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A NEW EFFICIENT SYNTHESIS AND REARRANGEMENTS OF [6]PARACYCLOPHANE

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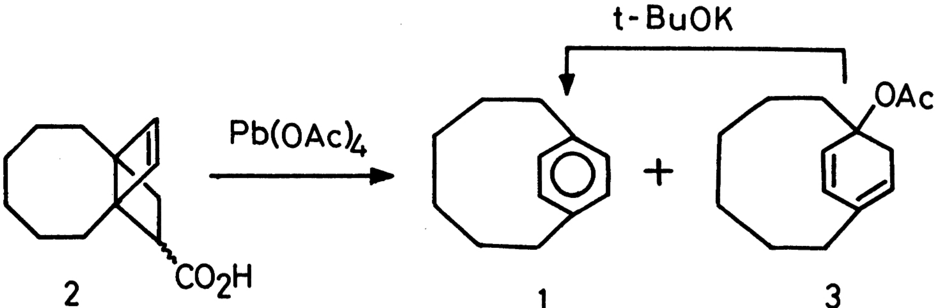
[6]paracyclophane (1) has been synthesized by oxidative decarboxylation of [6.2.2]propellenecarboxylic acid with lead tetraacetate. Vapor phase thermolysis of 1 affords 3-methylene-spiro[5.5]undeca-1,4-diene predominantly, while acid-catalyzed rearrangement of 1 gives the meta and ortho isomers in a ratio of 1:3.

Recently, we and Tochtermann et al. have developed independently new efficient routes to [6]paracyclophane derivatives having substituents on the aromatic ring[1,2a] and have found out that the benzene rings of them are highly deformed from planarity (≈20°) by means of their X-ray structure determination[1,2c] as well as that they show unusual chemical behaviors associated with the above deformation.[1,2b,d] Although the parent hydrocarbon 1 was first synthesized a decade ago,[3] the inaccesibility of 1 did not allow further investigation of the properties of 1. In this connection, we report here a new efficient synthetic route to 1 based on oxidative decarboxylation of [6.2.2]porpellenecarboxylic acid (2) by lead tetraacetate and thermal and acid-catalyzed rearrangements of 1 in order to clarify the chemical properties of 1.

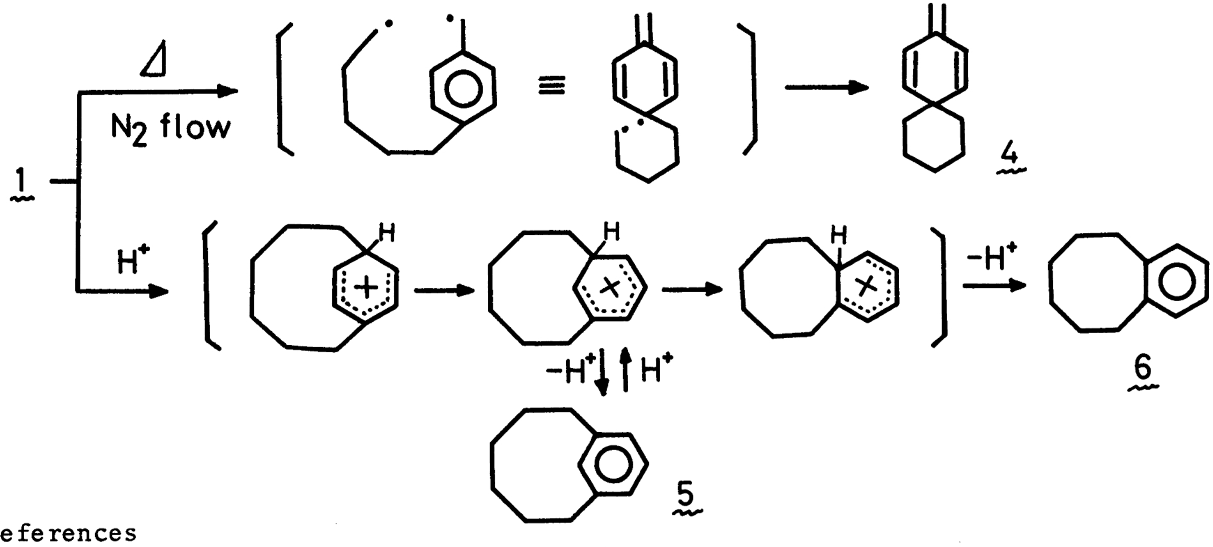
The acid 2[4] was prepared by alkaline hydrolysis of the corresponding methyl ester which was derived from bicyclo[6.3.0]undec-1(8)-en-9-one in 30% overall yield in seven steps.[1] Oxidative decarboxylation of 2 with lead tetraacetate (1.2 equiv.) in boiling benzene in the presence of pyridine (0.5 equiv.) and copper(II) acetate (0.5 equiv.) gave successfully 1 in 39% yield along with the acetate 3 in 21% yield. The structure of 1 was confirmed by the comparison with the reported UV and ^{1}H NMR data.[3a] Moreover, 3 was cleanly converted to 1 in 90% yield by treatment with potassium t-butoxide in dimethyl sulfoxide at room temperature. Thus total yield of 1 amounts to 58%.

