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

The Rearrangement of α,β-Epoxy Ketones. VI. 1,1-Disubstituted Ethylene Oxides

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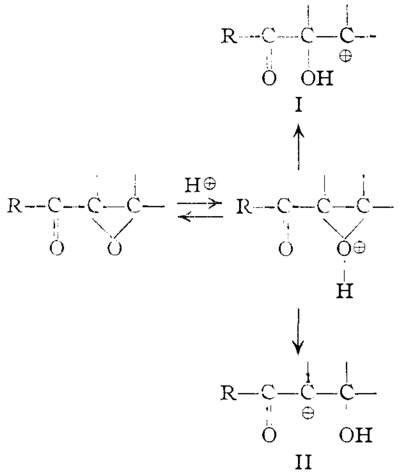
α,β-Epoxy-α-phenylpropiophenone, α,β-epoxy-α-ethylpropiophenone and 1,2-dimesityl-2,3-epoxy-1-propanone have been isomerized to α-formyldesoxybenzoin, α-formylbutyrophenone and the enol of α-formyldesoxymesitoin, respectively, by treatment with boron trifluoride. The analogous rearrangement of α,β-epoxypropiophenone produced 1,3,5-tribenzoylbenzene. The interpretation of the results suggests that a carbonium ion adjacent to a carbonyl group is either equivalent in stability or more stable than a primary carbonium ion.

The products derived from the acid-catalyzed isomerization of a variety of α,β-epoxy ketones have been rationalized by the assumption that the initial step in the isomerization involves cleavage of the oxirane ring to leave a positive charge on the carbon atom beta to the carbonyl group (I).[2,3] The fission of the oxirane ring to form the transient cation I rather than II appeared to be justified; the formation of structure II would be expected to be energetically unfavorable since this structure places partial positive charges on adjacent atoms.



Although a carbonyl group is usually considered to destabilize an adjacent carbonium ion (such as II),[4,5] there is little evidence bearing on the extent of this destabilization relative to the effect of other substituents. Since the mode of cleavage (*i.e.*, I or II) of the oxirane ring accompanying the acid-catalyzed rearrangement of α,β-epoxy ketones appeared to offer a measure of the relative stability of a carbonium ion (or a partial positive charge)[3] adjacent to a carbonyl group, we were led to study the isomerization of certain 1,1-disubstituted ethylene oxides III. The products formed by rearrangement of these oxides III would provide a measure of the relative stabilities of a primary carbonium ion (Fig. 1, reaction path A) and a carbonium ion adjacent to a carbonyl group (Fig. 1, reaction path B).

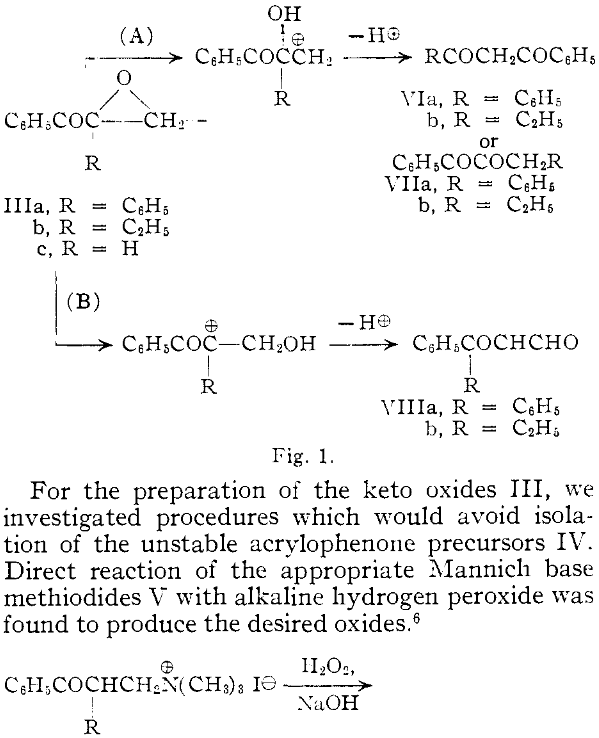
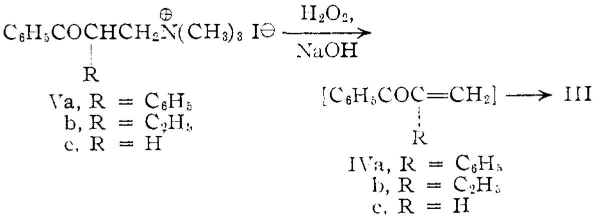


Fig. 1.

For the preparation of the keto oxides III, we investigated procedures which would avoid isolation of the unstable acrylophenone precursors IV. Direct reaction of the appropriate Mannich base methiodides V with alkaline hydrogen peroxide was found to produce the desired oxides.[6]



$$C_6H_5CO\underset{\displaystyle R}{C}HCH_2\overset{\oplus}{N}(CH_3)_3\ I^{\ominus} \xrightarrow[NaOH]{H_2O_2,} [C_6H_5CO\underset{\displaystyle R}{C}{=}CH_2] \longrightarrow III$$

Va, R = C_6H_5
b, R = C_2H_5
c, R = H

IVa, R = C_6H_5
b, R = C_2H_5
c, R = H

In a previous study[2b] the product derived from the isomerization of α-phenyl-*cis*-benzalacetophenone oxide appeared to be best explained by the assumption that the reaction proceeded *via* an ion of the type II. This observation suggested that the formation of a carbonium ion adjacent to a carbonyl group may occur without difficulty if the ion is stabilized by an adjoining aryl group.[7] We therefore chose α,β-epoxy-α-phenylpropiophenone (IIIa) for our initial studies in an effort to favor reaction path B (Fig. 1). The rearrangement of

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(1) Alfred P. Sloan Research Assistant, 1956.

(2) For previous papers in this series see THIS JOURNAL, (a) **76**, 1235 (1954); (b) **77**, 6525 (1955); (c) **78**, 2298 (1956); (d) **78**, 4394 (1956); (e) **79**, 1488 (1957).

