p-Dimethylaminoanil of 6-Carbonal-1,2,3,4-tetraphenylfulvene (IX).—A solution of 1.7 g. (4.3 mmoles) of VI and 1.2 g. (8.0 mmoles) of p-nitrosodimethylaniline in 25 ml. of dry benzene was heated to reflux and treated with 1 ml. of a 5% solution of sodium methoxide in methanol. The mixture darkened, became blood-red, and a dark solid separated on the sides of the flask. After refluxing for 15 min., the mixture was cooled and filtered. Washing the solid with methanol and drying gave 1.5 g. (2.8 mmoles, 66%) of brown crystals of IX, m.p. 215–218° dec. The product was contaminated with a decomposition product of p-nitrosodimethylaniline, which was brown, melted at 232–248°, and was soluble in 5% hydrochloric acid from which solution it was precipitated as a yellow solid by alkali. It could be separated from the anil by virtue of its solubility in a mixture of hot cyclohexane–benzene (from which it crystallized on cooling) in which the anil was insoluble. It was not separated from the anil by chromatography on alumina.

After washing with cold 5% hydrochloric acid until the washings were colorless, then with water, and drying, it melted 227–230.5° dec. A mixture with the dimethylaminoanil of tetracyclone melted at 215–218°. For analysis IX was recrystallized three times from benzene, m.p. 233–234° dec.

Anal. Calcd. for $C_{39}H_{32}N_2$: C, 88.60; H, 6.10; N, 5.30. Found: C, 89.06; H, 5.72; N, 5.29.

6-Carbonal-1,2,3,4-tetraphenylfulvene 2,4-Dinitrophenylhydrazone (X).—A mixture of 0.3 g. (0.57 mmole) of IX, 0.12 g. of 2,4-dinitrophenylhydrazine, 10 ml. of 1:1 hydrochloric acid and 10 ml. of benzene was refluxed under nitrogen for 15 min. The mixture was cooled, separated and the organic layer was washed with water, dried over anhydrous magnesium sulfate and chromatographed on alumina. A dark-gray band was eluted with benzene and appeared orange-brown in solution. A red-violet and a yellow band remained at the top of the column.

Distillation of the solution to dryness and trituration of the residue with Skellysolve A gave 0.115 g. (35%) of crude X which melted at 234–253° dec. Four recrystallizations from a mixture of dioxane (soluble)–95% ethanol (insoluble) gave a brown solid, m.p. 265–267° dec.

Anal. Calcd. for $C_{37}H_{26}N_4O_4$: C, 75.24; H, 4.44; N, 9.49. Found: C, 75.13; H, 4.70; N, 9.52.

1-(4′-Quinolyl)-2-(1″,2″,3″,4″-tetraphenylfulven-6″-yl)-ethylene (XI).—To a refluxing mixture of 0.4 g. (1.01 mmoles) of VI and 0.2 g. of quinoline-4-carbonal in a solvent mixture of 25 ml. of methanol and 15 ml. of benzene was added 5 ml. of 5% methanolic sodium methoxide. The solution became dark and on refluxing for 15 min. all of the VI was in solution. After refluxing for a total of 2.25 hr., cooling gave no crystals. The solution was then poured into water, separated and the aqueous layer was washed with benzene and then discarded. The combined benzene extracts were washed with water, dried over anhydrous magnesium sulfate, filtered and distilled to dryness. Trituration with Skellysolve A crystallized the residual oil. Purification was achieved by chromatography on alumina using cyclohexane as solvent and a mixture of cyclohexane and benzene as eluant. The lowest invisible band, which fluoresced blue-white under ultraviolet light (unreacted VI (?) was followed by a visible yellow band, and then by the main brown fulvene band, which was eluted with benzene.

Distillation of the solvent gave a semi-solid which melted at 216–217° after trituration with Skellysolve A, 0.175 g. (0.33 mmole, 32%). Two recrystallizations from acetonitrile raised the melting point to 217–218°.

Anal. Calcd. for $C_{41}H_{29}N$: C, 91.93; H, 5.46; N, 2.62. Found: C, 92.14; H, 5.64; N, 2.54.

