

the residue was fractionated at reduced pressure to yield 120 gr. of starting dibromide (b.p. 70° at 30 mm., n_D^{25} 1.4385) and 30 gr. of 2-methyl-2,3-butanediol, b.p. 93–95° at 24 mm., n_D^{25} 1.4375. The yield based upon 2-methyl-2,3-dibromobutane consumed, was 51%. The yield based upon dibromide used amounted to 27% conversion.

Treatment of isobutylene dibromide with aqueous potassium carbonate at 55° during 5 days resulted in its 40% conversion into isobutyraldehyde (b.p. 62°, n_D^{20} 1.3725), but no diol could be isolated.

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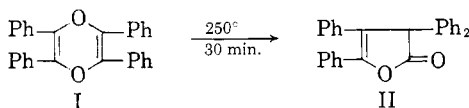
Thermal Rearrangement of Tetraphenyl-*p*-dioxadiene

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Tetraphenyl-*p*-dioxadiene (I) differs markedly from the analogous sulfur compound, 2,5-diphenyl-*p*-dithiadene, in that it rearranges on pyrolysis to give a lactone whereas the sulfur compound decomposes to give a thiophene derivative. Similarities in the chemistry of I and *cis*-dibenzoylstilbene (III), which gives the same lactone on pyrolysis, are discussed.

Parham and Traynelis have recently described the thermal decomposition of 2,5-diphenyl-*p*-dithiadene to give 2,4-diphenylthiophene and free sulfur.² With the thought that a similar reaction might occur in the *p*-dioxane series, the pyrolysis of tetraphenyl-*p*-dioxadiene (I) was carried out; the product, obtained in 90% yield, was not the anticipated tetraphenylfuran but was instead a rearrangement product, 2,2,3,4-tetraphenyl-3-buten-4-ylactone (II).



The product (II) was identified by its elemental analysis, its infrared spectrum [very strong band at 5.58 μ , consistent with a β,γ -unsaturated- γ -lactone,^{3a} weak absorption at 6.02 μ ($-\text{C}=\text{C}-$),^{3b} and medium absorption at 8.06 μ , expected for the system $-\text{O}-\text{C}=\text{C}$],^{3c} and its melting point.

The rearrangement is not acid-catalyzed. A sample of I which had been carefully freed from traces of acid gave a smoother reaction and better yield of II than did a sample of I which had been crystallized from acetic anhydride. Also, the formation of the lactone does not involve formation and subsequent air oxidation of tetraphenylfuran. Pyrolysis of the furan under the same conditions as pyrolysis of I led only to recovered starting material.

The lactone II was first reported by Zinin⁴ in

1872, and some of the chemistry of the compound has been reviewed by Japp and Klingemann.⁵ Zinin oxidized tetraphenylfuran to *cis*-dibenzoylstilbene (III), the pyrolysis of which gave the same lactone (II) as is now obtained upon pyrolysis of tetraphenyl-*p*-dioxadiene (I).

The formation of the same lactone on pyrolysis is not the only point of close resemblance between tetraphenyl-*p*-dioxadiene (I) and *cis*-dibenzoylstilbene (III). Many of the recorded properties are so similar that the actual existence of two compounds might be questioned. In fact, Irvine and McNicoll apparently did confuse the two compounds.⁶ They reduced their "dibenzoylstilbene" and obtained tetraphenylfuran, citing this reduction as proof that their compound was the same as Zinin's III,⁷ but Madelung and Oberwegner have since pointed out⁹ that the compound in question was really I. Both compounds have been prepared in this laboratory, and our work confirms the earlier finding that, although very similar, they are not identical. Both are isomers of $\text{C}_{28}\text{H}_{20}\text{O}_2$. The dioxadiene melts at

(5) F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **57**, 662 (1890).

(6) J. C. Irvine and D. McNicoll, *J. Chem. Soc.*, **93**, 950 (1908).

(7) Zinin reduced III to tetraphenylfuran with hydrogen iodide.⁸ Irvine and McNicoll⁶ state that their sample of I is the same as Zinin's III because of its elemental analysis and conversion to the furan; however, the only reduction of a "dibenzoylstilbene" described in the experimental involves hydrogen chloride rather than the iodide, and it is not clear whether the reaction is actually being performed on I or III. We have been unable to verify the formation of tetraphenylfuran upon treating I with hydrogen chloride in refluxing anhydrous methanol according to the procedure of reference (6); the yellow solution became colorless, but no furan precipitated. (After working up the reaction solution, however, there was obtained a small yield of benzoin, which could form tetraphenylfuran.)

(8) N. Zinin, *Chem. Zent.*, **38**, 373 (1867); *J. prakt. chem.*, [1] **101**, 160 (1867); *Jahresber. Fort. Chemie*, **20**, 417 (1867).

