and cyclopentanecarboxylic acids from ethylene and tetramethylene bromides, respectively. The hydrolysis of the ester resulting from ethylene bromide was effected by means of an aqueous solution of potassium hydroxide in order to avoid the cleavage of the cyclopropane ring which might have been formed, while a mixture of dioxane and concentrated hydrochloric acid was used for hydrolyzing the ester from tetramethylene bromide. Although suberic acid was obtained with an excellent yield in the latter reaction, the ethylene bromide failed to afford any acidic product other than acetic acid by means of this amide.

It seems safe to conclude from these results that the direct alkylation of *t*-butyl acetate is of value as an alternate of malonic ester synthesis for preparing mono- and dibasic carboxylic acids.

Experimental[6]

Alkylation.—To a suspension of 0.1 mole of lithium amide in 200 ml. of liquid ammonia 0.1 mole of *t*-butyl ester was added rapidly with continuous stirring at −40°. Since the use of anhydrous ether as a solvent of the ester lowered the yields of alkylated products, no solvent other than ammonia was used at this stage of the raction. After 15–40 minutes stirring at −40° 0.05 mole of organic halide (neat) or its solution in 20 ml. of anhydrous ether was added during 3–30 minutes. The stirring was continued for an additional 40–180 minutes and then ammonium chloride was added. Ammonia was evaporated by external heating, while 50 ml. of wet ether was added slowly. The reaction mixture was treated with 50 ml. of water, extracted with ether, the combined ethereal solutions were washed with water and dried over anhydrous sodium sulfate. Upon removing the solvent, followed by fractional distillation of the residue in the presence of magnesium oxide, the alkylated product could be isolated. The details of each experiment were summarized in Tables I and II. When the isolation of the *t*-butyl ester was accompanied with difficulties, the evaporation residue of the ethereal extracts was directly subjected to hydrolysis.

Hydrolysis of the *t*-Butyl Ester.—A mixture of 0.02 mole of the alkylation products, 6 ml. of dioxane and 10 ml. of concentrated hydrochloric acid was refluxed for 2–5 hours. After cooling to room temperature the mixture was extracted several times with ether, the combined ethereal solutions were washed with a small amount of water and then thoroughly extracted with 10% aqueous sodium hydroxide solution or saturated sodium bicarbonate solution. The combined alkaline solutions were washed with ether and acidified with concentrated hydrochloric acid. The carboxylic acid which separated was taken up in ether or collected through filtration and purified through distillation or by recrystallizations. Yields were almost quantitative in each case.

The condensation product obtained from ethylene bromide in the presence of sodium amide was hydrolyzed by heating with 50% excess of 50% aqueous potassium hydroxide solution. The reaction mixture was washed with ether and acidified with concentrated hydrochloric acid. The solution was extracted with ether, but failed to afford any acidic product. Though the non-saponifiable portion was examined to recover the condensation product, if any, no appreciable amount of neutral ester could be isolated.

KYÔTO, JAPAN

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[6] All temperatures are uncorrected. Analyses by Miss Kenko Ogawa.

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

Reactions of *t*-Butyl Peresters. I. The Reaction of Peresters with Olefins[1]

BY M. S. KHARASCH,[2] GEORGE SOSNOVSKY[3] AND N. C. YANG[3]

RECEIVED MAY 23, 1959

t-Butyl peresters react smoothly with olefins in the presence of copper or cobalt salt catalysts to form allylic esters in moderate to good yields. With terminal olefins, such as 1-octene, 1-hexene or allylbenzene, the only products isolated are the allylic esters with a terminal double bond. When the reaction of cyclohexene, *t*-butyl perbenzoate and cuprous bromide is carried out in an aliphatic acid as the solvent, the aliphatic ester of cyclohexenol instead of the benzoate is obtained. The scope and limitation of this reaction are discussed.

Tertiary alkyl peresters were first prepared by Milas and Surgenor.[4] However, the chemistry of these substances, except for several kinetic studies, has received little attention. Blomquist[5] and his associates studied the decomposition of *t*-butyl perbenzoate in great detail. They found that *t*-butyl perbenzoate decomposes about as rapidly at 115° as benzoyl peroxide does at 80°. In most aromatic solvents the rate of decomposition is of first order; in aliphatic solvents the situation is more complex, and it appears that an induced chain reaction (involving free radicals derived from solvent) takes place in addition to the unimolecular cleavage of the perester. More recently, Bartlett and Hiatt[6] examined the decomposition of various *t*-butyl peresters in chlorobenzene. They found that most of the peresters examined give a mixture of products with carbon dioxide as the major constituent. In view of these findings, it is not surprising that in a variety of substrates the decomposition of *t*-butyl perbenzoate gives a complex mixture of products; and that few useful preparative results have been obtained from such reactions.

In a previous communication[7] it was shown that the addition of catalytic amounts of copper or cobalt salts to the reactions of perester and olefins has a decisive effect on the composition of the end-products. Thus, *t*-butyl perbenzoate reacts with ethylenic compounds to give esters of benzoic acid. These reactions are stereospecific, namely, the benzoyloxy group enters the position alpha to the double bond, and there is no rearrangement of the ethylenic system. The present paper contains experimental details which amplify the original observations.