BROOKLYN 1, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

Epoxyethers. IV. Mechanism of the Opening of an Epoxyether with an Organic Acid[1]

BY CALVIN L. STEVENS AND STANLEY J. DYKSTRA[2]

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The reaction of an epoxyether I with 3,5-dinitrobenzoic acid is considered to proceed by initial attack of the acid on C_1 of the epoxyether followed by intramolecular ester interchange with the irreversible formation of alcohol and the ketoester III.

The purpose of this investigation was the determination of the mechanism of the reaction of organic acids with epoxyethers. The results indicated that in the example studied the organic acid opened the oxide ring of the epoxyether I by initial attack at the carbon atom (C_1) holding the two oxygen functions to give the ester of a hemiketal (II). This ester when heated or dissolved in an organic solvent, was converted to the ketoester IIIa.

A number of epoxyethers have been isolated recently in this Laboratory and the chemistry of these compounds has been investigated.[3-5] The epoxyethers (*cf.* I) have been characterized by hydrolysis reactions which gave α-hydroxyketones (*cf.* IV), methanolysis reactions which gave α-hydroxyketals (*cf.* V) and reactions with organic acids which gave ketoesters (*cf.* IIIa).

In the reaction with organic acids the reagent appeared in the product attached to carbon atom 2. The fact that in acid-catalyzed alcoholysis the reagent appeared in the product on carbon atom 1 indicated that the mechanism of the reaction with organic acids might involve an intermediate in which the reagent was also attached to carbon atom 1.

The epoxyether, 1,2-epoxy-2-methyl-1-methoxy-1-(p-biphenyl)-propane (I), chosen for this investigation was a solid and gave derivatives which were readily crystallizable. This epoxyether was prepared in 84% yield from the bromoketone by treatment with alcoholic sodium methoxide. Since p-phenylisobutyrophenone was prepared in 92% yield and brominated in 85% yield, I represented a readily available starting material.

The epoxyether was stable at high temperatures (250°) for a short period of time and was characterized by hydrolysis to the α-hydroxyketone IV in 79% yield, methanolysis to the α-hydroxyketal V in 83% yield, and reaction with benzoic acid to

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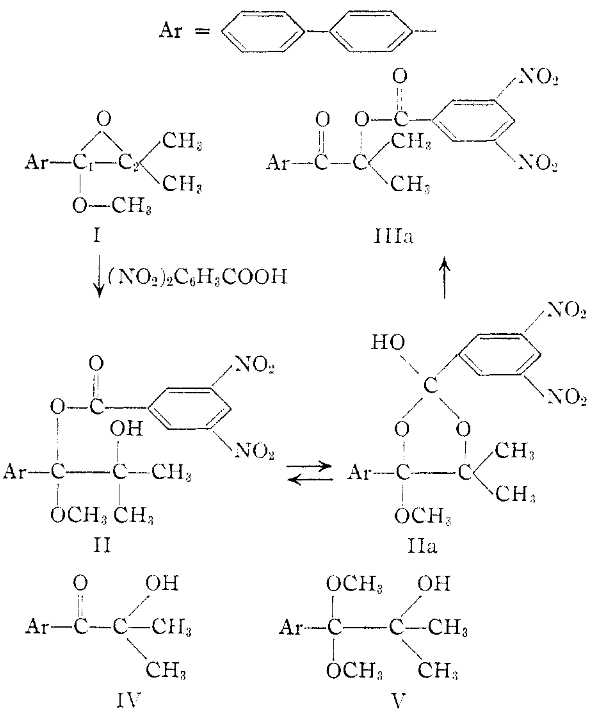
[1] Presented before the Organic Division of the 122nd Meeting of the American Chemical Society, Atlantic City, September, 1952.

[2] Abstracted in part from the Ph.D. thesis of Mr. Stanley J. Dykstra, Wayne University, June, 1953.

[3] C. L. Stevens, W. Malik and R. Pratt, THIS JOURNAL, **72**, 4758 (1950).

[4] C. L. Stevens and E. Farkas, *ibid.*, **74**, 618 (1952).

[5] C. L. Stevens, M. W. Weiner and R. C. Freeman, *ibid.*, **75**, 3977 (1953).



give α-hydroxy-*p*-phenylisobutyrophenone benzoate (IIIb) in 70% yield. The α-hydroxyketone acetate IIIc was formed in 77% yield from the epoxyether and acetic acid.

