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GENERATION OF 7-METHOXYCARBONYL[5]PARACYCLOPHANE

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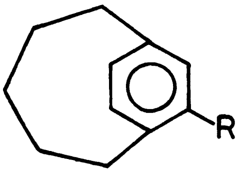
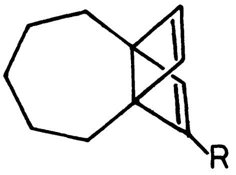
7-Methoxycarbonyl[5]paracyclophane generated by photochemical valence isomerization of 8-methoxycarbonyl[5.2.2]propella-8,10-diene has been successfully characterized by UV and ^{1}H NMR spectra.

Recently, we and Bickelhaupt succeeded in spectroscopic characterization of [5]paracyclophane (1), the smallest bridged [n]paracyclophane so far known,[1)] generated by photochemical valence isomerization of [5.2.2]propelladiene (3), the Dewar isomer of 1.[2)] However, more precise information about the present highly strained but still aromatic ring system has been keenly requested, since the out-of-plane deformation of the benzene ring of 1 should reach near the limit within which aromaticity can be kept.[1,3)] Herein we disclose the generation and characterization of 7-methoxycarbonyl[5]paracyclophane (2).



1 R=H
2 R=CO_2Me



3 R=H
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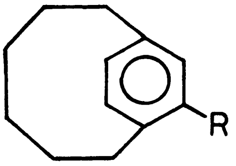


5 R=H
6 R=CO_2Me

On irradiation of a degassed hexane solution of 8-methoxycarbonyl[5.2.2]-propelladiene (4)[4)] (10^{-4} M) in a quartz cell with a low pressure mercury lamp at 0 °C, a new absorption appeared at 360 nm as shown in Fig. 1. The intensity of the absorption reached a maximum after 20 min irradiation, but on further irradiation it gradually decreased.[6)] This absorption band is attributable to

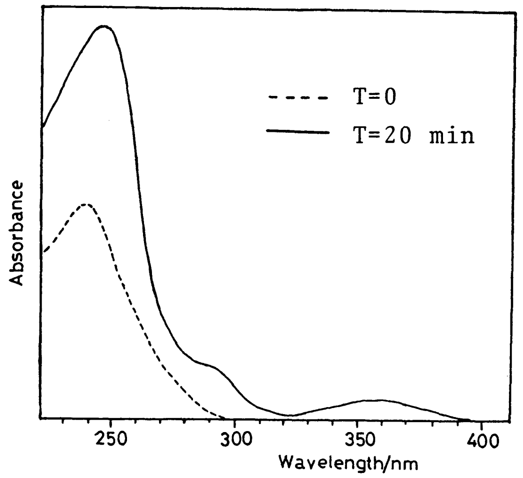
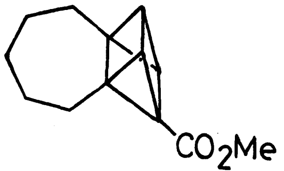


Fig. 1. Spectral change of 4 in hexane (10^{-4} M) on irradiation.



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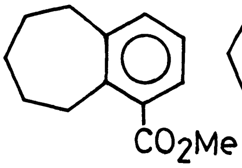

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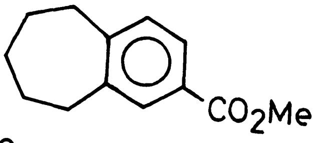

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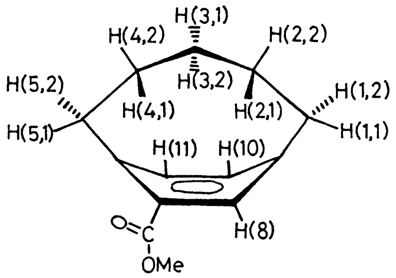
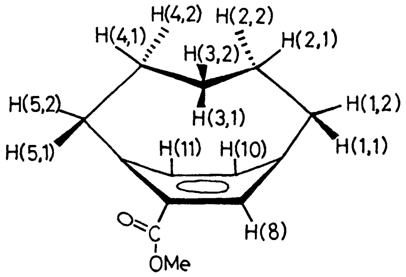
7-methoxycarbonyl[5]paracyclophane (2) in view of the difference in the absorption wave lengths between [5]paracyclophane (1) and [6]paracyclophane (5) [ca. 34 nm (observed);[2,8] 33 nm (calculated)[3b)]].[7] On standing in the dark at room temperature the absorption of 2 decreased slowly; the half-life of the decrease was measured to be about 70 h at 25 °C.[9]

