per cent of VII-5 in mixtures with VIII-5 was linear over the concentrations of interest with a maximum deviation of 1.0% and an average deviation of 0.7%. This served as a supplementary check on the analysis based on absorption at 13.1 μ. As II gave primarily rearranged product (little C—CH_3), this additional check was not used in the cyclohexane series.

Decarbonylation of the aldehydes (I and II). A solution of di-*t*-butyl peroxide (0.47 g., 0.6 ml., 3 mmoles, n_D^{20} 1.3890) in the appropriate aldehyde (I or II, 30 mmoles) was heated in a Wood's metal bath held at some constant temperature (see Table V for the specific temperatures used). Portions of more peroxide (to a limit of 9 mmoles) were added periodically, although such additions were not needed for I because of its rapid rate of decarbonylation. The gas liberated in the reaction was passed through a cold trap (−80°) and collected over water. Analysis of the gas for carbon monoxide was performed in a Fisher-Orsat apparatus using cuprous chloride absorbent. When no further gas was evolved, distillation was commenced under reduced pressure, all volatile materials being collected in the cold trap. The distillation was continued until the head temperature decreased, a temperature which in all cases was at least 20° below the boiling point of the parent aldehyde. The purification of the distillate from nonhydrocarbon contaminants was attempted by column chromatography, Girard-T separations, steam distillation, and permanganate oxidations. None of these methods were satisfactory. The distillate was, however, effectively and simply purified by the following technique: distillate (1 g.) was taken up in petroleum ether (10 ml.) and extracted twice with concd. sulfuric acid (10 ml.). The organic phase was separated and washed with sodium bicarbonate solution (10%), then with water, and dried over sodium sulfate. The solvent was removed at room temperature under reduced pressure and the residual oil held at 1 mm. for 5 min. This procedure was shown in control experiments not to affect the hydrocarbons VII and VIII in that the infrared spectra of the hydrocarbons and their mixtures were not altered. The purified hydrocarbons were then analyzed by use of infrared by comparison with the calibration curves obtained using authentic samples (see above). In one instance (an early experiment with II), vapor phase chromatography was employed in the analysis. The silicone oil column failed to resolve the hydrocarbon mixture at the temperature used (225°) although the curve obtained matched that of a synthetic mixture of VII-6 and VIII-6 made up in the proportions indicated by infrared analysis.

The acetone produced in each reaction was determined by the weight of its 2,4-dinitrophenylhydrazone derivatives obtained from the cold trap material: for experiment I-1 (0%), I-2 (0%); II-1 (37%), II-2 (41%), II-3 (37%), all based on the final amount of initiator used. No determinations were made in the other experiments.

The dilution experiments (I-3 and II-3) were performed as above except that the aldehyde (30 mmoles) was dissolved in distilled chlorobenzene (30 ml.). The experiments with mercaptan present (I-4 and II-4) were also performed as above, except that benzyl mercaptan (Eastman, 1.24 g., 10 mmoles) was added initially. The pot residues from all of these reactions were dark viscous materials ranging from 19–25% of the initial aldehyde weight in the case of I to 29–46% in the case of II. These figures do not include the experiments I-4 and II-4 where much of the residue was sulfur-containing material derived from the added mercaptan. The residues contained some unchanged aldehyde in every case as evidenced by the isolation of the correct 2,4-dinitrophenylhydrazone. Other than this, no further work was done on these residues.[50]

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[50] The possibility exists that dimeric hydrocarbons are present in these residues and that the relative rearrangement data might be thereby affected. Such dimer production has been reported by Curtin,[4] although such is normally not the course of the decarbonylation process because the concentration of radicals is kept low by the small amount of initiator present and by control of its rate of homolysis through the use of moderate temperatures for the decarbonylations. The intractable nature of these residues precluded effective work-up, but no crystalline or otherwise easily isolable substances appeared present.

