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[2.2](2,7)NAPHTHALENOPARACYCLOPHANES[1]

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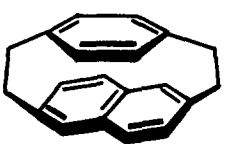
[2.2](1,4)Naphthalenoparacyclophane was first reported by Cram[2] and recently, two isomers of this structure, [2.2](1,5)- and [2.2](2,6)naphthalenoparacyclophane (1) were synthesized.[3] We wish to report here the synthesis of the related [2.2](2,7)naphthalenoparacyclophane (2) and the corresponding dienes 3 and 4.



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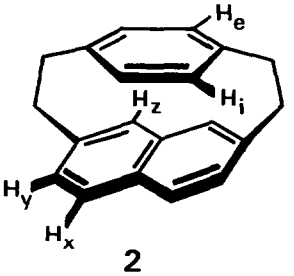

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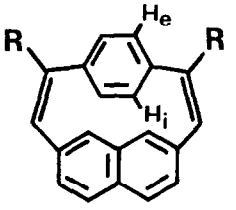
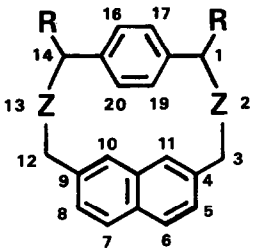
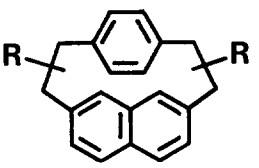


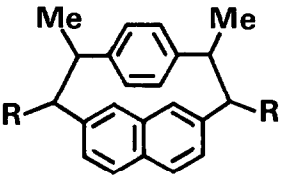
3 R=H

4 R=Me

Addition of a mixture of α,α'-dithia-p-xylene and 2,7-bis(bromomethyl)-naphthalene in benzene with a syringe-drive over 50h to ethanolic potassium hydroxide gave the dithiacyclophane 5[4] in 50% yield, mp 239-241°C. Similarly, the 1,14-dimethyl compound 6[4,5] was obtained in similar yield from p-bis(α-mercaptoethyl)benzene and 2,7-bis(bromomethyl)naphthalene. Treatment of either 5 or 6 in dichloromethane with dimethoxycarbonium tetrafluoroborate[6] led to a quantitative yield of the corresponding salt 7[4] or 8. Attempts to ring-contract the salt 7 to the [2.2]cyclophane 10 by treatment with bases such as potassium t-butoxide, n-butyl lithium, sodium hydride, sodium methoxide or basic ion-exchange resins (Stevens rearrangement conditions)[7,8] gave only polymeric products. Also, treatment of the cyclophane 5 in THF with n-butyl lithium followed by methyl iodide (Wittig rearrangement conditions)[9] gave very low yields of the desired







5 R=H, Z=S
6 R=Me, Z=S
7 R=H, Z=$\overset{+}{S}$MeBF$_4^-$
8 R=Me, Z=$\overset{+}{S}$MeBF$_4^-$
9 R=H, Z=SO_2

10 R=SMe
11 R=SC_6H_5
12 R=SOC_6H_5

13 R=SMe
14 R=$\overset{+}{S}Me_2BF_4^-$
15 R=SOMe

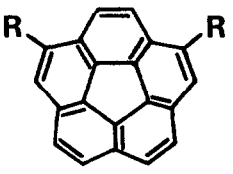
product 10. In contrast, the dimethyl cyclophanes 6 and 8 gave acceptable yields (47 and 12%) of the ring-contracted product 13[4,5] using the Wittig and Stevens procedures respectively.[10]

In an alternative approach to the diene 3, the dithiacyclophane 5, on reaction with benzyne generated in situ,[12] formed a high yield of the bis(phenylthio)cyclophane 11.[4,5] Compound 11, on oxidation with 2 equivalents of sodium metaperiodate gave the bis-sulphoxide 12 in quantitative yield, which on pyrolysis at 500°C/5x10^{-4}mm yielded the [2.2](2,7)naphthalenoparacyclophane-1,11-diene (3)[4] as yellow plates (mp 118-120°C, 63%). Its ^{1}H-NMR spectrum showed the H_i protons at δ 5.22, H_e 7.23, and the vinylic and naphthalene aromatic protons as the expected AB and AMX patterns (6.91 - 7.70). The upfield shift of the internal protons H_i confirmed the anticipated stepped structure of 3 in which the para-disubstituted benzene ring is tilted towards the naphthalene ring.