The formation of 2 was confirmed by 360 MHz ^{1}H NMR spectrum measured at -60 °C. When a THF-d_8 solution of 4 was irradiated as above, the appearance of new signals assignable to two conformational isomers (2a and 2b)[10] and to prismane derivative 7[11] were observed as shown in Fig. 2. The aromatic proton H(8) of the major conformer 2a appeared at δ 8.08 as a broad singlet while that of the minor 2b at δ 8.05 as a doublet (J=1 Hz). The other aromatic protons H(10) and H(11) of both 2a and 2b were observed as a broad unresolved singlet at δ 7.55. The methyl protons of 2a and 2b appeared at δ 3.84 (s) and 3.86 (s),



2a (major)



2b (minor)

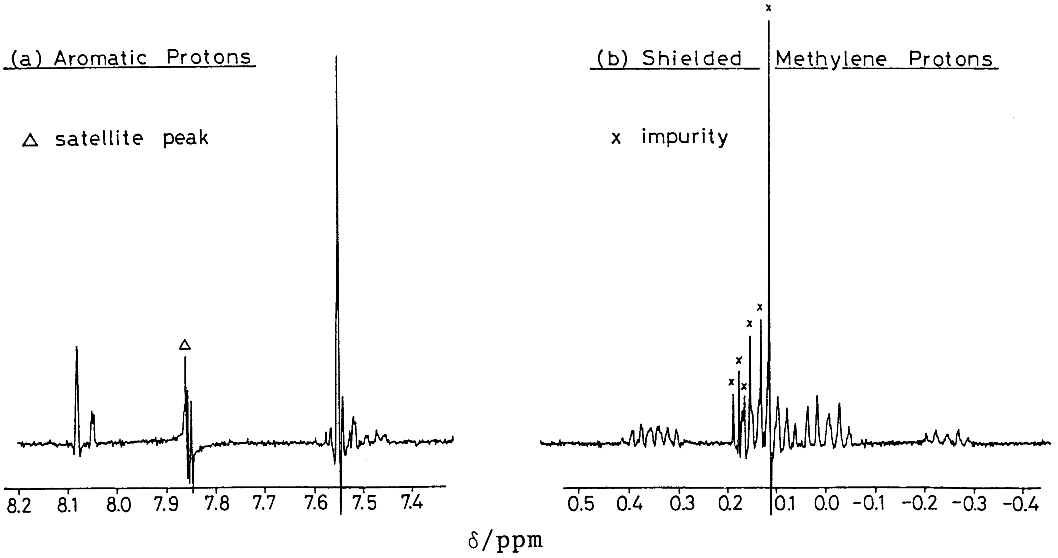


Fig. 2. ^{1}H NMR spectrum of 2 at -60 °C (THF-d_8).

respectively, in a ratio of 3:1. As for the major 2a, the benzyl proton H(1,1) could be observable at δ 2.84 (ddd, J=1, 6, 12 Hz) and H(1,2) and H(5,2) at δ 2.16 (apparent tt, J=5, 12 Hz). More importantly, the methylene protons shielded by the benzene ring were observed at considerably high fields; for 2a, the central proton H(3,2) was at δ -0.09 (apparent quintet, $J\approx7$ Hz) and the homobenzyl protons H(2,1) and H(4,1) were at δ 0.12 (apparent septet, $J\approx7$ Hz), while for 2b, H(3,1) at δ -0.25 (apparent quintet, $J\approx7$ Hz) and H(2,2) and H(4,2) at δ 0.35 (apparent septet, $J\approx7$ Hz). It was found that further irradiation gave 7 predominantly,$^{6)}$ which afforded 1- and 2-methoxycarbonylbenzocycloheptenes (8) and (9) in a ratio of 2:5 during chromatography on silica-gel.

