Syntheses and Reactions of [2,*n*]Paracyclophan-($n+7$)-enes

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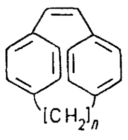
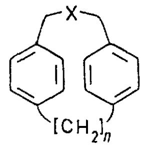
Summary Routes are described for the preparation of the [2,*n*]paracyclophanenes (**1**) from the corresponding thia-[3,*n*]paracyclophanes (**2**); photocyclisation of the olefins (**1**; $n \geqslant 7$) gives the bridged phenanthrenes (**12**); bromine in carbon tetrachloride gives predominantly the *cis*-dibromides (**10**) with increasing proportions of the *trans*-dibromides (**11**) as *n* increases.

The synthesis and properties of [2,2]paracyclophan-1-ene (**1**; $n = 2$) have been described,[1] and in view of the potential interest in the spectroscopic properties and electrophilic addition reactions of analogous olefins[1,2] we have investigated the synthesis of the series of paracyclophanenes (**1**; $n = 3$—10). The thia[3,*n*]paracyclophanes[3] (2; $n =$ 3—10) provided a convenient starting point since the synthesis of olefins from thioethers has recently been widely used.[4,5]

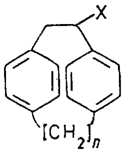
The conventional Ramberg–Bäcklund method,[4] using the sulphones (**3**), failed due to difficulty with the halogenation step, but the modified one-step procedure[6] proved reasonably effective and the olefins (**1**; $n = 5$—10) could be obtained in yields of 18—52%. This method proved unsatisfactory for the lower members of the series (**1**; $n \leqslant 5$) and alternative methods were therefore investigated. The Stevens rearrangement (NaH–Me_2SO) of the sulphonium salts (**4**) gave the thioethers (**5**), but for higher members of the series (**4**) the Sommelet–Hauser products (**6**) were also obtained ($n = 8$, 8%; $n = 9$, 55%) and this method is therefore only applicable for $n < 8$. The dimethylsulphonium salts (**7**) gave at best poor yields of the olefins (**1**) on attempted base-catalysed elimination, but pyrolysis of the sulphoxides (**8**) in boiling xylene[7] gave the olefins (**1**) in yields of 50—60% [based on the sulphides (**5**)]. The best method for the interconversion (**5**) → (**1**) was pyrolysis (boiling toluene) of the *N*-toluene-*p*-sulphonylsulphilimine derivatives[8] (**9**) (70—90% yields).



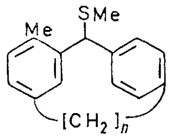
(1)



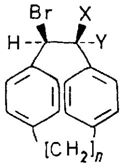
(2) X = S
(3) X = SO_2
(4) X = $\overset{+}{S}Me, BF_4^-$



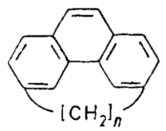
(5) X = SMe
(7) X = $\overset{+}{S}Me_2, BF_4^-$
(8) X = SOMe
(9) X = S(Me)=$NSO_2C_6H_4Me$



(6)



(10) X = Br, Y = H
(11) X = H, Y = Br



(12)

The olefins (**1**) showed an interesting sequence of changes[9] in their u.v. spectra (hexane solution), ranging from benzenoid in character with no well-defined maxima in the range 210—350 nm (**1**; $n = 3$—6) to nearly *cis*-stilbenoid with maxima at *ca.* 230 and 265 nm (**1**; $n =$ 9,10). This result reflects increasing torsional freedom, and hence aryl–olefin conjugation, as the bridge length increases. The addition of bromine in carbon tetrachloride also showed a series of gradual changes, giving the *cis*-dibromide (**10**) as the major product for the olefin (**1**; $n = 3$) (*cis*:*trans* 20:1) with a steadily increasing proportion of the *trans*-dibromide (**11**) as the length of the polymethylene bridge increases [*cis*:*trans* 1·7:1 for (**1**; $n = 10$)]. The assignment of stereochemistry to the dibromides (**10**) and (**11**) is based upon equilibration for lower members of the series (LiBr–DMF), which gives the *trans*-isomers (**11**), the stereoselective *trans*-elimination of HBr from the *cis*-isomers, and by analogy with the addition of bromine[1] to [2,2]paracyclophan-1-ene (**1**; $n = 2$) ($>$ 99% *cis*-addition). These results show an interesting relationship to the stereochemistry[10] of the addition of bromine to *cis*-stilbene under similar reaction conditions. Torsion angles about the two carbon bridge of the thioethers (**5**) show similar gradual changes, based upon n.m.r. coupling constant data for the CH_AH_B-CH_XSMe system, ranging from almost eclipsed [(**5**; $n = 3$) J_{AX} 9·3 J_{BX} 6·9 Hz] to nearly staggered [(**5**; $n = 8$) J_{AX} 5·5, J_{BX} 12·4 Hz]. The relationship, if any, between this result and the decreasing stereoselectivity of the addition of bromine requires further investigation.

Photocyclisation[11] of the olefins (**1**; $n = 7$—10) in cyclohexane solution, by irradiation at 253·7 nm in the presence of iodine, gave good yields of the corresponding bridged phenanthrenes (**12**). This reaction failed for shorter polymethylene bridges (**1**; $n \leqslant 6$), and this sharp cut-off, as opposed to the gradual changes observed in the u.v. spectra of the olefins (**1**) and the stereoselectivity of bromine addition, reflects the steric strain in the photocyclisation product for the shorter bridging groups.

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