bond is *concerted* with the cyclopropane opening. This question is considered in the following communication.[10]

Acknowledgment. The support of this work by the National Science Foundation is gratefully acknowledged.

(10) G. Stork and M. Gregson, *J. Am. Chem. Soc.*, **91**, 2373 (1969).

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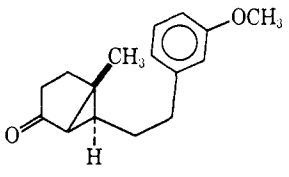
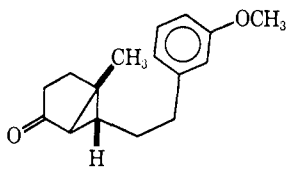
Aryl Participation in Concerted Cyclization of Cyclopropyl Ketones

Sir:

We have shown in the preceding communication[1] that a double bond may become involved in the acid-catalyzed opening of a suitably constituted cyclopropyl ketone. We now present evidence that this involvement is *concerted* with the breaking of the cyclopropyl bond.

In order to investigate this important mechanistic point, we chose a system which would lead to a bicyclic cation which would not be expected to become involved in structural rearrangements. The systems I and II appeared ideally suited to this purpose, especially


I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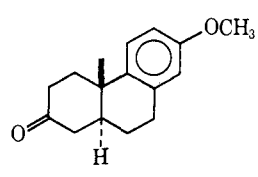
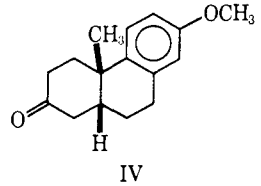

III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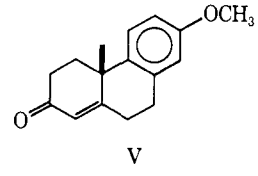
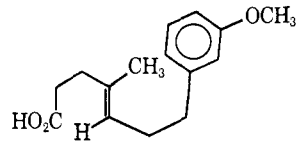
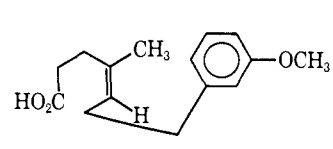
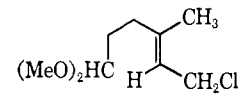

V

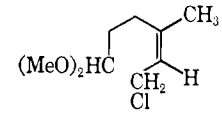
since the two most informative products (III and IV) from their cyclization were readily available from the well-known tricyclic ketone V.[2]

The preparation of I and II by the internal diazo ketone addition[3] required the pure geometric isomers VI and VII. These were prepared from geraniol and nerol, respectively, by the general synthesis we have described elsewhere involving the coupling of *m*-methoxybenzylmagnesium bromide with the chlorides VIII and IX[4] derived from geraniol and nerol, respectively,[5] followed by hydrolysis (20 ml of acetic acid, 15 ml of


VI

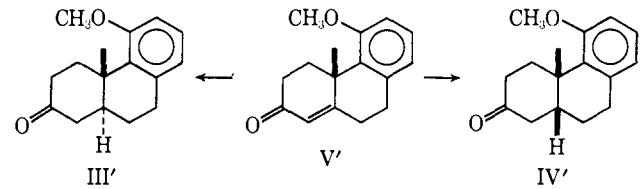

VII


VIII


IX

water, and 1.2 g of sodium acetate; 0.5 hr on a steam bath) and oxidation (silver nitrate in aqueous ethanol; slow addition of 1 *N* sodium hydroxide to pH 9; 60–70°; 1 hr). The two acids were converted to the cyclopropyl ketones I and II in the usual way.[1] The two cyclopropyl ketones I and II, obtained essentially pure after chromatography on silica gel, had very similar spectral characteristics but could readily be differentiated by vpc: the retention time of I was about 1 min longer (co-injection) than that of II on SF 96 at 210°. The homogeneity of I and II also follows from the results of acid cyclization, below.[6] Cyclization of I and II was carried out by allowing each isomer (200 mg) to stand at room temperature overnight with 3 ml of benzene containing 0.1 ml of stannic chloride and 10 μl of water. No starting material was left and the products (~80% yield) from I turned out to be a mixture of III and III′ (~5:1), while from II only IV and IV′ were obtained. The identity of these substances was established as follows.

