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.

MANHATTAN, KANSAS

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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.

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

# Bifurandione. I. Preparation and Characterization

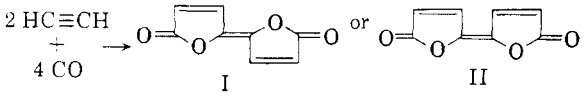
BY J. C. SAUER, R. D. CRAMER, V. A. ENGELHARDT, T. A. FORD, H. E. HOLMQUIST AND B. W. HOWK

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 acrylic compounds or hydroquinones.[1] The combination of acetylene with carbon monoxide under unspecified conditions has been reported to give a dimeric cyclopentadienone or hydrindone.[2]

The synthesis of an unusual unsaturated dilactone, $\Delta^{2,2'(5H,5'H)}$-bifuran-5,5′-dione, has now been accomplished by a remarkable catalyzed combination of two moles of acetylene and four moles of carbon monoxide. This paper deals primarily



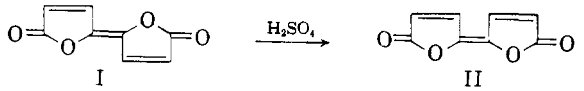
I II

with the preparation and structure proof of this new dilactone (hereafter referred to as bifurandione). Succeeding papers will be concerned with the chemistry of bifurandione.[2a]

**Preparation of Bifurandione.**—The synthesis of *trans*-bifurandione (I) readily takes place by the reaction of carbon monoxide with acetylene under pressure in an inert solvent containing a cobalt catalyst. Dicobalt octacarbonyl usually is used, but cobalt metal and other cobalt compounds also can be used, apparently because they are converted into soluble cobalt carbonyl derivatives under the conditions of the reaction. The optimum temperatures and pressures are 90–120° and 100–1000 atm., respectively. A molar ratio of carbon monoxide to acetylene of at least 4:1 is desirable for good yields. Conversions based on acetylene were 70% in acetonitrile solvent under carbon monoxide pressures of 1000 atm. At 300 atm. pressure, the best solvent was nitromethane, and conversions to bifurandione were 65%. A convenient method for preparing laboratory quantities of bifurandione utilized ethyl acetoacetate as solvent and cobalt acetate as catalyst. In this solvent, with relatively high acetylene concentrations, bifurandione was obtained in 60% conversion at 1000 atm. pressure, and the filtrate was reused as the solvent for subsequent runs.

A surprising variety of inert solvents can be used for this synthesis. In addition to the nitriles and nitroparaffins, mentioned above, ketones such as cyclohexanone or acetone were excellent media, while somewhat lower conversions were obtained with esters, ethers, hydrocarbons and halogenated hydrocarbons. To avoid the formation of insoluble, polymeric by-products, small amounts of hydroxylic or enolic compounds can be added to the reaction charge. This modification was unnecessary when cyclohexanone or ethyl acetoacetate was used as solvent. Due to its very low solubility in organic solvents at room temperature, bifurandione was conveniently isolated by filtration. A soluble by-product invariably was obtained by evaporation of the filtrate. Both soluble and insoluble by-products have empirical formulas corresponding approximately to a tetrahydrobifurandione.

While the *trans* isomer I was formed in most solvents, the *cis* isomer II was the sole product in tetramethylurea and was the major product in acetylacetone solvent. The *cis* isomer was best obtained by isomerization of the *trans* isomer; this transformation occurred quantitatively in hot concentrated sulfuric acid or phosphoric acid, and in lower yields in boiling pyridine.



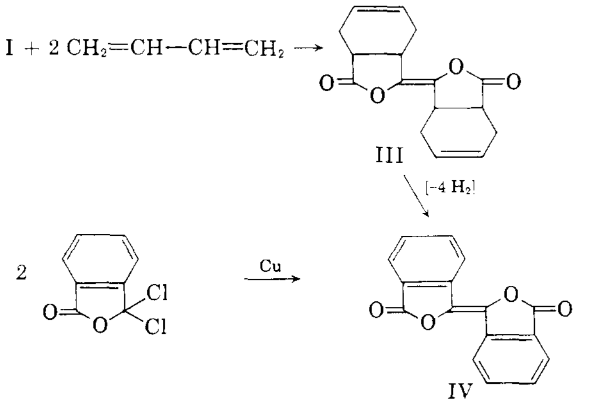
I II

The reverse isomerization of the *cis* to the *trans* form has not been observed.

