

in the nuclear magnetic resonance spectrum of III (Fig. 1) can be ascribed to the olefinic (3.92 τ ; rel. int. 3.99), ferrocenic (6.13 τ ; rel. int. 5.98) and allylic (7.33, 7.50 τ ; rel. int. 4.00) protons.²

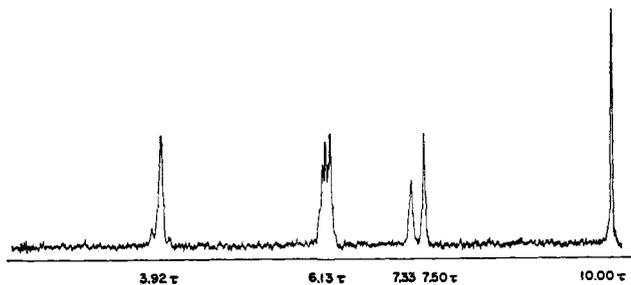


Fig. 1.—N.m.r. spectrum of III in CCl_4 determined at 60 Mc. with tetramethylsilane as an internal standard.

The ferrocene III in ether reacts with *t*-butyllithium (5 mole equivalents) in ether to yield at -40° a maroon solution, which on warming to -10° precipitates a brown solid. Addition of this suspension to excess dilute deuteriosulfuric acid and isolation of the product, as above, gives III containing two deuterium atoms (found³: 14.02, 14.42 atom % excess D, *i.e.*, 1.96, 2.02 atoms D/molecule). The n.m.r. spectrum of this material manifests the same peaks as the undeuterated compound, except that the allylic proton bands are broadened and diminished in intensity by a factor of two. (The integrated n.m.r. intensities of olefinic, ferrocenic and allylic hydrogens were found to be 3.94:6.08:2.10.)

If, however, the maroon solution formed at -40 to -50° is quenched by pouring it into 0.1 *N* deuterio-sulfuric acid (6 mole equivalents) at 0° , III is formed incorporating only one atom of deuterium (found: 7.44 atom % excess D, *i.e.*, 1.04 atoms D/molecule.⁴)

These data identify the species I and II and demonstrate their ease of formation and their stability.⁶

Acknowledgments.—We gratefully acknowledge the support of the National Science Foundation (NSF G-15561, GP-748) and the Alfred P. Sloan Foundation.

(2) The presence in the n.m.r. spectrum of two lines in the allylic region is attributed to the presence, in samples of III, of the isomers IIIa and IIIb, rather than to a chemical shift of protons *exo* and *endo* to the iron atom in one of these isomers. In the latter case, either the outer lines of the AB quartet are at least 1/10 as intense as the inner, implying that the spin-spin coupling constant is inordinately large (*ca.* 55 c.p.s.), or the outer lines overlap so closely with the inner that they cannot be resolved, implying that the coupling constant is exceptionally small (*ca.* 1 c.p.s.).

(3) Deuterium analyses by the falling drop method were performed by Josef Nemeth, Urbana, Illinois.

(4) Treatment of III with an excess of *n*-butyllithium, under a variety of conditions, and subsequent quenching of the reaction mixture with dilute D_2SO_4 , introduced only as much as 1.58 atoms of deuterium into the molecule. In other metalations *n*-butyllithium has been more effective than its branched isomers in ether, but has been less effective in petroleum ether.⁵

(5) H. Gilman and J. W. Morton, Jr., "Organic Reactions," Vol. 8, John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 284–285; H. Gilman, F. W. Moore and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

(6) Ferrocenylmethylolithium does not appear to be preparable by metalation of methylferrocene [A. N. Nesmeyanov, E. G. Perevalova and Yu. A. Ustynuk, *Dokl. Akad. Nauk SSSR*, **133**, 1105 (1960)]. *n*-Butyllithium does, however, metalate the ferrocene nucleus to form mono- and dilithio derivatives [A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *ibid.*, **97**, 459 (1954); R. A. Benkeser, D. Goggin and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954); D. W. Mayo, P. D. Shaw and M. Rausch, *Chem. Ind. (London)*, 1388 (1957)].

