of methyl iodide in 50 ml. of ether) was diluted with thiophene-free benzene (50 ml.) and most of the ether then was distilled off. Dry cuprous iodide (0.75 g.) now was added with vigorous stirring to the hot solution. The mixture was cooled in ice and a solution of the unsaturated cyanoester V (9 g.) in benzene (60 ml.) was gradually added with stirring. After being allowed to stand in an ice-bath for 0.5 hour, the reaction mixture was refluxed for 2 hours and finally decomposed with ice-cold dilute hydrochloric acid. On working up and removal of the solvent, the residue was crystallized from ethyl acetate, affording needles, 3.2 g. (37%), m.p. 169–170°. On recrystallization from the same solvent, the substance showed m.p. 171–172°. The sample was dried at 100° (0.01 mm.) for 6 hours.

Anal. Calcd. for $C_{20}H_{27}ON$: C, 80.8; H, 9.1; N, 4.7. $C_{21}H_{29}ON$ (methyl-addition compound): C, 81.0; H, 9.3; N, 4.5. Found: C, 80.7, 80.8; H, 8.7, 8.6; N, 4.9.

β,β-Dimethyl-α-(4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1)-acrylonitrile (XI).—The above hydroxy-compound (300 mg.) was dissolved in benzene (20 ml.) and the last traces of moisture were removed through distilling off 15 ml. of the solvent. Phosphorus pentoxide (400 mg.) was added and the reaction mixture was refluxed for 2 hours. The benzene extract was washed with a solution of sodium hydroxide, dried and evaporated. The residue crystallized on trituration with ethyl acetate. An oily impurity was removed on a porous plate and the resulting solid was crystallized repeatedly from the same solvent to yield 50 mg. (17.7%), m.p. 128–129°.

Anal. Calcd. for $C_{20}H_{25}N$: C, 86.0; H, 8.9. $C_{21}H_{27}N$ (methyl-addition compound): C, 86.0; H, 9.3. Found: C, 86.3; H, 8.6.

Methyl 1,4a-Dimethyl-9,10-diketo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (XIII).—To a solution of the ester VIII (310 mg.) in glacial acetic acid (3 ml.) was added a solution of chromic anhydride (390 mg.) in water (1 ml.) and acetic acid (3.5 ml.). The mixture was left, with occasional swirling, for 18 hours at room temperature (28–30°). The light-green reaction mixture was diluted with water (25 ml.), the solution was saturated with sodium chloride and extracted with chloroform (3 × 20 ml.). The light-yellow chloroform extract was washed with water, cold sodium hydroxide solution (5%; 2 × 10 ml.) and finally with water until neutral. The chloroform extract was dried over sodium sulfate and evaporated. Trituration of the residue with ethyl acetate–petroleum ether (40–60°), yielded shiny yellow crystals, m.p. 178–179°, contaminated with some oily material. After three recrystallizations from the same solvent mixture, yellow prisms, 75 mg. (22%), with m.p. 185–187° were obtained.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.0; H, 6.6. Found: C, 72.2; H, 6.8.

JADAVPUR, CALCUTTA 32, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Oxetanes. VIII. Synthesis and Reactions of 2-Oxaspiro[3,2]hexane[1,2]

BY SCOTT SEARLES, JR., AND EUGENE F. LUTZ

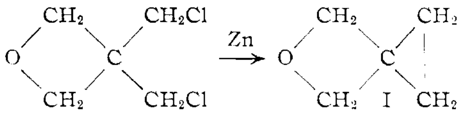
RECEIVED AUGUST 18, 1958

The preparation of the highly strained oxetane, 2-oxaspiro[3,2]hexane, is described. In its reactions with lithium aluminum hydride, hydrochloric acid, hydrogen bromide, oxygen and bromine enhanced reactivity of both rings appeared to be shown.

Few simple spiro compounds consisting of two small, strained rings, are known and practically nothing is known of their chemical reactivity. Considerable attention has been devoted to the synthesis of spiropentane,[3,4] the most strained such spiro compound, but only one reaction has been reported, catalytic hydrogenation to (mainly) 1,1-dimethylcyclopropane.[5] This result suggests that the additional strain of the spirane structure enhanced the ease of hydrogenolysis.

