K_t, and K_u are similar,[19] reasonable since R and R′ are both primary.

$$\mathrm{R'MgR} + \mathrm{MgBr_2} \overset{K_t}{\rightleftarrows} \mathrm{RMgBr} + \mathrm{R'MgBr} \qquad (5)$$

$$\mathrm{R'MgR'} + \mathrm{MgBr_2} \overset{K_u}{\rightleftarrows} 2\mathrm{R'MgBr} \qquad (6)$$

Since k_2, B, and $[\mathrm{R}]_0$ are known, k_1 and K_s can be determined from eq 4. This task is simplified by noting that when $[\mathrm{R_2Mg}] \ll [\mathrm{R}]_0$ and B, then the observed rate constant is approximated by eq 7. Values of K_s =

$$k_{\mathrm{obsd}} = \frac{2k_1[\mathrm{R}]_0}{K_sB} + k_2 \qquad (7)$$

42.1 and of $k_2 = 1.00 \times 10^{-6}$ sec^{-1} are obtained from a plot of $2k_1[\mathrm{R}]_0/B$ against k_{obsd}. Using these values in the more exact equation (eq 4) gives calculated rates in good agreement with the observed ones, particularly considering the errors in the approximation used to derive K_s and k_2 and in the experimental determinations of rate, $[\mathrm{R}]_0$, and B. The approximate equation (eq 7) should provide too large a value for K_s, and indeed a somewhat better agreement is obtained for slightly smaller values ($K_s \simeq 35$). Since k_2 is much smaller than k_1 and at the largest B (0.18 M) that could conveniently be used, the dialkylmagnesium species still contributed significantly to the rate, the determination of k_2 is subject to considerable error. Nevertheless, a much larger value of k_2 seems unlikely since at the highest value of B that was used, the observed rate was $< 2 \times 10^{-6}$ sec^{-1}. A value much nearer zero also seems unlikely, since then the agreement between calculated and observed rates (for any value of K_s) is not as satisfactory at both high B and at $B = 0$. Therefore, we conclude that $k_1 = 44.8 \times 10^{-6}$ sec^{-1}, $k_2 \simeq 1 \times 10^{-6}$ sec^{-1}, and $K_s \simeq 30$–40.[20]

Previous observations[6] of dependence of rate on the presence of substitutents at $>\mathrm{C{=}C}<$ and at $-\mathrm{CMgX}$ suggest that both the alkene and Grignard functions are involved in the rate-determining step. The present results indicate that this involvement can be no more than "first order" in each function. This conclusion is similar to the recent findings by Ashby and his coworkers that the transition states for addition in ether of methylmagnesium chloride or dimethylmagnesium to 2-methylbenzophenone or to benzonitrile contain only one molecule of organomagnesium species and one of ketone or nitrile.[21]

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[19] This would be precisely the case if $K_s = K_t/2 = K_u$.

[20] Extrapolation from activation parameters obtained at lower temperatures [M. B. Smith and W. E. Becker, *Tetrahedron*, **23**, 4215 (1967)] gives a value of K_s = 38 for the ethyl Grignard reagent (prepared from the bromide) in tetrahydrofuran at 100°.

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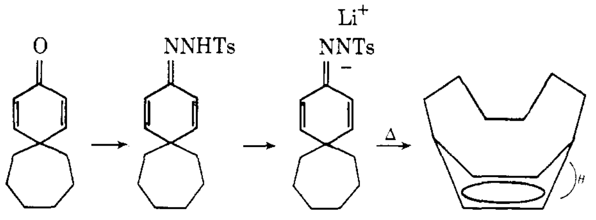
[6]Paracyclophane[1]

Sir:

Benzene is flat. Every undergraduate chemistry student learns early in his career that the extraordinary stability of benzene is associated with the cyclic overlap of six p orbitals. Planarity assures ideal overlap and thus maximizes the attendant stability. Naturally chemists have addressed themselves to the question of how much bending a benzene ring can withstand without giving up its "aromatic character."[2] The most successful experimental approach has been through the construction of [*m*,*n*]- and [*m*]paracyclophanes in which the para positions are bridged with ever-shortening chains.[3] The current limits in the [*m*] series are marked by Allinger and Walter's synthesis in 1972 of [7]paracyclophane-3-carboxylic acid[4] and our report last year of the formation of the parent hydrocarbon.[5] Here we describe the extension of our method and the construction of [6]paracyclophane.

Ketone **1** was synthesized from cycloheptane carboxaldehyde and methyl vinyl ketone and converted to the tosylhydrazone (**2**) in unexceptional fashion. Flash pyrolysis of the lithium salt **3** at 250–400° led to **4** as well as alkyl- and alkenylbenzenes. The yield of **4** measured by gas chromatography was as high as 5–10%, but the isolated yields were much lower because of the tedious gas chromatography required to separate **4** from other compounds. Purification was not a problem in the [7] series and, with luck, will not generally be a difficulty.[6]



1 2 3 4

Mass spectrometry established the composition as $C_{12}H_{16}$ (precise mass 160.128135; calcd 160.125194) and revealed the major fragmentation to involve formation of C_8H_8, probably *p*-xylylene. The ultraviolet spectrum [EtOH, nm (log ϵ): 212 (4.3), 253 (4.0), 296 (2.8)] is only moderately shifted from that of [7]paracyclophane.[5] The 60-MHz, room temperature pmr spectrum showed four approximately four-proton signals at τ 2.83 (singlet), 7.51 (broad triplet), 8.85 (center of multiplet), and 9.67 (center of multiplet). The 100-MHz spectrum is sharper at 90° but broadened considerably and otherwise changed at −80°. At the lower temperature the