**Characterization of Bifurandione.**—The method of formation of bifurandione from carbon monoxide and acetylene offered essentially no clues as regards its structure. Once the molecular formula of $C_8H_4O_4$ was determined, proof of a contiguous eight-carbon skeleton was obtained by hydrogenation to suberic acid over platinum catalyst at room temperature. As explained in detail in

$$C_8H_4O_4 \xrightarrow[Pt]{H_2} HOOC(CH_2)_6COOH$$

succeeding papers, the presence of three conjugated carbon-to-carbon double bonds was established by quantitative hydrogenation over palladium catalyst and by ultraviolet and infrared spectra. Similarly, the presence of lactone groups was indicated by saponification and by the infrared spectrum. Keto–enol isomerism in the saponified product was inferred on the basis of consumption of excess alkali over that required for the saponification of the lactone groups alone. The final structure proof consisted in converting bifurandione to biphthalyl (IV)[3] in the two-step synthesis indicated.



III

IV

The steric configurations of the two isomers of bifurandione were assigned on the basis of their infrared spectra[4] (Fig. 1). The intense band at

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[1] (a) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949; (b) J. W. Reppe, *et al.*, *Ann.*, **582**, 1 (1953); **596**, 1 (1955); **601**, 81 (1956); (c) E. R. H. Jones, T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, 230 (1950); 48, 763, 766 (1951); (d) E. R. H. Jones, G. H. Whitham and M. C. Whiting, *ibid.*, 1865 (1954); (e) P. Pino and A. Miglierina, THIS JOURNAL, **74**, 5551 (1952).

[2] Reference 1a, p. 293.

[2a] At the time the galley proof was received, an article describing the synthesis of bifurandione from acetylene and carbon monoxide came to the authors' attention. See G. Albanesi and M. Tovaglieri, *La Chimica L'Industria*, **41**, 189–194 (1959).

[3] J. Wislicenus, *Ber.*, **17**, 2178 (1884).

[4] Interpretations of the infrared spectra were made by Professor R. C. Lord of the Massachusetts Institute of Technology, to whom acknowledgment is made.

6.0$\mu$ (1668 cm.$^{-1}$) in the spectrum of the *cis* isomer, which has no center of symmetry, is due to the bridge double bond. This band is virtually absent in the spectrum of the *trans* isomer, since the bridge double bond is in this case astride a center of symmetry and no longer absorbs.[5] The absorption at 6.5 $\mu$ (1538 cm.$^{-1}$) is due to the endocyclic double bonds, and the doublet is expected in the case of the unsymmetrical *cis* isomer. The X-ray crystallographic data also indicate a center of symmetry for the isomer assigned the *trans* configuration.

The possibility that the *trans* form (I) may actually exist in another isomeric form appears improbable on the basis of both spectral and chemical evidence. The infrared absorption for the carbonyl group at 5.65$\mu$ (1770 cm.$^{-1}$) (*trans*) and 5.62$\mu$ (1780 cm.$^{-1}$) (*cis*) is well within the predicted range[6] expected of strained 5-membered rings. By contrast, the carbonyl absorption of a comparatively strain-free 6-membered ring would be expected to occur at a significantly higher wave length. Finally, as indicated above, the transformation of I to biphthalyl affords chemical evidence for the bifurandione structure (I).

The *cis* and *trans* isomers of bifurandione have limited solubility in hot organic solvents, with the *cis* isomer being less soluble. Concentrated sulfuric acid is the only satisfactory solvent at room temperature. It should be noted that the *cis* isomer is the more stable and higher melting one, an unusual occurrence. The spectral data, along with some of the physical properties of I and II, are summarized in Table I.