2-Oxaspiro[3,2]hexane (I) would be expected to be almost as strained as spiropentane but would have the advantage of a reactive ether linkage for study of reactivity. This compound has been synthesized now and some of its chemical reactions studied.

It was prepared in 25% yield by the reaction of 3,3-bis-(chloromethyl)-oxetane with zinc dust in molten acetamide according to a procedure similar to that used by Murray and Stevenson for the synthesis of spiropentane.[3] The product is a volatile, water-soluble liquid, boiling at 97°.



I

The main cause for low yield was undoubtedly the intermolecular condensation of 3,3-bis-(chloromethyl)-oxetane, but two side products resulting from ring enlargement were obtained in low yield. Cyclopentanone (II) was identified positively by its characteristic infrared absorption[6] and by isolation of its 2,4-DNP derivative. 1-Cyclobutenemethanol (III) also appeared to be present, as judged by the infrared spectrum containing absorption bands characteristic of a primary hydroxyl group and a double bond (unfortunately, a strong broad band at 902 cm.$^{-1}$ obscured any possible cyclobutane absorptions[7] that may have been present) and practically identical to those found in another preparation of this compound (see below).

It is believed that these products were formed from the Lewis acid-catalyzed rearrangement of the initially formed 2-oxaspiro[3,2]hexane by a sequence such as shown in I–II–III.

Although sodium carbonate was used to remove the zinc chloride as it was formed in the reaction, it seems likely that there could be some opportunity for zinc chloride or $ZnCl^{\oplus}$ to act on the molecule from which it was formed before interacting with

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[1] A portion of a dissertation presented by E. F. Lutz (1958) in partial fulfillment for the degree of Doctor of Philosophy in Chemistry at Kansas State College. Presented at the Southwest Regional Meeting American Chemical Society, December 5, 1957.

[2] (a) Supported in large part by a research grant from the National Science Foundation for which grateful acknowledgment is made. (b) The preceding paper in the series was S. Searles, K. A. Pollart and F. Block, THIS JOURNAL, **79**, 952 (1957).

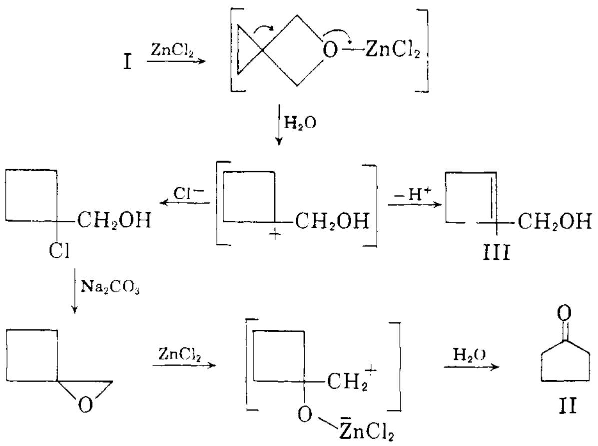
[3] M. J. Murray and E. H. Stevenson, *ibid.*, **66**, 812 (1944).

[4] V. A. Slabey, *ibid.*, **68**, 1335 (1946).

[5] V. A. Slabey, *ibid.*, **69**, 475 (1947).

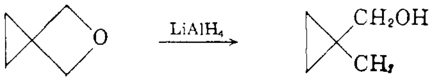
[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 128.

[7] *Ibid.*, p. 28.



sodium carbonate. Additional support for the scheme is furnished by the reaction with hydrochloric acid (see below) and by the report that 1-oxaspiro[2,5]octane produces cyclohexanecarboxaldehyde when heated with zinc chloride.[8]

The structure of the oxetane was demonstrated by lithium aluminum hydride reduction[9] to the known 1-methylcyclopropanemethanol and by its

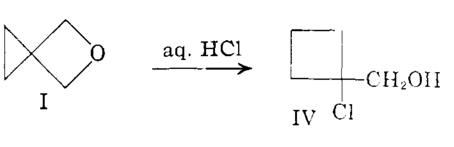


I

infrared spectrum which showed bands at 9.8 and 10.35 μ, characteristics of the cyclopropane[10] and the oxetane[11,12] groupings, respectively. It should be noted that the oxetane absorption band (usually at 10.20 μ) has been shifted to a higher wave length, indicating the highly strained nature of the ring system.