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[6] Best results were obtained by either sequential passes through a 6-ft, 10% DC 710 silicone oil column and a column composed of a 1:1 mixture of 6% Bentone 34 and 6% didecyl phthalate or single passes through a 10% OV-1 column. Either way is tedious.

triplet at τ 7.51 is split into two double doublets and the multiplet at τ 9.67 split into two multiplets of approximately equal areas, one of which is shifted downfield and the other upfield to τ 10.6. Such signals are consistent only with the paracyclophane structure **4**. Benzocyclooctene is eliminated as a possibility by a simple comparison of spectra[7] and [6]metacyclophane would be expected to show neither so simple a pmr spectrum nor so complex an ultraviolet spectrum.[5]

As **4** is a liquid, the determination of the amount of bending in the "benzene" ring must await X-ray analysis of an appropriate derivative. However, comparisons can be made with the estimates of Allinger and his coworkers. Early calculations[8] using the method of Pariser and Parr gave an angle of *ca.* 25–30° for θ. More recently an angle of 22.4° has been suggested[9] on the basis of force-field calculations which reproduce well the structures of [7]- and [8]paracyclophanes. Using this angle, an ultraviolet spectrum closely approximating the experimental was calculated.[9] There can be no doubt that **4** is substantially deformed.

The question of aromaticity of [6]- and [7]paracyclophanes requires most careful scrutiny, but the pmr spectrum clearly reveals a ring current and thus within the limits of this single criterion, these paracyclophanes are still aromatic.

We suspect the mechanism of formation of **4** involves radicals similar to those recently implicated in the formation of *p*-xylene from 4,4-dimethylcyclohexadienylidene.[10] We have not yet explicitly tested this surmise, however.

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Equivalence of Metal Centers in the Iron–Sulfur Protein Active Site Analogs $[Fe_4S_4(SR)_4]^{2-}$

Sir:

The synthetic clusters $[Fe_4S_4(SR)_4]^{2-}$[1,2] serve as close structural[2–4] and electronic[1,5,6] representations of the $[Fe_4S_4(S\text{-}Cys)_4]$ active sites of oxidized ferredoxin (Fd_{ox}) and reduced "high-potential" (HP_{red}) proteins.[7] The structures of the analogs $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$[2] and $(Me_4N)_2[Fe_4S_4(SPh)_4]$[8] reveal noncrystallographically imposed D_{2d} anion symmetry. Formal oxidation state considerations[1,2] imply a possible mixed valence [2Fe(II) + 2Fe(III)] property for the dianions. In view of the same total oxidation level for Fd_{ox}, HP_{red}, and $[Fe_4S_4(SR)_4]^{2-}$,[1,5,6] their structural similarities, and the current interest in mixed valence compounds,[9] the equivalence of all irons apparent in the crystalline state at ambient temperature[2,8] has been further investigated under different conditions in several laboratories. Techniques capable of detecting widely variant electronic state lifetimes (τ) have been employed in order to differentiate trapped valence (integral oxidation states) *vs.* delocalized properties of the dianions.

Pmr spectra of some 12 dianions (R = alkyl, aryl) obtained over a wide temperature interval in several solvents consistently reveal one set of contact-shifted R signals.[5] For example, single CH_2 resonances downfield of TMS are found for $[Fe_4S_4(SEt)_4]^{2-}$ at −78° (−9.82 ppm, acetone-d_6) and at 118° (−14.4 ppm, DMSO-d_6). From these and similar data $\tau \lesssim 10^{-4}$ sec is estimated for a distinct Fe(II, III) valence state.

Mössbauer spectra of $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ at room temperature, 77, 4.2, and 1.5°K in zero field (Figure 1a) are characterized by a single quadrupole doublet. The isomer shift $\delta = +0.36$ mm/sec (relative to iron metal), quadrupole splitting $\Delta E_Q = 1.10$ mm/sec, and line width $\Gamma = 0.23$ mm/sec at room temperature. At the two lower temperatures $\Delta E_Q = 1.26$ mm/sec, $\Gamma = 0.28$ mm/sec,[10] and δ is unchanged. Both components of the doublet are of equal intensity and width at all temperatures and have the expected Lorentzian line shape. Spectra obtained in external magnetic fields were compared with computer-generated spectra (Figure 1b). For all values of the applied field H_0, the spectra indicate a single iron site with the magnetic field at the nucleus $H_n = H_0$, the sign of the principal component of the electric field gradient positive, and the asymmetry parameter $\eta < 0.4$. These results provide strong evidence that all iron sites are structurally and electronically equivalent at temperatures down to 1.5°K; *i.e.*, $\tau \lesssim 10^{-7}$ sec. Similar conclusions follow from frozen solution measurements on several dianions at 77 and 4.2°K. For $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ δ is intermediate between the values given by Reiff, *et al.*,[11] for tetrahedral $Fe(II){-}S_4$ (*ca.* +0.60 mm/sec) and $Fe(III){-}S_4$ (*ca.* +0.20 mm/sec).

The existence of trapped valence states (class I, II species[9,12]) requires electronic spectral properties of distinct $Fe(II,III){-}S_4$ chromophores. Tetrahedral Fe(II) is spectrally characterized by one or more ligand field bands of $^5E \rightarrow {}^5T_2$ parentage in the near-infrared region. For the $Fe(II){-}S_4$ chromophore such bands

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