The possibility of utilizing *t*-butyl peresters as synthetic reagents was first noted when *t*-butyl

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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, Ill., September, 1958.

[2] Deceased.

[3] To whom inquiries of this publication may be sent.

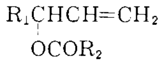
[4] N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 642 (1946).

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

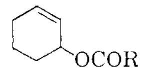
[6] P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

[7] M. S. Kharasch and G. Sosnovsky, *ibid.*, **80**, 756 (1958).

perbenzoate decomposed in the presence of cuprous bromide to give methyl benzoate. When this decomposition is carried out in solvents containing activated hydrogen atoms, benzoic esters are obtained. Of particular theoretical and practical interest are the reactions of *t*-butyl perbenzoate with allylic systems. Although radical reactions with allylic compounds usually result in a mixture of isomeric products,[8] the reaction of *t*-butyl perbenzoate and allylic compounds in the presence of cuprous bromide forms mainly one product. Thus, 1-hexene, 1-octene, allylbenzene, 2-octene, cyclohexene, 2,4,4-trimethyl-1-pentene, 4-vinylcyclohexene, cyclohexenyl acetate and α-pinene react smoothly to give monobenzoates. In the case of acrylonitrile, a very reactive olefin, high molecular weight substances were the main product. The position of the benzoyloxy group has been established in the esters derived from 1-hexene (Ia), 1-octene (Ib), cyclohexene (IIa) and allylbenzene (Ic), but there is still some uncertainty about the position of the benzoyloxy group in the esters derived from 2-octene (III), 2,4,4-trimethyl-1-pentene (IV), cyclohexen-1-yl acetate (V), 4-vinylcyclohexene (VIa) and α-pinene (VIIa).

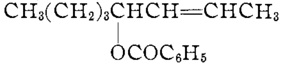


$$\underset{\textstyle OCOR_2}{R_1\underset{|}{C}H}CH{=}CH_2$$



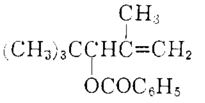
Ia, $R_1 = C_3H_7$, $R_2 = C_6H_5$
b, $R_1 = C_5H_{11}$, $R_2 = C_6H_5$
c, $R_1 = C_6H_5$, $R_2 = C_6H_5$
d, $R_1 = C_3H_7$, $R_2 = CH_3$
e, $R_1 = C_5H_{11}$, $R_2 = CH_3$

IIa, $R = C_6H_5$
b, $R = CH_3$



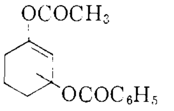
$$CH_3(CH_2)_3\underset{\textstyle OCOC_6H_5}{\underset{|}{C}H}CH{=}CHCH_3$$

III

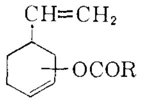


$$(CH_3)_3C\underset{\textstyle OCOC_6H_5}{\underset{|}{C}H}\overset{\textstyle CH_3}{\overset{|}{C}}{=}CH_2$$

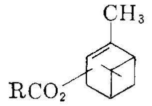
IV



V



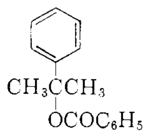
VIa, $R = C_6H_5$
b, $R = CH_3$



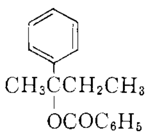
VIIa, $R = C_6H_5$
b, $R = CH_3$

Likewise, *t*-butyl peracetate reacts with 1-hexene, 1-octene, cyclohexene, pinene and vinylcyclohexene to give the esters of acetic acid, Id, Ie, IIb, VIIb and VIb, respectively.

The general applicability of this synthetic method is demonstrated by the reactions of *t*-butyl perbenzoate with compounds containing benzylic hydrogen atoms. With cumene, it forms 2-phenyl-2-benzoyloxypropane (VIII),[9] and with 2-phenylbutane, 2-phenyl-2-benzoyloxybutane (IX).[10] Triphenylmethane, however, failed to react under similar conditions.



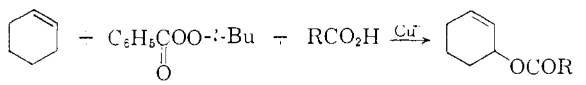
VIII



IX

The main limitation of this reaction is the temperature at which it may be performed. The most suitable temperatures lie between 80° and 125°. The reactions proceed slowly at 60–70°; highly volatile substances such as 1-pentene (b.p. 40°) do not react. However, the reaction with such volatile substances may be feasible at a higher temperature under elevated pressure. Substances of very low volatility (*e.g.*, benzyl benzoate, b.p. 323°) yield very high boiling esters which are difficult to separate from the polymeric by-products. In order to obtain the best results, the reaction between a perester and a compound containing a labile hydrogen atom should be carried out in the presence of an excess of the latter. When equimolar quantities of the reagents are employed, lower yields are obtained.

Another limitation of the reaction is the availability of the type of *t*-butyl peresters: only *t*-butyl perbenzoate and *t*-butyl peracetate are commercially available. This limitation may be partly overcome by using the desired acid as the solvent for the reaction. When cyclohexene dissolved in glacial acetic acid is treated with *t*-butyl perbenzoate in the presence of cuprous bromide, cyclohexenyl acetate (IIb) is formed instead of the corresponding benzoate (IIa). This modification has been applied successfully for the preparation of a number of cyclohexenyl esters (II) such as cyclohexenyl formate, acetate, propionate and *n*-butyrate. The yield of cyclohexenyl formate (IIe) is comparatively lower (30%) than the other esters, and there appears to be an extensive reaction between IIc or formic acid and the perester under the reaction condition.

