

Anal. Calcd. for $C_{34}H_{51}N$ (473.75): C, 86.19; H, 10.85. Found: C, 85.86; H, 10.81.

Ultraviolet spectrum. λ_{\max} 233 $m\mu$ (ϵ 35,000), 286 $m\mu$ (ϵ 6480), and 294 $m\mu$ (ϵ 6310).

*Reaction of 2 α -bromocholestan-3-one (6) with *N*-methyl-aniline.* A solution of 300 mg. (0.645 mmole) of 2 α -bromocholestan-3-one in 4 ml. of *N*-methylaniline was refluxed for 1 hr. under an atmosphere of nitrogen. The reaction mixture was diluted with ether and the excess amine removed by extraction with dilute hydrochloric acid. Evaporation of the dried ether layer left 295 mg. (97%) of colorless glass, λ_{\max} 232 $m\mu$ (ϵ 25,300), 286 $m\mu$ (ϵ 5600), and 292 $m\mu$ (ϵ 5270), whose infrared spectrum had no carbonyl absorption. Four recrystallizations from ethyl acetate gave 112 mg. (37%) of colorless needles of 13, m.p. 181–185°, $[\alpha]^{24}_D +69.5^\circ$ (c 2.36).

Ultraviolet spectrum. λ_{\max} 232 $m\mu$ (ϵ 40,000), 286 $m\mu$ (ϵ 7300), and 293 $m\mu$ (ϵ 6800).

Infrared spectrum. $\nu_{\max}^{CS_2}$ 738 cm^{-1} (s) (four adjacent hydrogens on benzene ring).

The mixture melting point with the *N*-methylindole (13) from cholestan-2-one was undepressed, m.p. 181–185°, but the mixture melting point with the indole 22 from cholestan-3-one was depressed to 145–179°.

*Estimation of *N*-methylaniline in *N,N*-dimethylaniline.* (a) A solution of 19.043 g. of the *N,N*-dimethylaniline used for dehydrobromination in 50 ml. of ether was stirred (magnetic bar) overnight with 1 g. of *p*-toluenesulfonyl chloride. Dimethylaniline was then removed by extraction with dilute hydrochloric acid; excess sulfonyl chloride was removed by stirring (magnetic bar) the ethereal solution with 10% potassium hydroxide solution. The dried ether solution was evaporated to leave 52.0 mg. of *N*-methylaniline *p*-toluenesulfonamide which corresponded to 0.112% of *N*-methylaniline contaminating the dimethylaniline.

(b) To prove that no hydrolysis of the sulfonamide was taking place 113 mg. of *N*-methylaniline *p*-toluenesulfonamide in 85 ml. of ether was stirred (magnetic bar) with 15 ml. of 10% potassium hydroxide solution for 22.5 hr. at room temperature. Evaporation of the washed and dried ether solution left 111.7 mg. (98.5% recovery) of starting material.

(c) To show that the reaction of *N*-methylaniline with *p*-toluenesulfonyl chloride was essentially complete, 9.390 g. of *N,N*-dimethylaniline containing 16.7 mg. of added *N*-methylaniline was treated as in (a). There was obtained

59.3 mg. (90%) of *p*-toluenesulfonamide. The total amount of *N*-methylaniline calculated to be present was (16.7) + (9.390 \times 0.00112) = 27.2 mg. equivalent to 66.3 mg. of *p*-toluenesulfonamide.

*Disproportionation of *N,N*-dimethylaniline hydrobromide.* A solution of 480 mg. (2.38 mmoles) of anhydrous *N,N*-dimethylaniline hydrobromide and 37.8 mg. (2.10 mmoles) of water in 6.686 g. of *N,N*-dimethylaniline was refluxed under nitrogen for 1 hour. A white solid appeared in the condenser. The reaction mixture was distributed between ether and dilute sodium bicarbonate solution. From the aqueous layer was precipitated 361 mg. (1.53 mmoles, 64%) of phenyltrimethylammonium perchlorate by addition of sodium perchlorate. Recrystallization from water gave 305 mg., m.p. 179–181.5°. The ether layer was dried and allowed to react with *p*-toluenesulfonyl chloride as described in part (a) above. The yield of *N*-methylaniline *p*-toluenesulfonamide was 552 mg. After allowance for the *N*-methylaniline in the dimethylaniline (6.686 \times 0.0011) the amide formed by disproportionation was 534 mg. (2.04 mmole, 86%). One recrystallization from 95% ethanol gave 499 mg., m.p. 95.5–96.5°, undepressed on admixture with an authentic specimen. When the same reaction was carried out without addition of water to the reaction mixture, the disproportionation still occurred.

