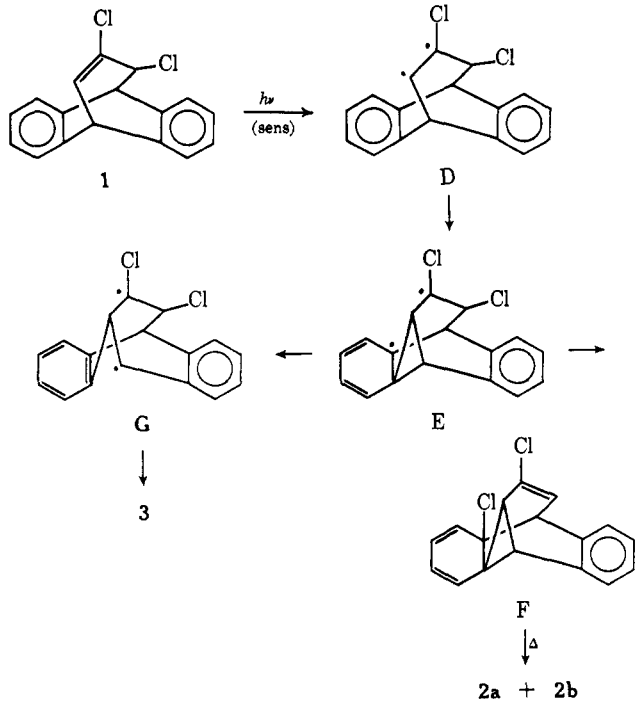
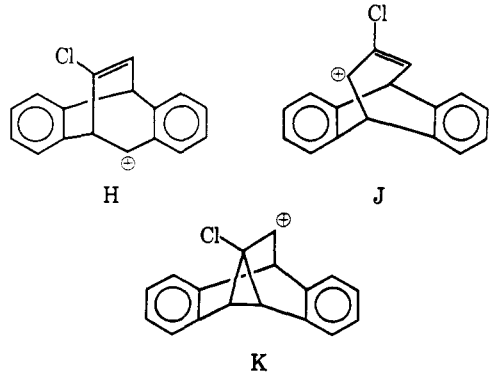
Scheme II



Scheme II. While benzo–vinyl bridging may account for the formation of **3**, it appears less likely for the formation of intermediate F, precursor of **2**.[14] Further, since **2** is the initially formed and predominant product (**3** being formed only to a small extent late in the reaction), it appears that this pathway is at best of minor importance.

It seems to us that the data compel a new mechanism for this reaction. A path in which photosensitization leads to a triplet state of **1** which then ionizes to a triplet carbonium ion–chloride ion ion pair seems energetically unattractive. However, the triplet state of **1** could decay to a vibrationally excited singlet[15–17] which then dissociates to a [R^+Cl^-] ion pair. This ion pair could recombine to give the thermodynamically unstable **2** isomers. It was shown[2] that cation H is more stable than J or K, and that kinetic products formed from this ion manifold are derived largely from H, while thermo-



dynamic products are formed from J and K. It is reasonable that the ion manifold produced photochemically should be similar to that produced in solvolytic reactions and that capture from this manifold should lead to the **2** epimers rather than to **1** or **3**.

Reports of photochemical reactions involving ionic intermediates (rather than zwitterions) are now beginning to appear.[18–20] In the present case one may speculate that the twisted aliphatic double bond (striving to become orthogonal in its π,π^* state) may aid the heterolytic departure of chloride ion.

We are investigating other cases to test predictions based upon the ionic mechanism.

(14) Preliminary work on the photorearrangement of the methanesulfonate of 3-chloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-3,6,8-trienol-2 vitiates this mechanism.
(15) Reference 8, pp 186–190.
(16) D. I. Schuster, B. R. Sckolnick, and F. H. Lee, *J. Amer. Chem. Soc.*, **90**, 1300 (1968).
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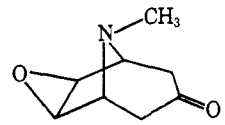
4,5-Homotropone

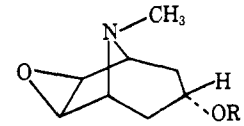
Sir:

Substantial interest has been shown recently in the chemistry of homoaromatic systems[1] and in the facile Cope rearrangements of *cis*-1,2-divinylcyclopropanes.[2] We wish to report the synthesis of 4,5-homotropone which is both a homoaromatic system and a *cis*-divinylcyclopropane. The synthesis of 2,3-homotropone has been described by Holmes and Pettit.[3]