(9) W. Madelung and M. E. Oberwegner, *Ann.*, **490**, 201 (1931).

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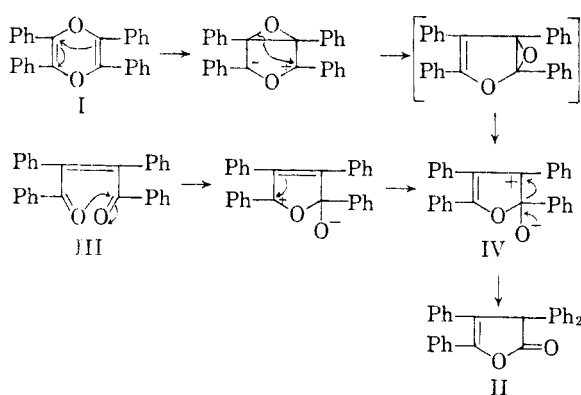
(2) W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **76**, 4960 (1954); see also W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **77**, 68 (1955); W. E. Parham, I. Nicholson, and V. J. Traynelis, *J. Am. Chem. Soc.*, **78**, 850 (1956) and H. H. Szmant and L. M. Alfonso, *J. Am. Chem. Soc.*, **78**, 1064 (1956).

(3) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, J. Wiley and Sons, New York, N. Y., 1954. (a) p. 159; (b) p. 31f; (c) p. 102.

(4) N. Zinin, *Ber.*, **5**, 1104 (1872).

218–219°, the stilbene at 216–217°. The former gives a dibromide of melting point 226°,¹⁰ the latter forms a dibromide of melting point 222°.¹¹ Both compounds give the same lactone (II) on pyrolysis, and both compounds have been reported to give tetraphenylfuran on reduction.^{7,12,13} Both compounds have previously been described as yellow, although in this laboratory the stilbene III is colorless whereas the dioxadiene I is a bright canary yellow.¹⁴ The infrared spectra of the two solids differ, however, and the mixed melting point is depressed.

The formation of the lactone II from the dioxadiene I or from the stilbene III may be interpreted as occurring through the common intermediate IV by the following paths¹⁵:



EXPERIMENTAL

Preparation of tetraphenyl-*p*-dioxadiene (I). 2,5-Bismethoxy-2,3,5,6-tetraphenyl-*p*-dioxane was prepared from benzoin by the method of Irvine and McNicoll,⁹ who incorrectly described the compound as 2-hydroxy-3,5-dimethoxytetraphenyltetrahydrofuran.⁹ The dioxane was heated for 10 min. in boiling acetic anhydride containing one drop of concentrated sulfuric acid; on cooling, yellow crystals of I were formed, m.p. (crude) 214–215° (reported,⁹ 214°). The yield of I ranged from 30 to 45%, based on benzoin.

Anal. Calcd. for C₂₈H₂₀O₂: C, 86.57; H, 5.19. Found: C, 86.76; H, 5.27.

Infrared absorption bands are as follows (reported as microns in a potassium bromide pellet; s, strong, m, medium, w, weak): 3.31w, 6.03s, 6.22w, 6.34w, 6.68m, 6.91m, 7.28w, 7.60w, 7.90s, 9.08m, 9.33s, 9.72s, 9.97m, 10.08s, 10.92m, 12.97s, 13.17s, 14.5s.

An alternate preparation of I was developed during the course of this work. The yield is not as good as that obtained above, but the method is much faster and does not involve the isolation of an intermediate. A solution of benzoin (3.0 g., 0.0141 mole), *p*-toluenesulfonic acid (0.1 g.) and petroleum hexane (Skellysolve B, 100 ml.) was heated under reflux for 48 hr., using an apparatus designed for

azeotropic removal of water as formed.¹⁶ The solvent was evaporated and replaced with ethanol to give, upon cooling, 0.45 g. of product, m.p. 203–209°, identical in the infrared with the tetraphenyl-*p*-dioxadiene prepared as above. A second crop, weighing 0.20 g., melted from 130–145°, and was shown by infrared to be a mixture of I and tetraphenylfuran. The yield of I (0.45 g.) was 16%.

Pyrolysis of tetraphenyl-*p*-dioxadiene (I). Three grams of I, recrystallized from acetic anhydride to m.p. 214–215°, was held in an open Pyrex test tube for 30 min. at 250°. The resulting red-brown tar was recrystallized, after treatment with Norite, from ethanol-chloroform, to give 2.1 g. of tan crystals, m.p. 136.2–136.6°, for a 70% yield of 2,2,3,4-tetraphenyl-3-buteno-4-lactone (II). Recrystallization from ethanol gave 1.7 g. of colorless platelets, m.p. 137.1–137.6° (reported,^{4,5} 136°).