It is of interest to note that the reductive cleavage proceeded smoothly and in 65% yield whereas the reductive cleavage of 3,3-dimethyloxetane gave only a 32% yield under more rigorous conditions.[9] Whether this difference is due to external steric factors and/or internal strain factors is uncertain.

When 2-oxaspiro[3,2]hexane (I) was treated with aqueous hydrochloric acid at 0°, cleavage of the ether linkage and enlargement of the carbocyclic ring occurred. 1-Chlorocyclobutanemethanol (IV) was isolated in 69% yield. The structure of this product was established by hydrolysis



to 1-hydroxymethylcyclobutanol which was oxidatively cleaved with lead tetraacetate to cyclobutanone,[13] identified by its 2,4-DNP derivative. The 1-chlorocyclobutanemethanol was treated also with methanolic potassium hydroxide to give 1-cyclobutenemethanol in 66% yield. Low pressure hydrogenation of the product gave cyclobutanemethanol.

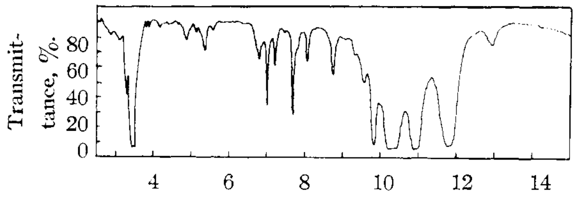
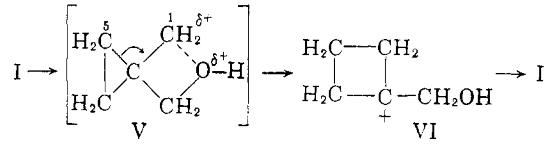


Fig. 1.—Infrared spectrum of 2-oxaspiro[3,2]hexane (liquid).

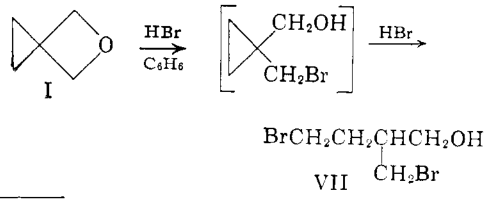
This Wagner–Meerwein ring enlargement of I seems to be rather unusual for a cyclopropylcarbinol or carbinyl ether. Such compounds usually react without rearrangement or rearrange to olefins, the cyclopropyl ring undergoing ring contraction rather than expansion. Thus, methylcyclopropylcarbinol is converted to its methyl ether without rearrangment when treated with methanolic *p*-toluenesulfonic acid for a short time, but on long refluxing it rearranges to 3-penten-1-yl methyl ether.[14] Also, cyclopropyl carbinyl *p*-toluenesulfonate rearranges to 3-penten-1-yl *p*-toluenesulfonate, presumably *via* a carbonium ion intermediate.[15]

With no evidence for any olefinic products of ring contraction in I, the observed ring expansion suggests that the bicyclic structure may facilitate migration of a carbon atom with its pair of electrons in the carbonium ion stage (V). This may be due to the Thorpe–Ingold effect of bond angle deformation,[16] causing closer proximity of position 1 and 5. Another factor probably is the tertiary



nature of the rearranged carbonium ion VI.[17] It seems likely that the process is closely related to the one leading to the by-products observed in the synthesis of I.

When 2-oxaspiro[3,2]hexane (I) was treated with dry hydrogen bromide in dry benzene at 0°, both rings were cleaved to form 4-bromo-2-bromomethyl-1-butanol (VII) in 38% yield. The structure of the dibromo alcohol VII was demonstrated by



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[8] M. Tiffeneau, P. Weill and B. Tchoubar, *Compt. rend.*, **205**, 54 (1937).

[9] S. Searles, K. A. Pollart and E. F. Lutz, THIS JOURNAL, **79**, 948 (1957).

[10] L. J. Bellamy, ref. 6, p. 28.

[11] G. M. Barrow and S. Searles, THIS JOURNAL, **75**, 1175 (1953).

[12] T. Campbell, *J. Org. Chem.*, **22**, 1035 (1957).