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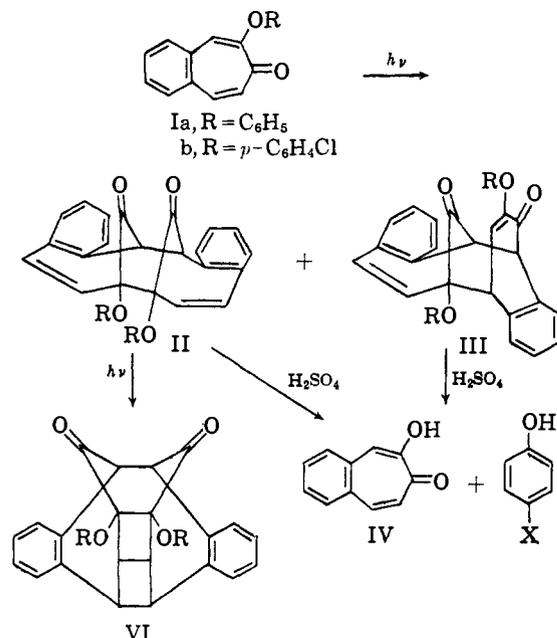
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A New Photodimerization Process

Sir:

The potential photochemical rearrangements of 2-phenoxy-4,5-benzotropone (Ia) are of special interest in that the usual photochemical valence tautomerization of tropolone ethers¹ is virtually forbidden. Irradiation of Ia in 2-propanol or tetrahydrofuran (mercury arc lamp, Pyrex filter) gives IIa (27%; m.p. 208.5–210°; 217 (45,200), 255 (infl., 24,950) and 260.5 $m\mu$ (26,250); 534 (osmometric)) and IIIa (14%; 196–198°; 216 (infl., 12,600) 264 (13,200) and 273 $m\mu$ (12,600); 504 (osmometric)). Similar dimers (IIb and IIIb) may be prepared by irradiation of Ib.

Treatment of IIa,b or IIIa,b with concentrated sulfuric acid gives 4,5-benzotropone (IV) and the corresponding phenol² precluding gross rearrangement



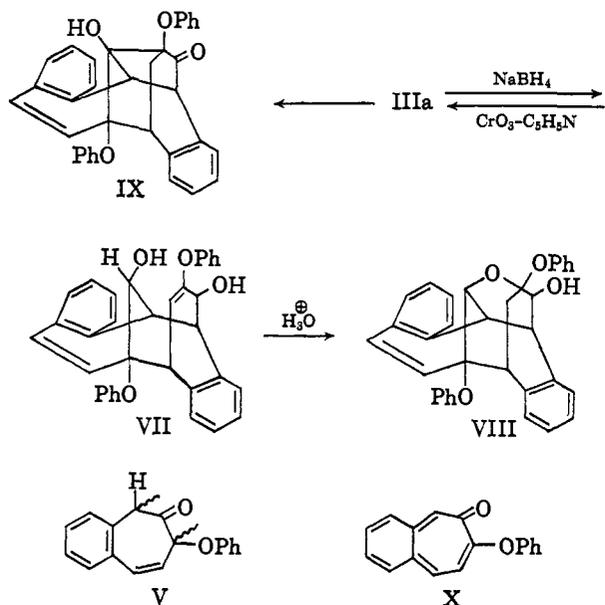
of the carbon skeleton and suggesting that the seven-carbon ring is still intact. The infrared carbonyl absorption of IIa (5.74 μ)³ eliminates from consideration structures in which the carbonyl function is conjugated with a double bond or aromatic system. IIa shows aromatic protons (2.83 τ), an AB pattern characteristic of a styryl double bond unperturbed by protons on adjacent carbons (3.41 and 4.10 τ , $J_{ab} = 12.3$ c.p.s.) and a sharp singlet (5.64 τ). The simplicity of the n.m.r. spectrum of IIa together with the infrared and ultraviolet absorption requires a dimer composed of two units of V. A unique choice among the four possible dimers based on V is provided by the observation that irradiation of IIa (without the Pyrex filter) gives in low yield a new dimer (VI). VI shows an A_2B_2 pattern (5.61 and 6.23 τ) and a two-proton singlet (5.46 τ) in the n.m.r. spectrum and $\lambda_{\text{max}}^{\text{EtOH}}$ 256 (infl.; 2319), 263 (3083), 269 (3834), 273 (3300) and 306 $m\mu$ (754).

