl and methoxy free radicals since trimers and tetramers are obtained in addition to 1,2-diphenylethane when these radicals are generated in toluene. (McBay and Tucker, unpublished results.) [b] Styles, A. R., Ph.D. Thesis, University of Chicago. 1946. [c] Kharasch, *et al.*, *J. Org. Chem.*, **10,** 394 (1945). [d] *Alpha* and *beta* to the carbomethoxy group.

the ethoxy free radical was generated in each of the solvents dimethyl malonate and dimethyl succinate no products resulting from cleavage reactions of the free radical were formed. The only non-volatile product obtained from each of these reactions representing approximately 100% disproportionation of the ethoxy free radical has been the ethylidene derivative of the respective ester used as the solvent.

One case is thus far recorded in the literature involving a stereospecific course of the dimerization of these residual free radicals resulting from cleavage by methyl or ethoxy free radical. The racemic form of 1,2,3,4-tetracarbomethoxybutane is obtained in 98 to 2 mole-percentage ratio when dimethyl succinate is reacted with methyl free radicals (2).[6] The theory that there exists repulsion between these carbomethoxy groups is consistent with this fact.



Meso form
2%



Racemic form
98%

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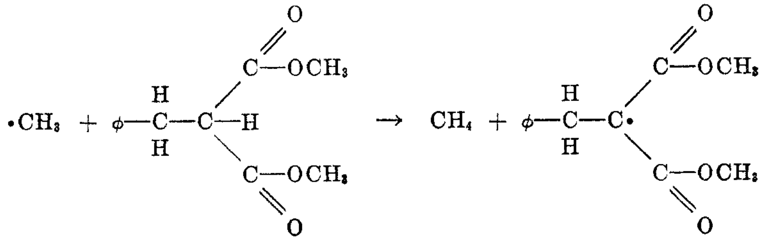
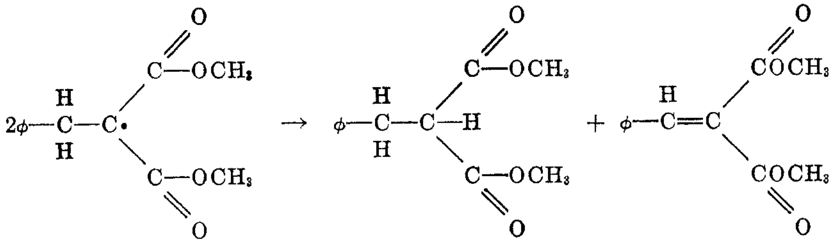
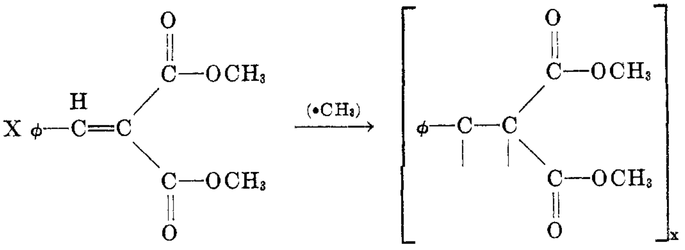
[6] One referee calls attention to the fact that Auwers and Jacobs, *Ber.*, **27**, 1114 (1894), have converted the meso and racemic forms of 1,2,3,4-butane tetracarboxylic acid one into the other by thermal means. He states that, therefore, these workers (2) have very probably obtained the usual 50% mixture of meso and racemic forms of this dimer, 1,2,3,4-tetracarbomethoxybutane; that heating during the reaction and the working-up of the products produces isomerization which gave the observed distribution of the racemic (98%) and meso (2%) forms of this tetra-ester; and that the idea of stereospecific dimerization is for this reason a mistaken interpretation. This criticism is invalid for the following reasons. Auwers and Jacobs have accomplished the quantitative conversion of the two forms of the free *tetracarboxylic acids* one into the other and not the *tetra-esters*. This was accomplished by converting them respectively first into a derived anhydride by heating the acids to their melting points in solution of dehydrating agents. The anhydrides were isolated and characterized. Apparently they are necessary intermediates in the interconversions of these stereoisomeric acids. They were then hydrolyzed in boiling aqueous HCl to give in each case the isomeric acid. This phenomenon reported by Auwers and Jacobs does not, therefore, offer a satisfactory explanation for the occurrence of the 98%–2% distribution of the racemic to meso forms which we have reported, for we have obtained the *tetra-esters* by the direct dimerization of dimethyl succinate. At no point in that work (2) have we handled the anhydrides. The temperature of those experiments (110°) is much lower than the temperatures (189 and 240°) at which Auwers and Jacobs worked. Finally, direct thermal isomerizations would for thermodynamic reasons be expected to result in an equilibrium composition with respect to these two forms which composition would result from heating either one of the two pure isomeric forms. This has not been the case in the work reported by Auwers and Jacobs, nor has it been the case in our own previous paper (2).