TABLE I

PHYSICAL PROPERTIES AND SPECTRAL DATA OF BIFURANDIONE

| | *rans*-Bifurandione | *cis*-Bifurandione |
|---|---|---|
| Melting point (uncor.), °C. | 237 dec. | 248 dec. |
| Color | Very pale yell. | Very pale yell |
| Density | 1.59 | 1.59 |
| Ultraviolet absorption | $\epsilon_{max}$ 33,085<br>$\lambda_{max}^{CH_3CN}$ 340 m$\mu$ | $\epsilon_{max}$ 36,100<br>$\lambda_{max}^{CH_3CN}$ 334 m$\mu$ |
| Infrared absorption (KBr wafer), $\mu$ (cm.$^{-1}$) | | |
| Carbonyl band | 5.65 (1770) | 5.62 (1780) |
| Conjugated unsatn. bands | 6.50 (1538)<br>(single) | 6.50 (1538)<br>(doublet)<br>6.00 (1668)<br>(very intense) |
| Unsaturated CH | 3.20 (3120) | 3.20 (3120) |
| X-Ray data | | |
| Form | Monoclinic | Monoclinic |
| *a*° | 8.42 | 7.25 |
| *b*° | 5.99 | 5.72 |
| *c*° | 6.84 | 16.58 |
| Angle | 96°20′ | 98°40′ |
| Space group | $C_{2h}^5$–$P^11/c$ | $C_{2h}^3$–$I^2/m$ |
| Formula wt. per unit cell | 2 | 4 |
| Nuclear magnetic resonance (in $H_2SO_4$ or $CF_3COOH$) | Two peaks (each a doublet) of equal intensity | Identical with *trans* |

**Preparation of Substituted Bifurandiones.**—Substituted bifurandiones were prepared readily by the interaction of carbon monoxide with alkyl- or arylacetylenes under synthesis conditions used for bifurandione itself. These substituted bifurandiones, along with some characterization data, are listed in Table II. Difficulties encountered in obtaining products of sharp melting point, and similar difficulties with derivatives, indicate that both stereoisomeric and positional isomers were present in the bifurandiones from monosubstituted acetylenes. Positional isomers at the 3,3′,4,4′- and 3,4′-positions are theoretically possible in addition to the *cis–trans* isomeric combinations. Due to the complexity of isomeric mixtures, precise structural determinations of these substituted bifurandiones were not attempted. It is interesting that three isomers of diphenylbifurandione were obtained from phenylacetylene and carbon monoxide by varying the conditions of synthesis.

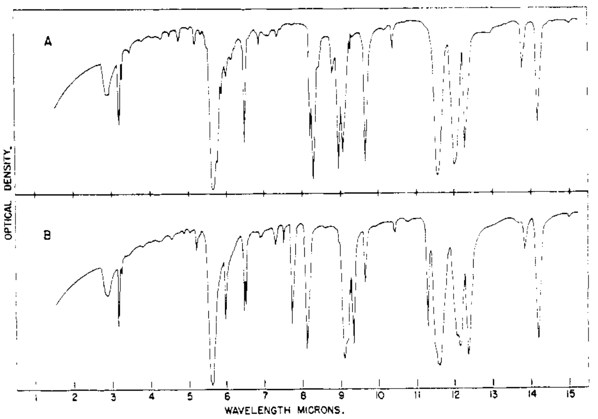

Fig. 1.—Absorption spectra: A, *trans*; B, *cis*.

As expected, the bifurandione from the symmetrically disubstituted acetylene, 3-hexyne, in which the 3,3′- and 4,4′-positions all contained the ethyl substituent, had a comparatively sharp melting point, since positional isomerism was not possible in this case.

## Experimental

**Synthesis of Bifurandione.[7] Typical Syntheses of *trans*-Bifurandione.**—A stainless steel rocker bomb was swept out with oxygen-free nitrogen and then was charged with a solution made by dissolving 1.5 g. of dicobalt octacarbonyl in 200 ml. of acetonitrile and adding 2.8 g. of methanol. The bomb was closed, cooled in a mixture of solid carbon dioxide–methanol, and evacuated to about 5 mm. pressure. The bomb was installed behind a heavy barricade, and all subsequent operations were controlled from the outside. Acetylene (7.5 g.) was introduced into the cold bomb by allowing the gas under 100–200 lb./sq. in. pressure to flow from a previously calibrated reservoir until the pressure drop in the reservoir indicated that the desired quantity of acetylene had been transferred. The bomb then was connected to a source of carbon monoxide and this gas injected to a cold pressure of 600 atm. The reaction mixture was agitated and heated to 90° for a period of 17 hours during which the gauge pressure was maintained at 900–1000 atm. by periodic repressuring with carbon monoxide. The bomb then was cooled to room temperature, pressure released, and contents removed. The reaction mixture was filtered, and the precipitate was rinsed with ether. After drying in a vacuum oven, the bifurandione (15.1 g.) was found to be 99.5% pure, based on its ultraviolet spectrum. Evaporation of the filtrate gave 10.7 g. of a residue which contained 1.2 g. of bifurandione based on the ultraviolet spectrum. Accordingly, the total yield of bifurandione was 16.3 g. (69% conversion).