*Reaction of *N*-methylaniline with 2 α ,4 α -dibromocholestan-3-one (1).* A solution of 1.000 g. (2.60 mmoles) of 1 in 10 ml. of *N*-methylaniline was refluxed (oil bath 210°) under nitrogen for 2 hr. Excess amine was removed by steam distillation after addition of sodium bicarbonate. The residue was taken up in ether, washed with dilute hydrochloric acid, water, and saturated sodium chloride solution. Evaporation of the dried ether solution left 734 mg. of an amber colored glass, λ_{\max} 231 and 289 $m\mu$, with no more than ca. 6% of 17 present. The infrared spectrum had no carbonyl absorption but did have peaks corresponding both to four and five adjacent hydrogens on a benzene ring. No crystalline material could be obtained from the crude product. Chromatography on activity II alumina gave no fractions that could be crystallized. Furthermore, infrared spectra showed that the material containing four adjacent aromatic hydrogens had not been separated from that with five adjacent aromatic hydrogens.

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Rearrangements of Certain α -Alkoxy- α -hydroperoxyacophenones. Alcoholysis of Acetic Benzoic Anhydride

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The decompositions of four different α -alkoxy- α -hydroperoxyacophenones in hot ethanol and methanol were studied. The decompositions were shown to occur by three different simultaneous routes, two of which (87%) apparently involve concerted rearrangement of the hydroperoxides with migration of the acyl group. Incidental to this was a study of the alcoholysis of acetic benzoic anhydride. The major nucleophilic attack occurred at the acetyl carbonyl group giving benzoic acid and acetates.

α -Alkoxy- α -hydroperoxyacophenones (I) are products obtained from ozonolysis of certain 1,2-dibenzoylalkenes^{1,2} and phenylacetylenes.³ Since,

as shown in the accompanying paper,³ it is not always possible to isolate these (I) from the phenyl-

(2) P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *J. Am. Chem. Soc.*, **82**, 6136 (1960).

(3) P. S. Bailey, Y. G. Chang, and W. W. L. Kwie, *J. Org. Chem.*, **27**, 1198 (1962).

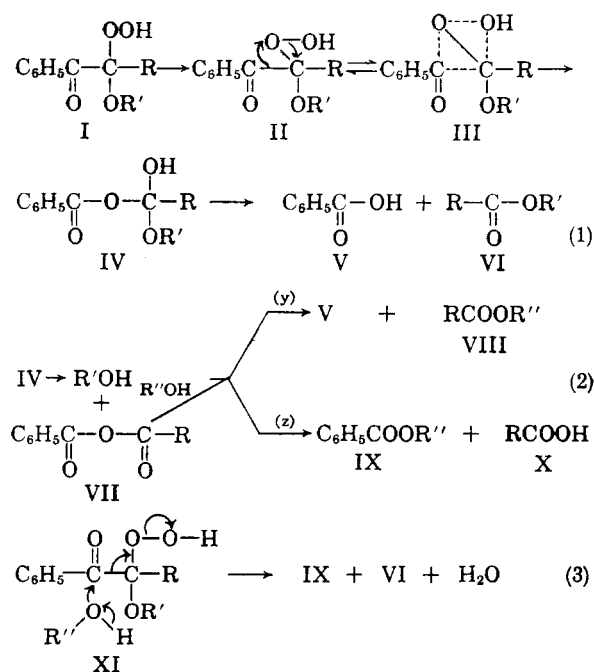
(1) P. S. Bailey and S. S. Bath, *J. Am. Chem. Soc.*, **79**, 3120 (1957).

acetylene reaction mixtures, it was necessary to know with certainty both how they decompose in the presence of alcohols and the exact proportions of the decomposition products, in order to elucidate the nature of the attack of ozone on acetylenes.