In order to study further the possible significance of this postulated "repulsion factor" in the cleavage process and at the same time to attempt to investigate its significance in the dimerization process, dimethyl benzylmalonate was reacted in separate experiments with methyl, methoxy, and ethoxy free radicals. The results were essentially the same when methoxy and ethoxy free radicals were used, but these results differ distinctly from those obtained with the methyl free radical. No crystalline dimeric product was obtained when methyl free radical was generated in dimethyl benzylmalonate. A glassy polymer was obtained in quantities less than can be directly accounted for on basis of the quantity of methane obtained. This polymer distilled over an extremely wide range without decomposition up to 212°/1 mm. Saponification and subsequent acidification gave no crystalline products, only gunks. This evidence together with the following data from the alkoxy studies suggest that the following reactions occurred.



VII VIIA

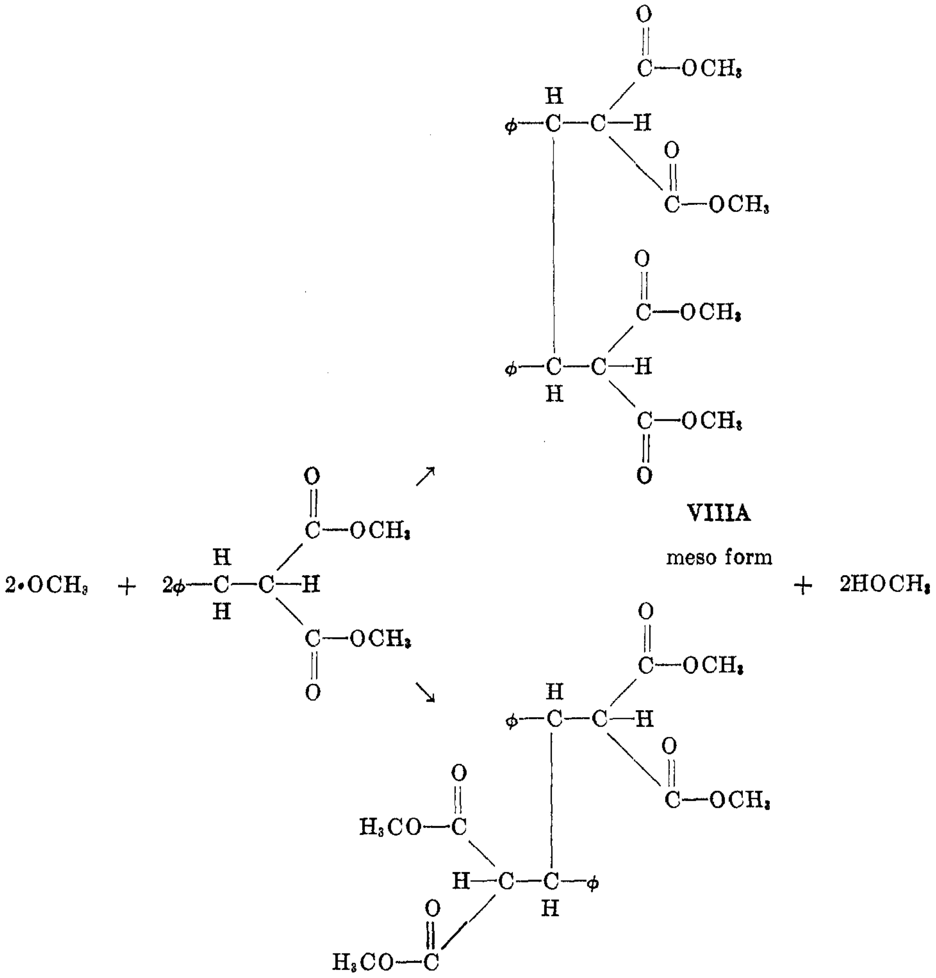




Polymer

The proposed theory of repulsion is entirely in keeping with the fact that dimerization of VIIA occurs with difficulty or not at all across the interface involving these four carbomethoxy groups. The course of the disproportionation and/or polymerization of these intermediate free radicals, VIIA, has not been elucidated.