The above results clearly indicate that 7-methoxycarbonyl[5]paracyclophane (2) is formed as an unstable aromatic intermediate and that the flipping of the methylene chain of 2 is frozen at low temperatures into two nonequivalent conformers 2a and 2b in a ratio of 3:1. Moreover, introduction of a methoxycarbonyl group on the aromatic nucleus has been shown to enhance the relative yield and stability of the strained cyclophane with highly bent benzene ring in comparison with the parent hydrocarbon.

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References

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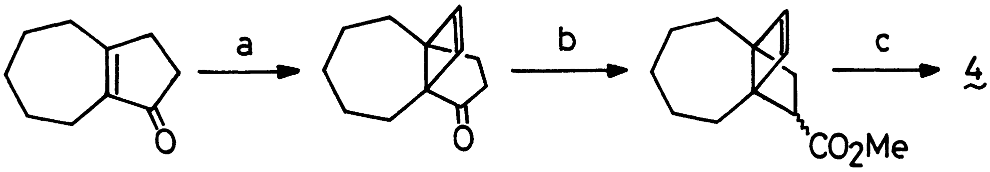
2) L. W. Jenneskens, F. J. J. de Kanter, P. A. Kraakman, L. A. M. Turkenburg, W. E. Koolhaas, W. H. de Wolf, F. Bickelhaupt, Y. Tobe, K. Kakiuchi, and Y. Odaira, J. Am. Chem. Soc., 107, 3716 (1985).

3) a) H. Wynberg, W. C. Nieuwpoort, and H. T. Jonkman, Tetrahedron Lett., 1973, 4623; b) N. L. Allinger, J. T. Sprague, and T. Liljefors, J. Am. Chem. Soc., 96, 5100 (1974); c) H. Schmidt, A. Schweig, W. Thiel, and M. Jones, Jr., Chem. Ber., 111, 1958 (1978).

4) Propelladiene 4 was prepared by the same method as the preparation of the corresponding [6.2.2]propelladiene[5] as shown below.



a i $ClHC=CHCl$, hν; ii $HOCH_2CH_2OH$, H^+; iii Na, NH_3, iv H^+; 66%.
b i HCO_2Et, NaOEt; ii TsN_3, Et_3N; iii hν, MeOH; 69%.
c i LDA, Ph_2Se_2; ii H_2O_2; 50%.

5) Y. Tobe, K. Kakiuchi, Y. Odaira, T. Hosaki, Y. Kai, and N. Kasai, J. Am. Chem. Soc., 105, 1376 (1983).

6) The maximum yield of 2 was estimated to be 14% by ^1H NMR spectra or to be 10% by UV spectra on assumption that 2 had the same absorption coefficient as that of the corresponding [6]-derivative (6)[7] at this band.

7) 8-Methoxycarbonyl[6]paracyclophane (6) showed λ_{max} (hexane) at 327 nm (ε 1170).

8) V. V. Kane, A. D. Wolf, and M. Jones, Jr., J. Am. Chem. Soc., 96, 2643 (1974).

9) The half-life of the parent hydrocarbon 1 was estimated to be about 22 h at 25 °C.

10) The assignment for the major and minor conformers 2a and 2b is based on the chemical shifts and the coupling pattern of the benzyl protons in ^1H NMR spectrum of the major one taking into account those of 1.[2] Such large bias between 2a and 2b may be due to steric repulsion between H(5,1) and the ester group in 2b.

11) The methine protons of 7 were observed at δ 2.98 (d, J=1 Hz), 2.56 (d, J=5 Hz), and 2.38 (dd, J=1, 5 Hz) and the methyl protons were at δ 3.56 (s).

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