The hydroxyketal V was hydrolyzed in dilute acid to the hydroxyketone IV in 83% yield. The ketobenzoate IIIb was saponified with dilute base to IV in 66% yield. Benzoylation and acetylation of IV gave the ketoesters (IIIb and IIIc) in 89 and 92% yield, respectively. The structure of IV was confirmed by preparation of the oxime in 98% yield followed by Beckmann rearrangements to give 80% of *p*-phenylbenzonitrile.

When an ether solution of 3,5-dinitrobenzoic acid and an ether solution of the epoxyether I were mixed and the solution warmed on a steam-bath the light yellow α-hydroxy-*p*-phenylisobutyrophenone 3,5-dinitrobenzoate (IIIa), m.p. 140–141°, was formed in 89% yield. The structure was shown by independent synthesis from the hydroxyketone IV. However, at 0° 3,5-dinitrobenzoic acid reacted with the epoxyether I to give a colorless solid melting sharply at 120–121°. After melting, this compound resolidified and melted again at 140–141°. The latter melting point corresponded to the ketoester IIIa and in a large scale pyrolysis of the 121° melting material the ketoester IIIa was isolated in 50% yield and proved by a mixture melting point determination.

The 121° melting intermediate was assigned the structure of the hemiketal ester II. The carbon, hydrogen and methoxyl content indicated that all the elements of the 3,5-dinitrobenzoic acid and the epoxyether were present in II. The fact that II was an ester of a hemiketal was proven by mild acid hydrolysis to the hydroxyketone (IV, 84%) and 3,5-dinitrobenzoic acid. Under these mild acid hydrolysis conditions IIa was not hydrolyzed. A structure for the 121° melting material such as the methyl hemiketal of IIIa, in which the 3,5-dinitrobenzoate was attached to carbon atom 2, was eliminated by this latter experiment.

3,5-Dinitrobenzoic acid is known to form addition complexes with biphenyl and biphenyl derivatives.[6] Such a complex was considered as a possible structure of the 121° melting material but rejected since complexes of 3,5-dinitrobenzoic acid and biphenyl compounds are highly colored whereas II is colorless.[7] Further, a solution in methanol of II gave hydroxyketal V by alcoholysis and ketoester IIIa by decomposition, while a solution in methanol of an intimate mixture of I and 3,5-dinitrobenzoic acid, the behavior of which might simulate a complex in which no valence bonds were broken, gave only hydroxyketal by reaction of methyl alcohol with I. Also, liquid analogs of II, stable enough to be distilled, have been isolated in this Laboratory from other epoxyethers and will be reported later.

In addition to the formation of IIIa from II by pyrolysis, II was readily converted to IIIa in ether solution at room temperature. Both of these reactions are interpreted as intramolecular ester interchange reactions involving the equilibrium II → IIa and which proceed irreversibly to the C_2 O-acyl derivative IIIa by the elimination of alcohol. O- to N-acyl migrations and *vice versa* can be conveniently studied by varying the driving force of the reaction by changing the acidity and basicity of the solution. O- to O-acyl migration is inherently very difficult to determine. The above example indicates that O- to O-acyl migration takes place very readily and the unique irreversible last step may allow a convenient study of the rearrangement.

The above results are considered to prove that in the case studied the reaction of organic acid on the epoxyether I to give the ketoester proceeded by initial attack of the acid on carbon atom 1 of the epoxyether. Similar examples recently reported[3–5] likely proceed by the same mechanism.

Experimental

α-Bromo-*p*-phenylisobutyrophenone.—*p*-Phenylisobutyrophenone, m.p. 62–63°, was prepared in 92% yield by a Friedel–Crafts reaction of biphenyl and isobutyryl chloride in carbon disulfide using anhydrous aluminum chloride catalyst, following the directions of Long.[8]

Following the procedure of Carpenter[9] the ketone was brominated in glacial acetic acid to give an 85% yield of α-bromo-*p*-phenylisobutyrophenone, m.p. 99–100°.