[13] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3928 (1949).

[14] R. G. Pearson and S. H. Lange, *ibid.*, **75**, 1065 (1953).

[15] C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

[16] R. M. Beesley, C. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, **107**, 1080 (1915).

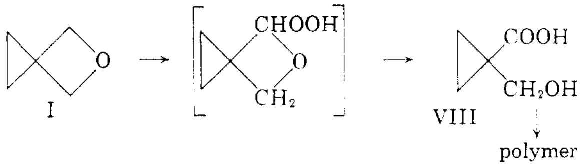
[17] *Cf.* discussion of cyclopropylcarbinyl–cyclobutyl–allylcarbinyl interconversion in J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951).

hydrogenolysis with lithium aluminum hydride to *dl*-2-methyl-1-butanol, identified by melting point and mixed melting point of its naphthylurethan.

It seems very likely that the reaction with hydrogen bromide proceeded by first cleaving the oxetane ring, since it is known that oxetanes are very sensitive to treatment with acids,[18] to produce the intermediate 1-bromomethyl-1-hydroxymethyl-cyclopropane. This would then react further with hydrogen bromide to cleave the cyclopropane ring and give the product 4-bromo-2-bromomethyl-1-butanol (VII). It is known that the presence of a *gem*-dialkyl group on a cyclopropane ring facilitates its cleavage with hydrogen bromide.[19] No indication of rearrangement was observed here. This is to be expected since benzene is a very poor ionizing solvent[20] and could not solvate the intermediate primary carbonium ion to any great extent.

It was found that 2-oxaspiro[3,2]hexane (I) was slowly oxidized in the air. After standing for a short time in the air, it gave a positive test for peroxides. When oxygen was passed through a sample of the oxetane at temperatures ranging from 65–80° and reaction times of 5 to 29 hours, a viscous, high boiling product formed which contained hydroxyl and non-aldehydic carbonyl groups, according to the infrared spectrum and chemical tests. The spectrum also showed that the cyclopropane ring (but not the oxetane ring) was retained during oxidation.

Attempted distillation of the oxidation product resulted in polymerization. Though the product was not specifically identified, the data collected suggested that the initial product of oxidation was the 1-hydroxymethylcyclopropanecarboxylic acid (VIII). Since it is known that the hydroperoxides of primary and secondary alcohols give the corresponding acids on mild heating,[21] the reaction path outlined above seems quite reasonable.



Preliminary work was done on bromination of 2-oxaspiro[3,2]hexane (I). The product, which appeared to be a mixture, contained labile bromine, hydroxyl and non-aldehydic carbonyl (probably acyl bromide), and it polymerized on heating. Since it contained neither cyclopropane nor oxetane ring, as shown by the infrared spectrum, it seems likely that bromine initially cleaves the cyclopropane ring, liberating hydrogen bromide which eventually cleaves the ether functions present. We plan to report further on the halogenation of oxetanes at a later date.

Experimental[22]

2-Oxaspiro[3,2]hexane.—To a stirred solution of 406 g. of zinc dust, 164.5 g. of sodium carbonate and 23.3 g. of sodium iodide dissolved in 400 g. of molten acetamide at 160° was added, drop by drop, 240.6 g. of 3,3-bis-(chloromethyl)-oxetane[23,24] in a manner similar to that used by Murray and Stevenson in the preparation of spiropentane.[13] The reaction apparatus was arranged so that the product, 2-oxaspiro[3,2]hexane, could be distilled from the reaction flask as it was formed and collected in one of two cold traps connected by a short condenser. Since a slow stream of nitrogen was passed through during the reaction to sweep the product out of the reaction mixture the first cold trap (ice-cooled) served to collect most of the acetamide that sublimed and the second trap (Dry Ice–acetone-cooled) served to collect the volatile product that had been swept through the first trap. The contents of the two traps were combined, ether was added, and the insoluble acetamide was removed by gravity filtration. After drying and distilling over sodium twice, taking the best cut each time, the product was distilled over sodium through a Fenske column; 32.2 g. (25%) of 2-oxaspiro[3,2]hexane was collected, b.p. 95–97°, $n^{20}\mathrm{D}$ 1.4352. After fractional distillation over sodium, the product had b.p. 97°, $n^{20}\mathrm{D}$ 1.4371. The infrared spectrum shown in Fig. 1 has absorption bands at 9.8 and 10.35 μ which are characteristic of the cyclopropane[10] and oxetane[11,12] groupings, respectively.

