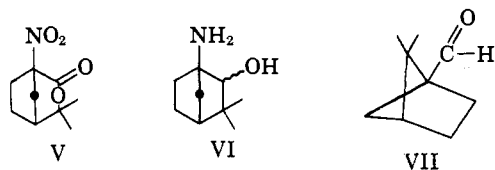


benzene); infrared spectrum ( $\text{CHCl}_3$ ): 5.70 (carbonyl) and 6.55, 7.30  $\mu$  (nitro group). *Anal.* Calcd. for  $\text{C}_9\text{H}_{13}\text{NO}_3$ : C, 59.00; H, 7.16; N, 7.64. Found: C, 58.97; H, 7.27; N, 7.68. The nitro ketone was remarkably unstable to strong acids or bases, and a dilute solution of ammonia in cold, anhydrous ethanol rapidly converted the ketone to the amide IV, 55% yield, m.p. 114–116.5°. *Anal.* Calcd. for  $\text{C}_9\text{H}_{13}\text{N}_2\text{O}_3$ : C, 53.97; H, 8.09; N, 13.98; O, 23.96. Found: C, 54.22; H, 8.10; N, 13.80; O, 24.16. The ease with which the cleavage was accomplished indicates that the compound is an  $\alpha$ -nitro ketone and not the ketone derived from the isomer II. Baeyer–Villiger oxidation of the nitro ketone III with peracetic acid gave the lactone V, 40% yield, m.p. 147.2–149.2°;  $[\alpha]^{23\text{D}} + 92.5^\circ$  (*c* 5.13, chloroform); infrared spectrum ( $\text{CHCl}_3$ ): 5.72, 8.51 (lactone), and 6.45, 7.28  $\mu$  (nitro group). *Anal.* Calcd. for  $\text{C}_{13}\text{H}_{13}\text{NO}_4$ : C, 54.26; H, 6.58; N, 7.03; O, 32.13. Found: C, 54.47; H, 6.59; N, 7.14; O, 32.03. The n.m.r. spectrum of the lactone in  $\text{CDCl}_3$  showed the *gem*-dimethyl group to be bonded to an oxygen atom<sup>12</sup> ( $\delta$  1.47, singlet, 3 H; 1.54, singlet, 3 H). The reactions of the tertiary nitro ketone differ markedly from the properties of a secondary nitro ketone.<sup>13</sup>

Catalytic reduction of the ketone III with platinum and hydrogen in glacial acetic acid gave the amino alcohol VI, 61% yield, m.p. 99–101.2°;  $[\alpha]^{23\text{D}} - 10.3^\circ$



(*c* 5.07, ethanol). *Anal.* Calcd. for  $\text{C}_9\text{H}_{17}\text{NO}$ : C, 69.63; H, 11.04; N, 9.02. Found: C, 69.69; H, 11.12; N, 9.12. The infrared spectrum showed the reduction to be complete.

Nitric acid deamination of the amino alcohol under nitrogen yielded the aldehyde VII which was rapidly oxidized by air, m.p. 84.5–88°;  $[\alpha]^{23\text{D}} - 6.8^\circ$  (*c* 5.08, benzene); infrared spectrum ( $\text{CCl}_4$ ): 3.58, 3.70, and 5.85  $\mu$ . Vapor phase chromatography on a silicone column indicated that the product of the reaction was homogeneous. The n.m.r. spectrum of the aldehyde in  $\text{CCl}_4$  was similar to the spectra of bicyclo[2.1.1]hexane derivatives already reported in the literature<sup>14,15</sup>: C-5- $\text{CH}_3$ ,  $\delta$  0.92 (singlet, 3 H); C-6-*endo*-H, 1.06 (doublet, *J* = 7.5 c.p.s., 1 H); C-5- $\text{CH}_3$ , 1.28 (singlet, 3 H); C-2- and C-3- $\text{H}_2$ , 1.77 (multiplet, 4 H); C-6-*exo*-H, 2.08 (multiplet, 1 H); C-4-H, 2.33 (broad, 1 H); and C-1-CHO, 9.67 (singlet, 1 H).