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(5) H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 154.

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958; E. Klingsberg, *Chem. Revs.*, **54**, 68 (1954).

(7) J. C. Sauer, U. S. Patent 2,840,570 (1958).

TABLE II

BIFURANDIONES[a] FROM CARBON MONOXIDE AND SUBSTITUTED ACETYLENES

| Acetylene | Yield, % | M.p., °C. | Analyses, % Calcd. | Analyses, % Found | Mol. wt. Calcd. | Mol. wt. Found | $\lambda_{max}$, mμ[c] | $\epsilon_{max}$ |
|---|---|---|---|---|---|---|---|---|
| $CH_3C\equiv CH$[b] | 41 | 183–184.5 | C 62.50<br>H 4.20 | C 62.07<br>H 4.11 | .. | ..... | 342(1) | 36,864 |
| $C_4H_9C\equiv CH$ | 58 | 190–205[d] | C 69.54<br>H 7.30 | C 69.23<br>H 7.37 | 276 | 265, 290 | 347.5(2) | 39,456 |
| $C_6H_5C\equiv CH$ | 6–21 | (A) 295–297 | | (A) C 75.89<br>H 3.83 | 316 | 323, 325, 340 | (A) 407(1) | 33,180 |
| | | (B) 176–178 | C 75.94 | (B) C 75.44<br>H 4.05 | | | (B) 381(1) | 35,708 |
| | | (C) 207-210 | H 3.82 | (C) C 75.92<br>H 3.81 | | | (C) 381(1) | 38,452 |
| (2-Napthyl)- | 57 | 218–220 | C 80.76<br>H 3.87 | C 81.05<br>H 4.16 | 416 | 445 | 393(3) | 32.448 |
| *p*-Chlorophenyl- | 55 | 243–258 | | ... | 385 | 380, 375 | 399(3) | 33,730 |
| *o*-Methoxyphenyl- | 47 | 186–220 | C 70.21<br>H 4.29 | C 70.12<br>H 4.35 | 376 | 391 | 430(3) | 30,832 |
| $C_2H_5C\equiv CC_2H_5$ | 6.3 | 95–96 | C 69.54<br>H 7.30 | C 69.84<br>H 7.36 | 276 | 265, 250 | 344(1) | 38,364 |

[a] The infrared spectra in all cases showed the characteristic lactone carbonyl absorption at 5.65–5.7 μ. [b] This bifurandione was prepared by Dr. R. E. Benson. [c] (1) in acetonitrile, (2) in ethanol, (3) in chloroform. [d] B.p. at 2–3 mm.

When the same procedure and catalyst were used, but with the pressure maintained at 300 atm., the best solvent was nitromethane. Under these conditions, the conversion to bifurandione was 65%.

The most convenient method for preparing laboratory quantities of bifurandione utilized a charge of 26 g. of acetylene, 200 ml. of ethyl acetoacetate as solvent and 2 g. of cobaltous acetate as catalyst. With a reaction temperature of 90° and applied carbon monoxide pressures of 800–1000 atm., the yield of bifurandione of moderate purity was 47–49 g. per run (57–60% conversion). The reaction liquid from a previous run was made up to 200 ml. with fresh solvent and used for the next run; no additions of fresh catalyst were necessary.

*trans*-Bifurandione (I) of highest purity (m.p. 237° dec.) was obtained conveniently by recrystallization from acetic acid, methyl ethyl ketone or dioxane. *Anal.* Calcd. for $C_8H_4O_4$: C, 58.55; H, 2.46; mol. wt., 164; moles $H_2$/mole, 3.0 (for hydrogenation of three double bonds); moles $H_2$/mole, 5.0 (for hydrogenation to suberic acid); sapn. no., 1030 (for consumption of 2 *M* alkali for lactone groups and 1 *M* alkali for enol group). Found: C, 58.60, 58.58; H, 2.49, 2.64; mol. wt., 163, 172; moles $H_2$/mole, 3.4 (Pd in dioxane); moles $H_2$/mole, 5.0 (Pt in acetic acid); sapn. no., 945.