An earlier paper¹ described briefly the decompositions of Ia and Ie, when heated in methanol or when treated with formic acid, sodium hydroxide, or pyridine, and suggested possible mechanisms for the decompositions. Not all of the products were isolated, however, and no attempt was made to distinguish between the two mechanisms proposed. This is the purpose of the present paper, in regard to the decompositions in refluxing alcohols. The decompositions in sodium hydroxide and in formic acid will be the subject of a later communication.

There are three most likely ways in which these hydroperoxides (I) could decompose in an alcohol solution, as shown in Chart I. The first two involve a concerted rearrangement of I to give intermediate IV which then could decompose either (1) to give benzoic acid (V) and ester VI or (2) to give an alcohol and a mixed anhydride (VII), which would then undergo alcoholysis to V and VIII or to IX and X. The third route involves an alcoholysis or displacement mechanism, as shown in XI to give IX, VI, and water.

CHART I



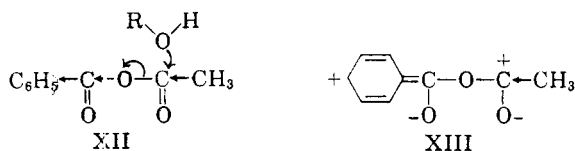
- a. R = H, R' = R'' = CH₃
- b. R = H, R' = CH₃, R'' = C₂H₅
- c. R = H, R' = C₂H₅, R'' = CH₃
- d. R = H, R' = R'' = C₂H₅
- e. R = R' = R'' = CH₃
- f. R = R' = CH₃, R'' = C₂H₅
- g. R = CH₃, R' = C₂H₅, R'' = CH₃
- h. R = CH₃, R' = R'' = C₂H₅

necessary to study the alcoholysis of one of the expected mixed anhydrides. The one chosen was acetic benzoic anhydride (VIIe) which was synthesized from ketene and benzoic acid.⁴

Freshly prepared acetic benzoic anhydride (VIIe) was used without further purification, since Hurd and Dull⁴ have reported that disproportionation to benzoic and acetic anhydrides occurs upon heating, or even upon standing at room temperature. The results from heating alcohol solutions of the mixed anhydride (VIIe) for fifteen minutes (Table I) show that no appreciable disproportionation occurred. Hurd and Dull⁴ reported that upon treatment with aniline, pure acetic benzoic anhydride was converted to benzoic acid and acetanilide in 88% and 83% yields, respectively. Neither acetic acid nor benzanilide was isolated.

Our alcoholysis experiments with VIIe show that although the major reaction results in benzoic acid and esters of acetic acid, a minor reaction giving acetic acid and esters of benzoic acid also occurs (Table I). Theoretically, the yield of benzoic acid should equal that of acetate, and the yield of acetic acid should equal that of benzoate. The actual results showed the ester yields to be roughly 4-5% greater than the acid yields in each case. This apparently was due largely to esterification of acetic acid to a slight degree during distillation of the reaction mixture after the alcoholysis. Benzoic acid was shown to undergo esterification under these conditions much less than acetic acid. Thus it appears adequate to conclude that alcoholysis of acetic benzoic anhydride occurs roughly 85% by route 2y (Chart I) to give benzoic acid and acetates and roughly 15% by route 2z (Chart I) to give acetic acid and benzoates.