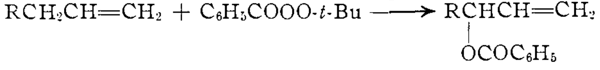


IIb, $R = CH_3$; d, $R = C_2H_5$
c, $R = H$; e, $R = n\text{-}C_3H_7$

The nature of the reaction described is independent of the solubility or valence of the copper salt catalyst introduced into the reaction mixture. Cuprous bromide and cupric 2-ethylhexoate are equally effective. When cuprous bromide is used, it enters the solution slowly, and the catalysis is homogeneous. Cobaltous 2-ethylhexoate is somewhat less effective giving a lower yield of the allylic ester, but zinc chloride and magnesium bromide are ineffective catalysts.

Discussion

A. Specificity.—Terminal olefins react with *t*-butyl peresters in the presence of a copper salt catalyst yielding only the unrearranged secondary allylic esters. The specificity of this reaction was first demonstrated by rigorous purification of the reaction product. When hex-1-en-3-yl benzoate (Ia), isolated by simple distillation of the reaction



$$RCH_2CH{=}CH_2 + C_6H_5COOO\text{-}t\text{-}Bu \xrightarrow{Cu^+} \underset{\textstyle OCOC_6H_5}{R\underset{|}{C}H}CH{=}CH_2$$

mixture, was carefully fractionated through a Piros–Glover spinning band column rated at 80

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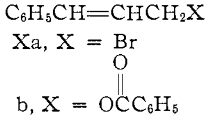
[8] (a) A. L. Bateman and J. I. Cuneen, *J. Chem. Soc.*, 941 (1950); (b) M. S. Kharasch, P. Pauson and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953); (c) M. S. Kharasch, R. Malec and N. C. Yang, *ibid.*, **22**, 1443 (1957); (d) M. S. Kharasch and A. Fono, *ibid.*, **24**, 72 (1959).

[9] M. S. Kharasch and A. Fono, *ibid.*, **23**, 324 (1958).

[10] P. A. Hallgarten, unpublished result.

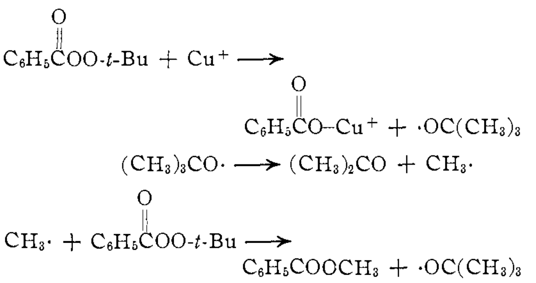
theoretical plates with a 40:1 reflux ratio,[11] a single fraction (87% of the total charge) was obtained which has an infrared spectrum identical with that of the original distilland. When oct-1-en-3-yl acetate (Ie), isolated in a similar manner, was analyzed by gas chromatography, there was detected only one component. However, small amounts of the rearranged ester may be formed in the reaction, but so far they have escaped detection. The specificity was further investigated with an olefinic system which is readily susceptible to rearrangement. Allylbenzene ordinarily undergoes free radical reactions accompanied by rearrangement; for example, the bromination of allylbenzene with N-bromosuccinimide gives only the rearranged cinnamyl bromide (X).[12] If cinnamyl benzoate (Xb) is formed in the reaction of allylbenzene and *t*-butyl perbenzoate in the presence of cuprous bromide, it may be easily detected by its characteristic ultraviolet absorption spectrum. Consequently, the ultraviolet absorption spectrum of the product was compared with the spectrum of authentic cinnamyl benzoate[13] and that of 1-phenylprop-3-en-1-yl benzoate (Ic).[13] The spectrum was found to be virtually identical with that of Ic. The absence of a strong absorption in 250 mμ region indicates that the product is contaminated with less than 1% of the rearranged cinnamyl benzoate. The infrared spectra of the product and Ic are superimposable.



$$C_6H_5CH{=}CHCH_2X \qquad \text{Xa}, X = Br \qquad \text{b}, X = O\overset{\overset{O}{\|}}{C}C_6H_5$$

B. Interpretation of Infrared Spectrum.—Compounds with *trans*-vinylene double bonds, HC=CH, absorb in the 960–970 cm.$^{-1}$ (strong) region, and compounds with vinyl double bonds, $-CH{=}CH_2$, absorb at 985–995 (medium) and 905–915 cm.$^{-1}$ (very strong).[14] The present work shows that when an acetoxy or a benzoyloxy group is introduced into a position alpha to the vinyl group the 905–915 cm.$^{-1}$ band is shifted to 925–935 cm.$^{-1}$ region,[15] and compounds such as hex-1-en-3-yl benzoate, hex-1-en-3-yl acetate, oct-1-en-3-yl acetate and 1-phenylprop-3-en-1-yl benzoate exhibit additional absorption bands in 955–980 cm.$^{-1}$ region. At first, this additional band was attributed to the presence of the vinylene isomer; but experimental investigation failed to detect any vinylene isomer. Therefore, this anomalous band is probably an intrinsic property of the esters and the interpretation of infrared spectra of allylic esters is to be done with care.