Anal. Calcd. for C₂₈H₂₀O₂: C, 86.57; H, 5.19. Found: C, 86.50; H, 5.19.

Infrared absorption bands are as follows (potassium bromide pellet): 3.26m, 5.58s, 6.02w, 6.22m, 6.70s, 6.91s, 7.46m, 8.06m, 8.38m, 8.68s, 9.06s, 9.34s, 9.57s, 9.89s, 9.96m, 10.39s, 10.83m, 11.86w, 12.82s, 13.06s, 13.24s, 13.83s, 14.3s (broad), 15.29w, 15.70w.

In order to determine if acid catalysis was involved, compound I was freed of acid by dissolving in chloroform and washing with 10% aqueous sodium hydroxide. The recovered material, obtained by adding ethanol to the dried (magnesium sulfate) solution, melted at 218–219°. Pyrolysis of 2.0 g. as before gave 1.8 g. (90%) of the same lactone, m.p., without recrystallization, 135.0–136.5°. This time, however, the melt did not form a tar upon cooling, but remained as a clear, yellow liquid, and treatment with Norite was not necessary.

Reaction of compound I with hydrogen chloride according to the method of Irvine and McNicoll⁶ did not give tetraphenylfuran as reported. Compound I (1.00 g.) was heated under reflux in 125 ml. of anhydrous methanol, passing hydrogen chloride gas through the solution. There was some yellow solid, but this gradually dissolved; after several hours the solution became colorless. Hydrogen chloride was added for another hour, and the solution was allowed to stand overnight at room temperature.

The solution was neutralized (phenolphthalein) with pellets of sodium hydroxide. The precipitated sodium chloride (which was completely water soluble) was filtered, and the filtrate was concentrated by distillation. Chloroform was added and the distillation was continued until most of the methanol had been removed. A small, light, water soluble layer was removed by use of a separatory funnel. The chloroform solution was dried over magnesium sulfate and concentrated to the point of being an oil. After standing for several weeks partial crystallization occurred; the crystals were washed with ethanol and filtered, m.p. 128–130°. They were identical in the infrared with authentic benzoin; the yield was 0.05 g.

Preparation of tetraphenylfuran. Tetraphenylfuran may be prepared by the method of Zinin,⁸ or the following procedure may be used:

Benzoin (50.0 g., 0.236 mole) and 0.1 g. of *p*-toluenesulfonic acid were heated under reflux for 12 hr. in 250 ml. of xylene, using a trap to remove water as it was formed.¹⁶ Two hundred ml. of solvent was then removed by distillation, and the residual oil was added to three times its volume of ethanol. The resulting crystals of tetraphenylfuran were recrystallized from ethanol-chloroform to give 11.0 g. of white needles, m.p. 173.5–175.0° (reported,⁸ 175°). The yield was 25%.

Anal. Calcd. for C₂₈H₂₀O: C, 90.29; H, 5.41. Found: C, 90.29; H, 5.36.

Pyrolysis of tetraphenylfuran. Tetraphenylfuran (0.15 g.) was pyrolyzed as described above for the pyrolysis of I,

(10) W. Madelung and M. E. Oberwegner, *Ann.*, **526**, 195 (1936).

(11) N. Zinin, *Jahresber. Fort. Chemie*, **29**, 426 (1876).

(12) E. Berlin, *Ann.*, **153**, 130 (1870).

(13) J. Dorn, *Ann.*, **153**, 349 (1870).

(14) Madelung and Oberwegner (reference 9) have also reported the stilbene to be colorless.

(15) The mechanism is shown as occurring stepwise for convenience; of course, the analogous concerted and free-radical mechanisms are possible.

(16) E. J. Salmi, *Ber.*, **71**, 1803 (1938).

heating to 250° for 1 hr. There was recovered 0.14 g. of starting material, m.p. 174.0–174.9°.

Preparation of cis-dibenzoylstilbene (III). Compound III may be prepared by the method of Zinin,⁸ or the following adaptation of his procedure may be used:

Tetraphenylfuran (1.0 g.) was heated to reflux for 1 hr. in 20 ml. of glacial acetic acid containing 0.2 g. of chromium trioxide. The resulting green solution was diluted with 50 ml. of water and washed three times with ether and once with chloroform. The combined extracts were washed twice with saturated aqueous sodium bicarbonate and once with water. The solvent was removed by distillation and replaced with ethanol. Crystallization gave 0.3 g. of III, as white needles, m.p. 216–217° (reported,⁸ 220°). The mixed melting point with I was 193–205°.