When the methoxy free radical was generated in dimethyl benzylmalonate a 2.9% yield of a white crystalline product was obtained which has been completely characterized as the meso form of dimethyl (α,α′-dicarbomethoxy β,β′-diphenyl)adipate.



VIIIA

meso form

VIIIB

racemic form

(not identified)

The major portion of the reaction products was a glassy material which did not crystallize upon standing for a year. This product decomposed upon attempts to distill it under 0.5 to 1 mm. The crude undistilled product was saponified, acidified, and refluxed at length under which conditions decarboxylation occurred as indicated by the loss of CO_2 through the reflux condenser.

From this acidified solution upon removal of some of the water there was obtained an additional small amount (1–2 g.) of the meso form of the β,γ-diphenyladipic acid. None of the racemic form of the dimeric tetra-ester or the degraded dimeric acid has been obtained from the reaction mixture.

While these data obtained from studying reactions in dimethyl benzylmalonate are suggestive they are inconclusive.

One fact is clear, however. The polymer from the action of methyl free radical upon dimethyl benzylmalonate and this thermally unstable resin obtained from the ethoxy free radical are distinctly different. The absorption spectra of the crude materials, as well as their solubilities, in cyclohexane together with the marked difference in their stabilities under conditions of reduced pressure distillation (0.5–1.0 mm.) support this belief. It is entirely possible that this reaction of ethoxy free radical and dimethyl benzylmalonate may exhibit another example of the stereospecific dimerization of residual free radicals and that the resin (97.1% of the total reaction product) which decomposed upon attempted distillation may contain the racemic form of the dimeric product contaminated with possible trimers, etc. By using some technique (possibly chromatography) which requires no heat one might isolate the racemic form. This problem is being investigated.

EXPERIMENTAL PART

Reagents. The *diacetyl peroxide* and the *dialkylperoxydicarbonates* have been prepared, purified, and analyzed by methods previously described (1, 2).

Diphenylmethane. Eastman's white label product was refractionated through a 20-plate column, b.p. 100–101°/1 mm., n_D^{19} 1.5788.

Methyl phenylacetate was prepared from Eastman's white label phenylacetic acid by direct esterification (13). The ester was purified by fractional distillation, b.p. 67.5–68°/1 mm., n_D^{19} 1.5052.

Dimethyl malonate was prepared from Eastman Kodak Company's white label malonic acid by exhaustive esterification. The product was distilled and collected at 41°/1 mm.; 68–69°/5 mm., n_D^{17} 1.4144.

Methyl hydrocinnamate was obtained by esterifying the hydrocinnamic acid prepared from dimethyl malonate and benzyl chloride (14). Fractionation of the final ester through a 20-plate column gave a product boiling at 68–70°/1 mm., n_D^{25} 1.4995.

Dimethyl succinate was obtained through direct esterification of Eastman's white label succinic acid. This ester was fractionated and the fraction used was collected at 50–51°/1 mm., n_D^{22} 1.4188.

Dimethyl benzylmalonate was obtained from dimethyl malonate and benzyl chloride by method of Conrad and Reinbach (14), b.p. 107°/0.5 mm., $n_D^{22.5}$ 1.5003.

Decomposition of the peroxides in the various solvents. The procedure for the preparation of these peroxides, the precautions to be taken in handling them, and the techniques of decomposing them thermally in the various solvents has been fully described elsewhere (1, 2). Only the results of the respective decompositions will be given here.

The decomposition of diacetyl peroxide in diphenylmethane. A solution of diacetyl peroxide (55.9 g., 0.465 mole) dissolved in diphenylmethane (352 g., 2.09 moles) was added dropwise beneath the surface of 147 g. (0.89 mole) of diphenylmethane heated to 140°. Carbon dioxide (35 g., 0.79 mole); methane (11.4 l., S.T.P., 0.508 mole); and methyl acetate (11 g., 0.174 mole) were obtained.