(3) The cleavage of the oxirane ring and the attendant rearrangement may well be concerted processes. If this is the case, the positive charge would not reside entirely on the β-carbon atom as depicted in I. Studies to determine the relative charge distribution in the transition state are currently in progress.

(4) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 150.

(5) The failure of certain α-halo ketones to react with silver nitrate has been attributed to such destabilization [for example, see R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 143].

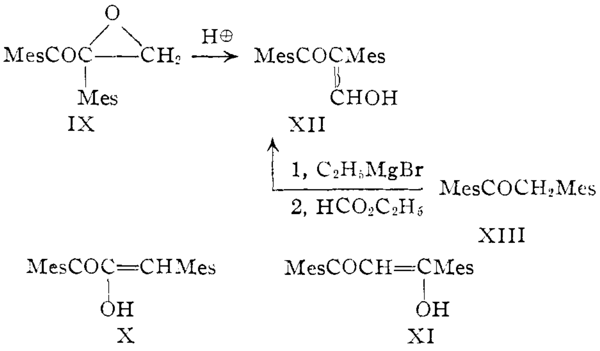
(6) This reaction is analogous to the use of the quaternary salts of Mannich bases as precursors for unsaturated ketones in the Michael reaction [see J. H. Brewster and E. L. Eliel, *Org. Reactions*, **7**, 99 (1953)].

(7) The successful use of α-aryl α-halo ketones as alkylating agents in the Friedel–Crafts reaction [P. Ruggli, H. Dahn and J. Wegmann, *Helv. Chim. Acta*, **29**, 113 (1946)] is in agreement with this idea.

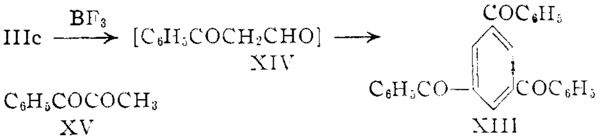
the oxide IIIa in the presence of boron trifluoride etherate yielded the keto aldehyde VIIIa, the product expected if the reaction followed path B (Fig. 1). We were unable to isolate either of the diketones VIa or VIIa.

A previous example of an acid-catalyzed isomerization of an oxide analogous to IIIa has been reported[8]; the reaction of 1,2-dimesityl-2,3-epoxy-1-propanone (IX) with a mixture of acetic and hydriodic acids was found to yield an unknown product isomeric with the starting ketone. We have effected the same reaction by treatment of the oxide IX with boron trifluoride etherate. The product is acidic and has an infrared spectrum which is suggestive of an enolized *β*-dicarbonyl compound. Since the product does not resemble either of the known, isomeric enolized diketones X[9] or XI,[10] the compound was assigned the enolized keto aldehyde structure XII, an analog of the keto aldehyde VIIIa derived from IIIa. This assignment was confirmed when compound XII was synthesized by the reaction of the bromomagnesium enolate of desoxymesitoin (XIII) with ethyl formate.

We next turned our attention to *α*,*β*-epoxy-*α*-ethylpropiophenone (IIIb). Rearrangement of the epoxide IIIb *via* reaction path B (Fig. 1) would involve a tertiary cation adjacent to a carbonyl group as was the case with IIIa; however, the formation of such an ion from IIIb would not be favored by an adjoining phenyl ring. The isomerization of the epoxide IIIb proceeded much more slowly than isomerizations previously studied as might be expected if the reaction involved the formation of a relatively unstable carbonium ion. Best results were obtained when the rearrangement was effected in the presence of a benzene solution of gaseous boron trifluoride rather than with boron trifluoride etherate.[11] The only products which could be isolated from the isomerization were the keto aldehyde VIIIb and its degradation product, butyrophenone; neither of the diketones VIb and VIIb or compounds derived from them, the products expected from rearrangement *via* path A (Fig. 1), could be isolated from the reaction mixture.



We therefore investigated the behavior of *α*,*β*-epoxypropiophenone (IIIc). Reaction of this oxide IIIc with boron trifluoride yielded the triketone XIII as the only isolable product. The triketone XIII was presumably derived from the intermediate keto aldehyde XIV; when an authentic sample of the keto aldehyde XIV was subjected to the conditions of the rearrangement, only the triketone XIII was produced. The alternative product, the diketone XV which might result from the isomerization of the oxide IIIc, has been found to be stable to acids[12] and, consequently, is not the precursor of the triketone XIII.



In order to determine which of the reaction paths C or D (Fig. 2) was operative in the conversion of the oxide IIIc to the triketone XIII, the isomerization of the partially deuterated oxide XVI was studied. The fate of the deuterium label in each reaction path is outlined in Fig. 2; 47% of the deuterium present in the oxide XVI was retained in the product XIII. Consequently, we are led to believe that approximately half of the isomerization of the oxide IIIc is proceeding *via* reaction path C (Fig. 2) and the remainder *via* path D (Fig. 2).

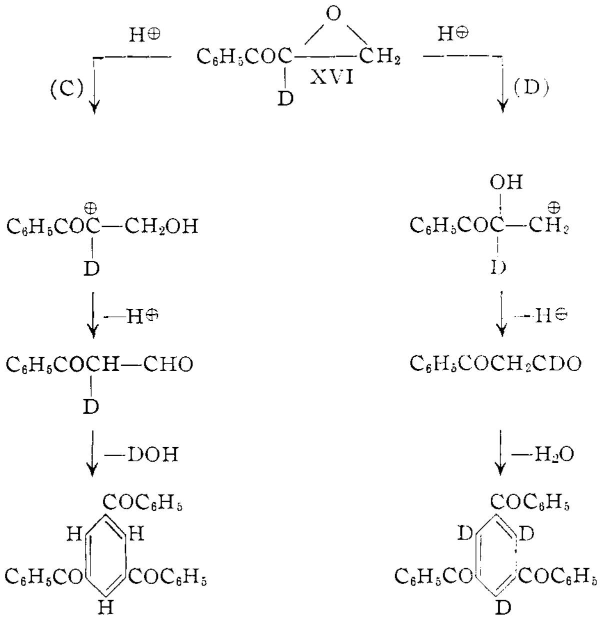
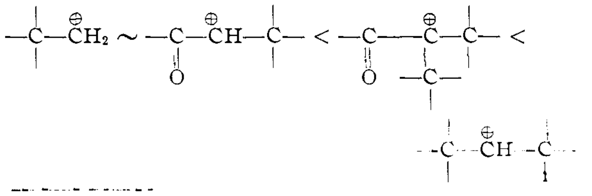


Fig. 2.

