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SYNTHESIS AND SPECTRA OF PARACYCLOPHANE DIENES

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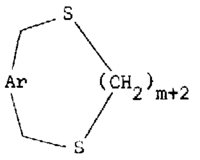
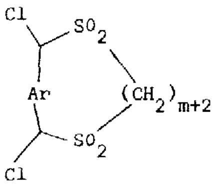
The ease with which sulfur to carbon bonds can be introduced and the numerous methods available for extruding sulfur make thioethers attractive intermediates in organic synthesis.[1] Recent reports[2] from Boekelheide's laboratory demonstrate the utility of sulfide linkages in the synthesis of strained binuclear cyclophanes. Following Boekelheide's initial report, Potter and Sutherland[3] reported syntheses of [2,n]paracyclophane-(n + 7)-enes, utilizing various methods for converting thioether linkages to carbon-carbon double bonds. However, they report that "the conventional Ramberg-Backlund method failed due to difficulty with the halogenation step." Several years ago we became interested in developing a general synthesis of cyclophanes that would serve as precursors of bridged annulenes. Our initial objective was the synthesis of [n]metacyclophanes that contained functional groups in the aliphatic bridge.[5] The Ramberg-Backlund reaction was selected as a means of converting two thioether linkages to carbon-carbon double bonds since the mechanistic details[6] and the synthetic utility of the reaction[1] are well documented This report deals with the synthesis (via the conventional Ramberg-Backlund reaction) and spectra of paracyclophane dienes (4a-c).

The previously known dithiaparacyclophanes (1a and 1b) were prepared according to Vogtle's procedure.[7] Similarly, the previously unreported dithiaparacyclophane 1c was obtained in 33% yield (mp 132° from methanol-chloroform) when 4,4'-(bromomethyl)diphenylmethane (from the bromomethylation of diphenylmethane[8]) and disodium 1,8-octanedimercaptide were allowed to react at high dilution. The dithiaparacyclophanes (1) were chlorinated with two equivalents of N-chlorosuccinimide in carbon tetrachloride.[9] The solution of bis-chlorosulfide was oxidized with four equivalents of m-chloroperoxybenzoic acid (MCPBA) in dichloromethane. Excess MCPBA was reduced with sodium bisulfite and m-chlorobenzoic acid was removed by extraction with base. The chlorocarbon solvents were removed completely, and the crude bis-chlorosulfones (2) were treated with approximately four equivalents of potassium t-butylate in dimethoxyethane. This led to the isolation of either diene 4 or chlorosulfone 3, depending on reaction time and conditions. Dienes (4) were isolated by evaporating the solvent and extracting the residue with equal volumes of water and dichloromethane. Purified paracyclophane dienes (4) were obtained in good yield based on sulfide 1 (Table I), by chromatographing (on alumina) the oily residues that were recovered from solvent evaporation.[10] As previously recognized,[3] the crucial step in the diene synthesis is the chlorination step. Thus long reaction times (> 4 hours) led to fragmentation products only, and an excess of two equivalents of N-chlorosuccinimide leads to chlorodiene contaminants in the final product.



1a Ar = $\underline{p}$-C_6H_4-, m = 5
1b Ar = $\underline{p}$-C_6H_4-, m = 7
1c Ar = $\underline{p}$-C_6H_4-CH_2-C_6H_4-, m = 6



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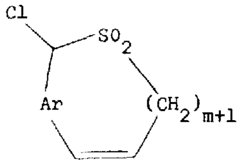

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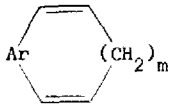

4a Ar = $\underline{p}$-C_6H_4-, m = 5
4b Ar = $\underline{p}$-C_6H_4-, m = 7
4c Ar = $\underline{p}$-C_6H_4-CH_2-C_6H_4-, m = 6

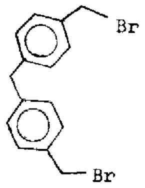

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TABLE I. YIELDS AND PMR DATA FOR PARACYCLOPHANE DIENES[a]

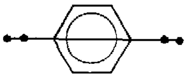
Compound	% Yield	H_a	H_b	H_c	H_d	M^+
4a	29	0.87	1.62	6.05	7.05	198
4b	55	0.66, 1.10	2.08	5.75	6.55	226
4c	42	0.80	1.78	5.50	6.28	302

[a] Chemical shifts are given in δ values relative to internal tetramethylsilane. H_a, H_b, H_c and H_d represent methylene, allyl, vinyl and benzal protons, respectively. A singlet appeared at δ3.75 for the benzyl protons of 4c. The expected resonance bands were observed for aromatic protons and relative intensities are consistent with assigned structures.