Preparation of the Epoxyether I.—In 200 ml. of refluxing absolute methanol 78.5 g. (0.061 mole) of α-bromoketone was dissolved. To the hot solution 25 ml. of 2.46 *N* sodium methoxide (0.061 mole) was added and the solution refluxed for two minutes. The reaction was quenched by pouring the solution onto cracked ice, after which a solid precipitated. The solid was extracted with methylcyclohexane, the solvent was removed immediately under reduced pressure at room temperature and the residue recrystallized from pentane. The yield of the epoxyether, 1,2-epoxy-2-methyl-1-methoxy-1-(*p*-biphenyl)-propane (I) was 13.0 g. (84%), m.p. 78–79°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13; OCH_3, 12.2. Found: C, 80.04; H, 7.11; OCH_3, 11.85.

One gram of the epoxyether I was heated for five minutes to 240–250° in the presence of 0.01 g. of dry sodium methoxide. The distillation flask was connected to a Dry Ice trap; however, no decomposition products were found.

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(6) D. Dermer and R. B. Smith, *ibid.*, **61**, 748 (1939).

(7) G. Bennett and G. Willis, *J. Chem. Soc.*, 256 (1929).

(8) L. M. Long and H. R. Henze, THIS JOURNAL, **63**, 1939 (1941).

(9) B. R. Carpenter and E. E. Turner, *J. Chem. Soc.*, 869 (1934).

After the liquid cooled it solidified to give a brown solid which dissolved in pentane leaving a small brown residue. From the pentane solution 0.7 g. of a solid, m.p. 73–75°, was obtained. When mixed with the starting epoxide I, m.p. 78–79°, the melting point was raised to 75–76°.

Hydrolysis of Epoxyether I.—A mixture of 2.15 g. of I and 150 ml. of water was made basic to litmus with sodium hydroxide. The mixture was heated on the steam-bath for ten minutes. After the solution had cooled, a solid formed which was removed by filtration. The precipitate was recrystallized from methylcyclohexane to give 1.61 g. (79%) of the α-hydroxyketone, α-hydroxy-*p*-phenylisobutyrophenone (IV), m.p. 94–95°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.95; H, 6.71. Found: C, 79.67; H, 6.82.

Following the procedure described by Shriner and Fuson,[10] 0.48 g. of α-hydroxyketone IV gave 0.63 g. of a yellow 2,4-dinitrophenylhydrazone, m.p. 213–215°. Repeated recrystallizations from alcohol lowered the melting point and finally gave a dark orange 2,4-dinitrophenylhydrazone, m.p. 188–189°. A mixture melted at an intermediate point, 205–208°.

Anal. Calcd. for $C_{22}H_{20}N_4O_5$ (m.p. 213–215°): C, 62.85; H, 4.80. Found: C, 62.85; H, 5.08. Calcd. for $C_{22}H_{20}O_5N_4$ (m.p. 188–189°): C, 62.85; H, 4.80. Found: C, 63.21; H, 5.17.

Using the method involving aqueous sodium hydroxide,[11] 2.0 g. of the α-hydroxyketone IV gave 2.06 g. (98%) of the oxime of α-hydroxy-*p*-phenylisobutyrophenone, m.p. 210–211°.

Anal. Calcd. for $C_{17}H_{19}NO$: C, 75.27; H, 6.71. Found: C, 75.06; H, 6.74.

Using the Beckmann rearrangement procedure of Buck,[12] 0.50 g. (0.002 mole) of the oxime was mixed with 10 ml. of 10% sodium hydroxide solution. To the suspension, cooled in an ice-bath, was added 0.70 g. (0.004 mole) of benzene sulfonyl chloride. The mixture was shaken until the odor of the chloride disappeared. Since some oxime still remained in suspension, an additional 0.35 g. (0.002 mole) of benzene sulfonyl chloride was added and the mixture was shaken until all the oxime was consumed. An oil remained on the bottom of the flask which eventually solidified and was collected on a buchner funnel. The solid was recrystallized from an ethanol–water mixture to give 0.28 g. (80%) of *p*-phenylbenzonitrile, m.p. 88–89°. The melting point of the known *p*-phenylbenzonitrile is 86°.[13] A small sample was hydrolyzed to the *p*-phenylbenzoic acid, m.p. 217–218°. Mixed with an authentic sample of *p*-phenylbenzoic acid the melting point was not depressed.