The semicarbazone of the aldehyde was isolated directly from the deamination reaction in 76% yield based on the amino alcohol, m.p. 192–193.2° dec. *Anal.* Calcd. for  $\text{C}_{10}\text{H}_{17}\text{N}_3\text{O}$ : C, 61.51; H, 8.78; N, 21.52. Found: C, 61.69; H, 8.80; N, 21.58. The dimedone derivative melted at 176–178°. *Anal.* Calcd. for  $\text{C}_{25}\text{H}_{36}\text{O}_4$ : C, 74.96; H, 9.06; O, 15.98.

(12) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 53.

(13) H. O. Larson and E. K. W. Wat, *J. Am. Chem. Soc.*, **85**, 827 (1963).

(14) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

(15) R. Srinivasan, *ibid.*, **83**, 4923 (1961).

Found: C, 74.91; H, 9.03; O, 16.01. The dimedone derivative was converted to the corresponding octahydroxanthene, m.p. 224.7–225.7° dec. *Anal.* calcd. for  $\text{C}_{25}\text{H}_{34}\text{O}_8$ : C, 78.49; H, 8.96; O, 12.55. Found: C, 78.75; H, 8.98; O, 12.52.

The aldehyde was oxidized with 30% hydrogen peroxide to 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxylic acid, 29% yield based on the amino alcohol, m.p. 118–120.2°;  $[\alpha]^{23\text{D}} + 11.2^\circ$  (*c* 5.03, benzene). *Anal.* Calcd. for  $\text{C}_9\text{H}_{14}\text{O}_2$ : C, 70.10; H, 9.15; O, 20.75. Found: C, 70.15; H, 9.20; O, 20.72; neut. equiv., 155. The n.m.r. spectrum of the acid in  $\text{CCl}_4$  showed that the bicyclo[2.1.1]hexane system had been retained: C-5- $\text{CH}_3$ ,  $\delta$  0.91 (singlet, 3 H); C-6-*endo*-H, 1.14 (doublet, *J* = 7.5 c.p.s., 1 H); C-5- $\text{CH}_3$ , 1.28 (singlet, 3 H); C-2- and C-3- $\text{H}_2$ , 1.80 (multiplet, *ca.* 4 H); C-6-*exo*-H, 2.02 (multiplet, *ca.* 1 H); C-4-H, 2.29 (broad, 1 H); and C-1-COOH, 12.15 (singlet, 1 H).<sup>16</sup>

The specificity of the bond migration (C-2–C-3) to the bridgehead carbonium ion derived from the amino alcohol with the formation of the bicyclo[2.1.1]hexane system is noteworthy. The product of a hydride shift to the carbonium ion was not detected even though the resulting ketone would be less strained than the product which was actually formed. The deamination of the bridgehead amino alcohol gave the product of ring contraction in excellent yield (isolated as the semicarbazone), and we suggest that the reaction may have substantial merit for the synthesis of highly strained cyclic systems.

(16) All n.m.r. spectra were obtained with a Varian A-60 spectrometer. The chemical shifts are given in p.p.m. ( $\delta$ ) downfield from tetramethylsilane used as an internal reference.

(17) N.D.E.A. Fellow, 1962 to present.

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## Photochemical Interactions in *ortho,ortho'*-Disubstituted Biphenyls<sup>1</sup>

Sir:

We wish to report two new photochemical reactions involving *ortho,ortho'* interactions in the biphenyl series. Irradiation of the *p*-chlorophenyl anil of *o*-nitro-*o'*-formylbiphenyl (1), m.p. 104° (*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{13}\text{N}_2\text{O}_2\text{Cl}$ : C, 67.76; H, 3.89; N, 8.32. Found: C, 68.70; H, 3.93; N, 8.43), in ethanol solution using a 450-w. Hanovia immersion lamp and a Corex filter, resulted in the formation of 5(6H)-phenanthridone (5), m.p. 290–292° (lit.<sup>2</sup> m.p. 290–292°) in 25% yield. Two mechanistically reasonable and sterically feasible pathways are possible for this intramolecular oxidation-reduction reaction. In path A, cycloaddition of the nitro group to the polarized anil C=N bond to give the oxadiazetidene N-oxide 2, followed by extrusion of *p*-chloronitrosobenzene, would give phenanthridine N-oxide (3),<sup>3,4</sup> which we have been

(1) This work was supported in part by a grant (CA 02551) to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service.