Our results suggest that the stability of a carbonium ion adjacent to a carbonyl group is approximately equivalent to the stability of a primary carbonium ion. The order of relative stabilities suggested by our present and previous[2] experiments is



$$-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{\oplus}{\mathrm{C}}\mathrm{H_2} \sim -\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\oplus}{\mathrm{C}}\mathrm{H}-\overset{|}{\underset{|}{\mathrm{C}}}- < -\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\overset{\oplus}{\underset{\underset{-\mathrm{C}-}{|}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}- < -\overset{|}{\underset{|}{\mathrm{C}}}-\overset{\oplus}{\mathrm{C}}\mathrm{H}-\overset{|}{\underset{|}{\mathrm{C}}}-$$

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[8] R. C. Fuson, D. J. Byers, C. A. Sperati, R. E. Foster and P. F. Warfield, *J. Org. Chem.*, **10**, 69 (1945).

[9] R. P. Barnes and A. E. Brandon, THIS JOURNAL, **65**, 2175 (1943).

[10] A. Behal and V. Auger, *Bull. soc. chim. France*, [3] **9**, 696 (1893).

[11] See ref. 2b, footnote 13.

[12] W. W. Hartman and L. J. Roll, *Org. Syntheses*, **23**, 1 (1943).

The authors wish to acknowledge the assistance of Dr. R. C. Fuson who kindly supplied samples of desoxymesitoin and mesityl α-mesitylvinyl ketone for this study.

Experimental[13,14,15]

The Methiodide of β-Dimethylamino-α-phenylpropiophenone (Va).—The reaction of 25 g. (0.128 mole) of desoxybenzoin with a solution of 23 ml. of 25% aqueous dimethylamine and 11.1 ml. of 37% aqueous formaldehyde in 50 ml. of ethanol according to the directions of Denton and co-workers[16] afforded an aqueous solution of the hydrochloride of β-dimethylamino-α-phenylpropiophenone. The aqueous solution was neutralized with sodium carbonate and extracted with ether. The ether was removed from a portion of the extract to leave the crude amine ketone. The pure **β-dimethylamino-α-phenylpropiophenone** crystallized from petroleum ether as white needles, m.p. 82.0–82.8°.

Anal. Calcd. for $C_{17}H_{19}NO$: C, 80.57; H, 7.56; N, 5.53. Found: C, 80.49; H, 7.47; N, 5.40.

The ether extract was dried over magnesium sulfate, treated with excess methyl iodide and allowed to stand at 15° for 12 hr. The crude product, collected on a filter, was recrystallized from aqueous ethanol. The methiodide separated as white crystals, m.p. 182.8–183.8° dec., yield 23.8 g. (48.5% based on desoxybenzoin).

Anal. Calcd. for $C_{18}H_{22}INO$: C, 54.71; H, 5.62; I, 32.11; N, 3.54. Found: C, 54.60; H, 5.56; I, 32.31; N, 3.76.

The Methiodide of β-Piperidino-α-phenylpropiophenone.—A solution of 10.5 g. (0.035 mole) of β-piperidino-α-phenylpropiophenone, m.p. 90.8–91.8° (lit.[17] 91°), in 40 ml. of ether was treated with excess methyl iodide and allowed to stand overnight. The crystalline methiodide (17% yield) was removed by filtration, additional methyl iodide was added and the process was repeated. When subsequent additions of methyl iodide produced no more quaternary salt the combined fractions of the product were recrystallized from ethanol. The quaternary salt separated as white crystals, m.p. 192.8–193.6° dec., yield 6.0 g. (40.5%).

Anal. Calcd. for $C_{21}H_{26}INO$: C, 57.88; H, 6.01; I, 29.11; N, 3.21. Found: C, 57.78; H, 6.24; I, 29.24; N, 3.05.

α,β-Epoxy-α-phenylpropiophenone (IIIa).—To a cold (0°) mixture of 10 g. (0.0253 mole) of the methiodide of β-dimethylamino-α-phenylpropiophenone, 12 ml. (0.124 mole) of 30% aqueous hydrogen peroxide and 100 ml. of methanol was added, dropwise and with stirring over a period of 25 minutes, 14 ml. (0.084 mole) of 6 *N* aqueous sodium hydroxide. Throughout the addition and subsequent reaction period the temperature of the mixture was kept below 2°. After the mixture had been stirred for an additional 1 hr., it was poured into 400 ml. of water and extracted with three portions of ether. The ethereal extract was dried over magnesium sulfate, concentrated and the residual oil crystallized from aqueous ethanol. Recrystallization of the crude solid from hexane afforded the pure oxide as white plates, m.p. 29.6–30.6°, yield 3.7 g. (66%). The infrared spectrum[18,19] of the oxide has an absorption band at 1670 cm.$^{-1}$ (conjugated C=O); the ultraviolet spectrum has a maximum at 252 mμ (ε 13,600).

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 80.18; H, 5.19.

Rearrangement of α,β-Epoxy-α-phenylpropiophenone (IIIa).—A solution of 260 mg. (0.00117 mole) of the oxide in 10 ml. of benzene was treated with 0.3 ml. (0.0024 mole) of boron trifluoride etherate and the resulting solution was allowed to stand at room temperature for 20 minutes. The reaction mixture was diluted with ether, washed with water and dried over magnesium sulfate. After the solvents had been removed, the residual oil was crystallized from hexane to give the **borofluoride complex** of α-formyldesoxybenzoin as yellow needles, m.p. 99.2–100° (lit.[20] 97–99°), yield 141 mg. (44%). In subsequent experiments the α-formyldesoxybenzoin was isolated as its copper complex, m.p. 223–224.5° (lit.[20] 220–221°), yield 65.3%, and, after treatment with phenylhydrazine as **1,4,5-triphenylpyrazole**, m.p. 211.2 212.2° (lit.[20] 210–211°), yield 75%. Each of the products was identified by a mixed melting-point determination with an authentic sample. As a control experiment a sample of the oxide IIIa was treated with phenylhydrazine under the same conditions which were employed to prepare 1,4,5-triphenylpyrazole from the crude isomerization product; none of the pyrazole could be isolated.