Reaction of Epoxyether I with Absolute Methanol.—In 15 ml. of absolute methanol 1.67 g. (0.0066 mole) of I was dissolved and a trace of hydrochloric acid was added to catalyze the reaction. A solid precipitated from the reaction mixture and was recrystallized in methylcyclohexane. The yield of α-hydroxy-*p*-phenylisobutyrophenone dimethyl ketal (V), m.p. 126–127°, was 1.56 g. (83%).

Anal. Calcd. for $C_{18}H_{22}O_3$: C, 75.49; H, 7.75; OCH_3, 21.67. Found: C, 75.00; H, 7.85; OCH_3, 21.70.

In 50 ml. of a slightly acidic water solution 1.7 g. (0.006 mole) of α-hydroxyketal V was heated for one hour. After cooling the mixture, the solid which formed was filtered and recrystallized from methylcyclohexane. The yield was 1.1 g. (83%) of α-hydroxyketone IV, m.p. 94–95°.

Reaction of Epoxyether I with Benzoic Acid.—In 45 ml. of anhydrous ether 2.62 g. (0.01 mole) of epoxyether I was dissolved and 1.34 g. (0.011 mole) of benzoic acid was added. The mixture was cooled and after three days 2.48 g. (70%) of the benzoate of α-hydroxy-*p*-phenylisobutyrophenone (IIIb), m.p. 118–119°, was obtained.

An analytical sample melted at 121–122°.

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.20; H, 5.85. Found: C, 80.13; H, 5.78.

To 2.0 g. (0.008 mole) of α-hydroxyketone IV in 50 ml. of dry pyridine, 2.0 g. (0.014 mole) of benzoyl chloride was added and the mixture refluxed for 18 hours. At the end of this time the mixture was poured on ice and the resulting solid recrystallized from alcohol. The yield of IIIb, m.p. 121–122°, was 2.56 g. (89%) of light tan needles. When mixed with the benzoate obtained from the epoxyether I, the melting point was not depressed.

The benzoate was hydrolyzed by refluxing for two hours a solution consisting of 25 ml. of 0.3 *N* sodium hydroxide and 20 ml. of methanol, 0.4 g. of the benzoate IIIb. The reaction mixture was poured on ice and the resulting solid was extracted with ether. The ether was removed and the residue on recrystallization from petroleum ether yielded 0.19 g. (66%) of hydroxyketone IV, m.p. 94–95°. When mixed with an authentic sample the melting point was not depressed.

Reaction of Epoxyether I with Acetic Acid.—A mixture of 0.12 g. (0.002 mole) of acetic acid, prepared by adding acetic anhydride to 95% acetic acid and 0.5 g. (0.02 mole) of I in 20 ml. of methylcyclohexane was heated until the odor of acetic acid was not perceptible. After cooling the solution, 0.34 g. (77%) of the acetate of α-hydroxy-*p*-phenylisobutyrophenone (IIIc), m.p. 125–126°, was isolated.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.54; H, 6.31.

In 20 ml. of dry pyridine 1.0 g. (0.004 mole) of α-hydroxyketone IV was mixed with 0.5 g. (0.005 mole) of 90% acetic anhydride and the solution was heated at the reflux temperature for six hours. The reaction mixture was poured onto cracked ice and the solid filtered. Recrystallization from petroleum ether gave 1.07 g. (92%) of IIIc, m.p. 126–127°. The melting point was not depressed when mixed with the acetate obtained from the epoxyether I.

Reaction of 3,5-Dinitrobenzoic Acid with Epoxyether I at 0°.—In 100 ml. of dry ether 1.00 g. (0.0047 mole) of acid was dissolved. The resulting solution was filtered and 1.22 g. (0.0046 mole) of epoxyether I was added to the filtrate. The mixture was cooled to 0° for 20 hours during which time colorless needles formed. The solid was filtered and washed with anhydrous ether to give 1.30 g. (61%) of the 3,5-dinitrobenzoate of the methyl hemiketal of α-hydroxy-*p*-phenylisobutyrophenone (II), m.p. 120–121°. After the melt had been heated to 130° and cooled the resulting solid melted at 140–141°.

Anal. Calcd. for $C_{24}H_{22}N_2O_8$: C, 61.80; H, 4.76; OCH_3, 6.65. Found: C, 62.00; H, 4.90; OCH_3, 6.64.