**Analyses of By-products.**—The filtrate from a typical reaction mixture was evaporated to dryness and the residue triturated with ether. The resulting tan solid contained small amounts of bifurandione and a major amount of what was probably a dimer of tetrahydrobifurandione. *Anal.* Calcd. for $C_{16}H_{16}O_8$: C, 57.14; H, 4.76; mol. wt., 336. Found: C, 58.39, 58.65; H, 4.75, 5.05; mol. wt., 327, 314.

Variable amounts of a tan, completely insoluble by-product were formed in some instances. This insoluble residue was formed, for example, in acetone or acetonitrile solvents with dicobalt octacarbonyl catalyst in the absence of methanol. After separating I by continuous extraction with acetone, this insoluble residue was found to have an empirical formula similar to that of a tetrahydrobifurandione. *Anal.* Calcd. for $[C_8H_8O_4]_x$: C, 57.14; H, 4.76. Found: C, 57.17; H, 4.48.

**Preparation of *cis*-Bifurandione. A. From Acetylene.**—The synthesis procedure outlined above was used. A reaction mixture containing tetramethylurea (200 ml.), dicobalt octacarbonyl (1.5 g.) and acetylene (7.5 g.) was heated under a bomb gauge pressure of 275–315 atm. maintained by injection of carbon monoxide at 90° for 15.8 hours. Conversion to *cis*-bifurandione, characterized by its ultraviolet spectrum, $\lambda_{max}^{CH_3CN}$ 334 mμ, ε 36,408, was 30%. No *trans*-bifurandione was detected.

**B. Isomerization of *trans*-Bifurandione to *cis*-Bifurandione. 1. In Sulfuric Acid.**—A solution of 210 g. of crude *trans*-bifurandione in 500 ml. of concentrated sulfuric acid was heated on a steam-bath for four hours, cooled, and poured into a mixture of 500 g. of ice and two liters of water. The precipitate was collected and recrystallized from cyclohexanone to give 176 g. (84%) of crude *cis*-bifurandione. After several recrystallizations from methyl ethyl ketone, pure II melted at 248°, $\lambda_{max}^{CH_3CN}$ 334 mμ, ε 36,736. Shorter or longer heating periods gave reduced yields. In cold concentrated sulfuric acid, complete isomerization required several weeks. The isomerization also takes place in 50–75% sulfuric acid at steam-bath temperatures.

**2. In Phosphoric Acid.**—Crude *trans*-bifurandione (19 g.) was heated with 85% phosphoric acid (300 ml.) on a steam-bath for several hours. The undissolved material (5.8 g.) was collected by filtration. The cooled filtrate yielded 4.8 g. of crystals. Each of these solids was recrystallized repeatedly from methyl ethyl ketone. Various crystallization fractions melted from 246 to 248°, and each was shown to be *cis*-bifurandione (total conversion 56%) $\lambda_{max}^{CH_3CN}$ 334 mμ, ε 36,080.

**3. In Pyridine.**—The *trans* isomer was converted into the *cis* form in 23% yield by refluxing 5 hours in pyridine. A portion of the bifurandione was carbonized under these conditions.

**Characterization of Bifurandione by Conversion to Known Derivatives. A. Hydrogenation of I to Suberic Acid.**[8]—Recrystallized *trans*-bifurandione (4.6 g., 0.028 mole), 0.05 g. of platinum oxide and 350 ml. of acetic acid were shaken at room temperature for eight hours with hydrogen at 45 lb./sq. in. Fresh catalyst and a few drops of concentrated hydrochloric acid were added twice. The absorption of hydrogen was 96% of the theoretical amount. The solution was filtered and then concentrated under reduced pressure to give 4.26 g. (87%) of suberic acid, m.p. 120–130° (137–138° after recrystallization from acetic acid). It was identified by mixed melting point and comparison of the infrared spectrum with that of an authentic sample.

**B. Conversion of I into Biphthalyl. Preparation of the Butadiene/Bifurandione Adduct (III).**[9]—*trans*-Bifurandione (16.4 g., 0.10 mole), 1,3-butadiene (25 g., 0.64 mole) and dioxane (200 ml.) were heated at 200° for 17 hours. The diadduct III (1.4 g.) separated from the solution. Another 2.3 g. was obtained from the mother liquor bringing the yield to 14%. The new dilactone could be recrystallized from either methyl ethyl ketone or ethyl acetate and melted at 232°. *Anal.* Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.44; H, 5.84.

