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A CYCLOÖCTATETRAENO-CYCLOPENTADIENONE

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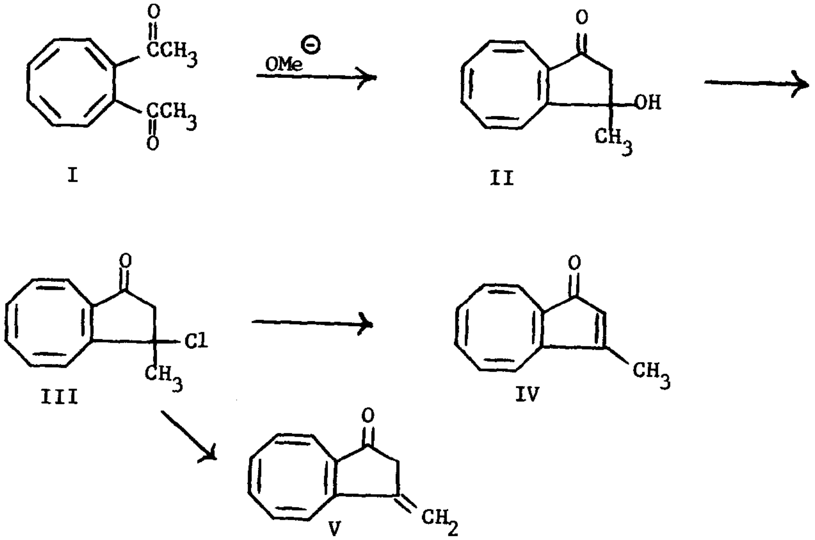
The fusion of two systems with 4n π electrons produces a composite with 4n + 2 π electrons. The intriguing possibility of producing an aromatic system by fusing two "antiaromatic" rings is also suggested by more detailed molecular orbital calculations; a number of such structures have been proposed.(1) We wish to report the synthesis of the first potential example of such a system, 2,3-cycloöctatetraeno-4-methylcyclopentadienone (IV).



1,2-Diacetylcycloöctatetraene (I) was prepared by a modification of the reported procedure,[(2)] in which our oxidation of 1,2-bis(hydroxyethyl)cycloöctatetraene[(2)] was performed with CrO_3-H_2SO_4. Treatment of I with sodium methoxide afforded the ketol II, purified by chromatography and distillation (160°C., 0.25 mm.) as a viscous oil (Calc'd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.42. Found: C, 76.52; H, 6.45. Infrared: 3400, 1705, 1630 cm.$^{-1}$ U.V.: λ_{max} 227 mμ (4.0). N.m.r.: 1.45 δ (CH_3), 2.53 δ (CH_2), 5.75, 5.88, 6.16 δ (vinyl) with the correct areas.) This was converted to the unstable chloride III with $SOCl_2$ and pyridine in cold ether (Infrared: no OH, C=O at 1715 cm.$^{-1}$ N.m.r.: 1.83 δ (CH_3), 2.95 δ (CH_2 as an AB quartet, J = 19 cps.) and the vinyl hydrogens, all in the correct ratio).

When III was slowly chromatographed on activity II neutral alumina with $CHCl_3$, a yellow-brown zone was eluted as an intensely colored solution which contained essentially pure cyclopentadienone derivative IV. The n.m.r. spectrum of this solution showed the CH_3 at 2.20 δ as a doublet split by the vinyl proton (J = 1.2 cps.); all other saturated aliphatic protons were missing, and the ratio of methyl to vinyl hydrogens (5.50 - 6.50 δ) was 3:7.2. When the solution was allowed to stand, or solvent removal was attempted, IV was destroyed in favor of a white flaky apparently polymeric substance. However, it was possible to replace the solvent $CHCl_3$ with benzene, without significant change in the n.m.r., and to hydrogenate the solution over Pd/C. The product was 87% distillable at 100° (0.75 mm.) and was identified as the cyclopentenone derived by reduction of the four least substituted double bonds in IV, on the basis of its mass spectrum (m/e = 178 (parent), 163 (parent - CH_3), etc.), n.m.r. (no vinyl hydrogen, doublet CH_3 at 1.15 δ (J = 7 cps.), aliphatic protons from 0.8 - 3.0 δ) u.v. (λ_{max} 239 mμ (4.23)) and infrared (1710 cm.$^{-1}$ strong and 1652 cm.$^{-1}$

medium). There was also a little completely saturated ketone (m/e = 180) and this was the major product of longer hydrogenation in ethyl acetate solution (m/e = 180, 165, etc.; infrared at 1740 cm.$^{-1}$).

Chromatography of III on silica gel afforded the β, γ-unsaturated ketone V as a yellow eluate, contaminated with IV. Ketone V can be purified by short path distillation at 105°C. (0.15 mm.) since under these conditions IV is destroyed (Calc'd. for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.99; H, 5.46. N.m.r.: COT protons at 5.70, 5.93, and 6.10 δ; two triplets (J = 1.5 cps.) at 5.15 and 5.03 δ (exo-CH_2 coupled to saturated CH_2); a triplet at 2.98 δ (J = 1.5 cps., sat'd. CH_2) all in the correct ratio. Infrared: exo-CH_2 at 895 cm.$^{-1}$). Chromatography of pure V on basic alumina afforded a 2:1 mixture of IV and V.

It is apparent that IV shares, at least to a considerable extent, the characteristic instability of most cyclopentadienone derivatives.$^{(3)}$ Kinetic instability is by no means a necessary indication of thermodynamic instability, as the alumina conversion of isolable V to reactive IV illustrates. However, the properties of IV, including the normal chemical shift of the cyclöoctatetraene protons in the n.m.r., certainly imply that it is not a new aromatic system. The chief piece of data suggesting some conjugative stabilization is our observation that IV is quite basic. It can be extracted from $CHCl_3$ solution with 65% H_2SO_4, and recovered unchanged (n.m.r.) on neutralization. The u.v. spectrum of IV has a maximum at 262 mμ, log ε ∼ 4, (heptane) or 272 mμ (H_2O) but it shifts to 296 mμ (65% H_2SO_4) or 298 mμ (97% H_2SO_4). The u.v. spectra in H_2O of varying acid concentrations give a rough titration curve whose midpoint, at 39% H_2SO_4, corresponds to a pK_a of -2.3 ± 0.2, which is consistent$^{(4)}$ with the extraction evidence. For comparison, the $pK_a$$^{(5)}$

of diphenylcyclopropenone is -2.5, that⁽⁶⁾ of dipropylcyclopropenone is -1.9, while the pK_a of 2-pentyl-3-methylcyclopentenone is -3.6. Thus there may be some special conjugative stabilization of the protonated ketone.

This is not an ideal case in which to test the fused-ring hypothesis, since electron delocalization in IV would require flattening of the COT ring and charge separation. However, it does suggest at least some limitations on our ability to produce stable compounds by fusing two anti-aromatic rings.(7)

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(7) We would like to acknowledge general support of this work by the National Science Foundation and the California Research Corporation, and an NSF Fellowship to William Vitale.