Anal. Calcd. for C_5H_8O: C, 71.39; H, 9.58. Found: C, 70.99; H, 9.52.

1-Methylcyclopropanemethanol.—To 2.51 g. of lithium aluminum hydride in 100 ml. of tetrahydrofuran was added 11.0 g. of 2-oxaspiro[3,2]hexane in 50 ml. of tetrahydrofuran and the mixture was refluxed for 7 hours as previously described[9]; 7.4 g. (66% yield) of 1-methylcyclopropanemethanol, b.p. 122–125.5° and $n^{19}\mathrm{D}$ 1.4312, was obtained. Its 3,5-dinitrobenzoate melted at 85.7–87°. The reported values[25] are: b.p. 128° at 750 mm., $n^{20}\mathrm{D}$ 1.4308, and m.p. of the 3,5-dinitrobenzoate 85.2–85.3°.

Side Products in 2-Oxaspiro[3,2]hexane Synthesis.—The residue from the distillation of 2-oxaspiro[3,2]hexane was found to distil at 124–130°, $n^{20}\mathrm{D}$ 1.4289. The infrared spectrum of this material showed absorption bands characteristic of the groups: hydroxyl (3333 cm.$^{-1}$), C=C—H (3030 cm.$^{-1}$), carbonyl (1733 cm.$^{-1}$), double bond (1680 cm.$^{-1}$) and primary alcohol (1036 cm.$^{-1}$). A strong, broad band was found at 902 cm.$^{-1}$ which would obscure any weak cyclobutane absorptions in this region. The b.p. and carbonyl absorption band are in close agreement with those properties of cyclopentanone.[6,26] A 2,4-DNP was obtained, m.p. 142–143°, in agreement with that for cyclopentanone,[27] and mixed m.p. with authentic 2,4-DNP of cyclopentanone showed no depression. The other bands in the infrared spectrum correlated closely with those for 1-cyclobutanemethanol, described below. (The small deviations may be reasonably ascribed to the presence of cyclopentanone and perhaps other substances in the mixture.)

1-Chlorocyclobutanemethanol.—To a stirred solution of 26 g. of concentrated hydrochloric acid, maintained at 0°, was added 20.2 g. of 2-oxaspiro[3,2]hexane. The mixture was stirred for two hours, the organic product was separated and, after neutralization, the water solution was extracted with ether. 1-Chlorocyclobutanemethanol (20.2 g., 70% yield), b.p. 107–110° (47 mm.), $n^{18.5}\mathrm{D}$ 1.4789, was collected by distillation. It gave an immediate precipitate when treated with alcoholic silver nitrate.

1-Hydroxymethylcyclobutanol.—A mixture of 6.0 g. of 1-chlorocyclobutanemethanol, 5.27 g. of sodium carbonate and 2.09 g. of sodium bicarbonate in 63 ml. of water was heated on a steam-cone until miscible. Saturation with sodium chloride and extraction with ether, followed by drying and distillation gave 2.3 g. (45.3% yield) of 1-hydroxymethylcyclobutanol, b.p. 94–97° (5 mm.), $n^{25}\mathrm{D}$ 1.4702. The reported values[13] are b.p. 93° (5 mm.), $n^{25}\mathrm{D}$ 1.4715.

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[18] S. Searles, K. A. Pollart and F. Block, THIS JOURNAL, **79**, 952 (1957).

[19] A. Klota, *J. prakt. Chem.*, **68**, 156 (1903).

[20] H. Meerwein and K. van Emster, *Ber.*, **55**, 2500 (1922).

[21] C. F. Wurster, Jr., L. J. Durham and H. S. Mosher, THIS JOURNAL, **80**, 327 (1958).

[22] All melting and boiling points are uncorrected. The microanalysis was performed by Geller Microanalytical Laboratories, West Englewood, N. J.

[23] F. Govaert and M. Beyaert, *Natuurw. Tijdschr.*, **22**, 73 (1940).

