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A STABLE DERIVATIVE OF THE PSEUDOAROMATIC s-INDACENE

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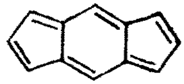
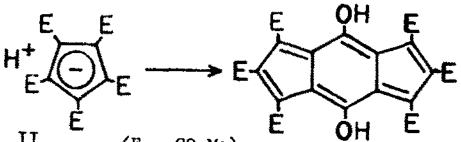
The recent preparation of the unstable pseudoaromatic, s-indacene, I, (1) has confirmed theoretical predictions (2,3) that this hydrocarbon should be quite reactive toward both electrophilic and nucleophilic attack. However, as with many unstable hydrocarbons, replacing hydrogens with certain stabilizing substituents can result in isolatable compounds. We have found such a derivative of s-indacene in the compound III, a deep red-green crystalline solid, m.p. 257-259° [Found: C, 54.39; H, 3.91; m.w., 546] (4) readily prepared in 40% yield by fusing pentacarbomethoxycyclopentadiene, II, (5) at 150-160° for 100 minutes. The infrared spectrum of III exhibit absorption bands at $\lambda_{max}^{HCCl_3}$ 4.05μ (-OH···O=C), 5.75 (ester), and 6.27 (C=C). The p.m.r. spectrum confirms the presence of strongly hydrogen bonded protons with a downfield absorption at τ = -6.05 [2H], while the two different types of carbomethoxy protons absorb at τ = 6.08 [12H] and 6.23 [6H]. III exhibits extensive absorption throughout the ultra-violet, visible and near-infrared regions: $\lambda_{max}^{CH_2Cl_2}$ mμ (log ϵ) 232 (4.36), 287 (4.68), 305 sh (4.59), 345 (4.81), 386 (3.87), 451 sh (3.84), 479 (4.29), 513 (4.63), 700 (2.59). The absorption maximum at 700 mμ tails off into the near infrared having a log ϵ = 2.43 at 800 mμ and a log ϵ = 1.49 at 900 mμ. This trailing off



I

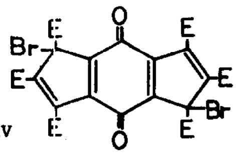


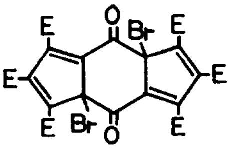
II (E = CO_2Me) III

into the near-infrared of the longest wave-length absorption peak is characteristic of several other pseudoaromatic compounds (6). While the rest of the spectrum remains essentially unchanged, the long wave-length absorption is sensitive to solvent exhibiting a long hypsochromic shift from 700 mμ in dichloromethane to 590 mμ in the more polar acetonitrile.

III forms in a 69% yield a dark red-orange 1:1 adduct of trinitrofluorenone, m.p. 239-241° [Found: C, 53.08; H, 3.49; N, 3.64]. The trinitrofluorenone is only weakly complexed, converting readily to III and TNF upon recrystallization.

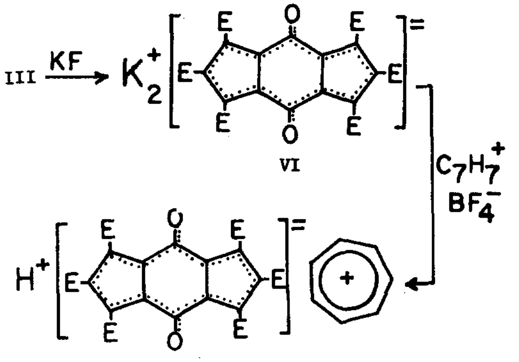
N-Bromosuccinimide converts III in a 77% yield to an extremely light-sensitive orange dibromo derivative, m.p. 213-215° [Found: C, 41.51; H, 2.77; Br, 24.13, m.w., 680, 693]. The infrared spectrum [$\lambda_{max}^{HCCl_3}$ 5.66μ (α-bromo ester carbonyl); 5.75, 5.82μ (α,β-unsaturated ester carbonyl); 6.01μ (quinone carbonyl), 6.25μ (C=C)] and p.m.r. spectrum [three different carbomethoxy proton, τ = 6.00, 6.13, 6.20, of equal intensity] favors the formulation IV, however, another structure, V, cannot be ruled out.