C. Possible Reaction Mechanisms.—In the absence of catalysts, the decomposition of *t*-butyl peresters in a variety of solvents proceeds by multiple cleavages to give a complex mixture of products.[6] In the presence of copper salt catalysts the type of the reaction is different. *t*-Butyl perbenzoate gives methyl benzoate and a little carbon dioxide beside much benzoic acid. The formation of these products may be accounted for by the reaction sequence



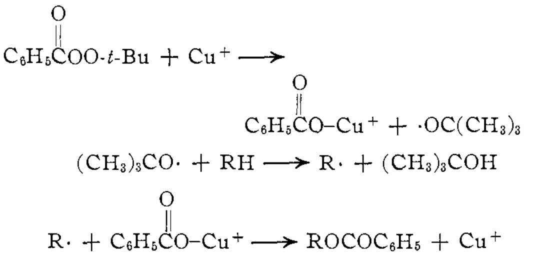
$$C_6H_5\overset{\overset{O}{\|}}{C}OO\text{-}t\text{-}Bu + Cu^+ \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}O\text{–}Cu^+ + \cdot OC(CH_3)_3 \quad (1)$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot \quad (2)$$

$$CH_3\cdot + C_6H_5\overset{\overset{O}{\|}}{C}OO\text{-}t\text{-}Bu \longrightarrow C_6H_5COOCH_3 + \cdot OC(CH_3)_3 \quad (3)$$

Methyl benzoate is probably formed by a chain reaction of which equations 2 and 3 are the propagating steps.

The metal salt-catalyzed decomposition of peresters in the presence of olefins containing allylic hydrogen atoms may be summarized in the steps



$$C_6H_5\overset{\overset{O}{\|}}{C}OO\text{-}t\text{-}Bu + Cu^+ \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}O\text{–}Cu^+ + \cdot OC(CH_3)_3 \quad (1)$$

$$(CH_3)_3CO\cdot + RH \longrightarrow R\cdot + (CH_3)_3COH \quad (4)$$

$$R\cdot + C_6H_5\overset{\overset{O}{\|}}{C}O\text{–}Cu^+ \longrightarrow ROCOC_6H_5 + Cu^+ \quad (5)$$

The absence of the primary allylic benzoates from the reactions of terminal olefins provides evidence against conventional free radical or carbonium ion intermediates which generally result in isomerization of the allylic system. This observation suggests that the displacement of the allylic hydrogen by the benzoyloxy radical (equations 4 and 5) probably occur in a concerted manner. The detailed mechanism of this reaction is now being investigated by kinetic and tracer[16] techniques.

This reaction requires as catalyst a metal salt which is capable to engage in rapid oxidation–reduction reactions. Transition metal salts, such as those of copper and cobalt are effective: ordinary metal salts, such as zinc chloride or magnesium bromide, are ineffective. The failure of triphenylmethane as a substrate may be attributed to the steric hindrance about the activated hydrogen atom.

When the reaction of cyclohexene, *t*-butyl perbenzoate and cuprous bromide is carried out in an excess of an aliphatic acid, the allylic ester of the aliphatic acid is obtained instead of the benzoate. Cyclohexenyl benzoate is converted to the acetate when it is heated in glacial acetic acid in the absence of a catalyst. This finding indicates that ester interchange occurs during these reactions.

Acknowledgment.—The authors are indebted to Professor T. P. Rudy for his assistance in analytical distillation and gas chromatography, to Mr. Wil-

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(11) Using the same column and similar operating conditions, various allylic isomers have been separated in this Laboratory; see ref. 8c and 8d.

(12) E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1116 (1952).

(13) E. A. Braude, D. W. Turner and E. S. Waight, *ibid.*, 2396 (1958).

(14) L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34.

(15) L. Bateman, *et al.*, *J. Chem. Soc.*, 915 (1950).

(16) Private communication, Professor Donald B. Denney, Rutgers University, New Brunswick, N. J.

Table I

Reactions of *t*-Butyl Perbenzoate and Olefins

Olefin	Mole olefin	Mole per-benzoate	Mmole catalyst	Temp., °C.	Products		
					Benzoic acid, g.(%)	Ester, g. (%)	Residue, g.
1-Octene	0.32	0.124	0.35	Reflux	8.5 (57)	Ib, 10.0 (35)	5
2-Octene	.32	.2	.35	Reflux	9.4 (39)	III, 13.0 (53)	
1-Hexene	.40	.2	.35	Reflux	9.0 (37)	Ia, 16.0 (40)	7
Cyclohexene	.5	.2	.35	Reflux		IIa, 29.5 (73)	3
Cyclohexene	.5	.2	.35[a]	Reflux	2.2 (9)	IIa, 31.0 (77)	4.5
Cyclohexene	.5	.2	.35[b]	Reflux	7.0 (29)	IIa, 22.5 (56)	5
Cyclohexene	.25	.2	.35	Reflux	2.2 (9)	IIa, 20.0 (50)	10
2,2,4-Trimethylpent-1-ene	.5	.2	.35	Reflux	9.0 (37)	IV, 17.0 (37)	6.5
Cyclohexanone enol acetate	.29	.2	.35	105–115	6.5 (27)	V, 15.0 (29)	
4-Vinylcyclohexene	.5	.2	.35	105–115	2.8 (12)	VIa, 28.0 (61)	6
α-Pinene	.5	.2	.35	105–115	9.0 (37)	VIIa, 17.0 (33)	4.5
Allylbenzene	.4	.2	.35	105–115	6.5 (27)	Ic, 26.0 (55)	5.5