Hurd and Dull's⁴ explanation of this preferential cleavage of the mixed anhydride, translated into modern terminology, was that the electron-attracting effect of the phenyl group and the

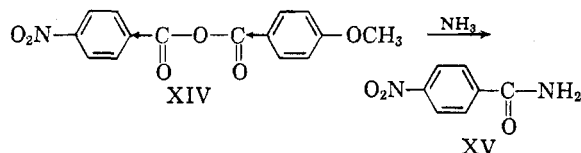


electron repelling effect of the methyl group would tend to weaken the carbon-oxygen bond involving the acetyl group and facilitate nucleophilic attack at the acetyl carbonyl, as shown in XII. This, however, is just the opposite of the findings of Denney and Greenbaum⁵ who showed that *p*-nitrobenzoic *p*-methoxybenzoic anhydride (XIV) and *p*-nitrobenzoic benzoic anhydride reacted with liquid ammonia to give high yields of *p*-nitrobenzamide (XV). A more logical explanation,

(4) C. D. Hurd and M. F. Dull, *J. Am. Chem. Soc.*, **54**, 3427 (1932).

(5) D. B. Denney and M. A. Greenbaum, *J. Am. Chem. Soc.*, **79**, 979 (1957).

which correlates both cases, is that, as shown in XIII, resonance in the benzoyl group would disperse the positive charge into the benzene ring making this carbonyl group less susceptible to nucleophilic attack than the acetyl carbonyl group,



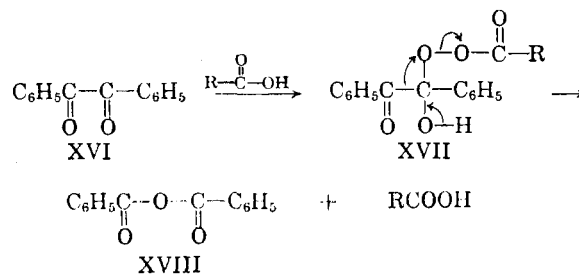
which would be polarized by the inductive effect of the methyl group. Similarly, in XIV, resonance in the *p*-anisoyl group would decrease its susceptibility to nucleophilic attack in comparison to the *p*-nitrobenzoyl group, where resonance would have no effect other than to increase the positive character of the carbonyl carbon inductively.

With this information it was then possible to draw valid conclusions concerning the extent to which the various mechanisms shown in Chart I are involved during the decompositions of the α -alkoxy- α -hydroperoxyacetophenones (I) in alcohols. Four of these were synthesized by ozonolysis of 1,2-dibenzoyl ethylene and 1,2-dibenzoyl propene in methanol and in ethanol (Ia, Ic, Ie, and Ig); two (Ic and Ig) are new compounds. Eight sets of decompositions were carried out by refluxing methanol and ethanol solutions of each of the four hydroperoxides for five minutes. The per cent yields of the products were determined in various ways, including gas chromatography. The most informative data (Table I) was obtained by using as solvent an alcohol with an alkoxy group different from that of the alkoxy hydroperoxide (*i.e.*, Chart I, examples Ib, Ic, If, and Ig, or Table I, examples Iib, IIIa, IVb, and Va). In this way the extent to which each mechanism is involved could be determined.

For example, the decomposition of α -hydroperoxy- α -methoxyacetophenone in ethanol (Chart I, Ib or Table I, Iib) gave 86.1% benzoic acid, 13.9% ethyl benzoate, 1.2% formic acid, 92.6% methyl formate, 5.9% ethyl formate, and 7.0% methanol. Since the methanol, formic acid (Xb), and ethyl formate (VIIIb) could come only from route 2, Chart I, one can conclude that roughly 7% of the reaction went by this path with roughly 6% by 2y and 1% by 2z. These latter two figures check reasonably well with the results obtained from alcoholysis of the mixed anhydride (VIIe), assuming that benzoic formic anhydride (VIIa) would behave similarly to acetic benzoic anhydride (VIIe). The data from IVb and Va (Table I), which involve the conversion of acetic benzoic anhydride to ethyl acetate and methyl acetate, respectively, bear out the validity of this assumption. Since benzoic acid (86.1%) could be produced by both routes 1 and 2 (Chart I) with only 6% coming from route 2, it can be concluded that

route 1 (Chart I) is the major route for the decomposition of the hydroperoxides and occurs to the extent of approximately 80%. Finally, ethyl benzoate (IXb, Chart I; 13.9%, Iib, Table I) can be produced by either of routes 2 or 3 (Chart I), but only approximately 1% of it comes from route 2. Thus route 3 (Chart I) appears to occur to the extent of approximately 13%. The extent to which route 3 occurs can also be determined from methyl formate (VIb) which is produced to the extent of roughly 93% by routes 1 and 3; since 80% comes from route 1, this leaves 13% from route 3. A scrutiny of the other data in Table I, especially examples IIIa, IVb, and Va shows that all of the hydroperoxide decompositions occur by routes 1, 2, and 3 (Chart I) in essentially the same percentages. There are perhaps other possible mechanisms by which some of these products could arise, but these appear insignificant, particularly in view of the excellent correlations just pointed out.