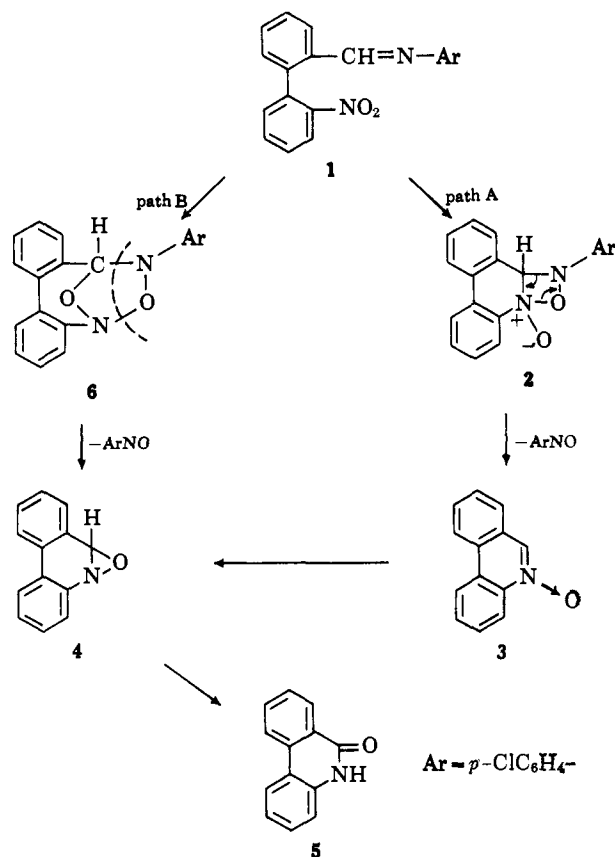
(2) E. C. Taylor and E. J. Strojny, *J. Am. Chem. Soc.*, **78**, 5104 (1956).

(3) P. Mamalis and V. Petrow, *J. Chem. Soc.*, 703 (1950).

(4) E. Hayashi and Y. Hotta, *J. Pharm. Soc. Japan*, **80**, 834 (1960).

able to show by independent experiment is converted by photolysis under the same conditions to **5** (86% yield), presumably *via* the intermediate formation and subsequent rearrangement of the oxaziridine **4**.<sup>5</sup> Alternatively (path B), cycloaddition of the nitro group to the anil C=N bond could give a 1,3,2-dioxazolidine (**6**). Subsequent collapse of this intermediate with loss of *p*-chloronitrosobenzene could lead to the same oxaziridine **4**. We favor path B since both photochemical and thermal additions of nitro groups to double bonds in this manner appear to have ample precedent.<sup>6-8</sup>

Irradiation of *o*-(cyanoanilinomethyl)-*o'*-nitrophenyl (**7**), m.p. 140° (formed from *o*-nitro-*o'*-formylbiphenyl, potassium cyanide, and aniline in 91% yield (*Anal.* Calcd. for C<sub>20</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C, 72.93; H, 4.59; N, 12.76. Found: C, 72.57; H, 4.68; N, 12.71) rapidly gave 6-cyanophenanthridine (**12**), m.p. 135° (lit.<sup>9</sup> m.p. 136–137°. *Anal.* Calcd. for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>: C, 82.33; H, 3.95; N, 13.72. Found: C, 82.16;



H, 4.08; N, 13.52) in 48% yield. The structure of **12** was further confirmed by hydrolysis and decarboxylation to phenanthridine, m.p. 106°, identical with an authentic sample, and by conversion with peracetic acid in chloroform to 6-cyanophenanthridine 5-N-oxide, m.p. 215° (lit.<sup>9</sup> m.p. 216–217°). Azobenzene and azoxybenzene were identified as by-products of the photochemical reaction by thin layer chromatography. We consider that this conversion proceeds by initial

(5) For a discussion and leading references, see (a) P. deMayo, *Advan. Org. Chem.*, **2**, 411 (1960); (b) O. L. Chapman, *Advan. Photochem.*, **1**, 410 (1963).