The contents of the reaction vessel were distilled through a 5-inch Claisen head and 420 g. (2.50 moles) of unreacted diphenylmethane was reclaimed at 100–104°/1 mm. Remaining in the distilling flask upon cooling to room temperature was 75 g. of a slightly yellow crystalline material which gave 60.5 g. of white crystals upon trituration with boiling ethanol.

Upon recrystallization from ethanol these white crystals melted at 210–211° and failed to depress the melting point of an authentic sample of 1,1,2,2-tetraphenylethane. The alcoholic solution resulting from the trituration of this product contained 10 g. of a light brown glassy polymer.

The decomposition of dimethylperoxydicarbonate in diphenylmethane. A solution containing 0.165 mole of the peroxide, dimethylperoxydicarbonate, dissolved in 344.5 g. (2.05 moles) of diphenylmethane was introduced drop after drop beneath the surface of pure diphenylmethane (46.5 g., 0.27 mole) held at 118°. The volatile materials collected and identified in the usual manner were carbon dioxide (13.0 g., 0.29 mole) and methyl alcohol (13.0 g., 0.40 mole, b.p. 63–64°). No formaldehyde was obtained. The less volatile contents of the reaction chamber were subjected to distillation under reduced pressure and 290.5 g. (1.72 moles), of unreacted diphenylmethane was collected at 102–108°/1 mm. The residue (84.9 g.) remaining in the reaction chamber after this distillation upon cooling to room temperature deposited white crystals from a yellow oil. This mass of crystals and oil was washed from the flask with ligroin and filtered through a fritted disk whereupon 34.9 g. (0.14 mole) of white crystals were obtained. These crystals were recrystallized from large volumes of ethanol and melted at 209°. They did not depress the melting point of an authentic sample of 1,1,2,2-tetraphenylethane. From the supernatant liquor after these crystals were removed the ligroin was removed, and vacuum-distillation gave an additional 45 g. of diphenylmethane, b.p. 82–84°/0.5 mm. together with 3 g. of a higher-boiling, 128°/0.5 mm., yellow oil which was not identified.

The decomposition of diethylperoxydicarbonate in diphenylmethane. A solution containing diethylperoxydicarbonate (0.401 mole) dissolved in diphenylmethane (375.9 g., 2.23 moles) was added dropwise beneath the surface of diphenylmethane (192.3 g., 1.16 moles) heated to 120°. Collected and identified in the manner already described (1) were carbon dioxide (35.8 g., 0.80 mole), ethanol (31.3 g., 0.68 mole, b.p. 74–76°), and acetaldehyde (1.2 g., 0.027 mole). The 3,5-dinitrobenzoate derivative of the alcohol melted at 91° and failed to depress the melting point of an authentic sample of this compound. The 2,4-dinitrophenylhydrazone derivative of the aldehyde melted at 147.5° and did not depress the melting point of an authentic sample of acetaldehyde 2,4-dinitrophenylhydrazone.

The contents of the reaction vessel were distilled *in vacuo*, and unreacted diphenylmethane (468.4 g., 2.79 moles) was reclaimed at 102°/1 mm. The residue (108 g.) remaining in the distilling flask deposited white crystals from a yellow oil. By filtration through a fritted disk there was obtained 81.6 g. (0.244 mole) of crystals which upon recrystallization from large volumes of ethanol melted at 208–209°. These crystals did not depress the melting point of an authentic sample of 1,1,2,2-tetraphenylethane (Lit m.p. 211°). The supernatant oil (26 g.) which had deposited these crystals was very probably the ester, ethyl diphenylmethylcarbonate (see reference 1). It decomposed when attempts were made to distill it *in vacuo*.

