into an excess of slightly acidulated water and the resultant gram of solid was collected on a filter. After drying and several recrystallizations from ligroin the hydroxy ester melted at 161–162° dec.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 81.05; H, 5.99. Found: C, 81.46; H, 5.89.

Ethyl 12-(α-Hydroxybenzyl)-9,10-dihydro-9,10-ethanoanthracene-11-carboxylate.—One gram of the ethyl ester of III was warmed on the steam-bath for 10 minutes with 0.2 g. of sodium borohydride in 20 ml. of ethyl alcohol. The product was precipitated by the addition of water and crystallized as the monohydrate from dilute alcohol; it melted at 77° dec. When dried for 24 hours at 60° and 10 mm., the anhydrous compound was obtained, m.p. 126°. It depressed the melting point of ethyl 12-benzoyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylate (m.p. 129°) by thirty or forty degrees.

Anal. (of hydrate) Calcd. for $C_{26}H_{24}O_3 \cdot H_2O$: C, 77.58; H, 6.51. Found: C, 77.79; H, 6.47. (Anhydrous material) Calcd. for $C_{26}H_{24}O_3$: C, 81.23; H, 6.29. Found: C, 81.24; H, 5.96.

11,12-Dibenzoyl-9,10-dihydro-9,10-ethanoanthracene.—*trans*-Dibenzoylethylene, m.p. 110°, was prepared from fumaryl chloride, benzene and aluminum chloride by the method of Conant and Lutz.[10]

Three grams of each of *trans*-dibenzoylethylene and anthracene were fused together at 200° for 5 minutes. Crystallization of the crude product from benzene–ligroin gave: (a) 1.0 g. of anthracene, (b) 2.0 g. of adduct melting 153–161°, and (c) 1.5 g. more material from which an additional gram of adduct was obtained on recrystallization from alcohol. The analytical sample was recrystallized several times from alcohol and melted 163–164°.

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 87.07; H, 5.22.

12-Phenyl-9,10-dihydro-9,10-ethanoanthracene-11-acetic Acid (X).—*trans*-Styrylacetic acid, m.p. 88°, was made from phenylacetaldehyde and malonic acid following both of two reported procedures.[11]

Seven grams of this *trans* acid and 14 g. of anthracene were fused at 220–230° for 5 hours. After cooling the mixture the solid mass was pulverized and extracted twice with hot 5% aqueous sodium carbonate solution. Unreacted anthracene was removed by filtration. Acidification of the filtrate yielded a mixture of solid acids which was treated with 50% acetic acid. This treatment caused solution of the unreacted styrylacetic acid without dissolving the adduct. The latter was dissolved in hot toluene and on cooling an acid separated; yield 4.0 g. (27%), m.p. 267° dec. The filtrate was processed for an isomeric acid (below).

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.88. Found: C, 84.30, 85.02; H, 6.08, 6.00.

The same product was formed but in lower yields if solvents (toluene or *o*-dichlorobenzene, both at reflux temperature) were employed.

The Lower Melting Adduct, Presumably 12-Benzyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acid (XI).—The filtered solution of toluene from the previous run was combined with filtrates of two other analogous runs and the total was evaporated. The residue weighed about 0.5 g. It was crystallized from benzene; m.p. 212° dec. Neither the higher or the lower melting adducts could be isomerized by refluxing for 6 hours in toluene or by boiling alcoholic potassium hydroxide, which means that X and XI were not *cis–trans* isomers.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.88. Found: C, 84.98; H, 6.13.

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[10] J. Conant and R. Lutz, THIS JOURNAL, **45**, 1303 (1923).

[11] D. Vorländer and E. Strunck, *Ann.*, **345**, 233 (1906); R. Linstead and L. Williams, *J. Chem. Soc.*, 2735 (1926).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE STATE UNIVERSITY]

Epoxyethers. XVII.[1] Synthesis from an α-Chloro-β-hydroxyether[2]

BY CALVIN L. STEVENS AND ROBERT L. MCLEAN

RECEIVED JULY 28, 1958

The α-hydroxyketal I has been used as a starting material for the synthesis of the epoxyether III in 83% yield. The key intermediate in this synthesis was the α-chloro-β-hydroxyether II prepared from I and trichloroacetyl chloride. The *p*-nitrobenzoate and 3,5-dinitrobenzoate esters of the α-hydroxyketal I were converted by acetyl chloride to the corresponding α-chloroether derivatives VI and VII in excellent yield. Treatment of these derivatives with liquid ammonia or sodamide in ether did not remove the protecting ester group, but rather led to the formation of nitrogen-containing products which were formulated as methoxy oxazolines VIII and IX.