Reaction of 3,5-Dinitrobenzoic Acid with Epoxyether I at 36°.—In 70 ml. of anhydrous ether 0.6 g. (0.003 mole) of 3,5-dinitrobenzoic acid was dissolved and added to 0.72 g. (0.003 mole) of epoxyether I. The volume of the solution was increased to 100 ml. and then the solution was warmed for ten minutes at 36°. After the solution cooled to room temperature, cubical, light yellow crystals had formed. Three crops of ketoester, m.p. 140–141°, were obtained and amounted to 1.08 g. (89%).

Anal. Calcd. for $C_{23}H_{18}N_2O_7$: C, 63.59; H, 4.176. Found: C, 63.72; H, 4.303.

Pyrolysis of Hemiketal Ester II.—In a test-tube suspended in an oil-bath, 0.75 g. of II was heated between 140–160° for 90 minutes. The melt was cooled and recrystallized from ether. The yield was 0.44 g. (63%) of the 3,5-dinitrobenzoate IIIa, m.p. 139–140°. When mixed with the ester obtained from I the melting point was 139–140°.

The hemiketal ester II also was readily converted to the ketoester IIIa in solution at room temperature. In 100 ml. of ether 2.8 g. of the hemiketal ester II slowly dissolved and after 24 hours crystals of the ketoester IIIa appeared. After the solution was cooled to 0°, 1.3 g. (50%) of the ketoester IIIa, m.p. 139–140°, was obtained and proved by a mixture melting point determination with an authentic sample.

Independent Synthesis of the 3,5-Dinitrobenzoate of α-Hydroxy-*p*-phenylisobutyrophenone (IIIa).—To 1.0 g. (0.004 mole) of α-hydroxyketone (IV) dissolved in 20 ml. of dry pyridine, 1.0 g. (0.0043 mole) of 3,5-dinitrobenzoyl chloride was added. The solution was refluxed for 20 hours, poured on ice and the solid which formed was collected by filtration and washed with sodium bicarbonate solution. Recrystallization from petroleum ether (b.p. 30–60°) gave 0.75 g. of the starting α-hydroxyketone, m.p. 93–94° (75% recovery). The mother liquors when concentrated yielded 0.11 g. (25% based on ketone used) of the 3,5-dinitrobenzoate (IIIa), m.p. 140–141°.

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[10] R. Shriner and R. Fuson, "Identification of Organic Compounds," 3rd ed., J. Wiley and Sons, Inc., New York, N. Y., 1948, p. 97.

[11] R. Shriner and R. Fuson, *ibid.*, p. 202.

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[13] M. Pestemer and E. Mayer-Pitsch, *Monatsh.*, **70**, 104 (1937).

Acid Hydrolysis of the Hemiketal Ester II.—A sample of 0.35 g. (0.75 millimole) of the hemiketal ester II was mixed in a separatory funnel with 70 ml. of ether and 20 ml. of 6 *N* hydrochloric acid. The reaction mixture was allowed to stand at room temperature for 15 hours with intermittent shaking. The ether layer was extracted with a sodium carbonate solution, washed once with water and dried over sodium sulfate. After concentration of the ether solution and the addition of petroleum ether, 0.05 g. (84%) of α-hydroxyketone IV, m.p. 94–95°, was obtained. When mixed with an authentic sample of IV, the melting point was 94–95°. On acidification of the sodium carbonate layer, 0.10 g. (62%) of 3,5-dinitrobenzoic acid, m.p. 195–198°, was obtained. A mixture melting point determination with an authentic sample of the acid, m.p. 204–205°, melted over the range 200–203°.

A sample of 0.35 g. of the 3,5-dinitrobenzoate IIIa was subjected to exactly the same procedure. After drying, the resulting ether solution was cooled and concentrated to give 0.27 g. (77%) of recovered starting keto 3,5-dinitrobenzoate. No acid was found upon acidification of the sodium bicarbonate layer.

