The Photolysis of Benzo[3,4]cyclobuta[1,2-*b*]quinoxaline[1,2]

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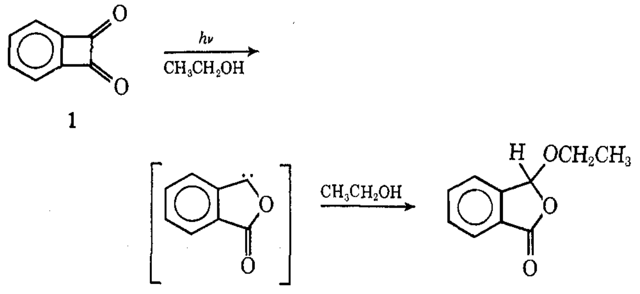
Benzocyclobutadienoquinone (**1**) has been shown to undergo a photochemical transformation which produces a species whose reactivity is characteristic of an intermediate containing a divalent carbon.[4] The reaction sequence shown in Scheme I has been offered as an explanation for the reaction of **1** with ethanol.

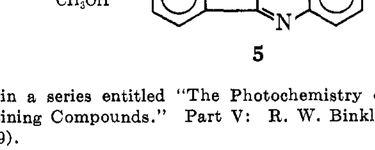
Scheme I

Photochemical Reaction of Benzocyclobutadienoquinone (1) with Ethanol



Our interest in the photochemistry of unsaturated nitrogen-containing systems[5] combined with this unusual photochemical transformation of benzocyclobutadienoquinone (**1**) prompted us to investigate the photochemistry of benzo[3.4]cyclobuta[1,2-*b*]quinoxaline, a nitrogen-containing analog of **1**. The particular reason for interest in compound **2** was the possibility that it might react in a manner similar to that suggested for **1** (Scheme II) and, if such reaction were to occur, the reactive intermediate **3** might have significant contribution from its zwitterionic resonance form. Significant participation by this resonance contributor would result in an intermediate which would possess a divalent center bearing considerable negative charge. In an effort to study the reactivity of **3**, benzo[3.4]cyclobuta[1,2-*b*]quinoxaline (**2**) was synthesized and irradiated.

Pyrex-filtered irradiation of a methanol solution of **2** under nitrogen produced, upon solvent removal, a yellow solid. Chromatography of this solid on silicic acid gave as the only product 11H-isoindolo[2,1-*a*]benzimidazole (**5**, 80% yield); none of the initially expected photoproduct **4** was detected. The fact that **5** undergoes photochemical decomposition suggests that the conversion of **2** into **5** may be essentially quantitative.



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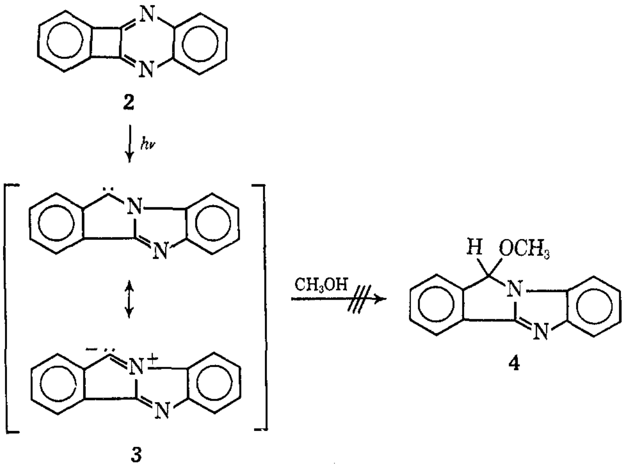
Scheme II

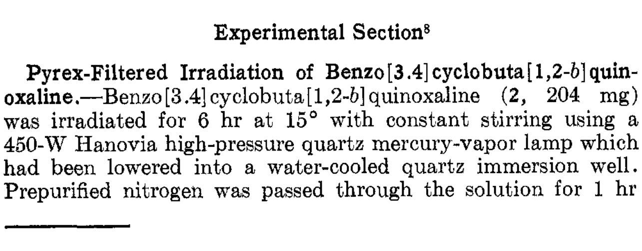
Potential (but Not Observed) Reaction Pathway for 2