Epoxyethers have been prepared easily from many α-halocarbonyl compounds by reaction with alkoxide ion.[3] The one main limitation of this preparation is that when a Favorski rearrangement is possible, an α-haloketone will undergo this rearrangement in many cases to the exclusion of epoxyether formation.[4] A vinyl ether has been converted to an epoxyether by oxidation with an organic peracid, but special precautions were necessary[5] since the organic acid that was formed reacted readily with the epoxyether. Since α-hydroxyketals can be prepared corresponding to the α-bromoketones that undergo the Favorski rearrangement,[6] the object of this investigation was the preparation of an epoxyether from a corresponding α-hydroxyketal.[7]

The essential feature of this preparation was the conversion of a ketal to an α-chloroether by an acid chloride as reported by Straus and Heinze[8] in 1932. As applied to the α-hydroxyketal in this investigation the resulting α-chloroether was at once a chlo-

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[1] Paper No. XVI in the Epoxyether series appears in THIS JOURNAL, **80**, 4072 (1958).

[2] Sponsored in part by the Office of Ordnance Research, U. S. Army, and in part by Grant No. A-769 from the National Institute of Arthritis and Metabolic Diseases, Public Health Service.

[3] The preparations of epoxyethers from various phenyl ketones have been published in THIS JOURNAL, **72**, 4758 (1950); **74**, 618 (1952); **75**, 3977 (1953); **76**, 718 (1954); **77**, 5412 (1955). The preparation from α-haloaldehydes appears in **76**, 2695 (1954) and **79**, 3448 (1957). The reaction of α-halotrimethyl cyclohexanone with alkoxide ion to form a bicycloepoxyether appears in **80**, 4072 (1958).

[4] R. B. Loftfield and L. Shaw discuss the possible control of the ratio of these reaction products in *ibid.*, **76**, 35 (1954).

[5] C. L. Stevens and J. Tazuma, *ibid.*, **76**, 715 (1954).

[6] *Cf.* C. L. Stevens and A. E. Sherr, *J. Org. Chem.*, **17**, 1228 (1952), for synthesis in the diphenylacetone series.

[7] An α-hydroxy diisopropylketal has been shown to lose isopropyl alcohol in the presence of an acid catalyst to give an epoxyether, but other attempts to prepare an epoxyether from an α-hydroxyketal have been fruitless; *cf.* THIS JOURNAL, **80**, 2276 (1958).

[8] F. Straus and H. Heinze, *Ann.*, **493**, 191 (1932).

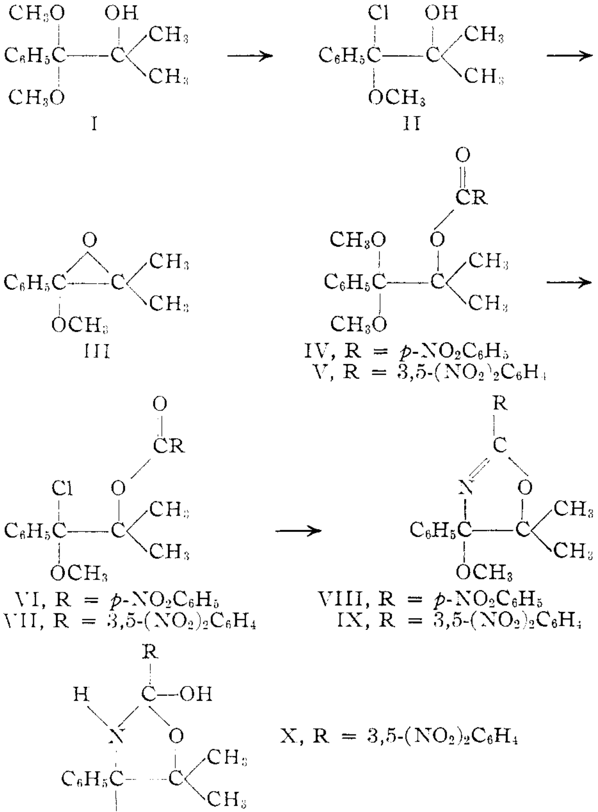
rohydrin and subject to epoxide formation with ammonia to yield the epoxyether.[9]