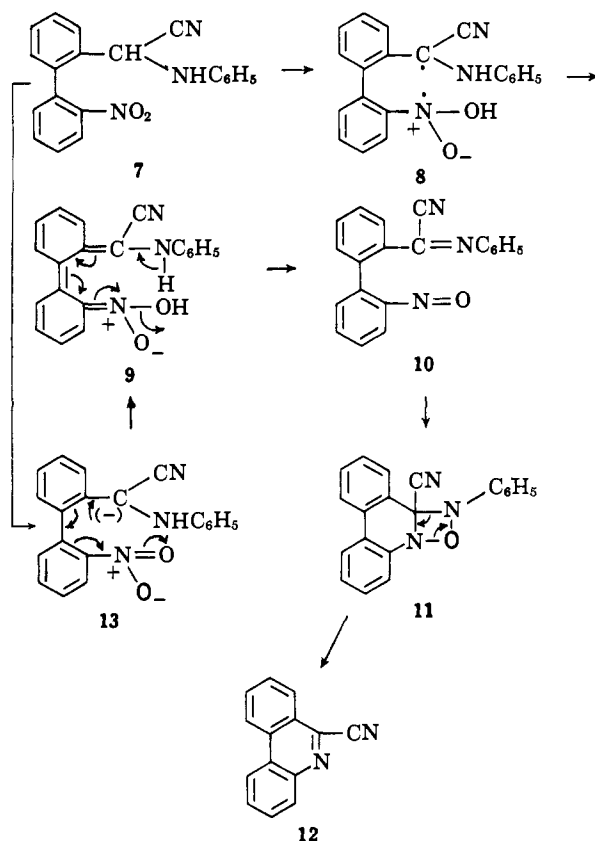
(6) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955).

(7) G. Büchi and D. E. Ayer, *J. Am. Chem. Soc.*, **78**, 689 (1956).

(8) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963).

(9) E. Hayashi and H. Ohki, *J. Pharm. Soc. Japan*, **81**, 1033 (1961).

hydrogen abstraction by the excited nitro group<sup>10</sup> to yield **8**, which gives the nitroso intermediate **10** by electron pairing and dehydration. Cycloaddition to the oxadiazetidene **11** followed by elimination of nitrosobenzene leads directly to **12**.



The cycloaddition step in the latter case need not be, and is probably not, photochemical in nature. We have observed that **7** is converted almost instantaneously to **12** nonphotochemically (43% yield) with a trace of sodium ethoxide in ethanol. The same nitroso intermediate **10** may be generated *via* the carbanion **13** as indicated, with cycloaddition and elimination proceeding spontaneously. Nitrosobenzene was identified (t.l.c.) as a product of this base-catalyzed reaction.

These observations are relevant to the recent report by Scheinbaum<sup>11</sup> that the products of photolysis of nitrobenzene and toluene can, in part, be rationalized in terms of intermediates arising from cycloaddition of nitro and nitroso groups to carbon-carbon double and triple bonds. Griffin<sup>12</sup> has also pointed out that the products formed by irradiation of a mixture of nitrosobenzene and 1,1-diphenylethylene can be interpreted in terms of an analogous cycloaddition intermediate. Although it has been claimed<sup>13</sup> that oxadiazetidines are formed by a nonphotochemical cycloaddition of aromatic nitroso compounds to Schiff bases, this apparent precedent for the formation of **11** should be

(10) For examples of analogous nitro → *aci*-nitro photochemical conversions, see J. D. Margerum, L. J. Miller, E. Saito, M. S. Brown, H. S. Mosher, and R. Hardwick, *J. Phys. Chem.*, **66**, 2434 (1962).

(11) M. L. Scheinbaum, *J. Org. Chem.*, **29**, 2200 (1964).

(12) C. E. Griffin, University of Pittsburgh, private communication (Jan. 9, 1965).