A possible mechanism for the photochemical formation of 11H-isoindolo[2,1-*a*]benzimidazole (**5**) is shown in Scheme III. The reason for the apparent failure of **2** to form a divalent intermediate is not known; however, the bridging of the ends of the nitrogen-containing diene system with a benzene ring may have restricted the movement of the atoms and altered the electronic nature of the molecule sufficiently to favor the observed reaction.[6]

Scheme III

Proposed Mechanism for Formation of 5



Experimental Section[8]

Pyrex-Filtered Irradiation of Benzo[3.4]cyclobuta[1,2-*b*]quinoxaline.—Benzo[3.4]cyclobuta[1,2-*b*]quinoxaline (**2**, 204 mg) was irradiated for 6 hr at 15° with constant stirring using a 450-W Hanovia high-pressure quartz mercury-vapor lamp which had been lowered into a water-cooled quartz immersion well. Prepurified nitrogen was passed through the solution for 1 hr

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[1] Part VI in a series entitled "The Photochemistry of Unsaturated Nitrogen Containing Compounds." Part V: R. W. Binkley, *Tetrahedron Lett.*, 1893 (1969).

[2] The title compound was synthesized according to the procedure of M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Amer. Chem. Soc.*, **85**, 2076 (1963).

[3] Taken in part from the M.S. thesis of J. I. S.

[4] (a) R. F. C. Brown and R. K. Solly, *Tetrahedron Lett.*, 169 (1966); (b) H. A. Staab and J. Ipaktschi, *ibid.*, 583 (1966); (c) H. A. Staab and J. Ipaktschi, *Chem. Ber.*, **101**, 1457 (1968).

[5] R. W. Binkley, *J. Org. Chem.*, **33**, 2311 (1968).

[6] (a) A slight variation of the proposed mechanism would involve a reversal of the last two steps shown in Scheme III; that is, the second hydrogen abstraction would occur before the cyclization to give the benzimidazole structure. There is reason to believe[7] that, if **6** did abstract an hydrogen atom from the solvent, cyclization to 11H-isoindolo[2,1-*a*]benzimidazole (**5**) would quickly occur. (b) It is interesting to note that this reaction also takes place when run in *t*-butyl alcohol, a much less effective hydrogen-donating solvent than methanol. In *t*-butyl alcohol, however, the yield of **5** decreases to 49%.

[7] K. Hofmann, "Imidazole and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1953, part I, pp 267–270.

[8] The nmr spectra were taken on a Varian T-60 nmr spectrometer.

prior to irradiation and a slow stream of nitrogen was continued during photolysis. A Pyrex filter was placed between the light source and the reaction mixture.

After 6 hr, the solvent was removed by distillation *in vacuo* below 30°, producing a distillate which was transparent in the uv and leaving a yellow solid. The residual solid was chromatographed on an 85 × 2.5 cm silicic acid column slurry packed in 1:3 ether–hexane; 60-ml fractions were collected. The column was eluted as follows: 0.5 l. of 1:3 ether–hexane; 0.5 l. of 1:1 ether–hexane; 0.5 l. of 3:1 ether–hexane; and 0.5 l. of ether. Fractions 15–19 gave 175 mg of a pale yellow solid, mp 203–209°, recrystallized from ethanol–water to yield 164 mg of white crystals: mp 214–215° (the uv spectrum and the melting point of the photoproduct were identical with the reported spectrum[9] and melting point[10] for 11H-isoindolo[2,1-*a*]benzimidazole); nmr (CCl_4) τ 5.08 (s, 2) and 1.80–2.95 (m, 8). The identity of the photoproduct as 11H-isoindolo[2,1-*a*]benzimidazole (**5**) was confirmed by ir and mixture melting point comparison with an authentic sample[10] of **5**.