α-Hydroxyisobutyrophenone dimethylketal (I) was chosen as the starting material for this investigation since the resulting epoxyether had been characterized previously.[10] Treatment of I with excess trichloroacetyl chloride at 0° for 20 hours gave 89% of the α-chloro-β-hydroxyether II, which could be isolated by rapid distillation at low pressure. Redistillation of II could not be used for purification since all fractions from a redistillation contained less chlorine than the original sample. The compound fumed when exposed to the laboratory atmosphere and was unstable at room temperature, although it was stored at 0° for one week. The infrared spectrum of the compound contained a hydroxyl band at 2.9 μ and had no appreciable carbonyl absorption. It could be hydrolyzed in 62% yield to the α-hydroxyketone, isolated as the semicarbazone. When an ether solution of the α-chloro-β-hydroxyether II was allowed to react with dry ammonia, the epoxyether III could be isolated in 55% yield. Without isolating II the over-all yield of epoxyether from α-hydroxyketal was 63%.

The successful conversion of I to II is attributed to the ability of the very powerful carbonyl group of trichloroacetyl chloride to convert the ketal group to a chloroether group at a temperature low enough to prevent reaction of the tertiary alcohol with the acid chloride. Any hydrogen chloride resulting from this latter reaction would cause the α-hydroxyketal to lose alcohol to form a dioxane-type product.[11] Acetyl chloride was not a useful reagent for the conversion of I to II. The infrared spectrum of the volatile material from such a reaction indicated a mixture in which the hydroxy group was partially acetylated and the ketal group was partially cleaved to ketone.

Since the hydroxyketal was very sensitive to changes of reagents or reaction conditions, one phase of this research involved an attempt to protect the hydroxyl group of the hydroxyketal during chloroether formation. The hydroxyketal I could be converted to the p-nitrobenzoyl ester IV in 74% yield. Reaction of this ketal ester with acetyl chloride gave 94% of the corresponding α-chloroether VI, which was crystalline but nevertheless also fumed in the laboratory atmosphere. Although the product was hydrolyzed readily to the ketoester in aqueous solutions, it is interesting that this chloroether is relatively stable in the presence of liquid ammonia. In an attempt to remove the protecting p-nitrobenzoyl group from VI, this chloroether was treated with liquid ammonia for 1.5 hours. From the reaction 52% of starting material was recovered along with 10% of ketoester and no p-nitrobenzamide could be isolated. The chloroether VI did react with sodium amide in ether solution but only with the formation of a nitrogen-containing compound which is provisionally formulated as the methoxyoxazoline VIII. Evidence for this structure was the carbon–nitrogen double bond absorption in the infrared spectrum and the easy hydrolysis in 98% yield to α-hydroxyisobutyrophenone p-nitrobenzoate.

Since the p-nitrobenzoate chloroether VI did not react with ammonia, the corresponding 3,5-dinitrobenzoate VII was prepared. This ester, with the more reactive carbonyl group, did react with liquid ammonia but a compound IX, analogous to the methoxyoxazoline VIII, was formed. This oxazoline IX also was hydrolyzed easily to the corresponding ketoester. In addition to IX, a new material was isolated which differed in composition from IX by the addition of the elements of water. Since the infrared spectrum of this compound had absorption bands corresponding to OH and NH and had lost the carbon–nitrogen double bond absorption, it was assigned the provisional formula X.



I

II

III

IV, R = p-$NO_2C_6H_5$
V, R = 3,5-$(NO_2)_2C_6H_4$

VI, R = p-$NO_2C_6H_5$
VII, R = 3,5-$(NO_2)_2C_6H_4$

VIII, R = p-$NO_2C_6H_5$
IX, R = 3,5-$(NO_2)_2C_6H_4$

X, R = 3,5-$(NO_2)_2C_6H_4$

Experimental

Reaction of α-Hydroxyisobutyrophenone Dimethylketal with Trichloroacetyl Chloride and Subsequent Ammonolysis.—A mixture of 5 g. (0.024 mole) of α-hydroxyisobutyrophenone dimethylketal[10] and 10 ml. of trichloroacetyl chloride was allowed to remain at 0° for 12 hours. The mixture then was brought to room temperature and the excess acid chloride removed over a 2-hour period at reduced pressure. The crude oil was dissolved in 75 ml. of ether and ammonia gas bubbled through the solution at room temperature for two hours. The mixture was filtered and gave the theoretical amount of ammonium chloride. After removal of the ether from the filtrate the residual oil was distilled through a Vigreux column and 2.68 g. (63%), b.p. 70–74° (5 mm.), $n^{25}D$ 1.4909, of 1,2-epoxy-1-methoxy-2-methyl-1-phenylpropane (III) was obtained, which was identical with an authentic sample. One gram of the epoxyether, isolated here,