Dimer IIa is converted thermally (210°) to dimer IIIa in good yield. This unique process bears on the mechanism of the Cope rearrangement and the Diels-Alder reaction. Dimer IIIa (5.82, 5.94 μ) shows in the n.m.r. spectrum aromatic protons (2.95 τ ; eighteen

(1) O. L. Chapman, chapter in "Advances in Photochemistry," edited by W. A. Noyes, G. S. Hammond and J. N. Pitts, Interscience Publ. Co., in press.

(2) It is significant that 2-phenoxy-4,5-benzotropone is not hydrolyzed to IV under these conditions.

(3) The carbonyl absorption (in CCl_4) is lower than expected, due to strain and the effect of the adjacent phenoxy group. Cyclohexane-1,4-dione shows lower wave length infrared absorption (5.80 μ) than cyclohexanone (5.85 μ).



aromatic protons plus the low field olefinic proton), a styryl AB pattern (3.99 and 4.69 τ , $J_{AB} = 13.0$ c.p.s.), a higher field AB pattern (5.36 and 5.73 τ ; $J_{AB} = 5.0$ c.p.s.) due to the adjacent, non-equivalent bridgehead protons and the high field half of an AX system (5.64 τ , $J_{AX} = 9.7$ c.p.s.). A double resonance experiment identifies the low field olefinic proton as the other half of the AX system. Saturation of the low field olefinic proton (151 c.p.s. downfield from the doublet) collapsed the high field doublet to a sharp singlet. Reduction of IIIa gives a diol (VII) which shows all the expected physical properties including an olefinic doublet (4.33 τ , $J_{AX} = 10.7$ c.p.s.) due to the vinyl proton of the enol ether function and exchanges two protons on shaking with deuterium oxide. Attempted acid hydrolysis of the enol ether function in VII gives the ether VIII which exchanges only one proton and forms a monoacetate. Catalytic reduction of IIIa gives a novel dihydro derivative IX, $\lambda_{\max}^{\text{EtOH}}$ 264 (12,290), 272 (11,440), 287 (infl., 2,900) and 297 μ (1,520) in good yield. IX shows an exchangeable hydroxyl proton (5.84 τ), a styryl AB system (3.98 and 4.66 τ , $J_{AB} = 6.5$ c.p.s.) and an ABX pattern (6.40, 6.76 and 7.88 τ , $J_{AB} = 7.1$ c.p.s., $J_{AX} \sim 0$, $J_{BX} = 12.9$ c.p.s.).

