

designated N)⁸ and D.³ We now wish to report a convenient synthesis of spinochrome D as well as syntheses of the remaining spinochromes of established identity, A, C, and E, not previously synthesized.

Condensation of 1,2-dihydroxy-3,4-dimethoxybenzene and chloromaleic anhydride in an aluminum chloride-sodium chloride melt produced a 50% yield of a 1:2:1 mixture of 2,3-dihydroxynaphthazarin, 2,3-dihydroxy-6-chloronaphthazarin, and 2,3-dihydroxy-6,7-dichloronaphthazarin. The crude mixture was methylated with diazomethane and separation of the dimethyl derivatives was achieved by thick-layer chromatography on silica gel to yield 2,3-dimethoxynaphthazarin, m.p. 136–137° (lit.⁹ m.p. 133.5°), 2,3-dimethoxy-6-chloronaphthazarin (7), m.p. 134–135°, and 2,3-dimethoxy-6,7-dichloronaphthazarin (8), m.p. 204–205°. Nucleophilic displacement of chlorine with methoxide converted 7 to 2,3,6-trimethoxynaphthazarin, m.p. 161–162°, in 42% yield (lit.¹⁰ m.p. 160°); ultraviolet spectrum¹¹: λ_{\max} 317, 472, 497, and 530 m μ ; n.m.r. spectrum: C-2, C-3, and C-6 methoxyl, δ 3.86, 3.98, and 4.06; C-7 hydrogen, 6.30; C-5 and C-8 hydroxyl, 12.86 and 12.98. Finally, hydrolysis of 2,3,6-trimethoxynaphthazarin in hydrobromic acid at reflux afforded *spinochrome D*, subl. 280–290° without melting, identical in all respects with an authentic sample; ultraviolet spectrum in acidic methanol: λ_{\max} 330, 462, 490, and 527 m μ .

2,3-Dimethoxy-6,7-dichloronaphthazarin (8) was obtained as described above or, more readily and in 75% yield, by condensing 1,2-dihydroxy-3,4-dimethoxybenzene with dichloromaleic anhydride in an aluminum chloride-sodium chloride melt followed by methylation of the resulting 2,3-dihydroxy-6,7-dichloronaphthazarin, m.p. 256–257°, with diazomethane. Compound 8 was allowed to react with methoxide to yield 34% of 2,3,6-trimethoxy-7-hydroxynaphthazarin (9), m.p. 134–135°; ultraviolet spectrum: λ_{\max} 333, 460, 490, and 522 m μ ; n.m.r. spectrum: C-2, C-3, and C-6 methoxyl, δ 4.04, 4.08, 4.16; C-7 hydroxyl, 6.90 (broad); C-5 and C-8 hydroxyl, 12.16 and 13.30. Methylation of 9 with diazomethane yielded 2,3,6,7-tetramethoxynaphthazarin, m.p. 185–186° (lit.⁸ m.p. 185°); n.m.r. spectrum: C-2, C-3, C-6, and C-7 methoxyl, δ 4.10; C-5 and C-8 hydroxyl, 12.68. Hydrolysis of 9 in hydrobromic acid at reflux gave *spinochrome E*, subl. 300–320° without melting, identical in every respect with the natural pigment; ultraviolet spectrum in acidic methanol: λ_{\max} 358, 455 (sh), 475, and 508 (sh) m μ .

Methoxynaphthazarin, m.p. 195–196° (lit.¹² m.p. 178°), obtained in 82% yield from chloronaphthazarin and methoxide, was oxidized to 2-methoxy-1,4,5,8-naphthodiquinone with lead tetraacetate in benzene and the crude diquinone was acetylated by the Thiele method. Mild hydrolysis with ethanolic hydrochloric acid furnished a 20% yield of 6-methoxy-2-hydroxynaphthazarin, m.p. 265–267° (λ_{\max} 311, 465, 493, 521, and 529 m μ), and a 55% yield of 7-methoxy-2-hydroxynaphthazarin (10), m.p. 240–241° (λ_{\max}

(8) J. Smith and R. H. Thomson, *J. Chem. Soc.*, 1008 (1961).