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY, THE UNIVERSITY OF CHICAGO]

Reactions of *t*-Butyl Peresters. II. The Reactions of Peresters with Compounds Containing Activated Hydrogens[1]

GEORGE SOSNOVSKY AND N. C. YANG

Received November 30, 1959

The reactions of *t*-butyl peresters with esters, ethers, aldehydes, ketones, tetralin, benzyl alcohol, dimethylaniline, and thiophenol were investigated. Cuprous bromide exerts a marked influence on both the nature and the rate in most of these reactions, and some of these reactions may be applied advantageously for preparative purposes.

In a previous communication, the reactions of *t*-butyl peresters with olefins in the presence of transition metal salts were described.[2] These reactions may be formulated as the displacement of an allylic hydrogen atom by an acyloxy group. Contrary to the results obtained by conventional free radical reactions, reactions with terminal olefins yielded only one type of allylic esters with terminal unsaturation. In the present investigation, the reactions of *t*-butyl peresters have been extended to substrates containing activated hydrogen atoms other than olefins. The compounds employed are esters, ethers, aldehydes, ketones, tetralin, benzyl alcohol, dimethylaniline, and thiophenol. Cuprous bromide was found to exert a

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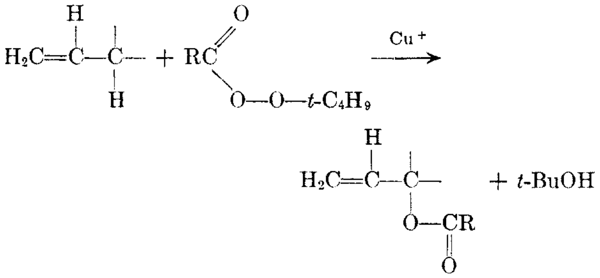
[1] This investigation was supported by a grant from the Office of Naval Research, Contract No. N6ori-02040. It was presented in part at the 134th Meeting of the American Chemical Society in Chicago, Illinois, September, 1958.

[2] M. S. Kharasch and G. Sosnovsky, *J. Am. Chem. Soc.*, **80**, 756 (1958); M. S. Kharasch, G. Sosnovsky, and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959).

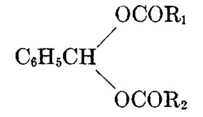


marked influence on both the nature and the rate in most of these reactions,[3] and some of these reactions may be used for preparative purposes

(a) *Reactions with ethers and esters.* Benzoyl peroxide[4] and *t*-butyl perbenzoate[5] decompose following first order kinetics in aromatic solvents. When the decompositions were carried out in aliphatic solvents, such as ethers and esters, the rate processes became more complex. The radicals derived from the solvents interacted with peroxides causing induced decomposition of the peroxy compounds, and the products of such interactions, acylals, had been isolated in few instances.[6] We found that the reaction of *t*-butyl peresters with ethers and esters bearing activated hydrogen atoms adjacent to the oxygen function may be advantageously used as a new method for the preparation of certain acylals.

Benzyl acetate (Ia) reacts with *t*-butyl perbenzoate in the presence of cuprous bromide to give benzylidene acetate benzoate (IIa). The same product (IIa) is obtained from the reaction of benzyl benzoate (Ib) with *t*-butyl peracetate, and benzylidene diacetate (IIb) can be prepared from benzyl acetate and *t*-butyl peracetate. In the absence of a copper catalyst, the decomposition of *t*-butyl peracetate in benzyl acetate proceeds at a much slower rate and a typical free radical type of reaction takes place.[7] The principal product from the reaction is a 1,2-dihydrobenzoin ester besides much carbon dioxide. The glycol ester is presumably formed by the dimerization of the intermediate benzyl radical (III).