(13) C. K. Ingold, *J. Chem. Soc.*, **125**, 87 (1924).

viewed with reserve in view of the recent refutation by Griffin<sup>14</sup> of analogous claims by the same author.

(14) N. F. Hepfinger and C. E. Griffin, *Tetrahedron Letters*, No. 21, 1361, 1365 (1963).

(15) NATO Postdoctoral Fellow.

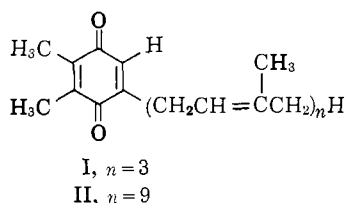
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Received January 15, 1965

## Identification of Plastoquinone-3 from Chloroplasts<sup>1</sup>

Sir:

Plastoquinone-3 (I) has been isolated from chloroplasts and identified for the first time as a natural product. This quinone could be functional in photosynthetic electron transfer.



New quinones of unknown structure, "PQB, PQC, and PQD," have been obtained<sup>2</sup> from chloroplasts of spinach along with tocopherylquinones, and two general statements were made about their restoration of photo-reductase activities; none of the quinones stimulated all activities and the tocopherylquinones tended to be effective at lower levels than the plastoquinones. We have carried out isolation and structure studies on the plastoquinones from chloroplasts of spinach.

A quinone fraction was eluted with 10% ether-hexane on a decalco column, giving a crystalline product, m.p. 44–46°; ultraviolet, infrared, and n.m.r. absorption spectra revealed this product to be 2,3-dimethyl-solanesyl-1,4-benzoquinone (II, plastoquinone-9). A second quinone fraction was eluted by 20% ether-hexane and was further purified by a decalco column and preparative thin layer chromatography. The chromatograms (silica gel G), developed by chloroform, showed several leucomethylene blue sensitive spots but two major spots with  $R_f$  0.32 and 0.62. The ultraviolet spectra and chromatographic behavior of the quinone  $R_f$  0.32 and of an authentic sample of  $\alpha$ -tocopherylquinone showed that these two compounds are identical. The quinone  $R_f$  0.62 was a red-yellow oil which was very unstable, even at 0°;  $R_f$  0.81 on silicon-impregnated paper in reverse phase chromatography. The ultraviolet spectrum of the eluted and still impure quinone showed  $\lambda_{\max}$  at 253 ( $E_{1\text{ cm}}^{1\%}$  115) and 261  $\mu$  (shoulder) in ethanol; reduction with sodium borohydride gave a hydroquinone with  $\lambda_{\max}$  289  $\mu$  ( $E_{1\text{ cm}}^{1\%}$  71) in ethanol. The infrared spectrum in carbon tetrachloride differed from that of plastoquinone-9 mainly in the presence of a band at 1730  $\text{cm}^{-1}$  and was analogous to the infrared spectrum of a mixture of plastoquinone-4 and the "dimers" of plastoquinone-4 and -9.<sup>3</sup> The n.m.r. spectrum showed signals at  $\tau$  3.62

(t), 4.44 (b), 4.92 (b), 6.90 (d), 7.34 (b), 8.03 (bs), 8.35, 8.42 (s), 8.75, 8.84 (s), and 9.0–9.3 (m) (s, singlet; d, doublet; t, triplet; m, multiplet; b, broad). This spectrum was very similar to the spectrum of the synthetic "dimer" of plastoquinone-9.<sup>3</sup> The mass spectrum at different temperatures showed significant peaks at  $m/e$  340, 271, 203, and 189 (base peak). No peaks were present beyond  $m/e$  340. The peaks can be assigned as follows:  $m/e$  340 ( $M^+$   $\text{C}_{23}\text{H}_{32}\text{O}_2$ );  $m/e$  271 ( $M^+ - \text{C}_5\text{H}_9$ ;  $\text{C}_{18}\text{H}_{23}\text{O}_2$ );  $m/e$  203 [ $M^+ - 2(\text{C}_5\text{H}_9)$ ;  $\text{C}_{13}\text{H}_{15}\text{O}_2$ ];  $m/e$  189 (base peak =  $\text{C}_{12}\text{H}_{13}\text{O}_2$ ). The spectroscopic and chromatographic data show that this quinone was 2,3-dimethyl-5-farnesyl-1,4-benzoquinone (plastoquinone-3) containing apparently some of the "dimers" of plastoquinone-3 and -9. 2,3-Dimethyl-5-farnesyl-1,4-benzoquinone (plastoquinone-3) was synthesized<sup>4</sup> and compared with the isolated quinone; in five chromatographic systems there was no difference, but there was a difference in  $R_f$  values between synthetic and isolated plastoquinone-3 (0.45 and 0.33, respectively) in ether-*n*-hexane. This difference may be a result of the impurities which are present in the isolated quinone and possibly a difference in side-chain stereochemistry. Dilley<sup>5</sup> has observed a difference in  $R_f$  values of 0.1 when synthetic plastoquinone-9 was compared with the natural compound.