The decomposition of diethylperoxydicarbonate in methyl phenylacetate. A solution containing 0.450 mole of diethylperoxydicarbonate dissolved in methyl phenylacetate (352.0 g., 2.34 moles) was added dropwise beneath the surface of pure methyl phenylacetate (68.0 g., 0.46 mole) heated to 140°. Carbon dioxide (38.7 g., 0.88 mole), ethanol (33.7 g., 0.73 mole), and acetaldehyde (5.3 g., 0.12 mole) were obtained and identified by methods already described. The contents of the reaction vessel were distilled through a Vigreux column of approximately ten plates and unreacted methyl phenylacetate (386.9 g., 2.64 moles, b.p. 69–74°/1 mm.) was obtained. Remining in the distilling flask was 37.2 g. of a white crystalline mass. These crystals were separated into two fractions of approximately equal masses with boiling methanol. The methanol-insoluble fraction melted after recrystallization from acetone at 217–219°. *meso*-Dimethyl α,α'-diphenylsuccinate is recorded in the literature as m.p. 218–219°.

Anal. Calc'd for $C_{18}H_{18}O_4$: C, 72.47; H, 5.94.

Found: C, 72.00; H, 5.84.

Saponification of this material with 25% aqueous sodium hydroxide and subsequent acidification gave an acid which upon recrystallization melted at 248–249°. The literature gives for meso α,α'-diphenylsuccinic acid, m.p. 252°.

From the methyl alcohol extract of the original crystalline mass there was obtained upon evaporation white crystals which upon recrystallization from methanol melted at 168–170°. Racemic dimethyl α,α'-diphenylsuccinate has a recorded melting point of 174°. Saponification of this racemic ester gave an acid melting at 179–183°. Racemic α,α'-diphenylsuccinic acid has a recorded melting point of 183°. The residual alcoholic solution remaining after removal of the racemic ester contained 10 g. of a glassy polymer from which no definite products were identified upon saponification.

The decomposition of diacetyl peroxide in dimethyl malonate. A solution of diacetyl peroxide (40 g., 0.33 mole) dissolved in dimethyl malonate (449.5 g., 3.40 moles) was introduced in single drops beneath the surface of pure dimethyl malonate (193.4 g., 1.46 moles) heated to 130°. Carbon dioxide (27.2 g., 0.61 mole), methane (10.3 l., S.T.P., 0.46 mole), and methyl acetate (5.2 g., 0.07 mole, b.p. 57.5°, n_D^{20} 1.3609) were collected by techniques described elsewhere (2).

The contents of the reaction flask were subjected to distillation at reduced pressure and 580.6 g. (4.40 moles) of unreacted dimethyl malonate was reclaimed at 68–72°/5 mm. Remaining in the distilling flask was 56.2 g. of an heavy oil which upon cooling to room temperature deposited beautiful white crystals. These crystals were separated from the supernatant oil by suction filtering on a fritted disk and subsequent washing with petroleum ether in which solvent they were but sparingly soluble. The crude material (30. g., 0.11 mole) thus obtained had m.p. 128–130°. Repeated recrystallizations from absolute methanol gave a product which melted at 133–134°. The literature for 1,1,2,2-tetracarbomethoxyethane lists m.p. 136–138°.

Anal. Calc'd for $C_{10}H_{14}O_8$: C, 45.97; H, 5.61.

Found: C, 46.02; H, 5.38.

Saponification and subsequent acidification of this tetraester yielded an acid which melted at 153–155°. The literature for 1,1,2,2-tetracarboxyethane gives m.p. 167–169°. An examination of these methods of obtaining this tetra-ester and tetra-acid suggests that the tetra-ester previously recorded in the literature is probably not completely esterified while the free acid here reported has a low melting point because of possible incomplete saponification due to steric hindrance. There remained unidentified 20 g. of a resinous material.

The decomposition of diethylperoxydicarbonate in dimethyl malonate. A solution containing 0.539 mole of diethylperoxydicarbonate dissolved in dimethyl malonate (436.1 g., 3.30 moles) was introduced slowly (one drop at the time) beneath the surface of pure dimethyl malonate (86.3 g., 0.65 mole) heated at 130°. Carbon dioxide (47.5 g., 1.07 moles), ethanol (24.8 g., 0.51 mole), and acetaldehyde (22.4 g., 0.50 mole) were obtained and identified by methods previously described. At the end of the absorption train a small amount (2.0 liters, S.T.P.) of a volatile hydrocarbon gas was collected over water.