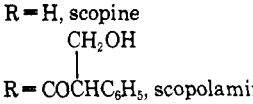
Our approach to the synthesis of 4,5-homotropone was based on the observation by Meinwald, *et al.*, that base-catalyzed degradation of tropinone methiodide gave a mixture of cycloheptadienones.[4] This approach takes advantage of the plane of symmetry in the final product and provides the first route to derivatives of scopinone, scopine, and scopolamine in which the oxirane oxygen has been replaced by a methylene group. Success in our pilot synthesis of 4,5-trimethylenetropone[5] and the availability of *cis*-cyclopropane-



scopinone



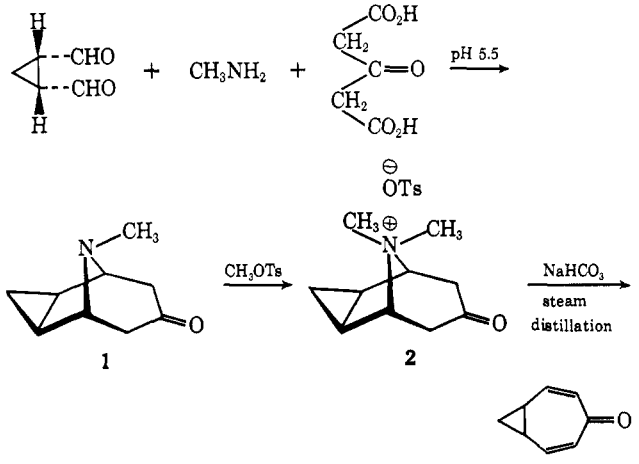
R = H, scopine



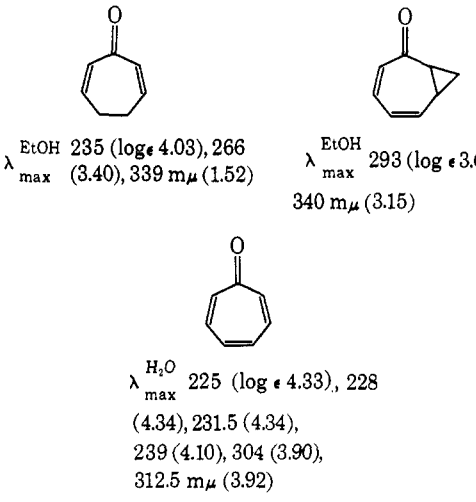
1,2-dicarboxaldehyde[6] encouraged us to undertake the synthesis of 4,5-homotropone *via* amino ketone **1**.

(1) For a review see S. Winstein, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 5.
(2) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); (b) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963); (c) G. Schröder, *Angew. Chem.*, **75**, 722 (1963); (d) M. Saunders, *Tetrahedron Letters*, 1699 (1963); (e) R. Merenyi, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **97**, 3150 (1964); (f) J. B. Lambert, *Tetrahedron Letters*, 1901 (1963); (g) J. M. Brown, *Chem. Commun.*, 226 (1965); (h) E. Vogel, R. Erg, G. Lenz, and A. Bothnerby, *Ann. Chem.*, **682**, 1 (1965); (i) M. Simonetta, G. Favini, C. Mariani, and P. Gramaccioni, *J. Amer. Chem. Soc.*, **90**, 1280 (1968); (j) O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968).
(3) J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963).
(4) J. Meinwald, S. L. Emmerman, N. C. Yang, and G. Büchi, *ibid.*, 77, 4401 (1955).
(5) O. L. Chapman and T. H. Koch, *J. Org. Chem.*, **31**, 1042 (1966).
(6) G. Maier and T. Sayrac, *Chem. Ber.*, **101**, 1354 (1968).

A solution of *cis*-cyclopropane-1,2-dicarboxaldehyde was prepared by warming (steam bath) 2,4-dimethoxy-3-oxabicyclo[3.1.0]hexane (6.48 g) with 0.1 *N* sulfuric acid (65 ml).[6] The aqueous solution of the aldehyde was added to a solution of acetonedicarboxylic acid (11.68 g), methylamine hydrochloride (5.4 g), and sodium dihydrogen phosphate (10 g) in water (2 l.). The solution was brought to pH 5.5 with saturated sodium carbonate solution and then stirred 3 days at room temperature. The solution was made basic (pH 10) with solid sodium carbonate and continuously extracted with ether. Evaporation of the ether after drying gave crude amino ketone **1** (94%) which crystallized. Sublimation (room temperature, 0.15 mm) gave the pure product (72%), mp 69–70°. The stereochemistry of the amino ketone (methylene bridge *cis* to the nitrogen bridge) was assigned by analogy to other products derived from Robinson–Schöpf condensation.[7,8] All such condensations involving *erythro*-2,3-disubstituted succindialdehydes for which the product stereochemistry is known give *cis,exo* products.[7] Direct evidence for the stereochemical assignment comes from the vigorous conditions necessary to quaternize the amino ketone. The amino ketone **1**, (5.06 g) was heated (96°) for 8 hr