In an effort to isolate any benzyl phenyl diketone present as its quinoxaline, a crude rearrangement product was boiled with a solution of *o*-phenylenediamine dihydrochloride in ethanol. The only crystalline product which could be isolated was desoxybenzoin, m.p. 60–61° (lit.[21] 60°), yield 35%, which formed a 2,4-dinitrophenylhydrazone melting at 202–203.5° (lit.[22] 203°). All of our attempts to isolate dibenzoylmethane or one of its derivatives from the reaction mixture were unsuccessful.

Rearrangement of 1,2-Dimesityl-2,3-epoxy-1-propanone (IX).—Mesityl α-mesitylvinyl ketone [infrared absorption[19,23] 1665 cm.$^{-1}$ (conjugated C=O), 1625 cm.$^{-1}$ (conjugated C=C), 975 cm.$^{-1}$ ($C=CH_2$ adjacent to a carbonyl group)[23]] was converted to the epoxy ketone IX, m.p. 150.5–151.5° (lit.[8] 152–152.5°), by the procedure previously described.[8] The infrared spectrum[19,23] of the oxide has a band at 1700 cm.$^{-1}$ (C=O of a sterically hindered aryl ketone) but lacks the absorption at 975 cm.$^{-1}$ found in the corresponding unsaturated ketone. A mixture of 0.50 g. (0.0016 mole) of the oxide, 2 ml. (0.016 mole) of boron trifluoride etherate and 25 ml. of cyclohexane was stirred for 2 minutes, diluted with ether, washed with water and concentrated. The residual solid crystallized from ligroin (b.p. 90–120°) as white needles, m.p. 250–252°, yield 0.27 g. (54%). An additional crystallization sharpened the melting point of the keto aldehyde to 251–252°.

Anal. Calcd. for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84; mol. wt., 308. Found: C, 81.76; H, 7.96; mol. wt., 245 (Rast).

An attempt to effect the same rearrangement in ether solution with boron trifluoride etherate resulted in isolation of the unchanged oxide (75% recovery).[11]

The infrared spectrum[19,25] of the enolized keto aldehyde has a broad intense band in the 3 μ region with its center at 2950 cm.$^{-1}$ (associated O–H); in the 6 μ region a band of medium intensity is found at 1630 cm.$^{-1}$ accompanied by a broad, intense band with its center at 1565 cm.$^{-1}$ (C=O and/or C=C of an enolized β-dicarbonyl compound). The product was shown to be identical with the sample, m.p. 250–253°, prepared by Fuson and co-workers[8] by means of a mixed melting-point determination. Although the compound dissolved readily in aqueous alkali, it was remarkably stable to cleavage. After a solution of the compound in 10% aqueous sodium hydroxide had been heated on a steam-bath for 1 hr., 98% of the unchanged, enolized keto aldehyde was recovered when the reaction mixture was acidified. The behavior of the compound was also anomalous in that an ethanolic solution of the product gave no color with ferric chloride.

1,2-Dimesityl-2-propen-3-ol-1-one (XII).—A solution of 280 mg. (0.001 mole) of desoxymesitoin and 1 ml. (0.001 mole) of a standard solution of ethylmagnesium bromide in 25 ml. of benzene was refluxed for 40 minutes and then treated with 3 ml. (0.037 mole) of ethyl formate. The resulting mixture was refluxed for 19 hr., diluted with ether and washed with aqueous ammonium chloride. After the

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(13) All melting points are corrected and all boiling points are uncorrected.

(14) The ultraviolet spectra were determined in 95% ethanol with a Cary recording spectrophotometer, model 11 MS.

(15) The microanalyses were performed by Dr. S. M. Nagy and his associates.

(16) J. J. Denton, R. J. Turner, W. B. Neier, V. A. Lawson and H. P. Schedl, THIS JOURNAL, **71**, 2048 (1949).

(17) C. Mannich and D. Lammering, *Ber.*, **55**, 3510 (1922).

(18) Determined in carbon tetrachloride solution.

(19) Determined either with a Baird, model B, or a Perkin-Elmer, model 21, double beam infrared recording spectrophotometer fitted with a sodium chloride prism.

(20) W. Wislicenus and A. Rutbing, *Ann.*, **379**, 229 (1911).

(21) C. Graebe and H. Bungener, *Ber.*, **12**, 1079 (1879).

(22) C. F. H. Allen and J. R. Richmond, *J. Org. Chem.*, **2**, 222 (1937).

(23) The abnormal location for the band attributable to the C–H bending vibration of a terminal methylene group of vinyl ketones has been reported previously by M. H. J. Davison and G. R. Bates.

(24) M. H. J. Davison and G. R. Bates, *J. Chem. Soc.*, 2607 (1953).

(25) Determined as a suspension in a potassium bromide pellet.

solvents had been removed from the organic layer, the residue was taken up in boiling methanol and the solution was decolorized with Norit, diluted with water and cooled. After the unchanged desoxymesitoin, m.p. 90–93°, recovery 182 mg. or 65%, had been removed, concentration of the mother liquor afforded 26 mg. of the crude enolized keto aldehyde, melting over the range 220–245°. The pure enolized dicarbonyl compound crystallized as white needles, m.p. 251–253°, yield 12 mg. (11% based on the unrecovered desoxymesitoin). The melting point of a mixture of the product with a sample obtained by rearrangement of 1,2-dimesityl-2,3-epoxy-1-propanone was not depressed.

