Further investigation of allyldiazomethane and of bicyclobutane is in progress.

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DEPARTMENT OF CHEMISTRY DAVID M. LEMAL
CHEMISTRY RESEARCH BLDG. FREDRIC MENGER
UNIVERSITY OF WISCONSIN GEORGE W. CLARK
MADISON 15, WISCONSIN

Electronic Interactions in Biradicals. 1. Reversible Bond Formation

Sir:

There is considerable interest in the chemistry of biradicals which, in some cases, may interact sufficiently to be termed triplets.[1] The synthesis of a potential triplet containing two phenoxyl radicals in a cross-conjugated system has been reported by Yang and Castro.[2] We have studied a system containing two individually stable phenoxyl radicals not connected to a single π-electron system but held together as closely as possible—bound to the same saturated carbon atom. The system we chose is derived from 2,2-bis-(3,5 di-t-butyl-4-hydroxyphenyl)-propane (I).[3]

R = t-butyl
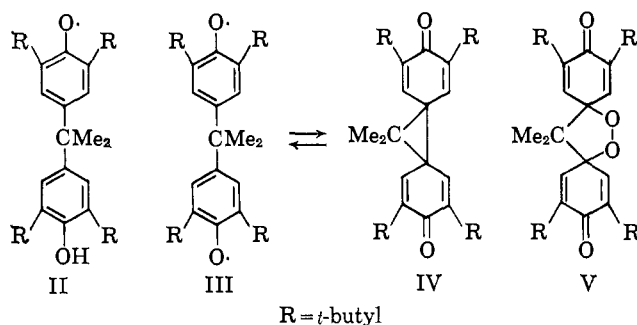
Metal oxides (PbO_2, Ag_2O, MnO_2) oxidized I readily, but treatment of a benzene solution of I with aqueous alkaline $K_3Fe(CN)_6$ was most effective for preparative scale work. Evaporation of the solvent with nitrogen left brick-red needles (m.p. *ca.* 120° dec.) which could be crystallized from pentane. Iodometric titration indicated the consumption of 1.85 equivalents of HI and regenerated I (55%, crystallized). The infrared spectrum of the product was interpretable in terms of structure IV, resulting from internal bond formation in the biradical III. There was no band at 6.4 μ, the characteristic absorption of phenoxyl radicals,[4] but there was a doublet, characteristic of this type of cyclohexadienone, at 6.08 and 6.16 μ.[4] Examination of a scale model of III indicated that the *para* positions of the radicals are held close together (the internuclear distance is 2.5 Å. when the central atom is tetrahedral) and a strained bond between these centers is conceivable. A simple spirodienone of this type has been reported by Baird and Winstein.[5]

The oxidation product, IV, was stable as a solid or in an inert solvent as long as it was protected from oxygen. The solid was decolorized slowly by air and solu-

tions of IV reacted readily with oxygen, forming an unstable addition compound. The latter is formulated as the peroxide V on the basis of its analysis (*Anal.* Calcd. for $C_{31}H_{46}O_4$: C, 77.13; H, 9.61. Found: C, 76.70; H, 9.84) and its infrared spectrum ($\lambda_{max}^{CH_2Cl_2}$ 5.97, 6.07 μ).

The oxidation of I (benzene or cyclohexane solution) also was carried out with Ag_2O or PbO_2 in a sealed, degassed system. The initially formed product was identified as the monoradical II by virtue of its e.p.r. spectrum. The major triplet splitting is attributable to the two equivalent *meta* protons ($\alpha = 1.67$ gauss) with further smaller coupling to the six equivalent protons of the isopropylidene group ($\alpha = 0.38$ gauss). There is no significant interaction with the adjacent unoxidized phenolic system although the optical spectrum lacks the long wave length band responsible for the blue color of 2.4.6-tri-t-butylphenoxyl. Further oxidation of the solution caused a marked decrease in the intensity of the e.p.r. spectrum; the addition of excess phenol I regenerated the original spectrum. These observations are readily interpretable in terms of the equilibrium I + IV $\rightleftarrows$ 2II. No e.p.r. signal attributable to biradical III was observed and there was no absorption in rigid media other than at $g = 2$.

The ultraviolet spectrum of phenol I is essentially that of a simple phenol and has a doublet maximum at 275 and 283 mμ. The optical absorption spectrum of the solution was monitored simultaneously with the e.p.r. spectrum as oxidation of the phenol progressed. Initially, a broad absorption at 325 mμ appears as well as a sharp peak at 263 mμ. As the oxidation proceeds, the latter increases in intensity while the former, which we attribute to the monoradical II, decreases. The peak at 263 mμ corresponds well with that reported for spiro(2,5)octa-(1,4)-diene-3-one by Baird and Winstein.[5] The long wave length peak tails into the visible and is responsible for the red color of the product. The variations in e.p.r. intensity as oxidation proceeded were in accord with the conclusions reached on the basis of the optical spectral data.