Test of the Stability of Benzo[3.4]cyclobuta[1,2-*b*]quinoxaline under Reaction and Isolation Conditions.—A control run in which 42 mg (0.21 mmol) of benzo[3.4]cyclobuta[1,2-*b*]quinoxaline (**2**) was subjected to the reaction and isolation conditions described in the previous experiment, except that no light was used, resulted in a quantitative recovery of starting material.

Pyrex-Filtered Irradiation of 11H-Isoindolo[2,1-*a*]benzimidazole (5) in Methanol.—11H-Isoindole[2,1-*a*]benzimidazole (**5**, 45 mg, 0.22 mmol) was irradiated in exactly the same manner as the irradiation of benzo[3.4]cyclobuta[1,2-*b*]quinoxaline (**2**). The isolation procedure was also the same. Fractions 14 and 15 from the chromatography column gave 30 mg of 11H-isoindolo[2,1-*a*]benzimidazole (**5**), mp 212–215°. No other compounds could be isolated. A stability test of **5** under reaction and isolation conditions but without the addition of light, similar to that described above for benzo[3.4]cyclobuta[1,2-*b*]quinoxaline (**2**), resulted in a quantitative recovery of **5**.

Registry No.—**2**, 259-57-4; **5**, 248-72-6.

[9] D. Amos and R. G. Gillis, *Aust. J. Chem.*, **17**, 1440 (1964).

[10] J. Thiele and K. G. Falk, *Justus Liebigs Ann. Chem.*, **347**, 114 (1906).

Deoxygenation of Benzoyl Cyanide[1]

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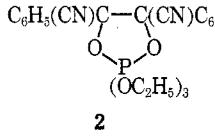
In refluxing benzene, triethyl phosphite and benzoyl cyanide (**1**) react over a period of 72 hr to form *cis*-α,β-dicyanostilbene oxide (**3**),[2,3] *trans*-α,β-dicyanostilbene (**4**),[2,3] and diethyl α-cyano-α-phenylpropylphosphonate (**5**). Intermediacy of a 1,3,2-dioxaphosph(V)olane **2**, a 2:1 adduct of starting materials which has been isolated when formed under milder conditions,[4,5] is assumed. Formation of **5** apparently requires an unprecedented 1,3 migration of an alkyl group from oxygen in a phosphonium ylide **8** to carbon.[6]

C_6H_5COCN

1



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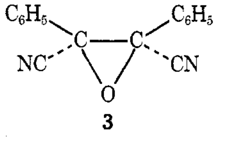

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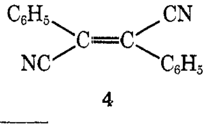

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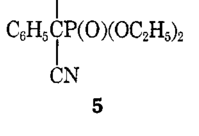
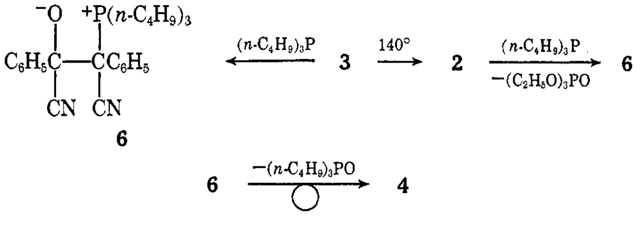


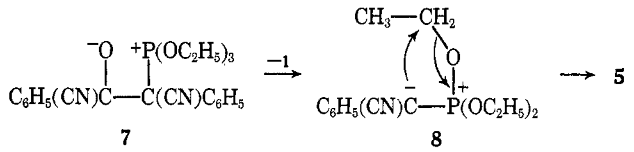
$C_6H_5\underset{CN}{\overset{C_2H_5}{C}}P(O)(OC_2H_5)_2$

5

Thermal elimination of **3** from **2** and the transformation of both **2** and **3**, on treatment with tri-*n*-butylphosphine, into **4** have been reported.[4,5] From either starting material, **4** is presumably formed by an elimination with inversion[3] from the common intermediate zwitterion **6**.