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[9] Brigl's anhydride (3,4,6-triacetyl-1,2-epoxyglucose), an epoxyether in the carbohydrate series, has been prepared from an α-chloro-β-hydroxy ether (3,4,6-triacetyl 1-β-chloroglucose); P. Brigl, *Z. physiol. Chem.*, **122**, 245 (1922).

[10] C. L. Stevens and T. H. Coffield, This Journal, **80**, 1919 (1958).

[11] C. L. Stevens and B. T. Gillis, *ibid.*, **79**, 3448 (1957).

gave 1.52 g. (75%), m.p. 151–152°, of α-hydroxyisobutyrophenone 3,5-dinitrobenzoate when allowed to react with 3,5-dinitrobenzoic acid.

Attempted Purification of the α-Chloro-β-hydroxyether II.—A mixture of 15 g. (0.071 mole) of α-hydroxyisobutyrophenone dimethylketal and 20 ml. of trichloroacetyl chloride was allowed to remain at 0° for 12 hours. The excess acid chloride was removed at reduced pressure. The crude material was distilled rapidly and material boiling from 82–90° (0.15 mm.) collected. This α,α-dimethyl-β-chloro-β-methoxyphenethyl alcohol amounted to 13.38 g. (89%), $n^{25}\text{D}$ 1.5260.

Anal. Calcd. for $C_{11}H_{15}O_2Cl$: Cl, 16.50. Found: Cl, 14.83.

This material was redistilled and three fractions collected. The first fraction amounted to 5.52 g., b.p. 83–85° (0.15 mm.), $n^{25}\text{D}$ 1.5264 (Found: Cl, 13.07). The second fraction amounted to 4.51 g., b.p. 85–86° (0.15 mm.), $n^{25}\text{D}$ 1.5264 (Found: Cl, 13.99). The third fraction amounted to 1.49 g., b.p. 86–87° (0.15 mm.), $n^{25}\text{D}$ 1.5275 (Found: Cl, 14.36).

Ammonia was bubbled slowly through a stirred solution of 9.67 g. (0.045 mole) of twice distilled II in 100 ml. of ether for two hours at room temperature. The resulting mixture was filtered to remove the ammonium chloride and the filtrate evaporated to remove the ether. The residual oil was distilled through a 12-cm. Vigreux column to give 4.38 g. (55%), b.p. 71–74° (5 mm.), $n^{25}\text{D}$ 1.4904, of the epoxyether III, identical with authentic material.

Hydrolysis of the α-Chloro-β-hydroxyether II.—A mixture of 1.09 g. (5.1 mmoles) of twice distilled II, 5 ml. of water and 10 ml. of ethanol was refluxed for two hours, then allowed to remain overnight at room temperature. The mixture was treated with 1 g. (9.0 mmoles) of semicarbazide hydrochloride and 1.5 g. (18 mmoles) of sodium acetate and then heated on a steam-bath for 10 minutes. Upon addition of hot water, 0.69 g. (62%) of product, m.p. 185–187°, crystallized. A mixture melting point determination with authentic α-hydroxyisobutyrophenone semicarbazone was not depressed.

α-Hydroxyisobutyrophenone Dimethylketal *p*-Nitrobenzoate (IV).—Sodium amide was prepared from 200 ml. of liquid ammonia, a crystal of ferric nitrate and 3.3 g. (0.14 mole) of sodium. To this mixture, after the reaction was complete, was added 30 g. (0.14 mole) of the hydroxyketal I in 150 ml. of ether. The mixture was refluxed to remove all the ammonia formed, and the remaining salt dispersed in 100 ml. of dry ether. The mixture was cooled to 0° and 28 g. (0.15 mole) of *p*-nitrobenzoyl chloride in 250 ml. of ether was added, after which time it was stirred for one hour at room temperature and then refluxed for one hour. The ether solution was separated and evaporated to dryness and the residue recrystallized from hexane. Several crops gave 41 g. of impure material melting from 117–126°. Recrystallization from heptane gave 37.8 g. (74%) of IV, m.p. 123.5–125°. An analytical sample melted at 125–126°.

