Tetrahedron Letters,Vol.24,No.41,pp 4413-4416,1983 0040-4039/83 $3.00 + .00
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A 1,10-HOFMANN ELIMINATION. SYNTHESIS OF A [6.6]PARACYCLOPHANE TETRAENE

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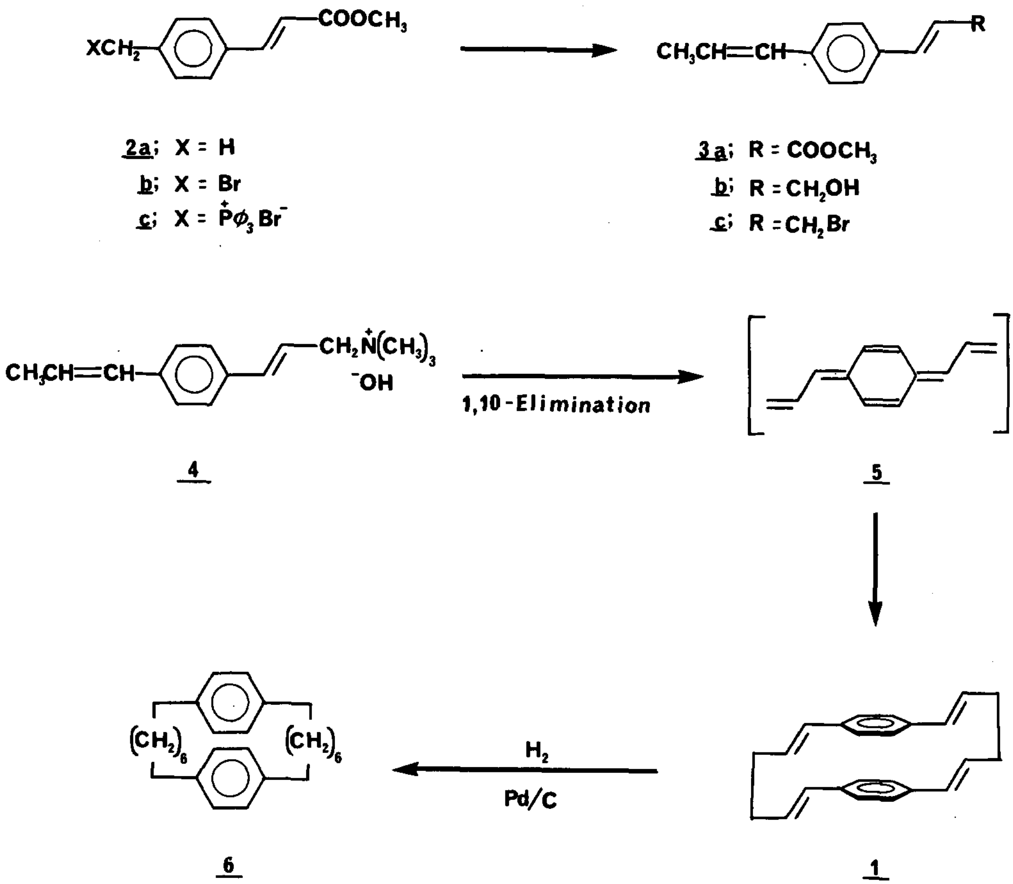
Summary: The synthesis of (E,E,E,E)-[6.6]paracyclophane-1,5,13,17-tetraene *via* the [10+10] cyclodimerization of 7,8-divinyl-*p*-quinodimethane is described.

The importance of 1,x-eliminations in the syntheses of bridged aromatic compounds is well established.[1] The overwhelming majority of such eliminations have been of the 1,6-Hofmann type affording *p*-xylylenes or their analogs and, on subsequent cyclodimerizations, [2.2]cyclophanes. Several 1,8-Hofmann eliminations have been described.[2,3] These provide direct syntheses of side-chain unsaturated [6.2], [4.4], and [4.2]cyclophanes.[2] We now report a facile 1,10-Hofmann elimination which affords in good yield a cyclophane with paired *p*-divinylbenzene moieties,(E,E,E,E)-[6.6]paracyclophane-1,5,13,17-tetraene (1).

Bromination of methyl *p*-methylcinnamate[4] (2a) with N-bromosuccinimide in CCl_4 gave the benzyl bromide 2b[6] in 82% yield, mp (pentane) 59.0-59.5°; IR (KBr), 975 cm^{-1} (*trans* alkene).[7] Treatment of 2b with triphenylphosphine in acetonitrile provided the phosphonium salt 2c in quantitative yield; mp (ethanol) 258.0-259.5°; IR (KBr), 980 cm^{-1}. The salt was condensed with acetaldehyde in the Wittig mode (lithium ethoxide as base) to give ester 3a in 76% yield;[8] mp (methanol) 82.5-83.5°; IR (KBr), 980 and 960 cm^{-1}. This ester was reduced with lithium aluminum hydride in ether affording alcohol 3b (93%); mp (methanol) 92.5-93.5°; IR (KBr), 970 and 960 cm^{-1}. Finally, bromide 3c was obtained by treatment of 3b with phosphorus tribromide in ether; 90% yield; mp (ether) 87.5-88.5°; IR (KBr), 970 and 960 cm^{-1}.