(9) C. Kuroda, *J. Sci. Res. Inst.* (Tokyo), 46, 188 (1952).

(10) C. Kuroda and H. Osima, *Proc. Imp. Acad.* (Tokyo), 16, 214 (1940).

(11) Ultraviolet spectra were determined in chloroform unless otherwise noted; n.m.r. spectra in deuteriochloroform.

(12) C. Kuroda, *Proc. Imp. Acad.* (Tokyo), 15, 226 (1939).

313, 488, 504 (sh), 518, 538 (sh), and 555 m μ), readily separable by chromatography on silica gel. Compound 10 was then reductively acetylated to 1,2,4,5,8-pentaacetoxy-7-methoxynaphthalene, m.p. 222–223°. Treatment with boron trifluoride in acetic acid followed by mild acid hydrolysis in the presence of air converted the leucoacetate to 2,7-diacetyl-3,6-dihydroxynaphthazarin (11), m.p. 237–238°, in 20% yield; ultraviolet spectrum: λ_{\max} 318, 531, 564, and 615 m μ ; n.m.r. spectrum: C-2 and C-7 acetyl, δ 2.85; mass spectrum: *m/e* 306. Further careful acid hydrolysis of 11 resulted in the removal of one acetyl group to yield *spinochrome A* (50%), identical with the natural product.

To produce spinochrome C, the leucoacetate of D, m.p. 212–213° (lit.¹³ m.p. 210°), was treated with boron trifluoride in acetic acid, followed by mild acid hydrolysis in the presence of air. After chromatography *spinochrome C* (5%), which was identical with the natural pigment, was obtained.

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(13) C. Kuroda and H. Iwakura, *ibid.*, 18, 74 (1942).

(14) Grantee of the East-West Center.

(15) N.D.E.A. Fellow, 1960–1963; National Institutes of Health Predoctoral Fellow, 1963–1964.

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The Photosensitized Reaction of Dichloromaleic Anhydride with Benzene. A Novel Variation in the Photochemistry of Maleic Anhydride Derivatives

Sir:

Maleic anhydride undergoes photosensitized addition to benzene^{1–3} to form the tricyclic dianhydride, Ia, while both methyl- and dimethylmaleic anhydride cyclodimerize under similar conditions.^{4,5}

In an attempt to determine which course dichloromaleic anhydride (DCMA) follows, we have discovered a third and unexpected variation in the photochemistry of maleic anhydride derivatives in which a 2:2 benzene-anhydride adduct is the major product isolated. Irradiation⁶ of DCMA (0.2–0.4 *M*) in benzene solutions containing benzophenone (0.2–0.4 *M*)

(1) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 2675 (1962).

(2) E. Grovenstein, D. V. Rao, and J. W. Taylor, *J. Am. Chem. Soc.*, 83, 1705 (1961).

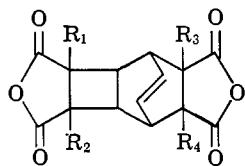
(3) G. O. Schenck and R. Steinmetz, *Tetrahedron Letters*, No. 21, 1 (1960).

(4) G. O. Schenck, W. Hartmann, S. P. Mannsfeld, and W. Metzner, *Ber.*, 95, 1642 (1962).

(5) G. O. Schenck, W. Hartmann, and R. Steinmetz, *ibid.*, 96, 498 (1963).

(6) Lamps having maximum intensity at 3500 Å. and an over-all range of 3000–4000 Å. were purchased from the Southern New England Ultraviolet Co.

resulted in the liberation of hydrogen chloride and the precipitation of 3,9,10-trichloro-4-phenyltricyclo[4.2.-2.0^{2,5}]dec-7-ene-3,4,9,10-tetracarboxylic dianhydride (Ib). Intermittent filtration of precipitated product