The contents of the reaction vessel were distilled at reduced pressure through an 18-inch Vigreux column and unreacted dimethyl malonate (505.8 g., 3.81 moles) was collected at 48–51°/2 mm., n_D^{17} 1.4144. While no dimeric product was formed there remained in the distilling flask 4.2 g. (0.026 mole) of oily material which was transferred to a smaller flask and distilled through a small column of approximately 10 plates, b.p. 90–100°/1 mm.

Saponification in aqueous ethanolic potassium hydroxide and subsequent acidification converted this oil to a crystalline acid melting at 128–129°. A sample of ethylidinemalonic acid prepared by the method of Goss (11) melted with rapid heating at 128.5°. A mixture of these two acids melted at 129.5–130°.

The decomposition of diethylperoxydicarbonate in methyl hydrocinnamate. A solution containing 0.478 mole of diethylperoxydicarbonate dissolved in methyl hydrocinnamate (392.8 g., 2.39 moles) was added in single drops beneath the surface of 64.3 g. (0.39 mole) of pure methyl hydrocinnamate heated to 125°. Carbon dioxide (36.6 g., 0.83 mole), ethanol (34.7 g., 0.76 mole), and acetaldehyde (2.0 g., 0.045 mole) were obtained and identified by techniques previously described. The contents of the reaction vessel were distilled at reduced pressure through a 10-inch Vigreux column and unreacted methyl hydrocinnamate (373.4 g., 2.27 moles) was collected at 71–72°/1 mm., n_D^{22} 1.4997. The residue from this distillation (83 g.) upon trituration with ethyl ether deposited white crystals (12.0 g., 0.037 mole). These crystals were collected on a fritted disk and washed with cold ether. The crude crystals thus obtained melted at 171–172°. Recrystallization from absolute methanol gave crystals melting at 173.5°. The literature (10) records the melting point of this ester as 175°. Direct saponification of this ester by method of Oomen and Vogel (10) gave a white crystalline acid melting at 272°. This acid did not depress the melting point of meso β,γ-diphenyladipic acid from a different source. The melting point given in literature for this acid is 270–271°.

After removal of the ether from the residue which had deposited the meso ester, the residue, a viscous oil, was distilled *in vacuo*, and after approximately 20 g. of methyl hydrocinnamate was collected a high-boiling oil (23.0 g., 0.69 mole), b.p. 145°/0.5 mm. was obtained. This soil did not crystallize upon standing for a year in a dilute solution of methyl ethyl ketone. Direct saponification gave a crude acid which melted at 169–170°. Recrystallization of this acid from large volumes of aqueous methanol gave crystals melting at 182°. The value recorded in the literature for racemic β,γ-diphenyladipic acid is 185–186°. The following table shows the comparison of the constants here reported with those obtained by earlier workers (10) for these esters and acids.

Remaining in the distilling flask after the distillation of the racemic ester was 26.9 g. of a glassy material which did not distill and could not be crystallized. This was not identified.

The decomposition of diethylperoxydicarbonate in dimethyl succinate. A solution of diethylperoxydicarbonate (0.568 mole) dissolved in dimethyl succinate (444.3 g., 3.04 moles) was introduced in single droplets beneath the surface of pure dimethyl succinate (163.0 g., 1.11 moles) held at 135°. Carbon dioxide (46.9 g., 1.06 moles), ethanol 25.8 g., 0.56 mole), and acetaldehyde (17.6 g., 0.40 mole) were collected and identified by procedures already described.

The contents of the reaction vessel were carefully fractionated through a column of approximately 20 plates. A first fraction (564.9 g., 3.86 moles), b.p. 48°/1 mm., n_D^{22} 1.4187, was unreacted dimethyl succinate. A small intermediate fraction, 3.5 g., was followed by a third fraction (26.3 g., 0.15 mole), b.p. 64–66°/1 mm. which was identified as dimethylethylidinesuccinate. A small sample of this oil was saponified with aqueous sodium hydroxide and acidification gave a solution from which was isolated a crystalline acid. When heated slowly this acid melted at 166–170°, but more rapid heating gave a melting point of 179–181°. The melting point of methyl itaconic acid is given (9) as 166°. An authentic sample of dimethylethylidinesuccinate was prepared by the method of Goss, Ingold, and Thorpe (9, 11). This authentic ester was hydrolyzed to the acid which melted with rapid heating at 180°. The acid here reported did not depress the melting point of this authentic sample. Collected over