[a] Cupric 2-ethylhexoate. [b] Cobaltous 2-ethylhexoate.

liam Saschek for microanalyses, and to Mr. Ihor Masnyk for molecular weight determinations.

Experimental[16a]

Starting Materials.—1-Octene, 1-hexene, 2,4,4-trimethyl-1-pentene and 4-vinylcyclohexene were pure grade (99 mole per cent. minimum) Phillips hydrocarbons which were used without purification. 2-Octene used was Practical Grade (95 mole per cent. minimum) Phillips hydrocarbon. α-Pinene, supplied by Matheson, Coleman and Bell Co., was freshly distilled before use. Cyclohexene and acrylonitrile, purchased from Eastman Kodak Co., were freshly distiled before use. Cyclohex-1-enyl acetate was prepared according to the method of Hagemeyer and Hull,[17] $n^{20}\mathrm{D}$ 1.4573. Allylbenzene was prepared according to the method of Hershberg.[18]

t-Butyl perbenzoate and *t*-butyl peracetate as a 75% benzene solution (Lupersol #7) were purchased from Lucidol Division, Wallace Tiernan, Inc. Unless otherwise specified the peresters were used without purification.

Anhydrous reagent grade cuprous bromide was dried and kept in a desiccator before use. Cupric or cobaltous 2-ethylhexoate was prepared from equivalents of potassium 2-ethylhexoate and the corresponding sulfate. The precipitate thus obtained was washed, dried and dissolved in benzene to make a 10% solution.

Authentic cinnamyl benzoate and 1-phenylprop-3-en-1-yl benzoate were prepared by the method of Braude, Turner and Waight.[13]

Analytical Methods.—*t*-Butyl peresters were analyzed by the addition of a weighed sample of the perester to a reagent consisting of glacial acetic acid, sodium iodide and traces of ferric chloride. The liberated iodine was titrated with 0.1 *N* sodium thiosulfate.[19]

The extent of unsaturation of the allylic esters formed in the perester reaction cannot be determined satisfactorily by conventional methods. Both hydrogenation and bromide–bromate titration gave values higher than those of theoretical, presumably due to hydrogenolysis and allylic bromination, respectively. The procedure used is a modification of the existing methods[20] developed in this Laboratory by Dr. Walter Nudenberg. A constant stream of ozonized oxygen of known ozone concentration (0.35–0.40 mmole/300 ml. of oxygen/min.) was passed into a solution of the sample (10–30 mmoles) in ethyl acetate (25–50 ml.) maintained at −40° to −20°. The end-point was taken when iodine was liberated in a potassium iodide trap connected after the ozonization vessel.[21] At the beginning of each series of determinations, the concentration of ozone in ozonized oxygen was determined iodimetrically using a ferrous–ferric system and the result was checked by ozonization of a standard sample (pure 1-octene). The accuracy of this method was found to be ± 2.5%. The success of this determination depends on the nature of olefins. Certain negatively substituted olefins such as enol acetates require a higher temperature (0°), and the method is not applicable for α,β-unsaturated carbonyl compounds, aromatic hydrocarbons and polyhalogenated olefins.

Decomposition of *t*-Butyl Perbenzoate in the Presence of Cuprous Bromide. Formation of Methyl Benzoate.—A mixture of *t*-butyl perbenzoate (0.1 mole) and cuprous bromide (0.1 g., 0.35 millimole) in benzene (100 ml.) was refluxed for 38 hours. During this period carbon dioxide (270 ml., 10%) evolved. The reaction mixture was extracted with a 2 *N* sodium carbonate solution to remove the copper salt and the benzoic acid, 8 g. (53%). The benzene solution was concentrated at reduced pressure. Distillation of the residue gave methyl benzoate (3.7 g., 34%, b.p. 197–198°, $n^{20}\mathrm{D}$ 1.5175), the infrared spectrum of which was identical to that of an authentic sample of methyl benzoate.

When *t*-butyl perbenzoate was refluxed in *n*-octane for 5 hours in the absence of copper catalyst, isolated were carbon dioxide (30%), benzoic acid (20%), acetone (1.8%, 2,4-dinitrophenylhydrazone, m.p. 125°), and an azeotropic mixture of *t*-butyl alcohol and benzene, 8 g., b.p. 73.° Only traces of methyl benzoate could be detected by infrared analysis.