The Methiodide of β-Dimethylamino-α-ethylpropiophenone (Vb).—The Mannich base hydrochloride was prepared from 40 g. (0.27 mole) of butyrophenone, 16.8 g. (0.56 mole) of paraformaldehyde and 49 g. (0.6 mole) of dimethylamine hydrochloride according to the general directions of Burckhalter and Fuson.[26] The paraformaldehyde and dimethylamine hydrochloride were added in two equal portions, the second portion being added after 4 hr.; a total reaction time of 16 hr. was employed. An aqueous solution of the Mannich base hydrochloride was neutralized with sodium carbonate and the amine was taken up in ether. The ethereal solution was dried over magnesium sulfate, treated with excess methyl iodide and allowed to stand for 12 hr. The methiodide separated as fine, white crystals, m.p. 188.8–189.8°, yield 59.3 g. (63%). The melting point of the product was not altered by recrystallization from an ethanol–ether mixture.

Anal. Calcd. for $C_{14}H_{22}INO$: C, 48.43; H, 6.40; I, 36.56; N, 4.03. Found: C, 48.47; H, 6.22; I, 36.58; N, 4.03.

α,β-Epoxy-α-ethylpropiophenone (IIIb). A. From the Methiodide Vb.—To a cold (−4°) solution of 58.8 g. (0.17 mole) of the quaternary salt and 81 ml. (0.84 mole) of 30% aqueous hydrogen peroxide in 500 ml. of methanol was added, dropwise and with stirring over a period of 20 minutes, 94 ml. (0.56 mole) of 6 *N* aqueous sodium hydroxide. The resulting mixture was stirred for 2 hr.; throughout the addition and subsequent reaction period the temperature of the mixture was kept at −2°. The reaction mixture was poured into water and the resulting mixture was extracted with ether. The extract was dried over magnesium sulfate and concentrated. The components of the extract were separated by repeated fractional distillation through a Holtzmann column. The α,β-epoxy-α-ethylpropiophenone (IIIb), a colorless liquid boiling at 60–61° (0.15 mm.), $n^{25}D$ 1.5249, amounted to 3.35 g. (11.2%). The infrared spectrum[19,27] of the oxide has a band at 1675 cm.$^{-1}$ (conjugated C=O); the ultraviolet spectrum has a maximum at 246.5 mμ (ε 11,600) with a minimum at 220 mμ (ε 2,210). The nuclear magnetic resonance spectrum of the oxide, determined as a pure liquid with a Varian Associates high-resolution nuclear magnetic resonance spectrometer, model V4300B, has the following peaks (expressed as cycles per second relative to the proton resonance of water): a triplet with its center at −174 sec.$^{-1}$ (CH_3 adjacent to CH_2); quadruplet with its center at −135 sec.$^{-1}$ (CH_2 adjacent to CH_3); a singlet at −96 sec.$^{-1}$ (CH_2 of an oxide ring); and two multiple peaks centered around +90 sec.$^{-1}$ and +108 sec.$^{-1}$ attributable to the nuclear resonance of protons bonded to an aromatic ring.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.05; H, 6.86.

The α-ethylacrylophenone (IVb), collected in the initial fractions of the distillation, amounted to 11.24 g. (41.5%), b.p. 49–50° (0.15 mm.), $n^{25}D$ 1.5300 [lit.[26] b.p. 85° (5 mm.), $n^{20}D$ 1.5267]. The infrared spectrum[19,27] of the unsaturated ketone has a band at 1645 cm.$^{-1}$ (conjugated C=O) with a shoulder at 1625 cm.$^{-1}$ (conjugated C=C). The spectrum also exhibits a band at 975 cm.$^{-1}$ ($C{=}CH_2$ adjacent to a carbonyl group)[24] which is not present in the spectrum of the oxide. The ultraviolet spectrum of the unsaturated ketone has a maximum at 246 mμ (ε 10,000) with a minimum at 220 mμ (ε 6,650).[28] The nuclear magnetic resonance spectrum of the unsaturated ketone, determined as previously described, has the following peaks (relative to the proton resonance of water): a triplet with its center at −170 sec.$^{-1}$ (CH_3 adjacent to CH_2); a quadruplet with its center at −115 sec.$^{-1}$ (CH_2 adjacent to CH_3); a doublet (+7 and +18 sec.$^{-1}$) attributable to the two non-equivalent hydrogen atoms of the terminal methylene group; and a series of peaks centered around +92 sec.$^{-1}$ attributable to the nuclear resonance of protons bonded to an aromatic ring. Because of the discrepancy in refractive index values the composition of the unsaturated ketone was also determined.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.30; H, 7.52.

B. Epoxidation of α-Ethylacrylophenone (IVb).—A solution of 11.1 g. (0.069 mole) of the unsaturated ketone and 20 ml. of 30% aqueous hydrogen peroxide in 70 ml. of methanol was cooled to 0°, and 6 ml. (0.036 mole) of 6 *N* aqueous sodium hydroxide was added dropwise and with stirring. The resulting mixture was stirred for 3 hr. at room temperature, diluted with water and extracted with ether. After the extract had been dried and concentrated, distillation of the residue through a 30-cm. Podbielniak concentric tube fractionating column, model GE-117, afforded 6.91 g. (56.5%) of α,β-epoxy-α-ethylpropiophenone, b.p. 68.5° (0.4 mm.), $n^{25}D$ 1.5258. The infrared and ultraviolet spectra of the product are identical with the spectra of the oxide sample previously described.

Rearrangement of α,β-Epoxy-α-ethylpropiophenone (IIIb).—A solution of 309 mg. (0.00175 mole) of the oxide in 15 ml. of benzene was saturated with gaseous boron trifluoride and the resulting solution was allowed to stand for 3 hr. The reaction mixture was diluted with ether, washed with water and extracted with three portions of 5% aqueous sodium hydroxide. When the remaining ether solution was concentrated, boiled with a solution of 2 ml. (0.012 mole) of 6 *N* aqueous sodium hydroxide for 24 hr. and then acidified and treated with 2,4-dinitrophenylhydrazine, no 2,4-dinitrophenylhydrazone could be isolated.