**Preparation of Biphthalyl (IV) from the Butadiene/Bifurandione Adduct (III).**—A solution of III (2.0 g.) in α-methylnaphthalene (250 ml.) was stirred with 10% palladium-on-carbon catalyst (1.5 g.) at reflux temperature under a nitrogen atmosphere for 48 hours. The mixture was filtered while hot and concentrated by distillation under

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(8) J. C. Sauer, U. S. Patent, 2840,609 (1958).

(9) J. C. Sauer, U. S. Patent 2,859,220 (1958).

reduced pressure to less than one-fifth of the original volume. Chloroform and petroleum ether were added. The solution was chilled and 20 mg. of crude IV, m.p. 300–308°, separated. Purification by recrystallization from chloroform gave IV melting at 331–334°. Further concentration of the mother liquor yielded another 50 mg., which was recrystallized from ethyl acetate to give a sample melting at 341–344°; infrared spectrum: 5.6 (lactone), 6.2, 6.25 and 6.75 μ (conjugated unsaturation); 13.15 and 14.65 μ (disubstituted aromatic). *Anal.* Calcd. for $C_{16}H_8O_4$: C, 72.73; H, 3.05. Found: C, 72.72; H, 3.27. Biphthalyl thus has the *trans* configuration, since the less symmetrical *cis* isomer would have absorption around 6.0 μ for the bridge double bond.

**Preparation of Biphthalyl from Phthaloyl Chloride.**—This preparation follows one described in the literature.[10] A mixture of unsymmetrical phthaloyl chloride[11] (8 g.), copper powder (10 g.) and pyridine (100 ml.) was stirred for six hours while being cooled externally by an ice-bath. The reactants were kept under a nitrogen atmosphere and were protected from moisture. The mixture was filtered to give 0.2 g. (3% yield) of the pale yellow IV, m.p. 339–341° after recrystallization from chloroform. A mixed melting point, taken at the same time, with the sample of biphthalyl prepared from III occurred at 338–339°. The two samples were found to have identical infrared spectra and X-ray patterns. Biphthalyl has the following ultraviolet spectrum: $\lambda_{\max}^{CH_3CN}$ 369 mμ, ε 22,440; $\lambda_{\max}^{CH_3CN}$ 357 mμ, ε 27,456; $\lambda_{\max}^{CH_3CN}$ 304 mμ, ε 13,200; $\lambda_{\max}^{CH_3CN}$ 292 mμ, ε 11,616; $\lambda_{\max}^{CH_3CN}$ 257 mμ, ε 13,200; $\lambda_{\max}^{CH_3CN}$ 226 mμ, ε 27,720; $\lambda_{\max}^{CH_3CN}$ 221 mμ, ε 24,816.

**Bifurandiones from Mono- and Disubstituted Acetylenes.**—The substituted acetylene (usually 0.2–1.0 mole) was charged into a shaker tube with 1–2 g. of dicobalt octacarbonyl catalyst dissolved in 100 ml. of acetone. The reaction was carried out at temperatures of 100–110° and carbon monoxide pressures of 800–1000 atm. The products, except for the bifuranidone from 1-hexyne, were purified by recrystallization (see Table II).

The reaction of phenylacetylene with carbon monoxide gave mainly the isomer of m.p. 295–297° (6% yield) from a reaction mixture consisting of phenylacetylene (100 ml.), acetone (50 ml.) and phenyl isocyanate (30 ml.). The more soluble isomer melting at 176–178° (3%) also was isolated in the experiment and was the main product (9%) in the absence of phenyl isocyanate, using an otherwise identical charge. The isomer of m.p. 207–210° (21%) was obtained in a run in which the charge consisted of phenylacetylene (80 ml.) and acetone (100 ml.). The catalyst in all cases was dicobalt octacarbonyl. The isomer melting at 207–210° has strong absorption in the 6.05–6.10 μ region, indicating lack of symmetry with respect to the bridge double bond. This isomer therefore must have the *cis*-4,4′ configuration, since the *cis*-3,3′ isomer is sterically impossible. The isomer of m.p. 176–178° has little absorption in this region, and the isomer of m.p. 295–297° none at all. They are the symmetrical or *trans* isomers, but it is not known which isomer is 3,3′ and which is 4,4′.