The mixture from the cyclization of I was resolved by vpc on SF 96 into two components which were separately collected. The lower retention time (minor) substance proved to be III′ by comparison of spectral properties and vpc behavior (co-injection) with the lithium–ammonia reduction product of V′.[7] The


III′ V′ IV′

longer retention isomer was identical with the known ketone III from the lithium–ammonia reduction of V.[8]

Similar separation of the two components obtained from II also gave a lower retention component (minor) which proved to be IV′ (identical with the catalytic hydrogenation product from V′), while the second isomer turned out to be IV (also formed by catalytic hydrogenation of V).

The important fact is that the *cis*-cyclopropyl ketone II gave only *cis*, and the *trans*-cyclopropyl ketone I only *trans* cyclized products. To the extent that cyclization accompanies cyclopropyl ring opening it is, therefore, a concerted reaction.

(1) G. Stork and M. Marx, *J. Am. Chem. Soc.*, **91**, 2371 (1969).
(2) G. Stork, A. Meisels, and J. Davies, *ibid.*, **85**, 3419 (1963).
(3) G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961).
(4) G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Letters*, in press.
(5) G. Stork, M. Gregson, and P. A. Grieco, *ibid.*, in press.
(6) It is worth noting that the fact that the internal diazo ketone addition[3] gives two different cyclopropyl ketones from the two isomeric diazo ketones derived from VI and VII demonstrates the (expected) stereospecificity of this reaction.
(7) D. A. H. Taylor, *W. African J. Biol. Appl. Chem.*, 7, 14 (1963).
(8) M. E. Kuehne, *J. Am. Chem. Soc.*, **83**, 1492 (1961).

Acknowledgment. The support of this work by the National Science Foundation is gratefully acknowledged.

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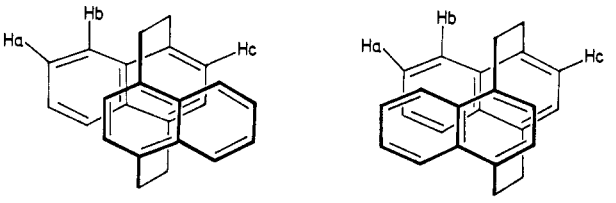
syn-[2.2]Paracyclonaphthane

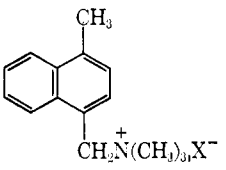
Sir:

The *syn*- and *anti*-[2,2]paracyclonaphthanes Ib and Ia are of special interest as potential substrates for a comparative study of transannular electronic and steric effects in the cyclophanes. To date, however, only *anti* forms have been isolated in systems of this type.[1-3] Thus, in the preparation of [2.2]paracyclonaphthane

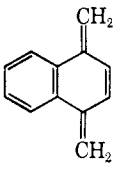


Ia

Ib



IIa, X = Br
b, X = OH



III

from the quaternary salt IIa, Cram[1] found that the dimerization of the naphthoquinodimethide intermediate III in toluene leads exclusively to the *anti* isomer Ia. Likewise, in an alternate solvolytic method[2] recently described for the generation of III, only the *anti* structure Ia was formed. We now wish to report the isolation of the *syn* form of [2.2]paracyclonaphthane (Ib) by a modification of earlier procedures[1,3] which employs a somewhat higher temperature for the decomposition of the quaternary hydroxide IIb.