in methyl tosylate (25 ml). Filtration and ether washing gave the quaternary tosylate **2** (10.33 g, 88%), mp 172.5–173.5°. A solution of quaternary tosylate **2** (12.12 g) and sodium bicarbonate (25 g) in water (25 ml) was steam distilled. Saturation of the steam distillate with sodium chloride, continuous ether extraction, successive washing with 5% hydrochloric acid and 5% sodium bicarbonate solution, drying ($MgSO_4$), and removal of the ether gave 4,5-homotropone (**3**, 2.11 g, 49%). The crude product was a mobile liquid and quite pure. Final purification was achieved by reduced-pressure distillation or collection from a vapor chromatograph. The infrared spectrum of 4,5-homotropone shows significant bands at λ_{max}^{neat} 3.32 (CH), 6.06 (C=O), 6.24 (C=C), 13.3 (*cis* -HC=CH-), and 14.1 μ (*cis* -HC=CH-). The ultraviolet spectrum, λ_{max}^{EtOH} 264 (log ϵ 3.88), 290 mμ (sh, 3.66), $\lambda_{max}^{cyclohexane}$ 248 (3.89), 275 (sh, 3.65), 360 (1.52), 390 (sh, 1.29), 410 mμ (sh, 0.80), suggests that there is relatively little delocalization through the cyclopropane ring. The ultraviolet absorption maxima of a few model systems

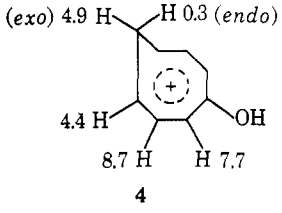


λ_{max}^{EtOH} 235 (log ϵ 4.03), 266 (3.40), 339 mμ (1.52)

λ_{max}^{EtOH} 293 (log ϵ 3.65), 340 mμ (3.15)

$\lambda_{max}^{H_2O}$ 225 (log ϵ 4.33), 228 (4.34), 231.5 (4.34), 239 (4.10), 304 (3.90), 312.5 mμ (3.92)

are given above for comparison. The nuclear magnetic resonance spectrum of 4,5-homotropone in carbon disulfide is unchanged from +40 to −55° and shows multiplets at δ 6.65 (2 H), 5.75 (2 H), 1.9 (3 H), and 0.45 (1 H). The coupling constant for the olefinic protons ($^3J \approx 12.5$ Hz) is in accord with expectation.[5,9] The fact that the nmr spectrum does not change over a 95° temperature range shows that 4,5-homotropone does not exhibit the facile Cope rearrangements common to many *cis*-1,2-divinylcyclopropanes. The nmr spectrum of 4,5-homotropone in sulfuric acid shows dramatic shifts in accord with expectation for the 4-hydroxyhomotropylium cation (**4**).[1,3,10] The large



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chemical shift difference, 4.6 ppm, between the two protons of the methylene group shows a high degree of delocalization in the 4-hydroxyhomotropylium cation. The mass spectrum of 4,5-homotropone shows a parent ion at *m/e* 120 (17.4%), an ion at *m/e* 92 (100%) due to loss of carbon monoxide, and an ion at *m/e* 91 (70.2%) due to further loss of a hydrogen atom. Appropriate metastable ions (*m/e* 70, 90) are observed for the 120 → 92 and 92 → 91 processes.

The most remarkable feature of 4,5-homotropone is its thermal stability. A Cope rearrangement in 4,5-homotropone would lead to a cyclopropanone derivative, and the thermal stability of 4,5-homotropone at room temperature may be ascribed to the greater energy requirement for formation of a cyclopropanone rather than a cyclopropane.

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(8) For references to the condensation see R. Robinson, *J. Chem. Soc.*, **111**, 762 (1917), and C. Schöpf and G. Lehmann, *Ann. Chem.*, **518**, 1 (1935).

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