Routes 1 and 2 (Chart I) both involve a rearrangement of the α -alkoxy- α -hydroperoxyacetophenone (I). The most logical explanation of this rearrangement is that it is completely concerted and goes through the double transition state III, similar to those proposed by Denney⁶ for certain other peroxide rearrangements. The preferential migration of an acyl group over that of hydrogen or alkyl is surprising, since the acyl group would be expected to have the lowest migratory aptitude of the three. A similar phenomenon (XVII \rightarrow XVIII) occurs in Baeyer-Villiger oxidations of benzil (XVI) and other 1,2-diketones.⁷



Leffler⁸ has suggested an alternative mechanism for Baeyer-Villiger oxidations of 1,2-diketones which does not involve migration of the acyl group. This cannot be applied to the present rearrangement, however. It may be that in the concerted mechanism suggested in Chart I the peroxy group starts the reaction by making a nucleophilic attack on the acyl group which migrates more as a positive than as a negative entity as shown in XIX. Alternatively, route 1 in Chart I could occur as shown in XX without going through IV at all. This would

(6)(a) D. B. Denney, *J. Am. Chem. Soc.*, **78**, 590 (1956);

(b) D. B. Denney and D. G. Denney, *J. Am. Chem. Soc.*, **79**, 4806 (1957).

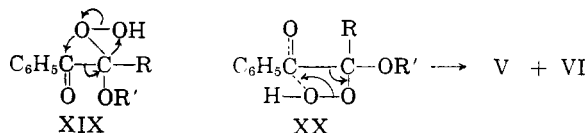
(7) C. H. Hassall, *Org. Reactions*, **IX**, 74, 82, 101 (1957).

(8) J. E. Leffler, *J. Org. Chem.*, **16**, 1785 (1951).

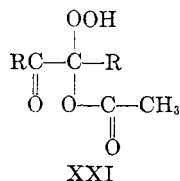
TABLE I

Decomposition Reaction	Products in Mole %									
	C_4H_7COOH	$RCOOCH_3$	$RCOOCH_2CH_3$	$RCOOH$	C_6H_5COOH	$C_6H_5COOCH_2CH_3$	CH_3OH	CH_3CH_2OH	CH_3CHO	CH_3CH_2CHO
I $C_6H_5C(O)OC(CH_3)_2C(O)H$	86.1 ^a	90.4 ^a	90.0 ^a	9.7 ^a	14.2 ^a					
a CH_3OH										
b CH_3CH_2OH	85.3 ^a			10.0 ^a		14.0 ^a				
II $C_6H_5C(O)OC(CH_3)_2C(O)H$	85.5 ^a	98.9		1.1	14.5 ^a					
a CH_3OH										
b CH_3CH_2OH	86.1 ^a	92.6	5.9	1.2		13.9 ^a	7.0			
III $C_6H_5C(O)OC(CH_3)_2C(O)H$	86.4 ^a	6.3	91.8	1.1	13.5 ^a					Present ^b
a CH_3OH										
b CH_3CH_2OH	86.6 ^a	98.5		1.2		13.6 ^a				
IV $C_6H_5C(O)OC(CH_3)_2C(O)H$	86.2 ^a	98.9		1.1	13.7 ^a					
a CH_3OH										
b CH_3CH_2OH	86.1 ^a	92.7	6.2	1.1		13.9 ^a	Present ^b			
V $C_6H_5C(O)OC(CH_3)_2C(O)H$	86.6 ^a	6.3	91.5	1.2	13.3 ^a					Present ^b
a CH_3OH										
b CH_3CH_2OH	86.9 ^a	98.7		1.2		13.8 ^a				