The crude bifurandione from 1-hexyne was distilled to give a liquid–solid mixture distilling at 190–205° (2–3 mm.) (58%). This cut was quite pure di-*n*-butylbifurandione as judged by elemental analysis. Repeated recrystallizations of the solid portion from ethyl acetate–petroleum ether gave an isomer, m.p. 123–124°, whose exact structure was not determined.

**Di-*n*-butylsuberic Acid from Di-*n*-butylbifurandione.**—The crystalline isomer of di-*n*-butylbifurandione (0.75 g.) was hydrogenated in acetic acid using platinum catalyst. Almost exactly 5 moles of hydrogen was absorbed. The reaction mixture was filtered, and the acetic acid was removed at 20–50 mm. on a steam-bath. The residual heavy oil was warmed for 2 hours on a steam-bath with 7 ml. of thionyl chloride and then evacuated at 80° and 20–30 mm. pressure for 30 minutes. Then aniline (8 g.) dissolved in ether (200 ml.) was added. After washing the mixture with water and dilute hydrochloric acid, the ether was removed by evaporation and the solid residue recrystallized from ethanol (0.44 g., m.p. 130–138°). This bis-anilide of a di-*n*-butylsuberic acid was characterized by elemental and infrared analyses. *Anal.* Calcd. for $C_{28}H_{40}O_2N_2$: N, 6.42. Found: N, 6.41, 6.54. The infrared spectrum showed strong absorption at 6.0 and 6.5 μ for secondary amide, 3.0 μ absorption for $\overset{\text{H}}{-\text{N}-}$, and the usual bands for saturated CH, $CH_3$ and monosubstituted aromatic groups.

Commercial-grade acetylene was purified according to a previously described procedure.[12] The infrared spectra were determined on a Perkin–Elmer double-beam spectrometer. The ultraviolet spectra were determined on a Cary model 11 spectrophotometer.

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[10] P. Karrer, W. Wehrli, E. Biedermann and M. dalla Vedova, *Helv. Chim. Acta*, **11**, 233 (1928).

[11] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 528.

[12] J. C. Sauer, THIS JOURNAL, **79**, 5314 (1957).

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[CONTRIBUTION NO. 497 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

# Bifurandione. II. Hydrogenation

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RECEIVED DECEMBER 17, 1958

Hydrogenation of $\Delta^{2,2'(5H,5'H)}$-bifuran-5,5′-dione in the presence of palladium, ruthenium or nickel gave γ,γ′-bibutyrolactone or γ-(γ-carboxypropyl)-butyrolactone, depending on the conditions, as principal product. Further hydrogenation of γ,γ′-bibutyrolactone over copper chromite gave 1,4,5,8-octanetetrol. Hydrogenation with ruthenium or nickel under more stringent conditions led to products with only one lactone ring intact, and with nickel molybdite to a dihydrobifurandione. Hydrogenation of bifurandione over copper chromite at 250–300° gave 1,8-octanediol, but at 160–190° yielded suberic acid. Electrolytic reduction of bifurandione resulted in 4,5-dioxoöctanedioic acid.

Hydrogenation of $\Delta^{(2,2'(5H,5'H)}$-bifuran-5,5′-dione[1,2] has made available a large number of compounds inaccessible through ordinary synthetic methods. The variety of ways in which the dilactone reacts with hydrogen can be explained by the fact that it is structurally both an α,β-unsaturated ester and an enol ester. Thus, with some catalysts the reactive bonds between the oxygen atoms and the bridge carbon atoms apparently are cleaved before any of the double bonds become saturated. An example of this, the hydrogenation of bifurandione over platinum to suberic acid in 87% yield, was described in Paper I of this series.[1]

Hydrogenation of the dilactone over supported palladium catalysts gave a mixture of γ,γ′-bibutyrolactone (III) and γ-(γ-carboxypropyl)-butyrolactone (IV). These compounds form an azeotrope but can be separated by careful neutralization of IV with sodium bicarbonate solution.

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[1] Paper I of this series, THIS JOURNAL, **81**, 3677 (1959).

[2] Throughout this paper, the compound is referred to as bifurandione.