Anal. Calcd. for C₂₈H₂₀O₂: C, 86.57; H, 5.19. Found: C, 86.74; H, 5.37.

Infrared absorption bands are as follows (potassium bromide pellet): 3.26w, 6.02s, 6.22m, 6.31m, 6.71w, 6.90m, 7.57m, 7.70m, 7.91s, 8.06m, 8.38m, 8.47m, 9.08w, 9.19w, 9.61w, 9.71w, 9.82m, 9.98w, 10.90w, 11.68w, 11.87w, 12.14m, 12.96s, 13.40w, 13.61s, 14.40s, 14.68s, 15.60w.

Pyrolysis of cis-dibenzoylstilbene. Compound III (0.1 g.) was heated to 270° for 15 min. Crystallization of the melt from ethanol-chloroform gave a quantitative yield of the same lactone (II), m.p. 135.5–137.0°, as was obtained upon the pyrolysis of I. The identity of the compounds was established by comparison of their infrared spectra.

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[CONTRIBUTION FROM ORGANIC CHEMISTRY DEPARTMENT, NATIONAL RESEARCH CENTRE]

Carbonyl and Thiocarbonyl Compounds. II.¹ Reaction of Halogenated *o*-Quinones with Certain Hydrazones and Diazocompounds

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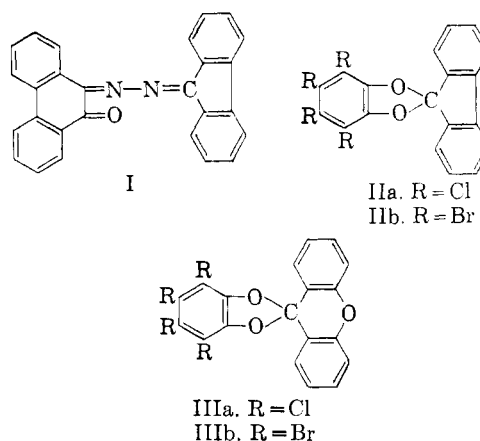
In contrast to other *o*-quinones, tetrachloro- and tetrabromo-*o*-benzoquinone react with fluorenone hydrazone at room temperature to give the cyclic ethers IIa and IIb respectively. With xanthone hydrazone the analogous products IIIa and IIIb are obtained. The mechanism proposed for this reaction suggests the formation of diazo derivatives as intermediate products.

The halogenated cyclic ethers IVa–IVf are obtained by the action of various diazomethane derivatives on tetrachloro- and tetrabromo-*o*-benzoquinone. 3,4-Dichloro-1,2-naphthoquinone reacts with 9-diazoxanthene giving the cyclic ether V. V is easily cleaved with hydrochloric acid in dioxane. An improved procedure for the preparation of 3,4-dichloro-1,2-naphthoquinone is described.

Gerhardt² has shown that aromatic ketohydrazones react with *o*-quinones to give ketazines of the type R₂—C=N—N=R=O.³ For example, when warming phenanthraquinone with fluorenone hydrazone in dry benzene, a 45% yield of the deeply colored phenanthraquinofluorenone ketazine I was obtained. Acenaphthenequinone, camphorquinone, and thianaphthenequinone have been found to react similarly.

In an attempt to prepare analogous ketazines from halogenated *o*-benzoquinone derivatives, it has been found, however, that the reaction between ketohydrazones and these quinones proceeds in a different manner. Thus, when fluorenone hydrazone is added to a dry ethereal solution of tetrachloro-*o*-benzoquinone, a vigorous reaction with evolution of gas occurs and the colorless cyclic ether IIa is obtained together with tetrachlorocatechol. The reaction proceeds easily at room temperature and the product is obtained in excellent yield. Tetrabromo-*o*-benzoquinone reacts similarly with the formation of the bromo-analogue IIb. IIa and IIb have been previously obtained by

the action of 9-diazo fluorene on the corresponding quinone:⁴



Xanthone hydrazone reacts similarly, but more vigorously, with these quinones with the formation of the analogous products IIIa and IIIb in almost quantitative yields. IIIa and IIIb have been obtained previously by the action of 9-diazoxanthene on the corresponding quinones.¹ IIIa and IIIb are hydrolyzed easily when boiled with a solution of hydrochloric acid in dioxane to give xanthone and the corresponding tetrahalocatechol.

(1) Previous paper in this series, *Can. J. Chem.*, **37**, 863 (1959).

(2) O. Gerhardt, *Monatsh*, **42**, 70 (1921); *Chem. Abstr.*, **15**, 3834 (1921).

(3) G. Rieveschl and F. E. Ray, *Chem. Rev.*, **23**, 304 (1938).

(4) A. Schönberg and N. Latif, *J. Chem. Soc.*, 446 (1952).