The Reaction of *t*-Butyl Perbenzoate and Olefins in the Presence of Cuprous Bromide.—The reactions were carried out under an atmosphere of Linde high purity nitrogen. *t*-Butyl perbenzoate was added over a period of one hour into a stirred mixture of the olefin and a small amount of the catalyst maintained at the reaction temperature. The progress of the reaction was followed by periodic examination of the infrared spectrum of the mixture. Heating was continued for 0.5 hour after the disappearance of the perester band from its infrared spectrum. The total reaction time was approximately 1–2 hours at 110° and 2–4 hours at 90° after the addition of the perester. There was little or no gas evolution. The mixture was next extracted with a 2 *N* solution of sodium carbonate to remove the catalyst and benzoic acid. In certain cases, the mixture was distilled prior to the extraction in order to isolate *t*-butyl alcohol. The yields of *t*-butyl alcohol were 76 and 68% in the reactions of 1-octene and 2-octene, respectively. Benzoic acid was recovered from the carbonate extracts by neutralization. The organic phase was washed with water, dried over sodium sulfate, and distilled under reduced pressure. In all the runs, appreciable quantities of starting olefins were recovered and the yields of allylic benzoates recorded were based on the amount of perbenzoate used. The results were given in Table I.

The catalyst used in these reactions was cuprous bromide unless otherwise specified. In some experiments, freshly distilled *t*-butyl perbenzoate (98^{+}%) was used and the re-

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(16a) Boiling points and melting points are uncorrected. Molecular weights were determined by the cryoscopic method in benzene. Infrared spectra were determined on a Perkin–Elmer model 21 spectrophotometer and ultraviolet spectra were determined on a Warren Spectrocord.

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TABLE II

REACTIONS OF *t*-BUTYL PERACETATE WITH OLEFINS

Olefins	Mole	Mole peracetate	Mmole catalyst	Heating, hr.	Temp., °C.	Products, g. (%)
Cyclohexene	0.49	0.2	0.35	4	Reflux	IIb, 15.0 (54)
1-Hexene	.40	.2	.35	22	Reflux	Id, incomplete reacn.
1-Octene	.32	.2	.35	2	Reflux	Ie, 8.5 (25)
4-Vinylcyclohexene	.50	.2	.35	2	105–110	VIb, 22.0 (44)
α-Pinene	.40	.3	.35	17	105–110	VIIb, 18.5 (30)

TABLE III

REACTIONS OF *t*-BUTYL PERBENZOATE AND CYCLOHEXENE IN ALIPHATIC ACIDS

				Products			
Acid	Moles	Temp.	Time, hr.	Benzoic acid, g. (%)	Alkanoate, g. (%)	Intermediate, g.	Benzoate, g.
Formic	1.15[a] 1.05[b]	Reflux	5	20.8 (86)	7.5 (30)	6	
Acetic	0.09	Reflux	3.5	21.0 (87)	16.0 (57)		
Propionic	.5	Reflux	12	18.0 (75)	18.0 (58)	6	
n-Butyric	.5	Reflux	6.5	18.0 (75)	15.0 (45)	5	5.3

[a] 50 ml. of 98% formic acid. [b] 50 ml. of 88% formic acid.

TABLE IV

PHYSICAL CONSTANTS OF THE PRODUCTS[a]

		B.p.,			Analyses, %					
					Calculated			Found		
Compound	Formula	°C.	Mm.	$n^{20}D$	C	H	Mol. wt.	C	H	Mol. wt.
Ib	$C_{15}H_{20}O_2$	85–87	0.1	1.4960	77.55	8.68	232	77.25	8.99	234
III	$C_{15}H_{20}O_2$	94–95	.2	1.4996	77.55	8.68	232	77.93	8.51	223
Ia	$C_{13}H_{16}O_2$	75–80	.25	1.5010	76.44	7.90	204	76.87	8.17	192
IIa	$C_{13}H_{14}O_2$	100–105	.25	1.5383	77.20	6.98	202	77.35	6.71	194
IV	$C_{15}H_{20}O_2$	93	.5	1.4998	77.55	8.68	232	77.53	8.83	235
V	$C_{15}H_{16}O_4$	127–130	.15	1.5332	69.21	6.20	262	69.81	6.32	246
VIa	$C_{17}H_{20}O_2$	120–122	.05	1.5330	79.65	7.86	256	79.39	8.13	257
Ic	$C_{16}H_{14}O_2$	108–112	.1	1.5641	80.64	5.92	238	80.77	5.96	232
IIb	$C_8H_{12}O_2$	58	9	1.4579	68.54	8.63	140	68.67	8.77	140
Ie	$C_{10}H_{18}O_2$	67–69	9	1.4290	70.54	10.66	170	70.85	10.46	165
Id	$C_8H_{14}O_2$	37–38	8	1.4172	67.57	9.93	142	67.83	9.77	135
VIb	$C_{10}H_{14}O_2$	55	0.2	1.4720	77.26	8.49	166	72.53	8.79	164
VIIb	$C_{12}H_{18}O_2$	53–54	0.2	1.4742	74.19	9.34	194	74.86	9.71	189
IIc	$C_7H_{10}O_2$	50–53	11	1.4590	66.64	7.99	126	66.84	7.78	126
IId	$C_9H_{14}O_2$	77–79	11	1.4581	70.10	9.15	154	70.01	9.01	148
IIe	$C_{10}H_{16}O_2$	88–90	10	1.4572	71.39	9.59	168	71.28	9.70	165

[a] The extents of unsaturation of these products were determined by quantitative ozonolysis, and were shown to be in agreement with theoretical values within experimental error.

sults obtained were identical with those using commercial grade perbenzoate.