Reaction of Hemiketal Ester II with Methanol.—In 25 ml. of absolute methanol 1.0 g. (0.002 mole) of II was heated on a steam-bath until solution was effected. After cooling the solution, a first crop of crystals gave 0.3 g. (33%) of the ketoester IIIa, m.p. 140–141°. A second crop, 0.17 g., corresponded to the α-hydroxyketal V, melting at 116–121°. When mixed with V the melting point was raised to 117–122°. The filtrate was evaporated to dryness and the residue was dissolved in ether and the ether solution was extracted with a 10% sodium bicarbonate solution. On acidification of the bicarbonate solution 0.14 g. of 3,5-dinitrobenzoic acid was obtained. The ether layer after evaporation left 0.15 g. of residue, m.p. 111–116°. An infrared spectrum of this solid showed absorption bands corresponding to the hydroxyketal (V) as the major constituent. Bands corresponding to the α-hydroxyketone IV and the 3,5-dinitrobenzoate ester IIIa were also present as minor constituents. The total yield of crude V was 76%.

Reaction of Epoxyether I with Absolute Methanol in the Presence of 3,5-Dinitrobenzoic Acid.—In a mortar 0.5 g. (0.002 mole) of I and 0.42 g. (0.002 mole) of 3,5-dinitrobenzoic acid were mixed thoroughly. The mixture was heated on a steam-bath with 25 ml. of absolute methanol until solution was effected. Treatment of this solution in the same manner as the solution of the hemiketal ester II gave no keto-3,5-dinitrobenzoate IIIa but only an 86% yield of crude hydroxyketal V as proved by mixture melting point determination and comparison of the infrared spectra.

DETROIT, MICHIGAN

[CONTRIBUTION NO. 69 FROM THE CENTRAL RESEARCH DEPARTMENT, MINNESOTA MINING AND MANUFACTURING COMPANY]

1,1-Di-H-perfluoroalkyl Halides

BY GEORGE V. D. TIERS, HARVEY A. BROWN AND THOMAS S. REID

RECEIVED MAY 28, 1953

A convenient, general method has been found for the preparation of 1,1-di-H-perfluoroalkyl halides from the corresponding alcohols, *via* the *p*-toluenesulfonyl (tosyl) esters. Good yields are obtained without the use of special apparatus. Physical properties are reported for the compounds prepared, and certain unusual features of the infrared spectra are discussed.

Although 1,1-di-H-perfluoroethyl chloride,[1,2,4] bromide,[2-4] and iodide[5] have previously been reported, the preparative methods are different for each halide, and are not readily extended to the synthesis of other 1,1-di-H-perfluoroalkyl halides. This article reports a convenient synthetic method of general applicability, which does not require the use of special apparatus.

The tosyl esters were readily obtained from the fluorinated alcohols, using reaction conditions satisfactory for the tosylation of phenols.[6a] The preparation of alkyl halides by reaction of alkyl tosylates with appropriate metal halides is well known.[6b,7,8] These tosyl esters, however, differ from alkyl tosylates in being quite unreactive at the usual temperatures of 50–100°. For example, it was necessary to heat 1,1-di-H-perfluorobutyl *p*-toluenesulfonate with sodium iodide in acetone in a sealed tube at 150° for 19 hours to afford a 40% yield of the corresponding iodide. No iodide was isolated after the tube was heated at 110° for 15 hours.

Much better results were obtained when higher-boiling solvents were tried. Thus, when 1,1-di-H-perfluorobutyl *p*-toluenesulfonate was heated with sodium iodide in diethylene glycol, triethylene glycol, tetraethylene glycol or tetraethylene glycol dimethyl ether, very good yields (80–95%) of 1,1-di-H-perfluorobutyl iodide were obtained.

It was necessary for both the sodium iodide and 1,1-di-H-perfluorobutyl *p*-toluenesulfonate to be dissolved in order for reaction to occur. For example, in one experiment, glycerol (in which sodium iodide is very soluble and the ester is in soluble) was used as a solvent and no reaction was noted.

In order to prepare the 1,1-di-H-perfluoroalkyl bromides and chlorides it was necessary to use lithium bromide and lithium chloride. No reaction occurred with sodium bromide or chloride, presumably due to the low solubility of these salts in the solvents used.

Now that the 1,1-di-H-perfluoroalkyl chlorides are readily accessible, they may be employed as starting materials for the preparation of the corresponding 1,1,1-trichloroperfluoroalkanes. The first member of this series, CCl_3CF_3, has been obtained by the chlorination of methylfluoroform,[9] but the higher 1,1,1-tri-H-perfluoroalkanes are not available. To illustrate the preparation, the photochlorination of 1,1-di-H-perfluorobutyl chloride was carried out by the method of Henne and Whaley.[10]

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