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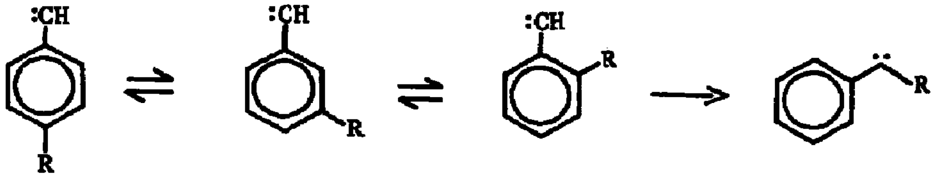
A CARBENE ROUTE TO DEHYDRO[m.n]PARACYCLOPHANES[1]

Michael Boxberger, Lothar Volbracht, and Maitland Jones, Jr.*
Department of Chemistry, Princeton University
Princeton, New Jersey 08544

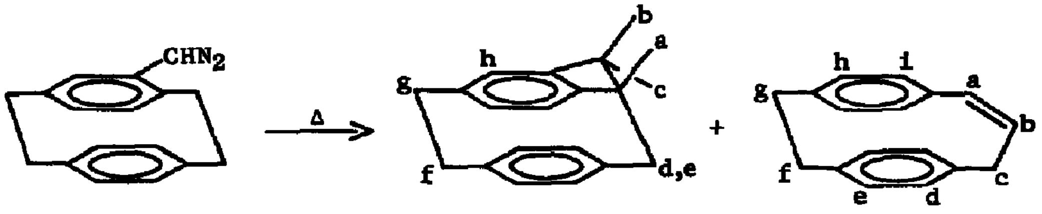
SUMMARY: Pyrolysis of the [2.2]paracyclophanyl diazomethane (1) at 270-300°C led to the product of carbon-hydrogen insertion (2) and _cis_-1,2-dehydro[3.2]paracyclophane (3).

We have been interested for some time in applications of the phenylcarbene rearrangement[2] in which a benzene ring in effect transports a divalent carbon from one position to another.



In the past we have used such a reaction to generate a number of metal-substituted carbenes.[3] Here we report the application of this idea to generate a "missing" member of the series of 1,2-dehydro[m.2]paracyclophanes.[4]

[2.2]Paracyclophanyl diazomethane, 1, was synthesized through an orthodox series of steps starting with [2.2]paracyclophane.[5] Following literature procedures, [2.2]paracyclophane was converted to the mono bromide[6] and the carboxaldehyde.[7] Treatment with tosylhydrazine in methanol led to a tosylhydrazone (mp 156-160°C) that could be converted to a lithium salt by treatment with butyllithium in dry tetrahydrofuran at -78°C. Careful pyrolysis of the salt at 80°C/0.01 torr led to a 26% yield of a red diazo compound, **1** (IR 2055 cm^{-1}). Flash vacuum pyrolysis at 270-300°C/0.01 torr led to two products, **2** and **3**, isolated by gas chromatography in _ca_. 3 and 12% yield, respectively. The yields are not optimized and do not reflect the large amounts of azine formed by the quite non-volatile **1**.



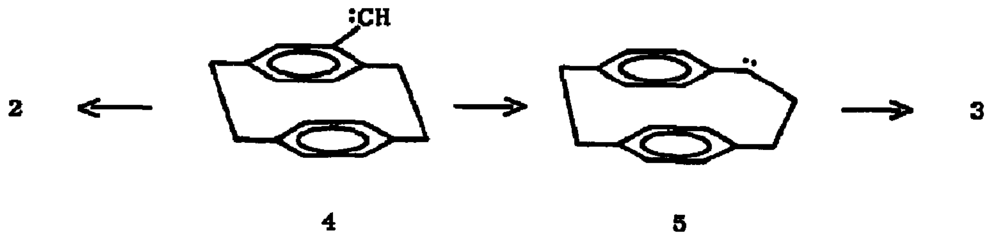
1 2 3

Both **2** and **3** were established as $C_{17}H_{16}$ isomers by high-resolution mass spectrometry. Dehydrocyclophane **3** could be identified by an examination of its 90 MHz proton NMR spectrum. The spectrum revealed the presence of eight aromatic protons. Thus the cyclophane skeleton is now only disubstituted. Four of these aromatic protons appear as a singlet at $\delta = 6.35$ ppm. These are presumably H_d and H_e. H_h and H_i are in more different environments than these because of the double bond proximate to H_i, and appear as an AB quartet centered at $\delta = 6.41$ ppm ($J = 6.5$ Hz). Two other low-field protons, H_a and H_b, appear as doublets of triplets [H_b, $\delta = 5.84$ ppm ($J = 12$, 5 Hz); H_a, $\delta = 6.74$ ppm ($J = 12$, 2.5 Hz)]. The allylic methylene protons, H_c, to which H_a and H_b are coupled appear at $\delta = 3.52$ ppm ($J = 5$, 2.5 Hz). Naturally, irradiation of H_c collapses the signals for H_a and H_b to doublets ($J = 12$ Hz). The remaining methylene protons (H_f and H_g) appear as a singlet at $\delta = 2.96$ ppm.

Compound **2** contains but seven aromatic protons spanning the range $\delta = 5.75$-7.2 ppm. Expansion reveals a number of AB systems and a single one-proton peak at $\delta = 5.75$ ppm (H_h). Six hydrogens ($H_{d,e,f,g}$) appear as a complex multiplet at $\delta = 2.88$-3.1 ppm. From this multiplet three other one-proton signals stand clear. Two, H_b and H_c, are an AB quartet, the two "wings" of which are centered at $\delta = 2.51$ ($J = 13.4$ Hz) and 3.46 ppm ($J = 13.4$, 5.5 Hz).

The lower field "wing" is further split into two doublets, as it represents the proton (H_b) cis to the cyclobutyl hydrogen H_a. As H_a is coupled not only to H_b but also to H_d and H_e, it appears as a multiplet centered at $\delta = 3.82$ ppm. The presence of only seven aromatic protons plus the details noted above leave us no doubt as to the structure.

Thus our hopes have been justified. The phenylcarbene rearrangement leads from 4 to 5 which then undergoes 1,2 carbon-hydrogen insertion to give 3 Prior to rearrangement 1 undergoes carbon-hydrogen insertion to give 2, which becomes the first example of a paracyclophane bridged through the four-membered ring of a benzocyclobutene.[8]



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REFERENCES AND NOTES

1. This work was supported by the National Science Foundation through grant CHE-77-24625.
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3. G. R. Chambers and M. Jones, Jr., *Tetrahedron Lett.*, 5193 (1978).
4. For 1,2-Dehydro[4.2]paracyclophane see: M. H. Delton and D. J. Cram, *J. Am. Chem. Soc.*, **94**, 1669 (1972). For 1,2-dehydro[2.2]paracyclophane see: R. E. Singer and D. J. Cram, *J. Am. Chem. Soc.*, **94**, 3512 (1972).
5. It is a pleasure to acknowledge the gift of a sample of [2.2]paracyclophane from Dr. Donald D. Stewart of the Union Carbide Corporation.
6. H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, **91**, 3534 (1969).
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8. There are other bridged benzocyclobutenes in which the bridges connect the aromatic rings only. See, for instance: R. Gray, L. G. Harruff, J. Krymowski, J. Paterson, and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2892 (1978).

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