Synthetic plastoquinone-3 and the isolated quinone were reduced and acetylated with acetic anhydride in the presence of zinc powder. The hydroquinone diacetate from synthetic plastoquinone-3 and the material obtained from the isolated quinone were chromatographically compared. The material from the isolated quinone showed three spots when detected by 2% aqueous potassium permanganate. One of these spots ( $R_f$  0.21, 20% ether-hexane, and 0.29, chloroform) showed the same  $R_f$  value (0.22, 20% ether-hexane, and 0.30, chloroform) observed for the hydroquinone diacetate of synthetic plastoquinone-3. The peak at  $m/e$  340 might have resulted from the loss of water from a " $\gamma$ -hydroxyquinone derivative" of plastoquinone-3, 2,3-dimethyl-5-(3'-hydroxy-3',7',11'-trimethyl-6',10'-dienedodecyl)-1,4-benzoquinone (mol. wt. 358). This possibility was eliminated by synthesis of the " $\gamma$ -hydroxyquinone derivative" through the steps: plastoquinone-3, chromenol, chromanol, and  $\gamma$ -hydroxyquinone. As expected, the  $R_f$  value (0.23 on silica gel G thin layer plates in chloroform) was different from that of plastoquinone-3 (0.62).

It is difficult to evaluate plastoquinone-3 in terms of quinones of unknown structure<sup>2</sup> from spinach chloroplasts; "PQB" ( $\lambda_{\max}^{\text{EtOH}}$  255  $\mu$  ( $E_{1\text{ cm}}^{1\%}$  202);  $R_f$  0.13 on silicon-impregnated paper); "PQC" (data from three publications:  $\lambda_{\max}^{\text{EtOH}}$  255  $\mu$  ( $E_{1\text{ cm}}^{1\%}$  66), 255, 262, ( $E_{1\text{ cm}}^{1\%}$  96); 262 ( $E_{1\text{ cm}}^{1\%}$  75), shoulder at 255;  $R_f$  values of 0.75 on silicon-impregnated paper, 0.0 on silica gel G thin layer plates in 15% trichloroethyl-acetate in benzene, and 0.49 on silica gel G plates in 1% ether in chloroform); and "PQD" ( $\lambda_{\max}^{\text{EtOH}}$  262  $\mu$  ( $E_{1\text{ cm}}^{1\%}$  75), shoulder at 255;  $R_f$  values at 0.0 on silica gel G thin layer plates in 15% trichloroethyl acetate in benzene and 0.40 on silica gel G thin layer plates in 1% ether in chloroform). A product corresponding to PQB was

(1) Coenzyme Q. LXIII.

(2) (a) L. P. Kegel, M. D. Henninger, and F. L. Crane, *Biochem. Biophys. Res. Commun.*, **8**, 294 (1962); (b) M. D. Henninger and F. L. Crane, *Plant Physiol.*, **39**, 598 (1964).

(3) N. Eck and A. Trebst, *Z. Naturforsch.*, **18B**, 446 (1963).

(4) N. R. Trenner, B. H. Arison, R. E. Erickson, C. H. Shunk, D. E. Wolf, and K. Folkers, *J. Am. Chem. Soc.*, **81**, 2026 (1959).

(5) R. A. Dilley, *Anal. Biochem.*, **7**, 240 (1964).