IV


V

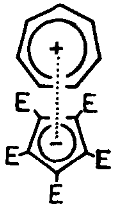
The yellow-orange dipotassium salt VI, m.p. > 360° [Found: C, 47.30; H, 3.17. Infrared: λ_{max}^{KBr} 5.77, 5.92, 6.02, 6.25μ. Ultraviolet-visible: $\lambda_{max}^{H_2O}$ mμ (log ε) 254 (4.64), 323 (5.62), 403 (3.98), 465 sh (3.20)] is readily prepared in an 84% yield by treating III with a methanolic solution of potassium fluoride (7).

If the dipotassium salt VI is treated with tropylium fluoroborate, the dark brownish-green monotropylium salt, VII, m.p. 191-192° [Found: C, 59.57; H, 4.41. Infrared: λ_{max}^{KBr} 5.81, 5.89, 6.24μ. P.M.R.: tropylium protons at τ = 0.8, carbomethoxy protons at τ = 6.22 and 6.35] is formed. With the



VI

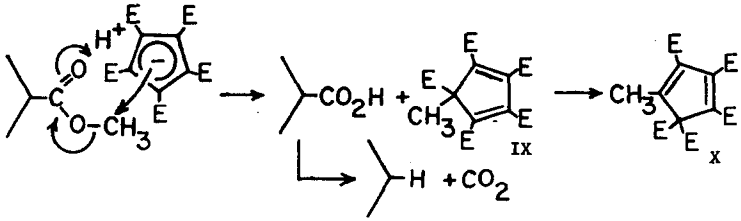
VII



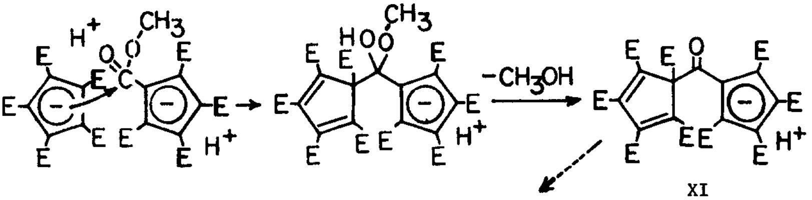
VIII

exception of a shoulder at 800 mμ, the ultraviolet-visible spectrum of VII [$\lambda_{max}^{CH_2Cl_2}$ mμ (log ε) 234 (4.32), 287 (4.64), 300 sh (4.57), 342 sh (3.61), 387 (3.73), 452 sh (3.83), 480 (4.25), 515 (4.80), 618 (3.02), 800 sh (2.33), with extensive tailing into the near-infrared, e.g., 900 mμ (log ε = 1.57)] is quite similar to that of III. The appearance of the 800 mμ absorption in VII may be a result of a charge-transfer transition in view of its similarity to the salt VIII which we have shown possesses a charge-transfer absorption band (8).

While the mechanism of formation of III from II remains unclear, identification of several by-products from this reaction [carbon dioxide, methanol, IX (5), and what appears to be a rearranged product of IX tentatively assigned the structure X], gives a clue to some of the intermediate steps in this strongly acidic mixture. IX and carbon dioxide could arise by nucleophilic attack of the anion of II on a methyl carbon of a carbomethoxy group followed by decarboxylation of the demethylated moeity:



while methanol and X could arise by nucleophilic attack of the anion of II on the carbonyl carbon of a carbomethoxy group followed by elimination of methanol to give a keto-ester, like XI, which, by internal nucleophilic attack, goes on to eventually form III:



XI

III

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2. R. D. Brown, *J. Chem. Soc.*, 2391 (1951).

3. D. Peters, *J. Chem. Soc.*, 1028 (1958).

4. Melting points are corrected. The molecular weight of III was determined by the p.m.r. method of Barcza, *J. Org. Chem.*, **28**, 1914 (1963). All other molecular weights were determined using a vapor phase osmometer.

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6. (a) Heptalene: H. J. Dauben, Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4659 (1961).
   (b) Triphenylbenzopentalene: E. LeGoff, *ibid.*, **84**, 1505 (1962).
   (c) Hexaphenylpentalene: E. LeGoff, *ibid.*, **84**, 3975 (1962).

7. Because of the strong hydrogen-bonding ability of fluoride anion, fluoride salts will function as bases and can be used to prepare alkali metal salts of compounds which are sensitive to bases such as hydroxides and carbonates; see reference 6c.

8. E. LeGoff and R. B. LaCount, *J. Am. Chem. Soc.*, **85**, 1354 (1963).