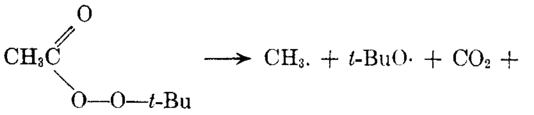
$C_6H_5CH_2OCOR$



$C_6H_5CH(OCOR_1)(OCOR_2)$

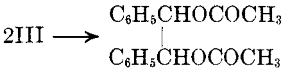
Ia. $R = CH_3$
Ib. $R = C_6H_5$

IIa. $R_1 = CH_3, R_2 = C_6H_5$
IIb. $R_1 = R_2, R_2 = CH_3$



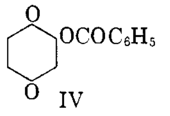
and other products

$$C_6H_5CH_2OCOCH_3 + \text{a radical} \longrightarrow C_6H_5\dot{C}HOCOCH_3 \quad \text{(III)}$$

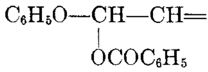


$$2\text{III} \longrightarrow \begin{array}{l} C_6H_5CHOCOCH_3 \\ | \\ C_6H_5CHOCOCH_3 \end{array}$$

1,4-Dioxane reacts sluggishly with benzoyl peroxide after a prolonged heating of twenty one days at 40° to give a poor yield ot dioxanyl benzoate (IV).[6] The reaction of dioxane with *t*-butyl perbenzoate remains incomplete after 72 hours of reflux, and only traces of IV are formed. These reactions may be accelerated, however, by the addition of cuprous bromide. The reaction of *t*-butyl perbenzoate and dioxane in the presence of cuprous bromide proceeds smoothly, and the product, IV, crystallized after one simple distillation. Under similar conditions, phenyl allyl ether gives 3-benzoyloxy-3-phenoxy-1-propene (V).



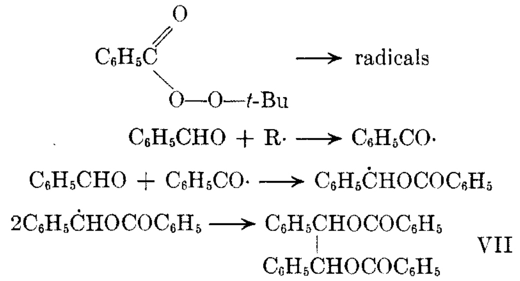
IV



$C_6H_5O{-}CH(OCOC_6H_5){-}CH{=}CH_2$

V

(b) *Reactions with aldehydes and ketones.* The decomposition of *t*-butyl perbenzoate in benzaldehyde corresponds closely to the decomposition of other peroxy compounds in the same solvent,[7] and dihydrobenzoin dibenzoate (VII) was found as the major product. Presumably VII is formed by the following reaction path.



$$C_6H_5CHO + R\cdot \longrightarrow C_6H_5CO\cdot$$

$$C_6H_5CHO + C_6H_5CO\cdot \longrightarrow C_6H_5\dot{C}HOCOC_6H_5$$

$$2C_6H_5\dot{C}HOCOC_6H_5 \longrightarrow \begin{array}{l} C_6H_5CHOCOC_6H_5 \\ | \\ C_6H_5CHOCOC_6H_5 \end{array} \quad \text{VII}$$

In the presence of cuprous bromide, benzaldehyde reacts smoothly with *t*-butyl perbenzoate to give benzoic anhydride (VIIIa), and butyraldehyde reacts with the same perbenzoate to give a mixture of anhydrides derived possibly from the disproportionation of the intermediate mixed anhydride (VIIIb). Under similar conditions, cyclohexanone and 2-methylcyclohexanone give good yields of benzoic acid and a small amount of high boiiling material while the major portions of these ketones are recovered unchanged.

$$RCHO + C_6H_5COOO{-}t\text{-}Bu \xrightarrow{\text{CuBr}} RCOOCOC_6H_5$$

VIIIa. $R = C_6H_5$
VIIIb. $R = n\text{-}C_3H_7$

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[3] M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24,** 606 (1959).

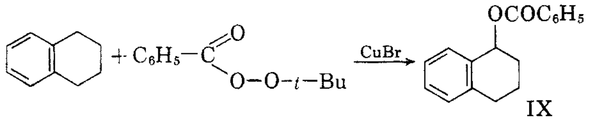
[4] K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68,** 1686 (1946).