^a These yields were corrected by the extent to which the organic acids esterified during the decomposition reaction, but not during the work-up procedure. ^b In these cases the separation of ethanol and methanol was not good enough for quantitative determinations.



not explain the occurrence of anhydride intermediates, however, which appear to be the major products from rearrangements of the similar acyloxy hydroperoxides (XXI).⁹



EXPERIMENTAL^{10,11}

Quantitative gas chromatographic analyses.¹² The ester and alcohol analyses were done by gas chromatography. For the higher boiling benzoates a 12-ft. coiled column of 1/4 in. O.D. copper tubing packed with Ucon nonpolar on 30/60 mesh acid-washed chromosorb¹³ was used. Identifications were made by comparison of peaks with those of authentic compounds under the same experimental conditions of 160° and a gas flow rate of 90 ml./min. A similar 10-ft. column packed with Carbowax 400 on the same chromosorb¹³ was used for the aliphatic ester and alcohol mixtures. Peak areas were determined by means of a planimeter¹⁴ and the percentage yield of each component was calculated after comparison of the peak area with an experimental plot of peak areas vs. mole per cents of each pure component in the solvent ethanol. This was necessary since the components of the mixture possess different thermal conductivities under the same experimental conditions. The gas flow rate was 90 ml./min. and the temperature 60°.

Acetic benzoic anhydride was prepared from ketene¹⁵ and pure benzoic acid (m.p. 122–123°) by the method of Hurd and Dull.⁴ At the conclusion of the reaction, complete removal of the ether solvent under vacuum gave a 99% yield of acetic benzoic anhydride having n_D^{20} 1.4955 and d_4 1.501.¹⁶

α -Hydroperoxy- α -methoxyacetophenone (Ia) was prepared by ozonolysis of 1,2-dibenzoyl ethylene in methanol and carbon tetrachloride (1:3)¹ in 63% yield; m.p. 81–82°;

(9) R. Criegee and M. Lederer, *Ann.*, **583**, 29 (1953).

(10) For more details see Ph. D. dissertation of Y. G. Chang, The University of Texas, June 1961.

(11) All melting points are corrected. Carbon and hydrogen analyses were done by The University of Texas Biochemical Institute. Infrared spectra were taken on a Baird double beam infrared spectrophotometer, either in chloroform (10%) or potassium bromide wafers. The ozonolysis set-up was as described in earlier papers.¹

(12) The apparatus had a Gow-Mac 30-S (Model 9454) thermal conductivity cell, four helix tungsten (Gow-Mac type 9225) hot wire filaments, a Mallory 5 ampere tapering charger (Model 12SAC5) for D.C. current and a Varian Model G-10 recorder. The sensitivity control possessed ten-step precision attenuation and reduced the signal by one-half each step. Dry helium was the carrier gas.

(13) Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

(14) Keuffel and Esser Co.

(15) J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 112 (1940).

(16) R. E. Dunbar and F. C. Garven, *J. Am. Chem. Soc.*, **77**, 4161 (1955), report these same constants.

recrystallized twice from ethyl acetate by addition of petroleum ether (b.p. 60–68°), m.p. 82°.²

α -Hydroperoxy- α -methoxypropioiphenone (Ie) was prepared by ozonolysis of 1,2-dibenzoylpropene in methanol-carbon tetrachloride (1:3)¹ in 88% yield (m.p. 57–60°); recrystallized from ethanol by addition of petroleum ether, m.p. 60°.¹

α -Ethoxy- α -hydroperoxyacetophenone (Ic) was prepared in the same way as was Ia except that ethanol-carbon tetrachloride was used as the solvent (1:3). The filtered peroxide had to be washed immediately with petroleum ether to prevent decomposition, *sometimes with violence*. A 62% yield of material melting at 70–78° was obtained; purification as with Ia raised the melting point to 77°. The material was very soluble in ethanol, methanol, and ethyl acetate, soluble in chloroform and insoluble in petroleum ether. The infrared spectrum was very similar to that of Ia,^{1,2} showing a broad hydroxyl band at 2.9–3.1 μ and a strong carbonyl band at 5.9 μ . The pure material is stable at room temperature, but decomposes rapidly in methanol or ethanol.

