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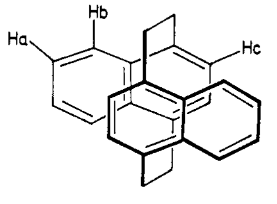
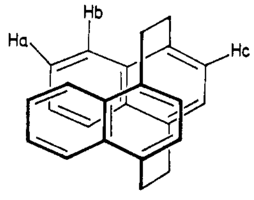
syn-[2.2]Paracyclonaphthane

Sir:

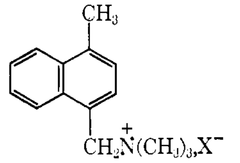
The *syn*- and *anti*-[2,2]paracyclonaphthanes Ib and Ia are of special interest as potential substrates for a comparative study of transannular electronic and steric effects in the cyclophanes. To date, however, only *anti* forms have been isolated in systems of this type.[1-3] Thus, in the preparation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



Ia

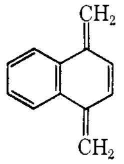


Ib



CH_3 / $CH_2\overset{+}{N}(CH_3)_3X^-$

IIa, X = Br
b, X = OH



CH_2 / CH_2

III

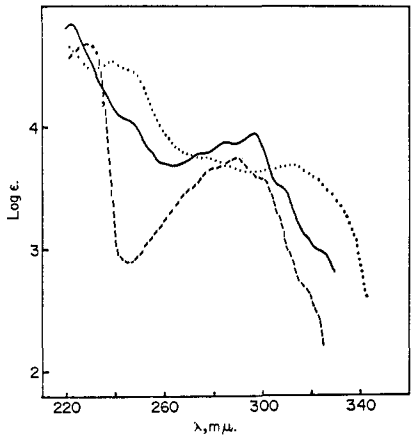


Figure 1. Ultraviolet absorption spectra in 95% ethanol of *syn*-[2.2]paracyclonaphthane (Ib) (————), *anti*-[2.2]paracyclonaphthane (Ia) (. . . . . . .), and 1,4-dimethylnaphthalene (- - - -).

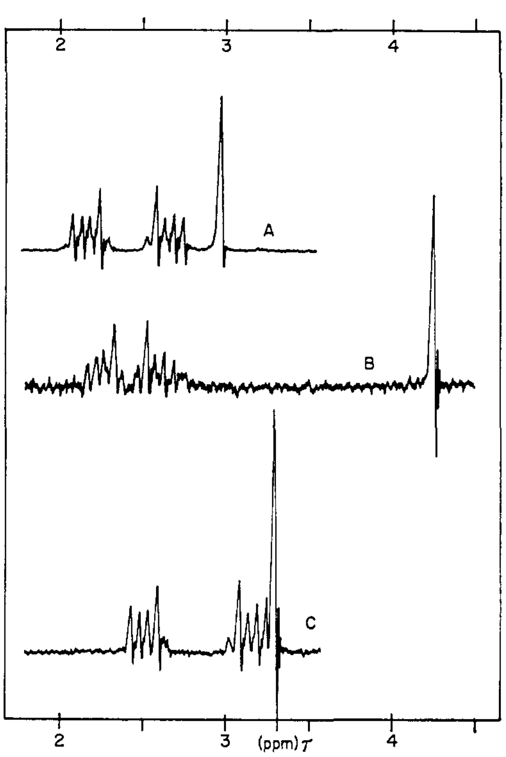


Figure 2. Nmr spectra (60 Mc) of (A) 1,4-dimethylnaphthalene, (B) *anti*-[2.2]paracyclonaphthane (Ia), and (C) *syn*-[2.2]paracyclonaphthane (Ib).

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]

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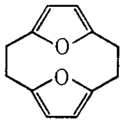
(1) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Amer. Chem. Soc.*, **85**, 1088 (1963).

(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).



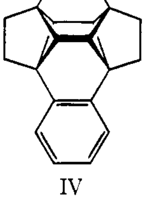
i

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

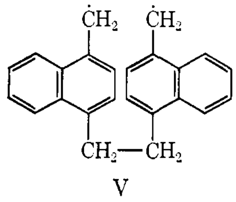
The mass spectrum shows a molecular ion peak at m/e 308 and a base peak at m/e 154. The ultraviolet spectrum (Figure 1) is strikingly similar to that of 1,4-dimethylnaphthalene and shows the typical bathochromic shifts characteristics of [2.2]cyclophanes.[6] In particular, the band at 244 mμ associated[1] with transannular effects is clearly evident.

The nmr spectrum, shown in Figure 2, provides strong support for the assigned (*syn*) structure. It is particularly interesting to compare this spectrum with the spectra of the *anti* form Ia and of 1,4-dimethylnaphthalene. As expected, the more highly shielded H_a and H_b protons of Ib show upfield absorption (symmetrical A_2B_2 multiplet, 8 H, centered at τ 2.85) compared to the H_a and H_b protons of Ia (m, 8 H, τ 2.5). The latter, in turn, have essentially the same chemical shifts as the corresponding protons of 1,4-dimethylnaphthalene. On the other hand, there is a striking difference between the peaks associated with H_c protons in the *syn* and *anti* forms. In the *anti* isomer, these H_c protons (s, 4 H, τ 4.28) are rigidly held in the fields of the transannular naphthalene nuclei and are shifted significantly upfield, while the H_c *syn* protons (s, 4 H, τ 3.28) experience relatively less shielding. The spectrum of the *syn* compound also contains a symmetrical multiplet at τ 6.42 assigned to the eight ethylene bridge protons.