In order to clarify the chemical properties of [6]paracyclophane system, thermally induced and acid-catalyzed rearrangements of 1 were examined.[5]



2 1 3

Thermolysis of 1 under nitrogen flow at 400 °C gave the spiro triene 4 predominantly (90%), via cleavage of the bridge at the benzyl position, together with a small amount of a few unidentified minor products.[6] Moreover, acid-catalyzed rearrangement of 1 with trifluoroacetic acid in chloroform took place smoothly to afford [6]metacyclophane (5)[7] and the ortho isomer 6 quantitatively in a ratio of 1:3.[8] Under the above conditions, 5 remained unchanged indicating that 6 is not formed via 5 but by successive 1,2-migration of the bridge, although isomerization of 5 to 6 also occurred with trifluoromethanesulfonic acid as a catalyst.[9]



References

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2) a) J. Liebe, C. Wolff, and W. Tochtermann, Tetrahedron Lett., 23, 171 (1982);
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   c) C. Krieger, J. Liebe, and W. Tochtermann, ibid., 24, 707 (1983);
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3) a) V. V. Cane, A. D. Wolf, and M. Jones, Jr., J. Am. Chem. Soc., 96, 2643 (1974); b) S. L. Kammula, L. D. Iroff, M. Jones, Jr., J. W. van Straten, W. H. de Wolf, and F. Bickelhaupt, ibid., 99, 5815 (1977).
4) All new compounds gave satisfactory analytical and spectral data. Selected data for 1, 3, and 4 are as follows:
   1: ^{13}C NMR (CDCl$_3$) δ 143.30 (s), 131.75 (d), 36.45 (t), 35.96 (t), 26.76 (t).
   3: ^{1}H NMR (CDCl$_3$) δ 0.7-2.5 (15H, m, s at 1.97), 2.48 (1H, dd, J=17 and 6 Hz), 2.87 (1H, dt, J=17 and 2 Hz), 5.68 (1H, dd, J=6 and 2 Hz), 5.98 (2H, s), ^{13}C NMR (CDCl$_3$) δ 170.21 (s), 136.60 (s), 131.26 (d), 128.47 (d), 121.28 (d), 85.27 (s), 37.53 (t), 36.06 (t), 33.32 (t), 29.40 (t), 28.82 (t), 27.40 (t), 26.71 (t), 22.51 (q).
   4: ^{1}H NMR (CDCl$_3$) δ 1.1-1.8 (10H, m), 4.77 (2H, s), 5.90, 6.15 (4H, ABq, J=10 Hz).
5) At the completion of this work, Professor Bickelhaupt informed us that he has also examined the thermal and acid-catalyzed rearrangements of 1; private communication and J. W. van Straten, Thesis, Vrije University, Amsterdam, 1978.
6) Thermolysis of the higher homologues of 4 has been shown to afford [7]- and [8]paracyclophanes; J. W. van Straten, W. H. de Wolf, and F. Bickelhaupt, Recl. Trav. Chem. Pays-Bas, 96, 88 (1977).
7) Identified with an authentic sample; S. Hirano, H. Hara, T. Hiyama, S. Fujita, and H. Nozaki, Tetrahedron, 31, 2219 (1975).
8) Isomerization of 1 to 5 and 6 (1:3) was also catalyzed by aluminum chloride in ether.
9) Acid-catalyzed rearrangement of [7]paracyclophane gave the meta isomer; K. L. Noble, H. Hopf, M. Jones, Jr., and S. L. Kammula, Angew. Chem. Int. Ed. Engl., 17, 602 (1978); and that of [5]metacyclophane afforded the ortho isomer; L. A. M. Turkenburg, W. H. de Wolf, and F. Bickelhaupt, Tetrahedron Lett., 24, 1817 (1983).

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