Anal. Calcd. for $C_{19}H_{21}NO_6$: C, 63.49; H, 5.89. Found: C, 63.75; H, 6.09.

Hydrolysis of the Ketal *p*-Nitrobenzoate IV.—A solution of 0.5 g. (1.44 mmoles) of the ketal ester IV, 20 ml. of acetone, 5 ml. of water and 2 drops of hydrochloric acid was refluxed for one hour and then diluted with hot water. Upon cooling 0.24 g. (58.5%), m.p. 135–137°, of the α-hydroxyisobutyrophenone *p*-nitrobenzoate crystallized. A mixture melting point with an authentic sample was not depressed. Also obtained were 0.03 g. (6%), m.p. 124–126°, of starting material and 0.06 g. (25%) of *p*-nitrobenzoic acid.

α-Hydroxyisobutyrophenone *p*-Nitrobenzoate.—Into 20 ml. of pyridine were placed 1.0 g. (6.1 mmoles) of α-hydroxyisobutyrophenone and 1.2 g. (6.5 mmoles) of *p*-nitrobenzoyl chloride. The mixture was refluxed for one hour and hot water added. Upon cooling 1.27 g. (71%) of ketoester was obtained, m.p. 137–139°. A similar experiment gave a 90% yield. Recrystallization from hexane gave an analytical sample which melted at 137–138°.

Anal. Calcd. for $C_{17}H_{15}NO_5$: C, 65.17; H, 4.83. Found: C, 65.30; H, 5.03.

α,α-Dimethyl-β-chloro-β-methoxyphenethyl Alcohol *p*-Nitrobenzoate (VI).—A mixture of 20.0 g. (0.056 mole) of the ketal ester IV and 20 ml. of acetyl chloride was refluxed for one hour and allowed to react overnight at room temperature. After the mixture was heated, hexane was added and from the solution 17.3 g., m.p. 125–126° dec., of the chloroether was obtained. A second crop of 1.7 g., m.p. 124–126° dec., was obtained for a total of 19 g. (94%). The compound was extremely unstable and fumed on exposure to air.

Anal. Calcd. for $C_{17}H_{18}NClO_5$: Cl, 9.75. Found: Cl, 9.70.

Hydrolysis of the Chloroether Ester VI.—A mixture of 0.52 g. (1.43 mmoles) of the chloroether ester VI, 20 ml. of acetone, 5 ml. of water and one drop of hydrochloric acid was refluxed for five minutes and then diluted with hot water. After the solution had cooled, 0.23 g. (51.5%), m.p. 137.5–138.5°, of the α-hydroxyisobutyrophenone *p*-nitrobenzoate was obtained; also formed was 0.1 g. (42%), m.p. 232–235°, of *p*-nitrobenzoic acid. Mixture melting points of both of these compounds with authentic samples were undepressed.

Reaction of the Chloroether Ester VI with Liquid Ammonia.—A mixture of 15.9 g. (0.044 mole) of the chloroether ester VI and 400 ml. of liquid ammonia was stirred for 1.5 hours, after which 300 ml. of ether was added and the ammonia evaporated. From the mixture were isolated 8.2 g. (51.6%), m.p. 122–125° dec., of starting material; 1.37 g. (10%), m.p. 137–139°, of the α-hydroxyisobutyrophenone *p*-nitrobenzoate; and 0.74 g., m.p. 185–186°, of α-hydroxyisobutyrophenone dimer.

Reaction of the Chloroether Ester VI with Sodium Amide.—Sodium amide was prepared by adding 1.3 g. (0.057 mole) of sodium and a crystal of ferric nitrate to 200 ml. of liquid ammonia. The sodium amide was suspended in 400 ml. of ether and 17.3 g. (0.048 mole) of the chloroether ester added. The mixture was stirred and refluxed for four hours. From this mixture was isolated 0.69 g. (8.75%), m.p. 230–235°, of *p*-nitrobenzoic acid and 4.89 g. (31.5%) of a compound, m.p. 185°, which has been assigned structure VIII.

Anal. Calcd. for $C_{18}N_{18}N_2O_4$: C, 66.25; H, 5.56. Found: C, 66.11, 66.19; H, 5.42, 5.30.