When Ib is heated above its melting point, it resolidifies at 250° and remelts at 300–303°, the melting point of the *anti* form.[1] The ultraviolet and nmr spectra of the resolidified material confirm the fact that complete conversion to the *anti* isomer takes place in this thermal process. Interconversion of the *syn* and *anti* forms may also be accomplished by photochemical means. Thus, irradiation[7] of pure Ib in degassed benzene at 3500 Å for 10 days yields predominantly (*ca.* 70%) isomer Ia with only traces of *syn* material remaining.[8] On the other hand, nmr analysis of the reaction mixture from photolysis[9] of pure *anti* isomer Ia in benzene clearly shows the presence of minor amounts of *syn* product Ib along with dibenzoequinine IV[10] (25%) and unreacted Ia (70%). Conversion of Ib to Ia most probably takes place through strain-relieving rupture of the ethylene bridge to form V which may then reclose to form the more stable *anti* isomer.

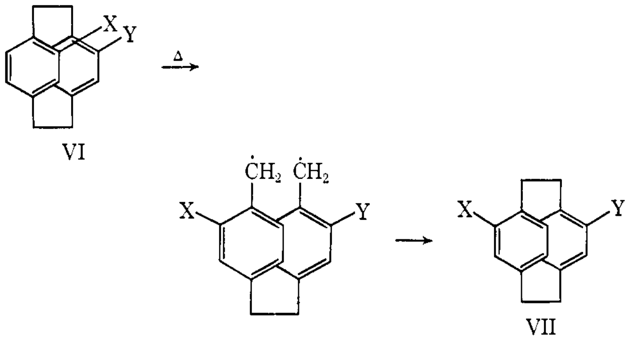


IV



V

Analogy for the formation of V may be found in the earlier work of Reich and Cram[11] who have demonstrated that thermal cleavage to biradical intermediates occurs in substituted [2.2]paracyclophanes, as in the isomerization of systems VI to VII.



VI

VII

Acknowledgments. This work was supported by National Institutes of Health Grant GM 13854. We thank Dr. Walter McMurray for the mass spectrum determination.

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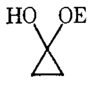
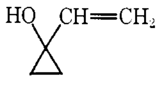
Cyclopropanone Reactions. Cyclobutanone Derivatives from Vinylic and Acetylenic Cyclopropanols

Sir:

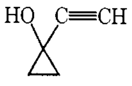
We have recently reported[1] that the ethyl hemiketal of cyclopropanone (I) provides a convenient source of the parent ketone for reactions with nucleophilic reagents. We now wish to describe examples of such reactions with vinylic and acetylenic Grignard reagents leading to novel cyclopropanol derivatives which may serve as convenient precursors of substituted cyclobutanones.



I



II



III

Addition of I[2,3] to an excess of vinylmagnesium bromide in refluxing THF yielded 1-vinylcyclopropanol (II; 64%): bp 44–51° (28 mm); nmr (CCl_4) τ 4.15–5.15 (m, 3 H), 5.55 (s, 1 H), and 9.21 (m, A_2B_2, 4 H); ir (liquid film) 3340, 3100, 3020, and 1645 cm^{-1}; mol wt (mass spectrum), 84; acetyl derivative:[4] nmr τ 4.05–4.50 (m, 1 H), 4.95–5.30 (m, 2 H), 8.08 (s, 3 H),

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[5] The X-ray structure determination by Dr. Albert Fratini, University of Dayton, will be reported separately.

[6] D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Amer. Chem. Soc.*, **76**, 6132 (1954).

[7] A Rayonet photochemical reactor was the light source.

[8] At the same time about 20% of dibenzoequinine[10] was also formed, presumably from the further photolysis of the *anti* isomer.

[9] As previously reported, the irradiation of Ia in benzene–methanol yields dibenzoequinine but no Ib.

[10] H. H. Wasserman and P. M. Keehn, *J. Amer. Chem. Soc.*, **89**, 2270 (1967).

[11] H. J. Reich and D. J. Cram, *ibid.*, **89**, 3078 (1967).

[12] National Institutes of Health Predoctoral Fellow, 1966–1968.

[1] H. H. Wasserman and D. C. Clagett, *J. Amer. Chem. Soc.*, **88**, 5368 (1966).

[2] The ethyl hemiketal may be conveniently prepared (43%) by the reaction of diazomethane with excess ketene in ether at −78°, in the presence of ethanol. Unreacted ketene is removed by extraction with aqueous bicarbonate solution. I, bp 60–62° (20 mm), may be purified by distillation and stored at 0° for several weeks without decomposition.

[3] In this work no attempt was made to generate solutions of the free ketone at low temperature as described by N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, **88**, 3672 (1966). See also S. E. Schaafsma, H. Steinberg, and T. J. DeBoer, *Rec. Trav. Chim.*, **85**, 1170 (1966).

[4] The acetate was formed by treatment of II with 1 equiv of ethylmagnesium bromide followed by acetyl chloride.