COMMUNICATIONS TO THE EDITOR

SYNTHESIS OF TROPONE

Sir:

Indications of aromaticity in the tropolones^{1a} and in azulene^{1b} direct attention to the need for determining the necessary minimum structural features for and the nature of this property in sevenmembered ring systems. We wish to report the synthesis of 2,4,6-cycloheptatrien-1-one (tropone) $(I)^2$ and evidence bearing on its aromatic character.



2-Cyclohepten-1-one on treatment with four equivalents of bromine in acetic acid and heating for fifteen hours yields 38% 2,4,7-tribromotropone, cream needles (MeOH), m.p. $182-183^{\circ}$ (calcd. for $C_7H_3OBr_3$: C, 24.51; H, 0.88; Br, 69.93. Found: C, 24.61; H, 1.11; Br, 70.80) (u.v. max. (EtOH): 275 m μ (22,100), 345 m μ (9400)), which absorbs (Pd-BaSO₄, EtOH) 6.0 moles of hydrogen to give cycloheptanone, is inert to ethanolic silver nitrate, and dissolves in ethanolic sodium hydroxide to furnish 88% dibromobenzoic acid(s), hydrogenolyzed to benzoic acid or fractionally crystallized to 2,5dibromobenzoic acid.

Hydrogenolysis of tribromotropone in absolute ethanolic potassium acetate using poisoned palladium-barium sulfate catalyst interrupted at 2.9 moles yields 95% ionic bromine and 40% tropone (I), b.p. 104–105.5° (10 mm.), n^{25} D 1.6070, viscous, almost colorless, hygroscopic (limited analyses to ca. C_7H_6O), (u.v. max. (HOH): 225 mµ (21,200); 228 m μ (22,100); 231.5 m μ (22,100); 239 m μ (12,700); 304 m μ inflection (8000); 312.5 m μ (8400)), (i.r. max.(liq.), 5-8 μ region; 5.86 μ (m); 6.09μ (s); 6.35μ (s); 6.60μ (s); 6.75μ (s); 7.98μ (s); 8.22 μ (s). Reactions of tropone: (i) salt formation: hydrochloride, white hygroscopic needles by ether-hydrogen chloride and sublimation; picrylsulfonate, m.p. 266-267°, pale needles from aqueous picrylsulfonic acid (calcd. for $C_{18}H_9O_{10}$ -N₈S: C, 39.10; H, 2.27. Found: C, 38.93; H, 2.54); dipicrate, m.p. 100–101°, yellow needles from aqueous picric acid, (calcd. for $C_{19}H_6O_{18}N_6$: C, 40.43; H, 2.14. Found: C, 39.99; H, 2.44); (ii) hydrogenation: (Pd-BaSO₄, EtOH) 3.0 moles (only) in 17 min. to give 91% cycloheptanone; (PtO₂, HOAc) 4.0 moles in 28 min.; (iii) carbonyl reactions: no 2,4-dinitrophenylhydrazone in ethanol-sulfuric acid or acetic acid; hydroxylamine consumption (titration) only on heating (0.67 equiv., 2 hr.); (iv) ring reactions: aqueous permanganate, rapidly decolorized; benzenediazonium chloride in aqueous sodium acetate, immediate orange pre-

Pertinent references in (a) M. J. S. Dewar, Nature, 166, 790 (1950);
(b) A. G. Anderson, Jr. and J. A. Nelson, THIS JOURNAL, 72, 3824 (1950).

(2) Cf. 4,5-benztropone, J. Thiele and E. Weitz, Ann., 377, 1 (1910).

cipitate; bromination at 25°, moderately rapid in water, slower in aqueous acetic acid, very slow in carbon tetrachloride, to give addition products which eliminate hydrogen bromide partially during preparation but more readily on heating to furnish crystalline bromotropones.

These reactions and properties of tropone resemble strikingly those of its isostere, 4-pyrone, and this similarity suggests that aromatic character in tropone may originate from analogous carbonyl polarization (II) and resonance of six π -electrons among seven π -orbitals (III). This system would acquire a benzene-like $2p_{\pi}$ molecular orbital energy pattern which has been considered³ as being largely responsible for aromatic behavior. Aromaticity in tropolone and azulene may arise from this type of resonance, stabilized by exocyclic structural features, or from other types.

(3) Cf. F. O. Rice and E. Teller, "The Structure of Matter," John Wiley and Sons, New York, N. Y., 1949, p. 107.

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CYCLOHEPTATRIENYLIUM OXIDE

Sir:

The general molecular orbital theory ascribing peculiar stability to cyclic molecular orbitals containing 2 + 4n electrons¹ has, among others, the corollary that the cycloheptatrienylium ion (I) should be more stable than the cyclopentadienylium ion (II) whereas the stability of the anions, $C_7H_7^$ and $C_5H_5^-$, should be reversed. We have now synthesized C_7H_6O (III) and found its properties to be represented by the structure cycloheptatrienylium oxide (IIIa) in accord with the theory.



Hydroxycycloheptatrienylium bromide (IV) is obtained from methoxytropilidene, prepared by the photochemical decomposition of diazomethane in anisole, by treatment with one equivalent of bromine, either directly or after preliminary acid hydrolysis to cycloheptadienone. IV is a colorless, sublimable salt from which aqueous sodium bicarbonate liberates III: m.p. -8 to -5° ; b.p. 113° at 15 mm.; n^{22} D 1.6172; d^{22}_4 1.095; $M_{\rm D}$ 33.9 (calcd. for "cycloheptatrienone" (IIIb), 30.9); C, 79.07; H, 5.88; miscible with water; crystallizable from ether. III is reconverted to IV with hydrogen bromide and forms a picrate: m.p. 99–100°; C, 46.65; H, 2.84. The infrared spectrum (we thank Mr. Alfred P. Wolf, Columbia University)

(1) E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, pp. 71-85.