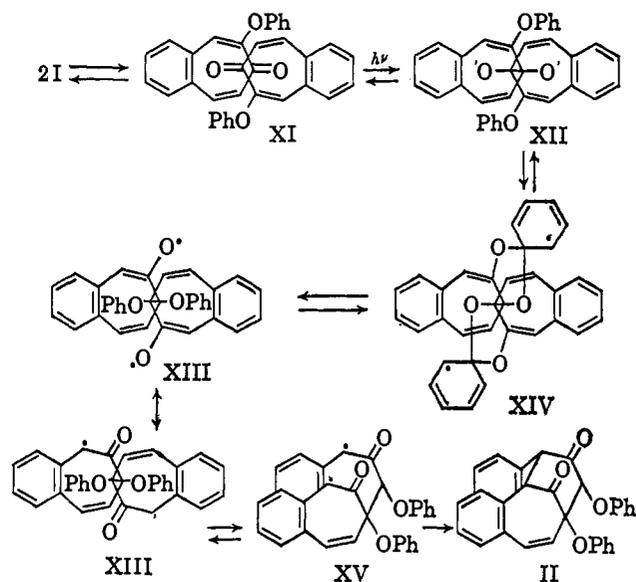
The dimers (II and III) appear to be derived formally from X rather than I. All attempts to trap X with dienophiles have failed. Dimer formation continues in the presence of dicarbomethoxyacetylene, maleic anhydride and tetracyanoethylene suggesting that dimerization does not involve X as an intermediate. Formation of II and III may be accounted for in the following manner. Complex formation between two molecules of I should lead to XI in which the ground state dipoles are properly oriented and the bulky phenoxy groups are on opposite sides of the complex.⁴ Excitation gives XII in which there is now a bond between the carbonyl carbons. An oxygen-oxygen phenyl shift analogous to previously observed carbon-oxygen phenyl shifts⁵⁻⁷ gives XIII via XIV. Rotation

(4) It is not necessary to assume complex formation in this mechanism. The same net result could be accomplished formally by addition of an excited molecule to a ground state molecule. 2-Phenoxy-4,5-benzotriene deviates significantly from Beer's law even in dilute (10^{-4} M) solution suggesting that complex formation does occur.

(5) H. Schmidt, H. Hochweber and H. von Halban, *Helv. Chim. Acta*, **30**, 1135 (1947), and references therein cited.

(6) G. W. Griffin and E. J. O'Connell, *J. Am. Chem. Soc.*, **84**, 4148 (1962).

(7) H. E. Zimmerman, H. G. C. Durr, R. G. Lewis and S. Bram, *ibid.*, **84**, 4149 (1962).



(180°) about the bond joining the two halves of the dimer gives XV which collapses to II. III may be produced by thermal rearrangement of dimer II molecules formed in a vibrationally excited state or by a separate photochemical process.⁸

Satisfactory analyses have been obtained for all new compounds.

Acknowledgment.—The authors acknowledge financial support of this investigation by grant CA-04253 from the National Institutes of Health, Public Health Service, and technical assistance by Miss Alice K. Peterson. The authors are indebted to Professor L. M. Jackman for stimulating discussion.

(8) It has been established that IIa is not derived from IIIa, but it has not been established that IIIa is derived from IIa.

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Tetracyanoethylene Oxide

Sir:

Unique reactivity has been uncovered for the previously unreported tetracyanoethylene oxide (I, TCNEO).¹ For example, TCNEO readily adds to olefinic, acetylenic, and aromatic systems to yield products derived from carbon-carbon cleavage of the epoxide molecule.

TCNEO, obtained in 65% yield by reaction of tetracyanoethylene with aqueous hydrogen peroxide in acetonitrile, is a colorless, sublimable compound, m.p. 177–178° (*Anal.* Calcd. for C₆N₄O: C, 50.00; N, 38.88; mol. wt., 144. Found: C, 50.00; N, 38.85, mass spectrum has parent peak at m/e 144). The compound shows no absorption in the ultraviolet, and the infrared spectrum (Nujol) is simple with absorption at 4.38, 7.68, 8.47, 8.66, 10.54 and 11.23 μ .

The strong electron-withdrawing character of the cyano groups is manifested in the ease with which TCNEO undergoes nucleophilic attack. Reaction with iodide ion gives cyanogen iodide and tricyanovinyl alcoholate.² With pyridine at 0°, the stable nitrogen

(1) Subsequent to our studies, we have learned that TCNEO has been isolated from ozonizations conducted in the presence of tetracyanoethylene (private communication from Prof. R. Criegee, Institut für Organische Chemie, Technische Hochschule, Karlsruhe, Germany).

(2) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).