[5] A. T. Blomquist, A. F. Ferris and I. A. Berstein, *J. Am. Chem. Soc.*, **73,** 3408, 3421, 5546 (1951).

[6] W. E. Cass, *J. Am. Chem. Soc.*, **69,** 500 (1947).

[7] F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70,** 3258 (1948).

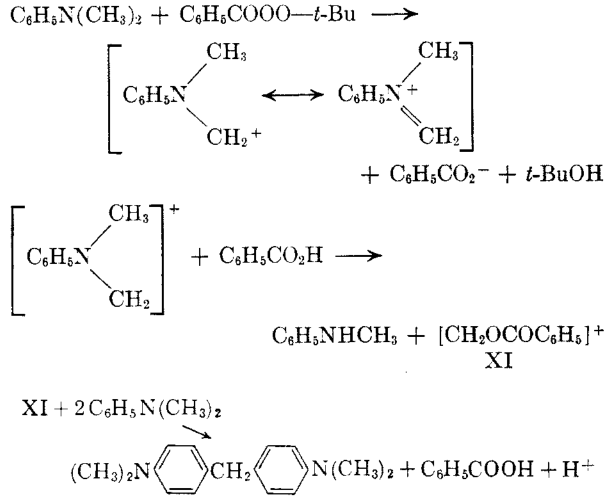
(c) *Reaction with tetralin. t*-Butyl perbenzoate reacts with tetralin in the presence of cuprous bromide to give 1-benzoyloxytetrahydronaphthalene (IX).



(d) *Reaction with dimethylaniline.* It has been demonstrated thus far that transition metal salts play a significant role in the reactions of peresters. However, these metal catalysts exert no effect on the reaction of *t*-butyl perbenzoate with dimethylaniline, benzyl alcohol, or thiophenol.

A moderate yield of bis(*p*-dimethylaminophenyl)methane (X) can be easily isolated by distillation from the reaction of *t*-butyl perbenzoate, and dimethylaniline as well as monomethylaniline is also detected in the reaction mixture. Horner and Betzel[8] obtained the same product (X) from the reaction of benzoyl peroxide and dimethylaniline. Their yield was lower (12%) and the method of isolation cumbersome.

The formation of X from the reaction of benzoyl peroxide and dimethylaniline has been reviewed by Walling.[9] A similar mechanism may apply in the reaction of *t*-butyl perbenzoate with dimethylaniline, such that a one carbon fragment in the oxidation stage of formaldehyde is an intermediate with monomethylaniline as the by-product. This intermediate (XI) reacts with dimethylaniline to form X.



$$C_6H_5N(CH_3)_2 + C_6H_5COOO\text{—}t\text{-Bu} \longrightarrow \left[C_6H_5N\begin{array}{l} CH_3 \\ CH_2{}^+ \end{array} \longleftrightarrow C_6H_5\overset{+}{N}\begin{array}{l} CH_3 \\ {=}CH_2 \end{array} \right] + C_6H_5CO_2^- + t\text{-BuOH}$$

$$\left[C_6H_5N\begin{array}{l} CH_3 \\ CH_2 \end{array} \right]^+ + C_6H_5CO_2H \longrightarrow C_6H_5NHCH_3 + \underset{\text{XI}}{[CH_2OCOC_6H_5]^+}$$

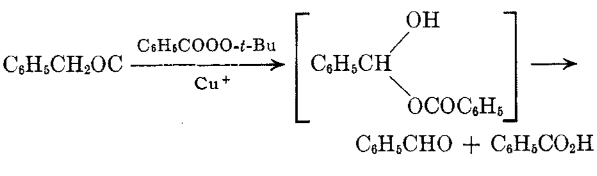
$$\text{XI} + 2C_6H_5N(CH_3)_2 \longrightarrow (CH_3)_2NC_6H_4CH_2C_6H_4N(CH_3)_2 + C_6H_5COOH + H^+$$