After ozonolysis of the allylic benzoates (Ia, Ib and Ic) obtained from the reactions of 1-hexene, 1-octene and allylbenzene, the ozonized samples were hydrogenated in the presence of Adams catalyst. By addition of dimedon to the distillate of the hydrogenated samples, the formaldehyde derivative of dimedon was isolated (m.p. 188°) indicating the presence of terminal double bonds. No acetaldehyde derivative was detected.

When a sample (9 g.) of hex-1-en-3-yl benzoate (Ia), b.p. 75–80° (0.25 mm.), $n^{20}D$ 1.5010, prepared by this method was fractionated through a Piros-Glover spinning band column rated at 80 theoretical plates with a 40:1 reflux ratio, the distillate was collected in eight 1-ml. fractions, b.p. 95–99° (1.5 mm.). All fractions exhibited identical infrared absorption spectra and refractive indices with the original distilland. The hold-up of the column was not further investigated.

1-Phenylprop-3-en-1-yl benzoate (Ic) prepared by this method and isolated by simple distillation exhibits the physical properties: b.p. 108–112° (0.1 mm.), $n^{20}D$ 1.5641; λ_{max} 280, 272, 263, 257 and 229 mμ (ϵ 890, 1090, 1180, 1280 and 18600) [lit.[13] values: b.p. 130–138° (0.05 mm.), $n^{21}D$ 1.5639; λ_{max} 281, 272, 265 and 256 mμ (ϵ 830, 970, 970, 1120)]. Isomeric cinnamyl benzoate exhibits λ_{max} at 247 and 251 mμ (ϵ 21600 and 21300).[13] By comparison with known mixtures, the concentration of cinnamyl benzoate in this sample of Ic is estimated to be 0.8%.

Reactions of Olefins and *t*-Butyl Perbenzoate in the Absence of Cuprous Bromide.—Over a period of 3 hours *t*-butyl perbenzoate (0.124 mole) was added dropwise into 0.32 mole of boiling 1-octene. The reaction mixture was refluxed for another 4 hours. During this period carbon dioxide (700 ml., 24%) and *t*-butyl alcohol (1.3 g.) was collected. The reaction mixture was extracted with a 2 *N* solution of sodium carbonate from which 1.5 g. (10%) of benzoic acid was recovered. The residue, a thick oil (31 g.), was of high molecular weight (1310) and could not be distilled at reduced pressure.

When the reaction was carried out with allylbenzene instead of 1-octene, there was obtained 3.5 g. (23%) of benzoic acid and a yellow brittle solid (molecular weight, 800) which was not further investigated.

The Reactions of *t*-Butyl Peracetate and Olefins in the Presence of Cuprous Bromide.—The reactions were carried out under the conditions similar to those for the reactions of perbenzoate. Indistinguishable results were obtained when Lupersol #7 was substituted by freshly distilled *t*-butyl peracetate. The progress of the reactions were again followed by periodic examination of the infrared spectrum of the reaction mixture. In general, *t*-butyl peracetate is qualitatively less reactive than *t*-butyl perbenzoate, and the yields of allylic acetates are lower than the corresponding benzoates. The results are summarized in Table II.

The reaction of 1-hexene and *t*-butyl peracetate in the presence of cuprous bromide was not complete even after prolonged reflux (22 hr.). A mixture of *t*-butyl peracetate and the allylic acetate (Id) was isolated. The mixture was treated with an excess of sodium iodide in acetic acid containing traces of ferric chloride to decompose the perester. The acetic acid solution was diluted with water 10 minutes later, cautiously neutralized with sodium carbonate, decolorized with sodium bisulfite and extracted with ether. Hex-1-en-3-yl acetate was isolated from the ether extracts by distillation.

When hex-1-en-3-yl acetate (Id) and oct-1-en-3-yl acetate (Ie) prepared by this procedure were analyzed by gas chromatography at 140° through a 6′ × 1/4″ column packed with Silicon SF 96 fluid on firebrick using helium as the effluent gas (60 ml. per minute); only a single peak was observed in each case.

Cuprous Bromide-catalyzed Reactions of *t*-Butyl Perbenzoate and Cyclohexene in Aliphatic Acids.—The reactions were again carried out under similar conditions. Over a period of one hour, *t*-butyl perbenzoate (0.2 mole) was added to a boiling mixture of cyclohexene (40.5 g., 0.49 mole), an aliphatic acid (0.5–1.15 moles) and cuprous bromide (0.1 g., 0.35 mmole). Heating was continued for 3 to 12 hours to assure complete ester interchange. After the addition of an equal volume of petroleum ether to the cooled solution, the mixture was extracted with sodium carbonate to remove benzoic acid and the catalyst. The non-aqueous layer was washed with water until neutral and was then concentrated under reduced pressure. The products were isolated by distillation of the residual oil. The results are summarized in Table III.