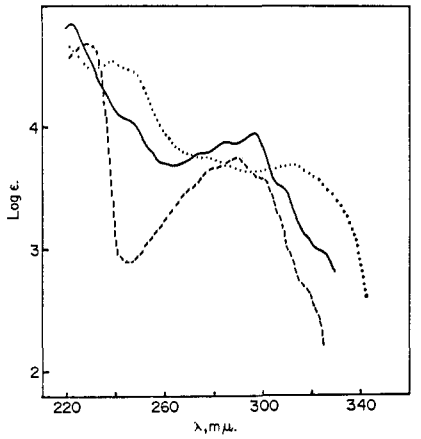


Figure 1. Ultraviolet absorption spectra in 95% ethanol of *syn*-[2.2]paracyclonaphthane (Ib) (————), *anti*-[2.2]paracyclonaphthane (Ia) (. . . . . .), and 1,4-dimethylnaphthalene (- - - -).

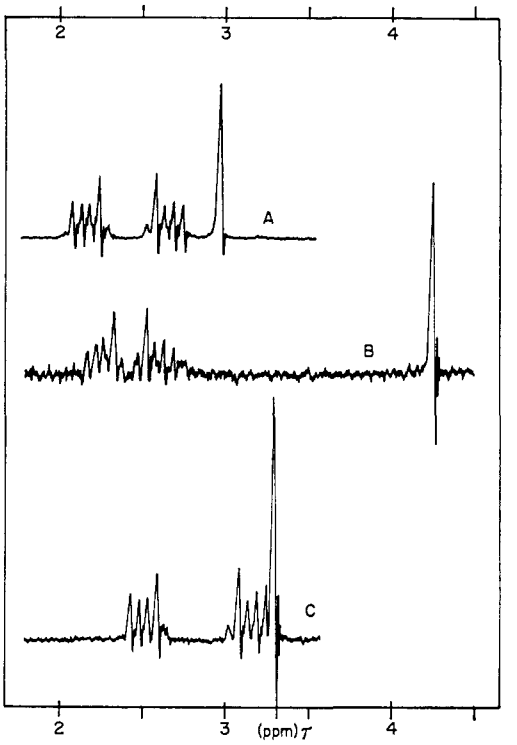
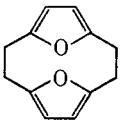


Figure 2. Nmr spectra (60 Mc) of (A) 1,4-dimethylnaphthalene, (B) *anti*-[2.2]paracyclonaphthane (Ia), and (C) *syn*-[2.2]paracyclonaphthane (Ib).

Treatment of the quaternary bromide IIa (58.8 g, 0.2 mol) with silver oxide (46 g, 0.2 mol) for 24 hr in the usual manner[1] followed by filtration and azeotropic removal of water in 3 l. of xylene[4] for 12 hr in the presence of phenothiazine (1 g) afforded a solution which was filtered to remove polymer. The filtrate was evaporated to dryness and the residue chromatographed on silica gel. Continuous elution with hexane afforded, first, 12.6 g (41%) of the *anti* isomer Ia, followed by fractions containing a mixture of *syn* and *anti* isomers. Fractional crystallization of these fractions from benzene and chromatography on preparative thin layer plates in hexane gave 1.3 g (4.1%) of pure Ib. The *syn* isomer crystallizes from benzene as white prisms, mp 243–245°. *Anal.* Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.35; H, 6.71. The *syn* structure was established by the spectroscopic data outlined below and confirmed by an independent X-ray crystallographic analysis.[5]

(1) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Amer. Chem. Soc.*, **85**, 1088 (1963).
(2) G. W. Brown and F. Sondheimer, *ibid.*, **89**, 7116 (1967).
(3) The related heterocyclophane i has been assumed to have an *anti* structure based on infrared and Raman spectral measurements: H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1928 (1960).



i

(4) Use of toluene as the medium for the thermal decomposition-dimerization phase of the reaction yielded only *anti* isomer, as reported.[1]