TABLE III

MELTING POINTS OF β,γ-DIPHENYLADIPIC ACIDS AND ESTERS

	THIS PAPER	OOMEN AND VOGEL[a]	HENLE[b]
Meso acid	272	270–271	270–271
Racemic acid	181–182 169–170	185–186 169–170	169–170
Meso dimethyl ester	171–172 173.5	170 175	175
Racemic dimethyl ester	b.p. 145–150/0.5 mm.	70–71 73–74	73

[a] Oomen and Vogel, *J. Chem. Soc.*, 2150 (1930). [b] Henle, *Ann.*, **348**, 16 (1906).

water at the end of the system during the decomposition reaction was a small amount (2.1 l. S.T.P.) of a flammable hydrocarbon gas.

The decomposition of dimethylperoxydicarbonate in dimethyl benzylmalonate. A solution containing 0.167 mole of dimethylperoxydicarbonate dissolved in dimethyl benzylmalonate (340.9 g., 1.53 moles) was added in single drops beneath the surface of pure dimethyl benzylmalonate (81.7 g., 0.37 mole) heated to 137°. Carbon dioxide (11.3 g., 0.25 mole) and methanol (10.7 g., 0.33 mole, b.p. 64–67°) were collected and identified in the usual manner. The nonvolatile products remaining in the reaction vessel were distilled at reduced pressure through a short (6-inch) Claisen head and 389.0 g. (1.8 moles) (b.p. 117°/2 mm.; 107°/0.5 mm., $n_D^{25.3}$ 1.4971) of unreacted dimethyl benzylmalonate was obtained. Remaining in the distilling flask was an oil (32 g.) which was diluted with approximately three times its volume of absolute ethyl ether and allowed to stand several days during which time white crystals (3.5 g., 0.08 mole) were deposited. These crystals were collected on a fritted disk and recrystallized repeatedly from absolute methanol. They were found to melt at 168°. The value recorded in the literature (12) for the meso form of dimethyl (α,α'-dicarbomethoxy-β,β'-diphenyl)adipate is 166°.

Anal. Calc'd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92.
Found: C, 65.58; H, 6.07.

All attempts to induce further crystallization from this mother liquid were futile. After the removal of the ether from this and analogous supernatant liquors from other runs, the liquors were subjected to distillation at reduced pressure. A small fraction was collected at 110–121°/0.5 mm., n_D^{22} 1.5003.

Anal. Calc'd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92.
Found: C, 64.84; H, 5.40.

Molecular weight determination by the cryoscopic method in benzene showed, however, that although this fraction boils at a distinctly higher temperature than the pure monomer, it is the monomer which had to be super-heated to remove last traces from the viscous residue.

Anal. M. W. Calc'd for $C_{24}H_{26}O_8$ (Dimer): 442. Found: (Cryoscopically in benzene) 230.
Calc'd for $C_{12}H_{14}O_4$ (Monomer): 222.

Attempts to distill the residue from the small pot through a 3-inch head electrically heated caused some material to distill at 135–170° with serious decomposition. Residues analogous to this obtained from other runs were subjected to saponification without further attempts at purification. Small quantities (1–2 g.) of meso β,γ-diphenyladipic acid, m.p. 268° have been obtained from these residues. This acid does not depress the melting point of meso β,γ-diphenyladipic acid obtained from another source.

The decomposition of diethylperoxydicarbonate in dimethyl benzylmalonate. Except for the isolation of a small amount of acetaldehyde and large quantities of ethanol, the products and their respective percentages yields obtained in this reaction have been the same as those obtained from the decomposition of dimethylperoxydicarbonate in this same solvent.

The decomposition of diacetyl peroxide in dimethyl benzylmalonate. A solution containing 0.38 mole of diacetyl peroxide dissolved in 457.7 g. (2.06 moles) of dimethyl benzylmalonate was added one drop at the time beneath the surface of pure dimethyl benzylmalonate (150.8 g., 0.67 mole) heated to 140°. Carbon dioxide (30.9 g., 0.70 mole), methane (10.1 l., S.T.P., 0.45 mole), and methyl acetate (11.4 g., 0.15 mole) were obtained and identified in the manner previously described.