A mixture of cyclohexenyl benzoate (19.2 g., 0.1 mole) and glacial acetic acid (50 ml.) was refluxed for 5 hours. After the usual workup, benzoic acid (6.3 g., 53%) was recovered from the carbonate extract, and cyclohexenyl acetate (7 g., 50%), b.p. 58° (9 mm.), was isolated from the organic layer.

Reaction of *t*-Butyl Perbenzoate and Triphenylmethane.—*t*-Butyl perbenzoate (10 ml., 0.05 mole) was added to a refluxing mixture of triphenylmethane (11.7 g., 0.05 mole) and cuprous bromide (0.1 g., 0.35 millimole) in benzene (50 ml.) over a period of one hour. The mixture was heated under reflux for an additional 12 hours. At the end of this period, it was filtered while hot, and 9.5 g. of a colorless solid separated from the filtrate upon cooling. The mother liquor was concentrated and the residue was triturated with a benzene–petroleum ether mixture (1:2), whereby an additional 2.1 g. of crystals was collected. The solid (11.6 g., 99%) was shown to be recovered triphenylmethane by comparison with the starting material.

CHICAGO 37, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Studies in Organic Peroxides. XXV. Preparation, Separation and Identification of Peroxides Derived from Methyl Ethyl Ketone and Hydrogen Peroxide

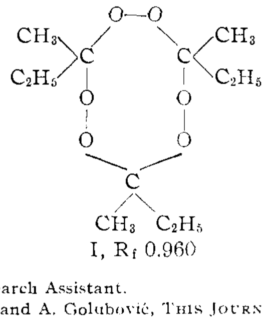
BY NICHOLAS A. MILAS AND ALEKSANDAR GOLUBOVIĆ[1]

RECEIVED MAY 9, 1959

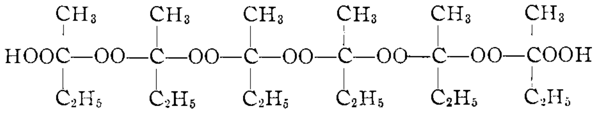
When methyl ethyl ketone is allowed to react with hydrogen peroxide in the presence of hydrogen ion, seven different peroxides are formed. Three have been separated by standard procedures and four by means of cellulose powder chromatography. 2,2-Dihydroperoxybutane has been shown to be the precursor from which all other peroxides can be formed. All peroxides of this series are highly sensitive to shock and explode with considerable brisance.

Although mixtures of organic peroxides derived from methyl ethyl ketone and hydrogen peroxide have been products of commerce for a long time, the complete separation of the individual peroxides present in these mixtures has never been accomplished and consequently their identity remained obscure. Quite frequently the properties of these peroxides would change on standing without an appreciable loss of active oxygen. This change, too, remained unexplained.

Our recent success in the separation and identification of the peroxides derived from diethyl ketone and hydrogen peroxide[2] prompted us to examine the peroxides derived from other simple ketones and hydrogen peroxide. When methyl ethyl ketone was allowed to react at 0 to −5° with 50% hydrogen peroxide in the presence of mineral acids, a mixture of peroxides was obtained which contained seven different peroxides as detected by paper chromatography[3] using hydrogen iodide–glacial acetic acid as the detecting agent. The probable structures of these peroxides are listed together with their R_f's in Fig. 1.

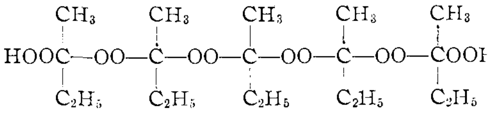


I, R_f 0.960



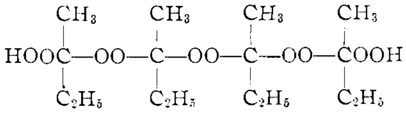
$$\mathrm{HOO}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\mathrm{OOH}$$

II, R_f 0.818



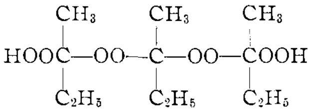
$$\mathrm{HOO}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\mathrm{OOH}$$

III, R_f 0.640



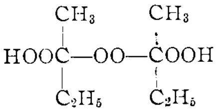
$$\mathrm{HOO}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\mathrm{OOH}$$

IV, R_f 0.475



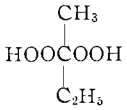
$$\mathrm{HOO}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\mathrm{OOH}$$

V, R_f 0.278



$$\mathrm{HOO}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\text{—OO—}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\mathrm{OOH}$$

VI, R_f 0.187



$$\mathrm{HOO}\overset{\mathrm{CH_3}}{\underset{\mathrm{C_2H_5}}{\mathrm{C}}}\mathrm{OOH}$$

VII, R_f 0.012

Fig. 1.—Peroxides derived from methyl ethyl ketone and hydrogen peroxide.

The percentage of each peroxide present in the mixture was estimated by paper chromatography to be approximately: I, 25; II, 1; III, 2; IV, 5; V, 12; VI, 45; and VII, 10%, respectively. Peroxides I, VI and VII were separated from the mixture without resorting to cellulose powder chromatography, while the other four peroxides were

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[1] Lucidol Research Assistant.

[2] N. A. Milas and A. Golubović, THIS JOURNAL, **81**, 3361 (1959).

[3] N. A. Milas and I. Belič, *ibid.*, **81**, 3358 (1959).