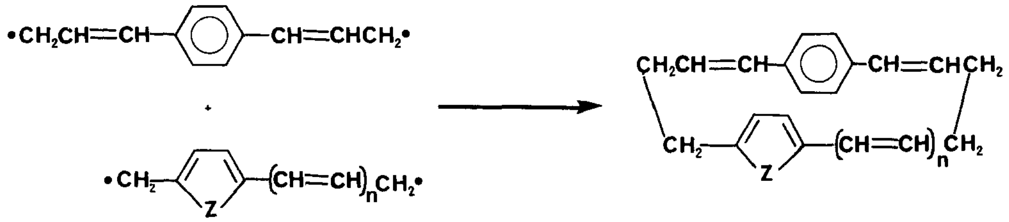
Conversion of 3c to the quaternary ammonium hydroxide 4 was done in the usual manner.[9] Heating an aqueous solution of 4 with toluene[9] gave smooth evolution of trimethylamine after water had been removed azeotropically. The ether extracts of the reaction solids eventually provided dimer 1 (30%); IR (KBr), 970 cm^{-1} strong; MS: m/e = 312 (M^+, 15%), 156 (100), 141 (27),



128 (29), 115 (68); NMR (60 MHz, $CDCl_3$): δ 6.77 (8H, s), 6.2-5.4 (8H, m), 2.33 (8H, m). The UV spectrum (cyclohexane) has maxima at 236 (sh, 4.29), 266 (sh, 4.59), 276 (4.69) and 316 nm (4.12). Compound 1 is sensitive to oxygen, adding increasing amounts with time;[10] it shows no melt but converts to an insoluble material when heated to 360°.

Catalytic (Pd/C) hydrogenation of 1 gives [6.6]paracyclophane (6) in 73% yield; mp (methanol) 99.0-99.5° (lit. mp 99.0-100.6°);[11] NMR ($CDCl_3$): δ 6.89 (8H, s), 2.59-2.35 (8H, m), 1.7-1.3 and 1.3-1.0 (16 H, m,m).

Two points regarding dimer 1 and its synthesis are of particular interest. Increasing the number of carbons in the bridges of [m.n]paracyclophanes generally increases the distance between the aromatic rings, leading to a reduction or loss of transannular electronic effects.[12] In [6.6]paracyclophane, for example, there is a complete absence of transannular electronic effects in the chemical and physical properties of the compound, each benzenoid ring acting independently.[13] In contrast, the presence of *trans* double bonds in 1 results in preferred conformations (by inspection of molecular models) where the two *p*-divinylbenzene segments are parallel and in close proximity to one another. Thus 1 may be expected[14] to exhibit transannular phenomena involving both the benzene rings and the side-chain double bonds. In addition to providing an ene-functionalized [6.6]paracyclophane, the unique *p*-quinodimethane vinylog 5 may allow direct access to similarly unsaturated [6.4] and [4.4]cyclophanes by crossed dimerizations[2] with other known *p*-quinodimethane type species (shown as the isoelectronic diradicals for structural clarity)[15]:



Z = (CH=CH), O, NH ; n = 0, 1

Acknowledgments. This research was supported by The Dow Chemical Company Foundation and by a fellowship grant to D.T.G. from The 3M Company and The Macromolecular Research Center of The University of Michigan.

References and Notes

1. F. Vögtle and P. Neumann, Synthesis, 85 (1973).
2. L. G. Kaufman and D. T. Longone, Tetrahedron Lett., 3229 (1974); P. S. Hammond and D. T. Longone, Tetrahedron Lett., 415 (1978); S. H. Küsefoglu and D. T. Longone, Tetrahedron Lett., 2391 (1978).
3. R. Luhowy and P. M. Keehn, J. Am. Chem. Soc., **99**, 3797 (1977).
4. Made from the corresponding acid[5] *via* the reaction of the acid chloride with methanol.
5. S. Dutt, J. Ind. Chem. Soc., **1**, 297 (1924).
6. Compound **2b** has been reported but without a full description of its physical properties: J.-Y. Wang and Y.-F. Jen, Yao Hsueh Hsueh Pao, **11**, 591 (1964).
7. All new compounds described give satisfactory combustion analyses and NMR and mass spectral data, except where noted.
8. The propenyl double bond in **3a** is generated as a mixture of geometric isomers, easily distinguishable by NMR. In all cases for compounds **3** and **4**, the analytical data refer to the *trans*-isomer, readily obtained by recrystallization of the mixture. For conversion of **3a** to **4**, the mixture of isomers was utilized.
9. H. E. Winberg and F. S. Fawcett, Organic Syntheses, Coll. Vol. V, 883 (1973).
10. After exposure to air for several days, compound **1** gives distinct M+16 and M+32 peaks in the MS as well as carbonyl (1700 cm^{-1}) and hydroxyl (3400 cm^{-1}) bands in the IR. Successive combustion analyses on a given analytical sample show increasing amounts of oxygen incorporation. Such sensitivity to oxygen has been observed in a structurally related side-chain unsaturated cyclophane: D. J. Cram and K. C. Dewhirst, J. Am. Chem. Soc., **81**, 5963 (1959).
11. J. Abell and D. J. Cram, J. Am. Chem. Soc., **76**, 4406 (1954).
12. The classic studies of Cram and coworkers are summarized and cited in: M. Sheehan and D. J. Cram, J. Am. Chem. Soc., **91**, 3544 (1969).
13. D. J. Cram and J. Abell, J. Am. Chem. Soc., **77**, 1179 (1955).
14. The NMR and UV spectra of **1**, relative to those of model compounds, exhibit features (shielding effects and broadening of absorption bands, respectively) consistent with this suggestion.
15. The species shown, not all properly *p*-quinodimethanes, are conveniently classified as such to stress their similarity in origin and chemical behavior.

(Received in USA 27 May 1983)