Hydrolysis of 5,5-Dimethyl-4-methoxy-4-phenyl-2-(*p*-nitrophenyl)-2-oxazoline (VIII).—A solution of 1.88 g. of VIII, 50 ml. of acetone, 20 ml. of water and 2 ml. of concentrated hydrochloric acid was refluxed for one hour, after which time 50 ml. of hot water was added. The solution was cooled, whereupon 1.5 g. of solid precipitated, m.p. 137–138°. Another crop amounted to 0.27 g., m.p. 135–137°, for total of 1.77 g. (98%), which gave no depression in a mixture melting point with authentic α-hydroxyisobutyrophenone *p*-nitrobenzoate.

α-Hydroxyisobutyrophenone Dimethylketal 3,5-Dinitrobenzoate (V).—Sodium amide was prepared by dissolving 2.09 g. (0.091 g. atom) of sodium in 200 ml. of liquid ammonia and adding a crushed crystal of ferric nitrate to initiate reaction. After completion of the reaction, the excess ammonia was evaporated and 18.23 g. (0.087 mole) of α-hydroxyisobutyrophenone dimethylketal in 100 ml. of dry ether was added. The reaction mixture was heated briefly to expel any ammonia and then cooled to 0° and 22 g. (0.096 mole) of 3,5-dinitrobenzoyl chloride in 300 ml. of ether was added. The cold mixture was stirred for one hour, then filtered through Super-cel. The filtrate was evaporated until most of the ether was gone and then methanol was added and heat applied to dissolve any solid material. The solution gave 22.84 g. (66%), m.p. 142–146°, of ketal ester V. Recrystallization from methanol gave material melting at 147–148°.

Anal. Calcd. for $C_{19}H_{20}N_2O_8$: C, 56.43; H, 4.99. Found: C, 56.74; H, 5.26.

The ketal 3,5-dinitrobenzoate V was hydrolyzed by refluxing a mixture of 0.5 g. (1.24 mmoles) of the ester, 20 ml. of acetone, 5 ml. of water and four drops of concentrated hydrochloric acid for four hours. The yield was 0.31 g. (70%), m.p. 151–152°. A mixture melting point with authentic α-hydroxyisobutyrophenone 3,5-dinitrobenzoate was 151–152°.

α,α-Dimethyl-β-chloro-β-methoxyphenethyl Alcohol 3,5-Dinitrobenzoate (VII).—A mixture of 5 g. (0.0124 mole) of the ketal ester V and 20 ml. of acetyl chloride was refluxed for 30 minutes, then allowed to remain overnight at room temperature. After removal of most of the acetyl chloride, petroleum ether was added, which precipitated 5 g. (99%) of a solid, m.p. 114–120° dec. Recrystallization from petroleum ether containing a small amount of acetyl chloride gave material, m.p. 124° dec.

Anal. Calcd. for $C_{18}H_{17}N_2ClO_7$: Cl, 8.67. Found: Cl, 8.51.

The chloroether ester VII was hydrolyzed by refluxing for five minutes a mixture of 0.3 g. (0.74 mmole) of XII, 5 ml. of water, 2 drops of 10% sodium hydroxide solution and enough acetone to effect complete solution. The mixture was neutralized with dilute acid and then evaporated to dryness at reduced pressure. An impure solid which amounted to 0.26 g., m.p. 126–145°, was obtained which upon recrystallization from methanol gave 0.11 g. (41%), m.p. 150–152°. A mixture melting point with authentic α-hydroxyisobutyrophenone 3,5-dinitrobenzoate was undepressed.

Reaction of the Chloroether Ester VII with Liquid Ammonia.—A mixture of 75 ml. of liquid ammonia and 5 g. of unrecrystallized chloroether ester VII was stirred for three hours at –80°. The mixture was then stirred at room temperature for 5.5 hours after which time all the ammonia had escaped. Addition of hexane caused a solid to form which upon recrystallization from acetone–water gave 2.5 g., m.p. 160–167°. Two recrystallizations from acetone–hexane gave 0.93 g., m.p. 163° dec., of the solid compound X [5,5-dimethyl-4-phenyl-4-methoxy-2-(3,5-dinitrophenyl)-oxazolidine].

Anal. Calcd. for $C_{18}H_{19}N_3O_7$: C, 55.52; H, 4.92; N, 10.79. Found: C, 54.70, 54.66; H, 4.99, 4.69; N, 11.13, 11.01.

From the mother liquors was obtained 0.3 g., m.p. 186–187°, of a crystalline compound IX [5,5-dimethyl-4-methoxy-4-phenyl-2-(3,5-dinitrophenyl)-2-oxazoline].