X

(e) *Reaction with thiophenol.* There was no effect of copper salt on the oxidation of thiophenol to diphenyl disulfide by *t*-butyl perbenzoate. Diphenyl disulfide is formed by the dimerization of phenylmercapto radicals which are generated from the oxidation of thiophenol by a radical or cupric ion.

$$C_6H_5SH \longrightarrow C_6H_5S\cdot \longrightarrow C_6H_5SSC_6H_5$$

(f) *Reaction with benzyl alcohol. t*-Butyl perbenzoate reacts with benzyl alcohol to form benzaldehyde. A hemiacylal (XII) may be formulate as an intermediate which decomposes to give benzaldehyde and benzoic acid.



$$C_6H_5CH_2OC \xrightarrow[Cu^+]{C_6H_5COOO\text{-}t\text{-Bu}} \left[C_6H_5CH\begin{array}{l} OH \\ OCOC_6H_5 \end{array} \right] \longrightarrow C_6H_5CHO + C_6H_5CO_2H$$

EXPERIMENTAL[10]

t-Butyl perbenzoate and *t*-butyl peracetate, purchased from Wallace Tiernan, Inc., were used without further purification. When freshly distilled peresters were used in these reactions, indistinguishable results were obtained.[2] The progress of the reactions was followed by periodic infrared analyses, and all experiments were conducted under an atmosphere of nitrogen.

General procedure for the reactions of peresters in the presence of cuprous bromide. t-Butyl perester (0.15–0.3 mole) was added over a period of 1 hr. to a stirring mixture of the substrate (0.27–0.5 mole) and cuprous bromide (0.1 g., 0.35 mmole) maintained at 105–110°. Heating was continued for 0.5 hr. after the perester band had disappeared from the infrared spectrum of the reaction mixture. The time required was approximately 3 hr. for *t*-butyl perbenzoate reactions and 17 hr. for *t*-butyl peracetate reactions. There was little or no gaseous evolution during these reactions. The cooled mixture was washed with 2*N* sodium carbonate followed by water. Benzoic acid might be recovered from the carbonate extract by neutralization. The products were isolated by distillation. The reactions were carried out in an excess of substrates which were partly recovered during the distillations. The results are tabulated in Table I and the listed yields were based on the amounts of peresters used.

Reaction of t-butyl peracetate and benzyl acetate. When benzyl acetate (0.5 mole) was treated with *t*-butyl peracetate (0.2 mole) in the absence of cuprous bromide according to the general procedure described previously, a different result was obtained. After 24 hr. of heating, the reaction mixture still contained 38% of unchanged perester. A large volume of gas was collected during the reaction. Following the usual work up, there were obtained unchanged benzyl acetate (0.34 mole), 13 g. of a high boiling residue, and 6 g. of dihydrobenzoin diacetate (IIb), b.p. 140–142° (0.2 mm.), m.p. 133° (from acetone) which was identical in all respects with an authentic sample.

Reaction of t-butyl perbenzoate and benzaldehyde. t-Butyl perbenzoate (0.2 mole) was added over a period of 1 hr. to benzaldehyde (0.5 mole) maintained at 115°. The reaction mixture was heated for 6 hr. During this period there was a continuous evolution of carbon dioxide (2 *l*., 58%). The mixture was then diluted with benzene and the benzene solution from which benzoic acid (14 g., 58%) was recovered. During washing, a white solid separated between the aqueous and the organic layers. The solid (3 g.) was collected by filtration and washed well with hot acetone, m.p. 242–244°. It was identified as *meso*-dihydrobenzoic dibenzoate by comparison with an authentic sample.[7]

Reaction of t-butyl perbenzoate and dioxane. A mixture of

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[8] L. Horner and C. Betzel, *Ann.*, **579**, 175 (1953).

[9] C. Walling, *Free Radicals in Solution*, John Wiley and Sons, New York, 1957, p. 590.