A comparable zwitterion intermediate **7** is now assigned to the transformation of both **2** and **3** into **4** when each is treated with triethyl phosphite. By an alternative dissociation of **7**, benzoyl cyanide **1** and the phosphonium ylide **8** are available. The latter is isomeric with **5** and, although unprecedented, its proposed rearrangement by 1,3 migration of an ethyl group from oxygen to carbon accounts for the formation of **5**.[6] The rearrangement is reminiscent of the Arbuzov reaction in which a monoalkylphosphonic ester is formed upon heating a mixture of an alkyl halide and a trialkyl phosphite with an unstable phosphonium salt presumably as an intermediate.[7,8]



$$(RO)_3P \xrightarrow{R'X} (RO)_3\overset{+}{P}R'\ \overset{-}{X} \longrightarrow (RO)_2P(O)R' + RX$$

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[1] Financial support was received from NASA Grant No. NGR 14-012-004.

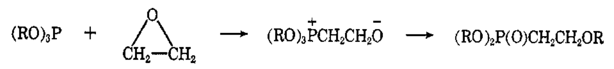
[2] J. H. Boyer and R. Selvarajan, Abstracts of 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p S 111.

[3] C. J. Timmons and S. C. Wallwork [*Chem. Ind.* (London), 62 (1955)] conclusively established the configuration of *trans*-α,β-dicyanostilbene **4**, mp 161°, by X-ray analysis. M. V. Sargent and C. J. Timmons [*J. Chem. Soc.*, 2222 (1964)] established the configuration of *cis*-α,β-dicyanostilbene, mp 134°. Formation of **4**, in turn, provides a tentative *cis*-configurational assignment to **3**, since an inverted olefin is reported to predominate when an epoxide is deoxygenated by a tertiary phosphine [G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955); C. B. Scott, *J. Org. Chem.*, **22**, 1118 (1957); M. J. Boskin and D. B. Denney, *Chem. Ind.* (London), 330 (1959)].

[4] T. Mukaiyaka, I. Kuwajima, and K. Ohno, [*Bull. Chem. Soc. Jap.*, **38**, 1954 (1965)] incorrectly reversed the configurational assignments for **3** and **4**.

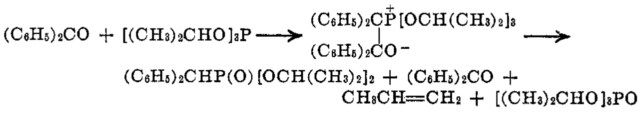
[5] P. C. Petrellis and G. W. Griffin [*Chem. Commun.*, 1099 (1968)] also observed the pyrolysis at 140° of **2** into **3**.[4]

[6] J. I. G. Cadogan [*Quart. Rev.*, **16**, 208 (1962)] discusses, p 216, a related reaction of epoxides with trialkyl phosphites which contain one or more secondary or tertiary alkyl groups. Phosphonates, rather than olefins and phosphates, are formed. An alkyl group migrates from oxygen to oxygen.



[7] R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 135–140.

[8] A. C. Poshkus and J. E. Herweh [*J. Org. Chem.*, **29**, 2567 (1964)] reported phosphonate formation by a related 1,3 migration of hydrogen in a reaction between benzophenone and triisopropyl phosphite.



$$(C_6H_5)_2CO + [(CH_3)_2CHO]_3P \longrightarrow \begin{matrix}(C_6H_5)_2C\overset{+}{P}[OCH(CH_3)_2]_3\\ (C_6H_5)_2CO^-\end{matrix} \longrightarrow (C_6H_5)_2CHP(O)[OCH(CH_3)_2]_2 + (C_6H_5)_2CO + CH_3CH{=}CH_2 + [(CH_3)_2CHO]_3PO$$