The alkaline extract of the reaction mixture was acidified and extracted with ether. When the ethereal solution was shaken with a saturated, aqueous solution of cupric acetate, concentrated and diluted with pentane, **the copper salt of α-formylbutyrophenone** separated as green needles, m.p. 181.5–183.5°, yield 60 mg. (16.5%). The product was identified by a mixed melting-point determination with an authentic sample whose preparation is subsequently described. The mother liquors from the copper salt were dissolved in a solution of sodium hydroxide in aqueous ethanol, and the solution was refluxed for 1 hr. When the resulting mixture was acidified and treated with 2,4-dinitrophenylhydrazine, the **2,4-dinitrophenylhydrazone of butyrophenone** separated as orange needles, m.p. 190–191° (lit.[29] 190°), yield 64 mg. (14%). The product was identified by a mixed melting-point determination with an authentic sample.

In subsequent experiments the alkali-soluble fraction of the reaction mixture was boiled with a solution of sodium hydroxide in aqueous ethanol and then acidified and treated with 2,4-dinitrophenylhydrazine. With reaction times for the rearrangement of 20 minutes and 3 hr. the yields of butyrophenone 2,4-dinitrophenylhydrazone were 50 and 49%, respectively. When a solution of 270 mg. (0.00153 mole) of the oxide and 0.5 ml. (0.004 mole) of boron trifluoride etherate in 15 ml. of benzene was allowed to stand for 1.5 hr. and then worked up in the same manner, the yield of butyrophenone 2,4-dinitrophenylhydrazone was 40%. In no case could either acetophenone 2,4-dinitrophenylhydrazone or benzoic acid be isolated. Treatment of the reaction mixture from the rearrangement with either phenylhydrazine or *o*-phenylenediamine dihydrochloride failed to yield crystalline products.

As a control experiment, α,β-epoxy-α-ethylpropiophenone was treated first with a boiling solution of sodium hydroxide and then with 2,4-dinitrophenylhydrazine as described previously. No 2,4-dinitrophenylhydrazone could be isolated.

α-Formylbutyrophenone (VIIIb).—This β-keto aldehyde was prepared from 14.8 g. (0.1 mole) of butyrophenone, 7.5 g. (0.1 mole) of ethyl formate and 4.8 g. (0.2 mole) of sodium hydride by the standard procedure.[30] The product was

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[26] J. H. Burckhalter and R. C. Fuson, THIS JOURNAL, **70**, 4184 (1948).

[27] Determined in a chloroform solution.

[28] The second band expected from the cross-conjugated system of the unsaturated ketone IVb is apparently masked by other absorption in the region 210–240 mμ. The oxide IIIb absorbs much less strongly in this region than does the unsaturated ketone IVb.

[29] D. P. Evans, *J. Chem. Soc.*, **785** (1936).

[30] C. R. Hauser, F. W. Swamer and J. T. Adams, *Org. Reactions*, **8**, 126 (1954).

separated from an ether solution of the organic components of the reaction mixture by extraction with a saturated, aqueous solution of sodium carbonate. The alkaline solution was acidified and extracted with ether. Evaporation of the ether followed by recrystallization of the residue afforded the pure keto aldehyde as white needles, m.p. 96–97°, yield 3.5 g. (20%). The infrared spectrum[19,25] has a broad band in the 3 μ region (associated O–H) as well as strong bands in the 6 μ region at 1645 and 1505 cm.$^{-1}$ (C=O and/or C=C of an enolized β-dicarbonyl compound). When the spectrum[19] of the product was determined in chloroform solution, two additional bands appeared in the 6μ region at 1675 cm.$^{-1}$ (conjugated C=O) and 1710 cm.$^{-1}$ (unconjugated C=O). Our product is, therefore, the enol form of α-formylbutyrophenone.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.95; H, 6.96.

The α-formylbutyrophenone sample, m.p. 86–87°, previously reported[31] is apparently the tautomer of the sample we have isolated.

A portion of the keto aldehyde was converted to its copper salt in the usual manner. **The copper salt of α-formylbutyrophenone** separated from an ether–pentane mixture as blue-green needles, m.p. 182.5–183.5°. The infrared spectrum[19,25] of the copper salt has broad absorption bands in the 6 μ region with their centers at 1585 and 1572 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{22}O_4Cu$: C, 63.86; H, 5.32. Found: C, 63.94; H, 5.36.

Alkaline Cleavage of α-Formylbutyrophenone (VIIIb).—A solution of 1.0 g. (0.0057 mole) of the keto aldehyde and 2 ml. (0.012 mole) of 6 *N* aqueous sodium hydroxide in 20 ml. of ethanol was boiled under reflux until an acidified sample of the reaction mixture no longer gave a color with ferric chloride (1 hr.). The mixture was diluted with water and extracted with ether. Treatment of the residue from the ether solution with 2,4-dinitrophenylhydrazine yielded 1.62 g. (95%) of butyrophenone 2,4-dinitrophenylhydrazone, m.p. 190–191°.

1-Phenyl-1,3-pentanedione (VIb).—The reaction of 13.7 g. (0.114 mole) of acetophenone with 5.5 g. (0.228 mole) of sodium hydride and 23.3 g. (0.228 mole) of ethyl propionate in the usual manner[30] produced the β-diketone, b.p. 131–135° (6 mm.), n^{25}D 1.5820 [lit.[32] b.p. 120–122° (5 mm.), n^{20}D 1.5837], yield 12.4 g. (62%). The infrared spectrum[19,27] of the product has a broad band in the 6 μ region with its center at 1625 cm.$^{-1}$ (enolized β-diketone).

Alkaline Cleavage of 1-Phenyl-1,3-pentanedione (VIb).—A solution of 1.0 g. (0.0057 mole) of the diketone and 1.5 ml. (0.009 mole) of 6 *N* aqueous sodium hydroxide in 20 ml. of ethanol was refluxed until an acidified sample from the reaction mixture gave no color with ferric chloride (24 hr.). The mixture was diluted with water and extracted with ether. Evaporation of the ether followed by treatment with 2,4-dinitrophenylhydrazine yielded acetophenone 2,4-dinitrophenylhydrazone, m.p. 249–250° (lit.[33] 249–250°), yield 1.10 g. (65%). Acidification of the aqueous solution from the reaction mixture followed by appropriate manipulations afforded 0.10 g. (14.4%) of benzoic acid, m.p. 120–121°. Both products were identified by mixed melting point determinations with authentic samples.