[10] Melting and boiling points are uncorrected. The molecular weights were determined cryoscopically in benzene.

TABLE I

Substrate (mole)	Perester (mole)	Benzoic Acid (%)	Yield Residue (g.)	Structure	Product, g.	%	B.P.	Mm.	n_D^{20}	M.P., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. Wt. Calcd.	Mol. Wt. Found
Benzyl acetate (0.5)	Perbenzoate (0.2)	25		IIa	18.7	35	135–138	0.2		70–71	$C_{16}H_{14}O_4$	71.10	71.12	5.22	5.14	270	268
Benzyl benzoate (0.5)	Peracetate (0.3)		20	IIa	15.0	18											
Benzyl acetate (0.5)	Peracetate (0.3)		8.5	IIb	24.5	40	133–135	10		43.5–44.0	$C_{11}H_{12}O_4$	63.45	63.75	5.81	5.87	208	211
Phenyl allyl ether (0.27)	Perbenzoate (0.15)	8.5	8.5	V	19.0	50	110–112	0.15	1.5662		$C_{16}H_{14}O_3$	75.57	75.37	5.55	5.73	254	244
Benzaldehyde (0.5)	Perbenzoate (0.2)	17		Benzoic anhydride	32.0	70	140–142	0.2								226	228
Tetralin (0.4)	Perbenzoate (0.2)	86		IX	7.4	15	130–135	0.05	1.5780		$C_{17}H_{12}O_2$	80.92	80.92	6.39	6.71	252	248

t-butyl perbenzoate (0.2 mole), dioxane (0.5 mole), and cuprous bromide (0.1 g.) was allowed to react in the usual manner. The cooled reaction mixture was diluted with ether (100 ml.) and extracted with carbonate to remove benzoic acid (2.5 g., 10%). The ethereal solution was washed with water, dried over sodium sulfate, and concentrated on a steam bath. The remaining oil was distilled under reduced pressure. There were obtained 6 g. of a gummy residue and 23 g. (56%) of the product (IV), b.p. 105–107° (0.1 mm.), which crystallized upon standing, m.p. 54° (methanol) (lit.[6] b.p. 108–110° at 0.3 mm.).

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81; mol. wt., 208. Found: C, 63.29; H, 6.07; mol. wt., 211.

When the reaction was carried out in the absence of cuprous bromide, a different reaction was observed. The reaction mixture contained 3.5% of the unchanged perester after 72 hr. of reflux. Following the usual work up there were obtained 600 ml. of carbon dioxide, traces of IV, and 18 g. of an oily alkali soluble material consisting mainly of benzoic acid.

Reaction of benzoyl peroxide and dioxane in the presence of cuprous bromide. A mixture of dioxane (0.6 mole), benzoyl peroxide (0.1 mole), and cuprous bromide (0.1 g., 0.35 mmole) was stirred at 55–60° for 13 hr. The temperature was raised slowly until the mixture began to boil. After 4 hr. of reflux, the reaction mixture was worked up as described in the preceding experiment. There were obtained 13 g. (55%) of benzoic acid, 800 ml. of carbon dioxide, 4 g. of a gummy residue, and 7 g. (34%) of IV.

Reaction of t-butyl perbenzoate and n-butyraldehyde in the presence of cuprous bromide. t-Butyl perbenzoate (0.2 mole) was added to a refluxing mixture of butyraldehyde (0.6 mole) and cuprous bromide (0.1 g., 0.35 mmole) over a period of 45 min. After 2 hr. of reflux, the mixture was worked up by the usual procedure. There were obtained benzoic acid (5 g., 20.5%), butyric anhydride (4 g., b.p. 75–78° at 10 mm. and n_D^{20} 1.4150), benzoic anhydride (9 g., b.p. 125–128° at 0.1 mm. and n_D^{20} 1.5778), and an intermediate fraction (11 g.) which was shown to be a mixture of anhydrides by infrared spectral analysis.