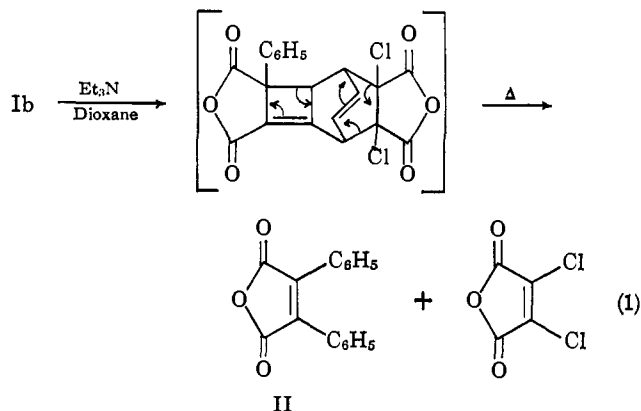


- Ia, $R_1 = R_2 = R_3 = R_4 = H$
 b, $R_1 = C_6H_5, R_2 = R_3 = R_4 = Cl$
 c, $R_1 = R_2 = R_4 = Cl, R_3 = C_6H_5$
 d, $R_1 = R_2 = C_6H_5, R_3 = R_4 = Cl$

(m.p. 290.0–290.5° dec., after two recrystallizations from *o*-dichlorobenzene) has resulted in conversions of 25–30% and yields of 40–45% after 200 hr. irradiation under nitrogen. The n.m.r. spectrum⁷ of Ib consisted of a complex multiplet centered at τ 2.49 (5 H), a broad singlet at τ 3.92 (2 H), and four doublets (total area 4 H) at τ 5.81 ($J = 12$ c.p.s.), 6.11 ($J = 9$ c.p.s.), 6.58 ($J = 12$ c.p.s.), and 6.88 ($J = 9$ c.p.s.). This latter pattern is consistent with two overlapping AB patterns. The infrared spectrum (KBr) was also consistent with the proposed structure, dianhydride peaks appearing at 1800 and 1870 cm^{-1} (both doublets) and phenyl absorptions at 1505, 753, and 700 cm^{-1} .

Anal. Calcd. for $C_{20}H_{11}Cl_3O_6$: C, 52.9; H, 2.4; Cl, 23.5. Found: C, 53.1; H, 2.5; Cl, 23.5.

The molecular weight determined ebullioscopically in dioxane was 412 (theoretical, 454). Solid Ib can be decomposed above its melting point (and also in refluxing 1,2,4-trichlorobenzene) to yield benzene, dichloromaleic anhydride, and chlorophenylmaleic anhydride. The latter compound was isolated in about 17% yield by preparative gas chromatography and was identified by comparison of its infrared and ultraviolet spectra with those of an authentic sample. The assignment of the phenyl group to the 4 position was confirmed by the isolation (preparative g.l.p.c.) of small quantities of diphenylmaleic anhydride (II) from the dehydrochlorination and subsequent thermal decomposition of Ib, presumably *via* eq. 1.

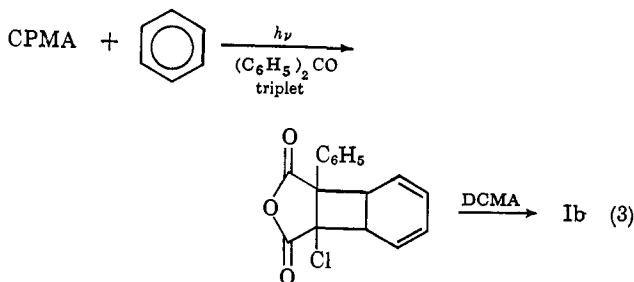
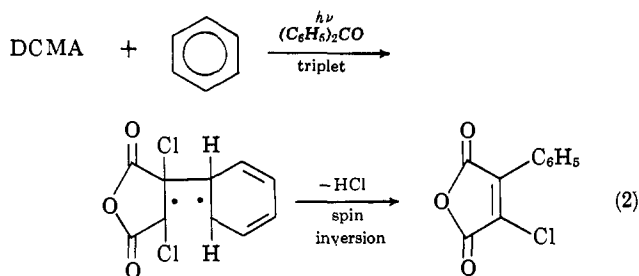


A sample of II was obtained for infrared analysis by trapping the solid on a cold germanium prism as it exited from a gas chromatograph. The spectrum was determined on a Perkin-Elmer Model 21 infrared

(7) The n.m.r. spectrum was determined on a Varian A-60 spectrometer using deuterated dimethyl sulfoxide as solvent and tetramethylsilane as an external reference.