The intensity of the e.p.r. spectrum of II decreased as the temperature was lowered, indicating that a thermal equilibrium was present. This is the disproportionation of II into I and IV. The Curie dependence of magnetic susceptibility may be allowed for by taking intensity (I) $\times$ temperature (T) as a measure of radical concentration. An Arrhenius plot of log IT *vs.* $1/T$ over the range 25 to $-56°$ (CH_2Cl_2 solution) was linear and gave $\Delta H = -3.7$ kcal. The low value reflects the weakness of the strained cyclopropane bond in IV.

It appears that IV is in equilibrium with biradical III on the basis of both physical and chemical evidence although III itself could not be detected. Dienone IV would not be expected to be destroyed rapidly by oxygen, but the reaction takes only a few minutes in solution at 25°. The n.m.r. spectrum of I was in accord with its assigned structure (τ scale: t-C_4H_9, 1.33; CH_3, 1.55; OH, 4.76; ArH, 6.81). In solutions of IV, however, only a single moderately broad line was observed (1.33 τ). The absence of the vinyl proton line can be explained by rapid interconversion of III and IV. The amount of monoradical II in solution was too small to permit an explanation based on hydrogen atom exchange.[6] The sharpness of the butyl line may be explained by the low spin density at this position.[7,8] The t-butyl proton splitting was not resolved in the e.p.r. spectrum.

(1) See S. I. Weissman, *Ann. Rev. Phys. Chem.*, **12**, 151 (1961).

(2) N. C. Yang and A. J. Castro, *J. Am. Chem. Soc.*, **82**, 6208 (1960).

(3) We thank the Ethyl Corp., Detroit, Michigan, for a gift of this compound. It was prepared by butylation of the corresponding bisphenol with isobutylene and Al(OC₆H₅)₃. I has m.p. 155-156°. *Anal.* Found: C, 81.94; H, 10.74.

(4) E. Müller and K. Ley, *Chem. Ber.*, **87**, 922 (1954).

(5) R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **85**, 567 (1963).

(6) R. Kreilick and S. I. Weissman, *ibid.*, **84**, 306 (1962).

(7) This phenomenon has been observed by Weissman and Kreilick in line broadening due to hydrogen atom exchange.

(8) H. McConnell and S. B. Berger, *J. Chem. Phys.*, **27**, 230 (1957).

It seems likely that the bond formation observed in this system could be avoided if the isopropylidene group were replaced by a cyclohexane or smaller ring system. Attempts to synthesize such compounds are in progress.

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BELL TELEPHONE LABORATORIES, INC.   EDWIN A. CHANDROSS
MURRAY HILL, NEW JERSEY

DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY   ROBERT KREILICK
ST. LOUIS 30, MISSOURI

## The Synthesis and Properties of Homotropone

Sir:

Following the recent synthesis of the homotropylium cation (I),[1] it became of interest to study the related ketone (II) for which the trivial name homotropone is applicable.[2]

I   II

One probable factor which contributes to the stability of the cation I is the presence of a "pseudoaromatic" sextet of electrons, two of which in a classical structure are part of a cyclopropane ring. Since many of the unusual properties of tropone (cycloheptatrienone), in particular its high basic strength,[3a,b] can be attributed to the stability of the aromatic tropylium cation it was considered desirable to determine whether homotropone would exhibit abnormal properties for analogous reasons.

We have synthesized homotropone by means of the reaction sequence
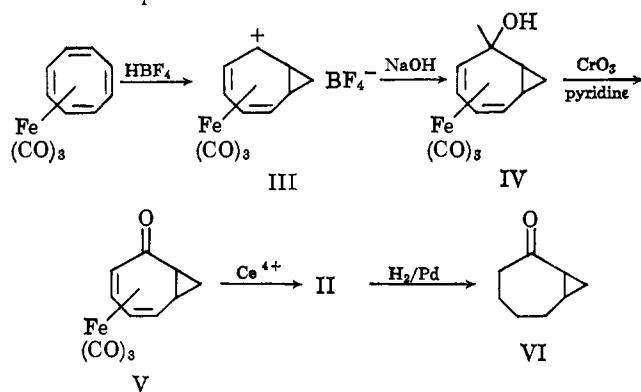
Cyclooctatetraeneiron tricarbonyl[4] was converted to the salt (III) following published procedures.[5a,b] Treatment of the salt with sodium hydroxide in aqueous acetone at low temperatures afforded the alcohol complex IV. (Yellow needles from petroleum ether, m.p. 90–91.5°; *Anal.* Calcd. for $C_{11}H_{10}O_4Fe$: C, 50.41; H, 3.81. Found: C, 50.36; H, 3.85.) Oxidation of IV with chromic oxide in pyridine gave the complex ketone V. (Yellow needles from benzene–petroleum ether,

(1) J. L. von Rosenberg, Jr., J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962).