[24] Part of the 3,3-bis-(chloromethyl)-oxetane used in this work was the generous gift of the Hercules Powder Co. Thanks also are due to Dr. Albert S. Matlock for his interest and valuable suggestions on synthesis of precursors.

[25] S. Siegel and C. G. Bergstrom, THIS JOURNAL, **72**, 3815 (1950).

[26] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Order I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 380.

[27] C. F. H. Allen, THIS JOURNAL, **52**, 2958 (1930).

The infrared spectrum was identical with that which has been reported previously.[13]

Cyclobutanone.—1-Hydroxymethylcyclobutanol (2.1 g.) in 65 ml. of methylene chloride was oxidatively cleaved with 10.0 g. of lead tetraacetate as described by Roberts and Sauer.[13] Cyclobutanone was isolated as its 2,4-DNP derivative, m.p. 146–147°, in 38.4% yield. The reported[13] m.p. is 146–146.5°.

1-Cyclobutenemethanol.—To 5.6 g. of potassium hydroxide dissolved in 100 ml. of methanol was added 9.6 g. of 1-chlorocyclobutanemethanol. After refluxing for two hours on a steam-cone, 4.4 g. (66%) of 1-cyclobutanemethanol, b.p. 148–160°, $n^{19}\text{D}$ 1.4407, was obtained. The infrared spectrum showed strong bands at 3310, 3040, 1645, 1698 and 1048 cm.$^{-1}$, and weak bands at 932 and 973 cm.$^{-1}$ (cyclobutane ring). Reduction of 1-chlorocyclobutanemethanol with lithium aluminum hydride in tetrahydrofuran for 34 hours gave a product, b.p. 116–185°, which appeared to be primarily 1-cyclobutenemethanol. The infrared spectrum supported this view.

Cyclobutanemethanol.—A solution of 210 g. of 1-cyclobutenemethanol in 50 cc. of methanol containing 50 mg. of platinum oxide was shaken under hydrogen at 50 p.s.i. initially and 30° for 18 hours. Distillation gave 1.0 g. (49%) of cyclobutanol, b.p. 140–155°, $n^{20}\text{D}$ 1.4430. A few drops were collected as a middle cut, $n^{20}\text{D}$ 1.4440. The reported[28] values are b.p. 142° (750 mm.), $n^{19}\text{D}$ 1.4449. The infrared spectrum showed no absorption in the 1620 cm.$^{-1}$ region, indicating that complete reduction had been obtained.

4-Bromo-2-bromomethyl-1-butanol.—Dry hydrogen bromide was passed through a solution of 6.0 g. of 2-oxaspiro[3,2]hexane in 30 ml. of dry benzene, maintained at 0°. When the gas uptake was complete, the benzene solution was washed with 5% sodium bicarbonate. Distillation gave 5.8 g. of 4-bromo-2-bromomethyl-1-butanol, b.p. 89–93° (23 mm.), $n^{25}\text{D}$ 1.5172. The total yield was 39%. The infrared spectrum showed hydroxyl absorption but lacked absorption bands characteristic of the cyclopropane and oxetane rings. The products turned dark on standing. A 3,5-dinitrobenzoate, m.p. 92°, was prepared, but its analysis indicated that it had lost about a third of its bromine.

DL-2-Methyl-1-butanol.—To 2.33 g. of lithium aluminum hydride in 90 ml. of tetrahydrofuran was added 5.8 g. of 4-bromo-2-bromomethyl-1-butanol according to the general procedure described by Johnson, Blizzard and Carhart.[29] The mixture was refluxed for 14 hours and then hydrolyzed as described above. Three fractions were obtained on distillation: (1) 0.6 g., b.p. 110–116°, $n^{20}\text{D}$ 1.4185; (2) 0.5 g., b.p. 116°, $n^{20}\text{D}$ 1.4171; and (3) 0.3 g., b.p. 116–125°, $n^{20}\text{D}$ 1.4362. Their infrared spectra showed that they were all mixtures of the same alcohol with tetrahydrofuran. The α-naphthylurethan was prepared, m.p. 76–77° (literature[30] value 76°), undepressed by mixture with the α-naphthylurethan of authentic *dl*-2-methyl-1-butanol (Eastman Kodak Co.). The phenylurethan was found to melt at 54.5–55°, rather than 30°, as previously reported.[30] The hydrogen 3-nitrobenzoate and 3,5-dinitrobenzoate melted at 147–148° and 52.5–54°, respectively. (There appear to be no literature values for these derivatives of the *dl*-alcohol; those for the *d*-alcohol are somewhat different.[31])

Oxidation of 2-Oxaspiro[3,2]hexane.—Oxygen was passed through 3–5 g. of 2-oxaspiro[3,2]hexane under a variety of conditions. The typical results are recorded in Table I.