Reaction of 1-Phenyl-1,3-pentanedione (VIb) with Boron Trifluoride.—A solution of 1.0 g. (0.0057 mole) of the diketone in 20 ml. of benzene was saturated with gaseous boron trifluoride, and the solution was allowed to stand for 2 hr. The benzene was removed and the residue crystallized from a hexane–ether mixture. **The borofluoride complex of 1-phenyl-1,3-pentanedione** separated as white needles, m.p. 68.4–69.2°, yield 638 mg. (50%). The infrared spectrum[19,27] of the product has a broad absorption band in the 6 μ region with its center at 1552 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{11}BF_2O_2$: C, 59.00; H, 4.91; B, 4.82; F, 16.97. Found: C, 58.89; H, 5.09; B, 4.83; F, 16.76.

When a solution of 200 mg. (0.0009 mole) of the complex and 2.0 ml. (0.012 mole) of 6 *N* aqueous sodium hydroxide in 20 ml. of ethanol was refluxed for 24 hr. and the neutral fraction of the product treated with 2,4-dinitrophenylhydrazine as previously described, the yield of acetophenone 2,4-dinitrophenylhydrazone, m.p. 249–250°, was 180 mg. (67%). In a second control experiment a solution of 100 mg. of the borofluoride complex in 20 ml. of ether was extracted with three portions of 5% aqueous sodium hydroxide. Concentration of the ether solution left 60 mg. of the unchanged borofluoride complex, m.p. 67–69°. The alkaline extract was acidified and extracted with ether; treatment of the ethereal extract with saturated, aqueous cupric acetate yielded 33 mg. (28%) of the copper complex of 1-phenyl-1,3-pentanedione, m.p. 153–154° (lit.[32] 151°). The product was identified by a mixed melting-point determination with an authentic sample.

α,β-Epoxypropiophenone (IIIc).—A suspension of 3.0 g. (0.0094 mole) of the crude methiodide of β-dimethylaminopropiophenone,[34] m.p. 203–209°, and 5 ml. (0.052 mole) of aqueous 30% hydrogen peroxide in 55 ml. of methanol was cooled to 0°, and 6 ml. (0.036 mole) of 6 *N* aqueous sodium hydroxide was added dropwise and with stirring. The resulting mixture was stirred for 1 hr. at 0°, diluted with 150 ml. of water and extracted with 3 portions of ether. The ether extract was dried and concentrated to leave an oil which crystallized from an ether–petroleum ether mixture. The oxide separated as white plates, m.p. 52–53° (lit.[35] 53°), yield 0.78 g. (60.6%). The infrared spectrum[19,27] of the product has a band at 1675 cm.$^{-1}$ (conjugated C=O).

Rearrangement of α,β-Epoxypropiophenone (IIIc).—A solution of 0.1 g. (0.0007 mole) of the oxide in 25 ml. of benzene was saturated with gaseous boron trifluoride over a period of 2 minutes and then worked up in the usual manner. None of the copper salt of benzoylacetaldehyde could be isolated from the crude rearrangement product. The reaction product, **1,3,5-tribenzoylbenzene** (XIII), crystallized from ethanol as white plates, m.p. 118–120° (lit.[36] 119°), yield 0.05 g. (56%). The infrared spectrum[19,26] of the compound has a band at 1685 cm.$^{-1}$ (conjugated C=O). When a benzene solution of the oxide was heated with 0.5 equivalent of boron trifluoride etherate for 15 minutes, the yield of the triketone XIII was 20%. As in the former case no benzoylacetaldehyde could be isolated.

Benzoylacetaldehyde (XIV).—The sodium salt of the keto aldehyde was prepared by the reaction of 60 g. (0.5 mole) of acetophenone with sodium hydride (12 g., 0.5 mole) and ethyl formate (45 g., 0.6 mole) in the usual manner.[30] Reaction of the crude sodium salt with cupric acetate afforded the **copper salt of benzoylacetaldehyde** which crystallized from an ether–pentane mixture as dark green needles, m.p. 212–213° dec., yield 110.7 g. (62%).

Anal. Calcd. for $C_{18}H_{14}O_4Cu$: C, 60.42; H, 3.92. Found: C, 60.61; H, 4.16.

A sample of benzoylacetaldehyde derived from 0.34 g. (0.0013 mole) of the copper salt was dissolved in ether and treated with 0.5 ml. (0.004 mole) of boron trifluoride etherate. The solution was refluxed for 15 minutes and then worked up in the usual way. None of the benzoylacetaldehyde could be recovered; instead 1,3,5-tribenzoylbenzene was isolated, m.p. 117–119°, yield 0.28 g. (80%). The compound was shown to be identical with the sample prepared by rearrangement of α,β-epoxypropiophenone both by a mixed melting-point determination and by comparison of the infrared spectra of the two samples.

Partially Deuterated α,β-Epoxypropiophenone (XVI).—A solution of 12 g. (0.1 mole) of acetophenone and 1 g. of sodium hydroxide in a mixture of 20 ml. of deuterium oxide and 20 ml. of ethanol was refluxed for 18 hr. The deuterium content of the recovered acetophenone was 21.92 atom per cent. deuterium or 1.75 gram atoms of deuterium per mole.[37] The acetophenone was converted to the methiodide of β-dimethylaminopropiophenone and subsequently to α,β-epoxypropiophenone by the procedures described previously. The deuterium content of the epoxy ketone was 1.40 atom per cent. deuterium or 0.112 gram atom of deuterium per mole.[37]

Rearrangement of Partially Deuterated α,β-Epoxypropiophenone (XVI).—A 1.0-g. (0.0067 mole) sample of the oxide was isomerized as previously described. The yield of par-

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[31] L. Claisen and L. Meyerowitz, *Ber.*, **22**, 3273 (1889).