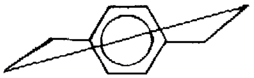
[11]Paracyclophane-1,10-diene (4b) was obtained as white crystalline solid from methanol, mp 65°. The 60 MHz pmr spectrum ($CDCl_3$) of 4b contained multiplets at δ0.66 and 1.10 for the methylene protons (10H), a quartet at δ2.08 for the allyl protons (4H), an hextet at δ5.75 for the vinyl hydrogens (2H), a doublet at δ6.55 (J = 10 Hz) for benzal protons (2H) and a singlet at δ7.03 for the four aromatic hydrogens. Compound 4b gave an intense molecular ion at m/e 226 in the 70 eV mass spectrum also. Dienes 4a and 4c were obtained as pale yellow viscous oils. The structure of 4c is supported by pmr data and an intense peak in its mass spectrum at m/e 302 Minor peaks appeared at m/e 336 and 338 corresponding to clorodiene (i.e., 4c that contains Cl

in place of a benzal hydrogen atom) that arose through trichlorination.[11] The paracyclophane dienes are stable compared to simple divinylbenzenes. Thus 4 could be stored at room temperature for months without significant decomposition or polymerization.

The paracyclophane dienes (4) may serve as good models for examining the interaction of π-orbitals that are twisted out of plane, although conjugated in the classical sense. Previous theoretical considerations indicate that the resonance integral for two interacting groups (R and S) having an angle θ between their planes is given by $\beta^{\theta}_{RS} = \beta^{0}_{RS} \cos \theta$.[12] Examination of molecular models and calculations of molecular dimensions (assuming normal bond angles and distances) indicate that the least strained conformation of 4b is one that carries the aliphatic bridge across the face of the benzene nucleus. Specifically, the singlet for aromatic protons and the high field multiplets for methylene groups in the pmr spectrum indicate that the aliphatic bridge is either symmetrically disposed across the face of the aromatic nucleus (A, i.e., carbons 1 and 4 of the benzene ring and those of the vinyl groups lie in a plane), or each vinyl linkage is tilted by some angle θ to opposite edges of the benzene nucleus(B). Conformations that would require the aliphatic bridge to lie along an edge of the benzene nucleus seem remote since such a structure would be expected to lead to large chemical shift differences of aromatic protons.



A



B

Ultraviolet spectra of 4a (λ_{max} = 244 nm, logϵ = 3.75) and 4b (λ_{max} = 251 nm, logϵ = 4.03) suggest that the vinyl groups interact strongly with the aromatic π-system although these groups are twisted out of plane to a position that approaches orthogonality. Comparison of the ultraviolet spectrum of 4a with those of cis-β-methylstyrene (λ_{max} = 241, logϵ = 4.1)[13] and 1,4-divinyl-2,3,5,6-tetrachlorobenzene (λ_{max} = 261 nm, logϵ = 4.0)[14] indicates that the effect of two orthogonal (or nearly so) vinyl groups is approximately equivalent to that of a single vinyl group in the acyclic models in terms of the energy of the $\pi \rightarrow \pi^*$ transition. The intensity of this band in 4a suffers a 50% reduction in intensity compared to the model compounds, indicating a major deviation from the coplanar conformation required for maximum overlap. On the other hand, the relatively strain free homologue, 4b, exhibits a low energy band that is comparable in energy and intensity to the one observed for 1,4-divinyl-2,3,5,6-tetrachlorobenzene. These data suggest that the energy and intensity of the $\pi \rightarrow \pi^*$ transition give only rough qualitative estimates of the deviation from coplanarity. Application of Braude's treatment[15] to our ultraviolet data leads to unreasonably small angles of twist for 4a and 4b (49° and 23°, respectively) when molecular dimensions and nmr data are considered. These data can be reconciled if one assumes highly mobile conformations for 4a and 4b (e.g., fast equilibration between conformation B and its mirror image). The ultraviolet spectrum of 4c (λ_{max} = 235, 255 nm, logϵ = 4.11, 3.97) suggests that the vinyl groups interact with the aromatic π-system also. The intensity is only ca 50% of what would be predicted for two independent styrenes on the basis of spectra for the model compounds. It is recognized that diphenylmethane derivatives exhibit unique features that are characteristic of aromatic nuclei in close proximity.[16] We are continuing our efforts to elucidate factors that influence $\pi\rightarrow\pi^*$ transitions of cyclophane dienes, with particular emphasis on the effect of bridge size.

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