Conversion of the dimethyl cyclophane 13 to the diene 4 was best achieved by methylation[6] to produce the salt 14 which on treatment with sodium hydride in THF gave a very low yield of the 1,12-dimethyl[2.2](2,7)naphthalenophane-1,11-diene (4)[4] as yellow prisms mp 105-106°C together with two other rearrangement products.[13] The ^{1}H-NMR of 4 was similar to that of compound 3 and in particular showed H_i at δ 5.20 and H_e 7.26. The ^{13}C-NMR was also consistent for the structure of the diene 4. Oxidation of the bis(methylthio) compound 13 with two equivalents of sodium metaperiodate gave the bis-sulphoxide 15[4,5] in high yield. However, on pyrolysis in a variety of solvents (dioxan, toluene, o-xylene) compound 15 gave

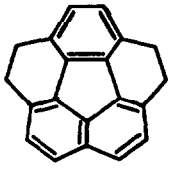
none of the desired diene 4.

The [2.2]cyclophane with saturated bridges, compound 2, was readily prepared by irradiation of the dithiacyclophane 5 in trimethylphosphite under nitrogen with a high-pressure mercury-quartz lamp. The cyclophane 2[4] was obtained in 30% yield as white prisms mp 114-115°C (^{1}H-NMR in $CDCl_3$, δ 2.11-3.19, m, benzylic H; 5.11, bs, H_i; 6.58, d, J 1.5Hz, H_z; 6.95, bs, H_e; 6.99, dd, J 8.5 and 1.5Hz, H_y; 7.56, d, J 8.5Hz, H_x). Vacuum pyrolysis of the sulphone 9[4] at temperatures between 200-500°C gave none of the ring-contracted cyclophane 2 and only polymeric material resulted. This is a reflection of the inherent strain in the [2.2](2,7)naphthalenoparacyclophane structure. We have also noted that the dienes 3 and 4 are labile compounds in solution and appear to be susceptible to oxidation which is in contrast to the many other cyclophane dienes which have been prepared by ourselves and others.



16 R = H

17 R = Me



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Several attempts were made to convert the [2.2](2,7)naphthalenoparacyclophanes 2, 3 and 4 to corannulene 16[14] or the related derivatives 17 and 18 but all without success. Irradiation of degassed solutions of the diene 3 produced new upfield resonances in the ^{1}H-NMR at δ 5.1 and 0.1 suggesting the formation of tetrahydrocorannulene intermediates, but under oxidative conditions (I_2 and O_2), none of the expected corannulene could be detected. Treatment of the cyclophane 2 with a variety of catalysts and reagents (10% Pd/C, $AlCl_3$, pyridinium hydrobromide perbromide) also failed to produce corannulene 16 or the related partially hydrogenated compound 18. We suspect that these *experiments may have failed in part due to the susceptibility of corannulene itself to* oxidation under the reaction conditions.

Acknowledgement. We thank the Australian Research Grants Committee for financial support.

References and Notes

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2. D.J. Cram, C.K. Dalton and G.R. Knox, J.Am.Chem.Soc., 85, 1088 (1963).
3. M.W. Haenel, Tetrahedron Lett., 4191 (1977).
4. Satisfactory elemental analysis and/or accurate mass measurement together with NMR data were obtained.
5. The product was obtained as a mixture of stereoisomers.
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9. R.H. Mitchell and V. Boekelheide, J.Am.Chem.Soc., 96, 1547 (1974).
10. We have noted elsewhere[11] that the presence of the methyl groups at the 3- and 10-positions decreases the kinetic and thermodynamic acidity of the protons at this site relative to those of the naphthyl benzylic positions. This in turn prevents (or decreases) an alternative 1,6-elimination reaction leading to polymer formation from a reactive p-xylylene intermediate.
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12. T.Otsubo and V. Boekelheide, Tetrahedron Lett., 3881 (1975).
13. These two products presumably arose by Stevens rearrangements of the salt 13, and their structures will be reported elsewhere.
14. W.E. Barth and R.G. Lawton, J.Am.Chem.Soc., 93, 1730 (1971).

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