spectrophotometer equipped for multipass attenuated total reflectance (a.t.r.-infrared) measurements. Strong absorptions at 1840, 1775, 1278, and 738 cm^{-1} were characteristic of a phenyl-substituted cyclic anhydride. The ultraviolet spectrum (λ_{max}^{EtOH} 257, 275, and 350 $m\mu$; lit.⁸ λ_{max}^{EtOH} 256, 275, and 349 $m\mu$) confirmed the structural assignment. We were unable to observe any chlorophenylmaleic anhydride, the expected product if the adduct was Ic. The facile elimination of exactly 1 equiv. of HCl suggests that the stereochemistry about the cyclobutane ring in Ib is the same as that reported² for Ia.

Equations 2 and 3 summarize the mechanism we believe responsible for the formation of Ib. Strong support for this mechanism was obtained with the isolation (g.l.p.c.) and identification (a.t.r.-infrared, ultraviolet) of chlorophenylmaleic anhydride (CPMA)



from the irradiated mixture. The CPMA appeared as a minor (about 1% of the benzophenone) peak in the chromatograph just preceding the benzophenone. Its concentration remained approximately constant throughout most of the reaction. We demonstrated that the peak did not arise from the thermal decomposition of Ib in the gas chromatograph.

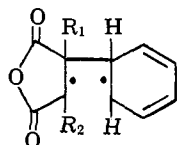
At least one of the two photochemical processes required benzophenone as indicated by our failure to obtain Ib after unsensitized irradiation at 3000–4000 Å. or with a low-pressure mercury resonance lamp.⁹ The CPMA peak was not observed in the gas chromatograph, even after large amounts of DCMA were consumed (presumably forming polymer). This suggests that the first step requires benzophenone. The reaction of chlorophenylmaleic anhydride with benzene also requires sensitization. Adduct Ib could not be isolated by irradiating a benzene solution containing DCMA and CPMA in the absence of benzophenone.¹⁰

(8) J. E. Banfield, *J. Chem. Soc.*, 2108 (1960).

(9) The nonadditivity of the benzene and DCMA spectra in the 280 $m\mu$ region suggests the formation and possible intermediacy of a complex similar to that reported¹ for maleic anhydride in benzene.

(10) Benzophenone-sensitized irradiation of the DCMA-CPMA mixture led to the expected product but in yields less than that theoretically possible from the DCMA itself.

The need for benzophenone can be equated with triplet intermediates.¹¹⁻¹³ Although the formation of triplet IV would be expected to be highly favored over III, the absence of diphenylmaleic anhydride and Id in the irradiated mixture and the isolation of Ib in high yields lead us to conclude that this is not the case.



III, $R_1 = C_6H_5$, $R_2 = Cl$

IV, $R_1 = Cl$, $R_2 = C_6H_5$

We have been unable to isolate analogs of Ib from the irradiation of DCMA in toluene or chlorobenzene. Unlike the maleic anhydride case,¹⁴ it is not simply a matter of low relative rates; even after 60–70% of the DCMA has been lost, no adduct can be isolated.

Acknowledgment. The authors are indebted to Professors D. Bryce-Smith and J. H. Richards for their aid in the solution of this problem.

(11) G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959).

(12) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Chem. Phys.*, **32**, 1594 (1960).

(13) H. L. J. Bockström and K. Sandras, *ibid.*, **23**, 2197 (1955).

(14) D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.*, 918 (1965).

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Phosphoranyl Radical Intermediates. Free-Radical Addition of Bromotrichloromethane to an Unsaturated Cyclic Oxyphosphorane

Sir:

Examples of free-radical additions of small molecules to carbon-carbon double bonds are extremely nu-