The less volatile material remaining in the reaction vessel after decomposition of the peroxide was distilled through a 5-inch Claisen head, and 522.0 g. (2.35 moles) of unreacted dimethyl benzylmalonate, b.p. 107–110°/1 mm., were obtained. Remaining in the distilling flask was 86 g. of an orange-brown glassy material which could not be induced to crystallize by orthodox techniques. A 30-g. sample of this extremely viscous oil was diluted with approximately three times its volume of absolute diethyl ether and left to stand indefinitely. Unlike the analogous viscous product obtained from the reactions of ethoxy and methoxy free radicals in this solvent, this solution has deposited no crystals. Samples of this undiluted glassy material were distilled through a 12-inch column electrically heated, and unlike the analogous product obtained using the alkoxy free radicals, this product distilled without decomposition. Fractions were obtained over the following range: Fraction I, b.p., 146–158°/1 mm.; Fraction II, b.p. 162–180°/1 mm.; and Fraction III, b.p. 190–212°/1 mm. Fraction III does not flow at room temperature. These fractions had about equal masses and there was in such case a small amount (7 to 10 g.) of unrecrystallizable material left in the distilling flask. All attempts to crystallize these fractions were unsuccessful. All had molecular weights greater than that of the dimer. Samples of this viscous oil before and after distillation were saponified and refluxed in aqueous acid media in attempts to decarboxylate the product to some known crystallizable acid. All such attempts yielded resins.

Acknowledgments. This work has been supported by a Frederick Gardiner Cottrell grant-in-aid from the Research Corporation. We are also grateful for financial assistance from the Atlanta University Carnegie Corporation Grant-In-Aid Committee. Some of the microanalyses reported in this paper were done at the Clark Microanalytical Laboratory, Urbana, Illinois.

SUMMARY

This paper reports evidence that the chemical inertia associated with reactions involving free radical displacements on carbon is dependent upon both the nature of the cleaving free radical and the nature of the substituents attached in close proximity to the site of the cleavage attack in the molecule from which an univalent atom is cleft. Here also is discussed the effect of the nature of these substituents upon the stereochemistry of the process of the dimerization of the residual free radicals resulting from these initial cleavage attacks on solvent molecules.

The free radicals used in this study have been the methyl, methoxy, and ethoxy free radicals. The solvents have been diphenylmethane, methyl phenylacetate, dimethyl malonate, methyl hydrocinnamate, dimethyl benzylmalonate, and dimethyl succinate. A correlation between percentage of cleavage attack, the nature of the attacking free radical, and the nature of the solvent molecule being attcked is observed. A theory of repulsion consistent with these facts is proposed.

ATLANTA, GEORGIA

REFERENCES

(1) Paper number I of this series, *J. Org. Chem.*, **19,** 869 (1954).
(2) KHARASCH, MCBAY, AND URRY, *J. Org. Chem.*, **10,** 394 (1945).
(3) MCBAY AND TUCKER, Unpublished results.
(4) STYLES, A., Ph.D. Thesis, Department of Chemistry, University of Chicago, 1946.
(5) KHARASCH, MCBAY, AND URRY, *J. Org. Chem.*, **10,** 401 (1945).
(6) WATERS, *The Chemistry of Free Radicals*, Oxford University at the Clarendon Press, London, 1946, pp. 138 ff.
(7) HEY AND WATERS, *Chem. Revs.*, **21,** 169 (1937).
(8) STRAIN, *et al.*, *J. Am. Chem. Soc.*, **72,** 1254 (1950).
(9) INGOLD, *J. Chem. Soc.*, **121,** 2689 (1922).
(10) OOMEN AND VOGEL, *J. Chem. Soc.*, 2150 (1930).
(11) DOEBNER, *Ber.*, **33,** 2140 (1900); **35,** 1136 (1902). AUWERS, *et al.*, *Ann.*, **432,** 46 (1923). GOSS, INGOLD, AND THORPE, *J. Chem. Soc.*, 3353 (1923).
(12) BACHER, *J. Pr. Chem.*, **120,** 131 (1928).
(13) FISCHER AND SPEIER, *Ber.*, **28,** 3252 (1895).
(14) CONRAD AND REINBACH, *Ber.*, **35,** 1821 (1902).