bis(p-Dimethylaminophenyl)methane (X). Over a period of 2 hr., *t*-butyl perbenzoate (0.2 mole) was added to dimethylaniline (0.6 mole) maintained at 105–115°. After the reaction mixture had been heated for 2 additional hr., *t*-butyl alcohol, 9.5 g., b.p. 81°, n_D^{20} 1.3870, was removed by distillation. The remaining liquid was washed with a solution of 2*N* sodium carbonate to remove benzoic acid (23 g., 96%) followed by water, dried over sodium sulfate, and distilled at reduced pressure. There was obtained 29 g. of an oil consisting of mono- and dimethylaniline, b.p. 75° (10 mm.). An aliquot of this mixture (2.14 g.) was acetylated with acetic anhydride at room temperature, and 0.6 g. of *N*-methylacetanilide was obtained, m.p. 99° alone or admixed with an authentic sample. Further distillation of the reaction mixture gave, beside 10 g. of a high boiling residue, 16.5 g. (32%) of X, b.p. 155–157° (0.1 mm.) which solidified on standing, m.p. 89° (from petroleum ether). The compound is identical in all respects with an authentic sample.[8]

When the reaction was carried out in the presence of cuprous bromide, the same result was obtained.

Reaction of t-butyl perbenzoate and thiophenol. To thiophenol (0.5 mole) maintained at 105–115°, *t*-butyl perbenzoate (0.2 mole) was added over a period of 1 hr. After the mixture had been heated for another 2 hr., *t*-butyl alcohol (11 ml.) was removed by distillation. The residual mixture was then diluted with ether and extracted with a 2*N* solution of sodium carbonate to remove benzoic acid (22 g., 92%). The organic phase was concentrated under reduced pressure and the remaining solid was recrystallized from acetone. There were obtained 40 g. (90%) of diphenyl disulfide, m.p. 58.5–59.0°.

When the reaction was carried out in the presence of cuprous bromide, the same result was obtained.

Reaction of t-butyl perbenzoate and benzyl alcohol. When a mixture of *t*-butyl perbenzoate (0.2 mole) and benzyl alcohol (0.5 mole) was treated in the usual manner, there were obtained benzoic acid (24 g., 99%), benzaldehyde (7 g., identified through its 2,4-dinitrophenylhydrazone, m.p. 237°), recovered benzyl alcohol (15 g.), and a higher boiling fraction (13 g., b.p. 50–90° at 0.2 mm.) which was not further investigated. When this reaction was carried out in the presence of cuprous bromide, a similar result was obtained.

Acknowledgment. This work is a continuation of the reactions of *t*-butyl peresters initiated by the late Professor M. S. Kharasch to whom this work is dedicated. The authors are indebted to Mr. William Saschek for the microanalyses and to Mr. Ihor Masnyk for the molecular weight determination.

CHICAGO 37, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

γ-Radiation-Induced Addition of Aldehydes to Esters of Maleic, Fumaric, and Acetylenedicarboxylic Acids

RICHARD H. WILEY AND J. R. HARRELL

Received November 23, 1959

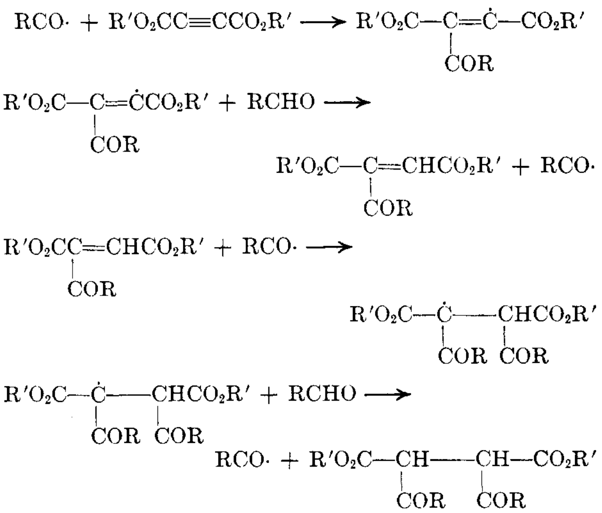
The γ-radiation (Co-60) initiated addition of aldehydes to maleates and fumarates gives acylsuccinates identical with those obtained with peroxide initiation. The reaction has been extended for the first time to additions with isobutyraldehyde and to the addition of aldehydes to acetylenedicarboxylates. Both radical and radiation initiation give products having a 2 3-diacyl structure from the acetylenedicarboxylates.