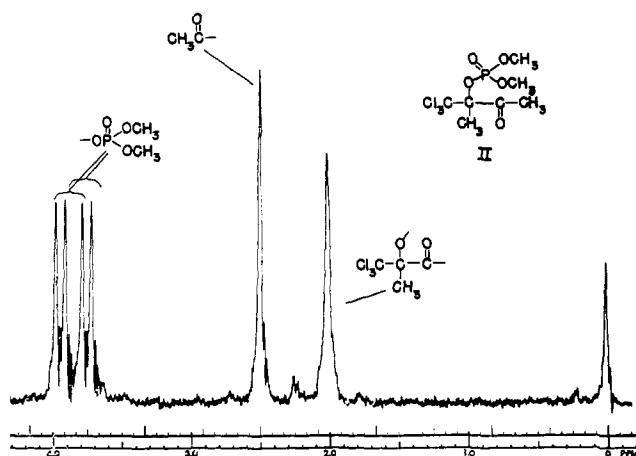
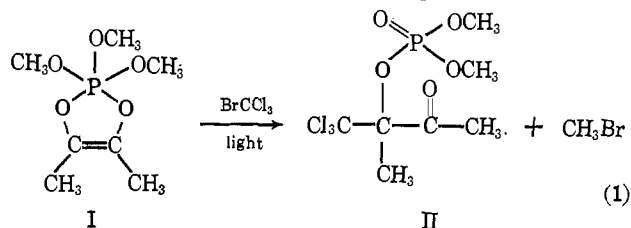


Figure 1. N.m.r. spectrum of product II (~40% in CCl_4).

merous¹ and often give high yields of 1:1 adducts. We wish to report the light-induced reaction of $BrCCl_3$ with the unsaturated cyclic oxyphosphorane, I.²

(1) See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 239–346.

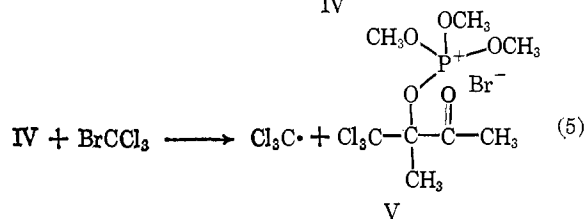
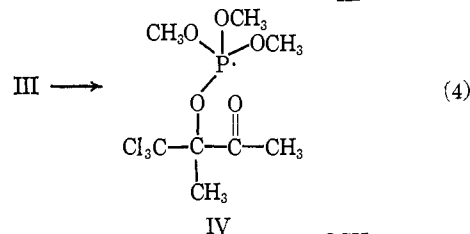
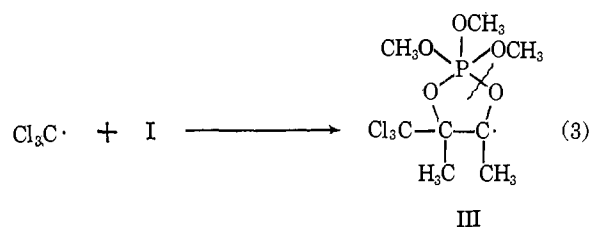
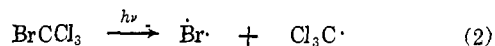
The major identified product, II, was isolated in 83% yield. This reaction, the first reported free-radical



addition involving the relatively new class of compounds represented by I, is also of interest because of its reasonable explanation in terms of a novel ring-opening sequence involving a phosphoranyl radical intermediate. In addition, the proton n.m.r. spectrum of II (Figure 1) exhibits a somewhat unusual long-range molecular asymmetry effect which is discussed later.

The reaction was carried out at 30–40° in a Pyrex flask irradiated with a 150-w. tungsten filament flood lamp. $BrCCl_3$ was in excess as solvent (9.5 g. of I in 40 ml. of $BrCCl_3$). Reaction progress was monitored by v.p.c. which showed II to be formed steadily as virtually the only high-boiling product. A very volatile product, which is likely methyl bromide (required in the above equation), was also noted. In an analogous reaction involving the phosphorane formed from biacetyl and triisopropyl phosphite (MeO in I becomes *i*-PrO), isopropyl bromide was detected by v.p.c., isolated by distillation, and identified by its n.m.r. spectrum. II, a colorless liquid, was isolated by fractional distillation, b.p. 104° (0.15 mm.), n_D^{25} 1.4760. *Anal.* Calcd. for $C_7H_{12}O_5Cl_3P$: C, 26.82; H, 3.86; P, 9.88; mol. wt., 315. Found: C, 26.67; H, 3.96; P, 10.16; mol. wt., 320.

The most obvious reaction series to explain the formation of II is



(2) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **85**, 3252 (1963).