(2) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3244 (1961).

(3) (a) H. J. Dauben, Jr., and H. J. Ringold, *ibid.*, **73**, 876 (1951); (b) W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).

(4) T. A. Manuel and F. G. A. Stone, *ibid.*, **82**, 366 (1960).

(5) (a) G. N. Schrauzer, *ibid.*, **83**, 2966 (1961); (b) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

m.p. 131–132.5°; *Anal.* Calcd. for $C_{11}H_8O_4Fe$: C, 50.80; H, 3.08. Found: C, 50.85; H, 3.19.) Oxidative degradation of the ketone complex with ceric ammonium nitrate removed the iron tricarbonyl residue and liberated homotropone. The ketone was obtained as a pale yellow oil. *Anal.* Calcd. for C_8H_8O: C, 79.97; H, 6.71; O, 13.32. Found: C, 80.05; H, 6.88; O, 13.5. The semicarbazone of II crystallized as yellow plates from aqueous alcohol; m.p. 146–147°. *Anal.* Calcd. for $C_9H_{11}ON_4$: C, 61.00; H, 6.26; N, 23.71. Found: C, 60.98; H, 6.28; N, 23.80.

Proof of structure of the ketone was provided by reduction with H_2/Pd (hydrogen uptake, 1.84 moles) to give bicyclo-(5,1,0)-octan-2-one (VI). The dinitrophenylhydrazone derivative of this ketone had identical properties (ultraviolet and infrared spectra, m.p., and mixture m.p.) with an authentic specimen.[6]

The most revealing property of ketone II concerns its basic strength. The basicity of II was measured using spectrophotometric methods in aqueous sulfuric acid solutions and Hammett's H_0 acidity values.[7] The pK_{BH^+} of II is found to be -2.8, which is significantly higher (2.1 pK units) than that found for eucarvone (2,6,6-trimethylcyclohepta-2,4-dienone, $pK_{BH^+} = -4.9$). For purposes of comparison the introduction of two methoxyl groups in the p,p'-positions of benzophenone has the effect of raising the pK_{BH^-} value by 1.8 pK units, from -6.16 to -4.39.[8]

It would be desirable to compare the basicity of II with a planar heptatrienone molecule but unfortunately no such system appears readily available. However, the value of -2.8 for the pK_{BH^+} value for II lies significantly higher than that which would be predicted on the basis of molecular orbital theory for such a planar heptatrienone molecule, the predicted value being -4.7.[9,10]

Homotropone, when treated with $HSbCl_6$ in a benzene–methylene chloride mixture, forms a pale yellow, crystalline hexachloroantimonate salt; m.p. 89–90° dec. *Anal.* Calcd. for $C_8H_9OSbCl_6$: C, 21.09; H, 1.99, Cl, 46.69. Found: C, 20.76; H, 2.41; Cl, 46.5. The salt is stable when stored under nitrogen but rapidly decomposes in moist air. We have not been able to isolate crystalline hydrogen halide salts of II; tropone, on the other hand, forms such salts readily.[3]

The most ready explanation for the high basicity of homotropone would appear to involve enhanced conjugation of the cyclopropane ring in the protonated form of II.

The n.m.r. spectrum of homotropone is also interesting. Taken neat the spectrum of II consists of unresolved multiplets centered at 3.5, 4.2, 7.6, 8.0, and 8.5 τ with areas of 2:2:1:2:1, respectively. In concentrated sulfuric acid the bands are centered at 2.2, 3.0, 6.2, and 9.3 τ with areas of 2:2:3:1, respectively. The appearance, in the protonated form, of three of the cyclopropyl hydrogens at low field and one at high field is analogous to that seen in the n.m.r. spectrum of the cation I[1] and is compatible with the existence of a ring current present in the system.

(6) We are very grateful to Professor A. C. Cope for providing us with an authentic specimen of the dinitrophenylhydrazone derivative of the ketone (VI).

(7) L. A. Flexser, L. P. Hammett, and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

(8) R. Stewart, M. R. Granger, R. B. Moodie, and L. J. Muenster, *Can. J. Chem.*, **41**, 1065 (1963).

(9) The value of a_{or}^2 for heptatrienone is 0.25; this predicts a pK_{BH^+} value of -4.7 for this ketone according to the linear relationship between pK_{BH^+} and a_{or}^{2}.[10] Justification for the use of this relationship in the present series of compounds is seen in the reasonable agreement of the observed basicity of eucarvone ($pK_{BH^+} = -4.9$) and that predicted for heptadienone [$pK_{BH^+} = -5.3$; $a_{or}^2 = 0.33$].

(10) G. Culbertson and R. Pettit, *J. Am. Chem. Soc.*, **85**, 741 (1963).