[32] L. I. Smith and V. A. Engelhardt, THIS JOURNAL, **71**, 2671 (1949).

[33] N. R. Campbell, *Analyst*, **61**, 391 (1936).

[34] C. E. Maxwell, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 305; C. Schopf and J. Thesing, *Angew. Chem.*, **63**, 377 (1951).

[35] M. Cahnmann, *Bull. soc. chim. France*, [5] **4**, 226 (1937).

[36] A. W. Johnson, *J. Chem. Soc.*, 1626 (1947).

[37] The deuterium analyses were performed by Mr. Jozsef Nemeth, Department of Chemistry, University of Illinois.

tially deuterated 1,3,5-tribenzoylbenzene, m.p. 118–119.5°, was 0.30 g. (34%). The deuterium content of the triketone was 0.87 atom per cent. deuterium or 0.157 gram atom of deuterium per mole (47% retention of the deuterium present in the epoxy ketone).

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Reaction of Arenes with Silver Fluoride in Hydrogen Fluoride Solution

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Silver fluoride, dissolved in anhydrous hydrogen fluoride, reacts with arenes to form a stable complex containing 3 moles of arene. The complex reverts to silver fluoride and arene as the hydrogen fluoride is removed by distillation. AgF–HF is therefore a useful solvent for separating arenes from other hydrocarbons. In contrast with other metal fluorides that complex with arenes, AgF in HF is a base; it inhibits rather than promotes such reactions as alkyl-group migration. The stability of the arene–silver fluoride complex is almost independent of the number and orientation of the alkyl groups on the ring. It differs from the σ-complexes formed by the action on arenes of HF plus other metal fluorides, such as BF_3, TiF_4, CbF_5, TaF_5, and acts more like a π-complex.

A few metal fluorides act as co-acids with liquid anhydrous hydrogen fluoride. A criterion used in previous work to establish such co-acid properties was whether the fluoride enabled a proton to add to a xylene molecule.[1] In the presence of a sufficiently strong co-acid, normally insoluble xylene accepts a proton and dissolves in the hydrogen fluoride. On the other hand, certain metal fluorides that are obviously bases in the hydrogen fluoride system also cause arenes to dissolve in this medium. Thus, Klatt[2] found that silver fluoride, which is soluble and ionizes in hydrogen fluoride probably according to the equation[3] can

$$AgF + HF \rightleftarrows AgFH^+ + F^-$$

bring into solution up to four mole-equivalents of arene.

In the present study, batch extractions of hydrocarbon mixtures and petroleum fractions with AgF–HF have been used to elucidate the action of silver fluoride on arenes. Our objects were to determine how silver fluoride differs from the acidic fluorides and to learn whether it could be used to extract arenes from hydrocarbon mixtures, separate arenes from each other, or promote such reactions as alkylation and disproportionation.

Experimental

Silver fluoride, obtained from the Beta Research Laboratory, was dissolved in hydrogen fluoride and heated to 100° under vacuum to drive off any moisture present with the hydrogen fluoride. The hydrogen fluoride, a commercial grade of 99.6% purity supplied by the Matheson Co., was distilled before each experiment. The hydrocarbons, C.P. grades obtained from commercial suppliers, were used without further purification. The petroleum fractions used were typical straight-run and reformed West Texas naphthas.

The extraction runs were carried out in a 1.5-liter carbon-steel autoclave. Silver fluoride, hydrocarbon and a measured volume of hydrogen fluoride were added to the autoclave and stirred for 1 hr. After a settling period of 2 hr., the acid layer was withdrawn from the bottom of the autoclave into a polyethylene flask cooled in Dry Ice. In most cases, the extracted arenes were sprung by slowly adding water to the chilled acid phase. After a large excess of water had been added, the displaced arenes were decanted from the aqueous acid. The raffinate layer was drained from the autoclave. Both hydrocarbon products were then washed with ammonium hydroxide and were analyzed by appropriate means, such as refractive index measurement and infrared and ultraviolet absorption.

In a few experiments designed to show whether the silver fluoride could be regenerated and used again the technique differed. After the mixing step, the autoclave was heated to 50° and the hydrocarbon and hydrogen fluoride were distilled into an evacuated flask to recover the silver fluoride residue for re-use.

Extraction of Known Mixtures.—Four mixtures of known hydrocarbons were each extracted with an equal volume of hydrogen fluoride plus silver fluoride. The results are shown in Table I.

TABLE I

EXTRACTION OF ARENES FROM SYNTHETIC MIXTURES

Arene	Benzene	Xylene[a]	C_8-Alkylbenzenes[b]	
Moles AgF per mole arene	0.17	0.17	1.0	1.0
Feed, vol. %				
Arene	40	40	32	32
n-Heptane	60	60	60	66.5
Olefin	....	...	8[c]	....
Propyl sulfide	....	...	....	1.5
Raffinate, vol. %				
Arene	22.5	25	0	0.4
Olefin	....	...	0	....
Propyl sulfide	....	...	....	0
Extract, vol. %				
Arene	97	95	97	94.5
Olefin	....	...	0	....
Propyl sulfide	....	...	....	4.5
Arene removed				
%	56.5	50	100	99
Moles per mole AgF	3.3	3.0	1.0	1.0
Separation factor, β[d]	144	57	>1000	1220

[a] Equal parts of *m*- and *p*-xylene. [b] Equal parts of all four. [c] Equal parts of *n*-octene and cyclohexene. [d] Quotient of the arene-to-heptane ratio in the extract phase divided by the arene-to-heptane ratio in the raffinate.

The mixture of benzene and *n*-heptane was about 56% dearomatized to give an extract containing 97% benzene. The separation factor, β, which measures the relative distribution of benzene and *n*-heptane between the two phases, has the high value of 144. Conventional solvents, such as diethylene glycol or sulfur dioxide, give β's ranging from 5

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[1] D. A. McCaulay, W. S. Higley and A. P. Lien, THIS JOURNAL, **78**, 3009 (1956).

[2] W. Klatt, *Z. anorg. allgem. Chem.*, **234**, 189 (1937).

[3] J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 237.