TABLE I

CONDITIONS AND PRINCIPAL INFRARED ABSORPTION BANDS OF THE PRODUCTS OF AUTOÖXIDATION

Condition	Infrared bands, cm.$^{-1\,a}$
Eight hours at 80°	3380(s and b), 3029(w), 1720(s), 1018(m-s), 978(s and b), 913(s)
Pot residue (very viscous) from distillation of the above product[c]	3380(s and b), 3020(w), 1720(s), 1018(?),[b] 804(s and b), 755-(m)
13 hours at 65–75°[d]	1021(m), 802(s and b)

[a] The letters in parentheses designate: s = strong, m = medium, w = weak, b = broad. [b] Somewhat uncertain because on edge of a very strong, adjacent absorption band. [c] The characteristic oxetane absorption band at 978 cm.$^{-1}$ was absent. [d] No absorption bands for hydroxyl or carbonyl groups were present.

After standing in the air for a short time, 2-oxaspiro[3,2]hexane gave a positive potassium iodide test for peroxides.

The product from oxidation for 13 hours at 65–75° decolorized bromine in carbon tetrachloride.

Bromination of 2-Oxaspiro[3,2]hexane.—To a stirred solution of 2.0 g. of 2-oxaspiro[3,2]hexane in 25 ml. of carbon tetrachloride was added 3.8 g. of bromine. After stirring for 24 hours in the absence of strong light, a 200 watt tungsten bulb was placed near the reaction flask. After one hour the liberation of hydrogen bromide was noted. The solution was washed with 10% aqueous sodium hydroxide, dried and concentrated under vacuum. The residue, $n^{20}\text{D}$ 1.5150, gave an immediate precipitate with alcoholic silver nitrate, a negative test with Fehling solution and infrared bands at 3500, 1720, 970 (weak), 787 and 763 cm.$^{-1}$.

Distillation gave a few drops of liquid, b.p. 90–130° (21 mm.), $n^{21}\text{D}$ 1.5028, and a black, viscous residue. The distillate gave an immediate precipitate with alcoholic silver nitrate and no Fehling test.

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[28] N. J. Demjanov, *Ber.*, **40**, 4960 (1907).

[29] C. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948).

[30] S. M. Gordon, *J. Am. Pharm. Assoc.*, **16**, 419 (1927).

[31] Reference 26, p. 440.

MANHATTAN, KANSAS

[CONTRIBUTION NO. 496 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Bifurandione. I. Preparation and Characterization

BY J. C. SAUER, R. D. CRAMER, V. A. ENGELHARDT, T. A. FORD, H. E. HOLMQUIST AND B. W. HOWK

RECEIVED DECEMBER 17, 1958

Synthesis of an unusual unsaturated dilactone has been accomplished by the combination of two moles of acetylene with four moles of carbon monoxide. The reaction is carried out under carbon monoxide pressures of 100–1000 atm. at 90–120° in an inert solvent containing a cobalt carbonyl catalyst to give the dilactone in conversions up to 70% based on acetylene. Both *cis* and *trans* isomers have been obtained and shown to have the structure *cis*- or *trans*-$\Delta^{2,2'(5H,5'H)}$-bifuran-5,5′-dione by functional group analysis and spectral data, by a one-step catalytic hydrogenation to suberic acid, and by conversion to biphthalyl in two steps. Analogous dilactones have been prepared from substituted acetylenes bearing alkyl or aryl substituents.

The literature contains many references to the reactions of acetylene or substituted acetylenes with carbon monoxide that in general involved various metallic carbonyls as catalysts and reactants. In the presence of a solvent containing a reactive hydrogen atom, the products were mainly