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_4$: C, 61.22; H, 6.16. Found: C, 60.40; H, 6.49.¹⁷

α -Ethoxy- α -hydroperoxypropioiphenone (Ig) was prepared in the same way as was Ie, except using ethanol-carbon tetrachloride (1:3). It was necessary to wash the filtered peroxide immediately with petroleum ether to prevent decomposition, *sometimes with violence*. The yield was 69% and the melting point 52–57°; recrystallization as with Ia raised the melting point to 57°. Solubility behavior was the same as with Ic. The pure material was fairly stable at room temperature, very stable at 0°, but decomposed rapidly in organic solvents. The infrared spectrum (potassium bromide disk) was quite similar to that of Ie with a broad hydroxyl band at 2.9–3.1 μ and a strong carbonyl band at 5.9 μ .

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_4$: C, 62.84; H, 6.71. Found: C, 62.65; H, 6.58.

Reaction of acetic acid with ethanol. A solution of 0.3168 g. of redistilled glacial acetic acid in 15 ml. of anhydrous ethanol was refluxed for 15 min., after which it was cooled to room temperature and titrated with standard base. Calculations showed a loss of 2.5% of the acetic acid. From a similar unrefluxed solution, 99.7% of the acetic acid was accounted for. Thus 2.2% of the acetic acid is esterified under these conditions.

Benzoic acid and ethanol under the same conditions showed only 0.7% esterification.

Decompositions of α -alkoxy- α -hydroperoxyacetophenones (I) in methanol or ethanol. The percentage yields of products from the eight different decompositions are shown in Table I. A typical run is described below. A suspension of 0.6971 g. (0.00383 mole) of freshly prepared α -hydroperoxy- α -methoxyacetophenone (Ia) at 0° and 1.2 ml. of cold (0°) anhydrous ethanol was allowed to come to room temperature in a 50-ml. round bottom flask equipped with a condenser connected at the upper end with a small side-arm trap placed in an acetone-Dry Ice bath to prevent the loss of low-boiling materials. The low volume of solvent (mole ratio solvent to peroxide approx. 5:1) was necessary in order to make concentrations of decomposition products sufficiently high for gas chromatographic analysis. In this case the peroxide did not decompose in the solvent at room temperature, although this did happen with Ic, Ie, and Ig. In each case, however, the reaction mixture was refluxed for 5 min. and allowed to return to room temperature. At this point the reaction mixture was no longer peroxidic. The set-up was then rearranged for distillation using the same condenser and cold trap. The fraction boiling at 30–78° was collected. The condenser, adapter, and trap were carefully washed with a small amount of ethanol which was added to the distillate.

A. *The residue* in the distillation flask partially crystallized

(17) The low carbon result appears to be due to sudden decomposition during analysis.

at room temperature. It was treated with just enough saturated sodium bicarbonate solution to convert the acids present to sodium salts, and the resulting mixture was extracted six times with 30 ml. of ether each time. The aqueous solution was acidified with 2.5 ml. of concd. hydrochloric acid and the precipitated benzoic acid (0.3365 g., 71.9%, m.p. 121–122°, no depression in mixture melting point with an authentic sample) was filtered off. Since the volume of the filtrate and washings was 20 ml., the benzoic acid remaining therein was determined by suspending 3 g. of benzoic acid in 17.5 ml. of water and 2.5 ml. of concd. hydrochloric acid and allowing the mixture to come to equilibrium. The undissolved benzoic acid was filtered off, and the filtrate was continuously extracted with ether for 24 hr. Titration of the ether extract, to which water had been added, with standard sodium hydroxide solution gave the amount of dissolved benzoic acid. Addition of this, plus the very small amount of benzoic acid which reacts with ethanol during such decompositions, to the amount of benzoic acid obtained by filtration gave a total yield of 86.1% benzoic acid. The filtrate from the reaction mixture was then continuously extracted with ether for 24 hr., and the ether extract was titrated with standard sodium hydroxide solution. Subtraction of the amount of benzoic acid shown (above) to be present gave a total formic acid yield of 1.2%. The ether extract of the residue was dried over anhydrous sodium sulfate and the ether was entirely removed under the reduced pressure of a water aspirator, leaving 0.0833 g. (14.5% yield) of an oil which was identified as pure ethyl benzoate by gas chromatography. Correction for the reaction of benzoic acid with ethanol during the peroxide decomposition lowered the yield to 13.9%.