Anal. Calcd. for $C_{18}H_{17}N_3O_6$: C, 58.22; H, 4.61. Found: C, 58.09; H, 4.69.

Compound IX was hydrolyzed by dissolving 0.5 g. (1.35 mmoles) in 25 ml. of acetone, 5 ml. of water and 1 ml. of concentrated hydrochloric acid and refluxing the solution for one hour. After 20 ml. of hot water was added, 0.48 g. (98%) of solid crystallized, m.p. 150–151°. A mixture melting point determination with authentic α-hydroxyisobutyrophenone 3,5-dinitrobenzoate was undepressed. The infrared spectra also were identical.

Acknowledgment.—The authors wish to thank Mr. C. Childs and associates of Parke, Davis and Co. for the analyses and Dr. J. M. Vandenbelt and associates of the same company for the spectral data.

Detroit 2, Mich.

[Contribution from the Department of Chemistry of the University of South Carolina]

Diacyl Peroxide Reactions. V. Simultaneous Rupture of Two or Three Bonds in the Initial Cleavage of δ-Phenylvaleryl Peroxide[1,2]

By DeLos F. DeTar and Robert C. Lamb[3]

Received August 20, 1958

In toluene and in carbon tetrachloride δ-phenylvaleryl peroxide gives 1.7 moles of carbon dioxide per mole of peroxide. In the presence of iodine and water the yield drops to 1.4 moles, while the rate of decomposition is essentially unchanged. This result indicates that it is possible to "trap" some of the free δ-phenylvaleryloxy radicals, and together with the previously reported detailed product study leads to the conclusion that most of the initial cleavage of the peroxide occurs by the simultaneous rupture of two or three bonds. It is significant that many reagents are suitable for "trapping" the benzoyloxy radicals from benzoyl peroxide while the iodine–water mixture was the only one of those tried that was also effective with δ-phenylvaleryl peroxide.

In the homolytic cleavage of a molecule into free radical fragments the ultimate products are often derived from units whose formation has required the cleavage of more than one bond of the original molecule. Diacyl peroxides, for example, give carbon dioxide and products derived from alkyl or aryl radicals as well as products from acyloxy radicals, and azo compounds lose nitrogen to give products arising from two alkyl free radicals. Thus these compounds must have reacted by breaking at least two bonds. There has been some speculation whether these bond cleavages occur in stepwise fashion or whether in some cases the primary break consists of the simultaneous cleavage of two or more bonds.

Some years ago Hammond and Soffer showed that the principal cleavage of benzoyl peroxide involved one bond to give two benzoyloxy fragments.[4] Accordingly the products incorporating phenyl radicals must be derived from successive reactions in one of which the benzoyloxy radical loses the carbon dioxide fragment. Recently Bartlett and his co-workers have studied the kinetics and the products of the thermal decomposition of an extensive series of peresters and have suggested that an initial two-bond cleavage occurs providing that a relatively stable alkyl radical is thereby formed, but that otherwise one-bond cleavage occurs.[5]

Because of our interest in the detailed mechanisms of diacyl peroxide reactions we have reinvestigated the Hammond and Soffer technique and have tested briefly a number of potentially useful modifications. The principle of the method is to carry out the peroxide decomposition in the presence of a "trapping" or "scavenging" agent capable of reacting rapidly with acyloxy radicals to give a product in which carbon dioxide is retained. Hammond and Soffer used an iodine and water combination for this purpose. Hammond first observed that the rate of decomposition of benzoyl peroxide in benzene or in carbon tetrachloride is not markedly affected

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[1] We wish to acknowledge with gratitude the generous support of this research by the Tennessee Eastman Co., and by the National Science Foundation (under G 4179). In addition this research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] (a) IV, D. F. DeTar and R. A. J. Long, This Journal, **80**, 4742 (1958); (b) III, D. F. DeTar and C. Weis, *ibid.*, **79**, 3045 (1957).

[3] Tennessee Eastman Research Fellow, 1956–1957. This work is based on the thesis of Robert C. Lamb submitted to the Graduate School of the University of South Carolina in partial fulfillment of the requirements for the Ph.D. degree.

[4] G. S. Hammond, This Journal, **72**, 3737 (1950); G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

[5] P. D. Bartlett, *Experientia, Suppl.*, **7**, 275 (1957); P. D. Bartlett and R. R. Hiatt, This Journal, **80**, 1398 (1958).