The radical initiated addition of aldehydes to maleates and fumarates has been described[1,2] using benzoyl peroxide and ultraviolet light as initiators. The only similar peroxide-initiated addition to an acetylenic bond that has been reported[3] is that with propionaldehyde and acetylene. We have studied these reactions using γ-rays from cobalt-60 as the initiator and wish to record the results of these studies at this time.

The γ-radiation induced addition of aldehydes to diethyl maleate takes place readily with butyraldehyde, isobutyraldehyde, and benzaldehyde. Yields from 14% (G = 9) for benzaldehyde, 27% (G = 35) for isobutyraldehyde, and 84% (G = 70) for butyraldehyde were observed at total dose levels of 17.4–27.6 megarep. The product from butyraldehyde, diethyl 2-butyrylsuccinate, was identical with that obtained by the peroxide initiated reaction.[1] On saponification it gave γ-oxoheptanoic acid, m.p. 50°.[4] Dimethyl fumarate gives the same product from butyraldehyde but in lower yield 36% (G = 23). The isobutyraldehyde product, diethyl 2-isobutyrylsuccinate, has not been described previously. It was obtained in liquid and solid (m.p. 134–136°) forms thought to be tautomeric.

The addition of aldehydes to acetylenedicarboxylic acids has not been described previously. It has been observed that butyraldehyde, isobutyraldehyde, and acetaldehyde add to dimethyl or diethyl acetylenedicarboxylate in yields varying from 9–31% with G values of 11–54 at total dose levels of 10.4–18.8 megarep. The product from acetaldehyde, diethyl 2,3-diacetylsuccinate, m.p. 90°, has been shown to have the 2,3-diacetyl structure by comparison with an authentic sample of this material, m.p. 89°, prepared by coupling ethyl acetoacetate.[5] The infrared spectra of the two samples are superimposable and identical in all respects. Identical products have also been obtained using peroxide initiation.

It is believed that these data indicate that the γ-radiation initiated addition of aldehydes to acetylenedicarboxylic ester proceeds *via* a free-radical mechanism. The first acyl radical to add



$$\mathrm{RCHO} \longrightarrow \mathrm{RCO\cdot} + \mathrm{H\cdot}$$

$$\mathrm{RCO\cdot} + \mathrm{R'O_2CC{\equiv}CCO_2R'} \longrightarrow \mathrm{R'O_2C{-}\underset{COR}{C}{=}\dot{C}{-}CO_2R'}$$

$$\mathrm{R'O_2C{-}\underset{COR}{C}{=}\dot{C}CO_2R'} + \mathrm{RCHO} \longrightarrow \mathrm{R'O_2C{-}\underset{COR}{C}{=}CHCO_2R'} + \mathrm{RCO\cdot}$$

$$\mathrm{R'O_2\underset{COR}{C}C{=}CHCO_2R'} + \mathrm{RCO\cdot} \longrightarrow \mathrm{R'O_2C{-}\underset{COR}{\dot{C}}{-}\underset{COR}{C}HCO_2R'}$$

$$\mathrm{R'O_2C{-}\underset{COR}{\dot{C}}{-}\underset{COR}{C}HCO_2R'} + \mathrm{RCHO} \longrightarrow \mathrm{RCO\cdot} + \mathrm{R'O_2C{-}\underset{COR}{CH}{-}\underset{COR}{CH}{-}CO_2R'}$$

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