B. *The low-boiling distillate* weighed 2.6404 g. Gas chromatographic analysis gave the four peaks shown in Table II. A sample calculation follows, all figures coming from Table II.

TABLE II

GAS CHROMATOGRAPHIC ANALYSIS OF LOW-BOILING DISTILLATE (2.6404 g.) FROM DECOMPOSITION OF 0.00383 MOLE PER CENT OF α -HYDROPEROXY- α -METHOXYACETOPHENONE (Ia)

Peak	Compound	Mol. Wt.	Peak Area	Mole % from Plots
1	HCOOCH ₃	60.05	6.31	6.31
2	HCOOCH ₂ CH ₃	74.08	0.40	0.40
3	CH ₃ OH	32.04	0.40	0.48
4	CH ₃ CH ₂ OH	46.07	—	92.81

Wt. of methyl formate in low-boiling distillate =

$$\frac{(6.31 \times 60.05) \times 2.6404 \text{ g. sample}}{(6.31 \times 60.05) + (0.40 \times 74.08) + (0.48 \times 32.04) + (92.81 \times 46.07)} = 0.2129 \text{ g.}$$

$$\text{Percentage yield methyl formate} = \frac{0.2129 \text{ g.} \times 100}{60.05 \times 0.00383 \text{ moles peroxide}} = 92.6\%$$

Similarly the yields of ethyl formate and methanol were calculated as 5.9% and 7.0%, respectively.

Reaction of acetic benzoic anhydride (VIIe) with alcohols. In the case of ethanol this was done in two ways, whereas in the case of methanol only method B was used (Chart I).

A. A solution of 10.11 g. (0.0616 mole) of freshly prepared acetic benzoic anhydride in 25 ml. of anhydrous ethanol was refluxed for 15 min. in the apparatus described in the peroxide decomposition. The decomposition mixture was made slightly basic with saturated sodium carbonate solution and then extracted 6 times with 30 ml. of ether each time. The aqueous layer was acidified with concd. hydrochloric acid. The precipitated benzoic acid weighed 6.26 g. and melted at 121–122°. The filtrate was continuously extracted with ether for 24 hr. after which the ether was completely evaporated from the extract under reduced pressure. The residue was carefully distilled, giving 0.36 g. (9.7% yield) of acetic acid boiling at 115–120°. Correction for the small amount lost by esterification during the decomposition raised the yield to 10.0%. The remaining residue was recrystallized from water giving 0.12 g. of benzoic acid melting at 121–122°. The total benzoic acid yield, after correction for the small amount lost by esterification during the decomposition, was 85.3%. Identification was by the mixture melting point method. The ether extract from the original reaction mixture was dried and completely removed of ether by evaporation, after which it was fractionally distilled. The fraction boiling at 77–79° was analyzed gas chromatographically, showing ethyl acetate and ethanol peaks. Calculations as shown in the peroxide decomposition experiment gave a yield of 4.87 g. of ethyl acetate. Correction for the small amount produced by esterification of acetic acid during the decomposition made the yield 90.0%. The remaining fraction boiled at 210–212° and weighed 1.35 g. Correcting for the small amount produced by esterification of benzoic acid during the esterification gave a yield of 14.0%.

B. A solution of 13.0728 g. (0.07971 mole) of freshly prepared acetic benzoic anhydride and 23 ml. of anhydrous ethanol was refluxed as described in part A. The products, determined in the same manner described under the peroxide decomposition, were 86.7% benzoic acid, 10.0% acetic acid, 13.3% ethyl benzoate, and 89.0% ethyl acetate.

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