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# SYMMETRY ALLOWED ELECTROCYCLIC REACTIONS OF RADICALS: CLEAVAGE OF THE ANION RADICALS OF 9,10-DIARYL-9,10-DIHYDROACENAPHTHYLENES.

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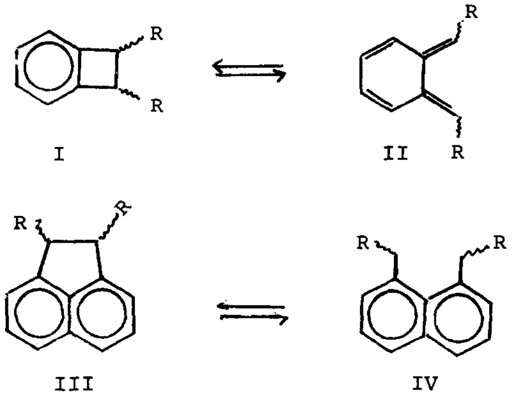
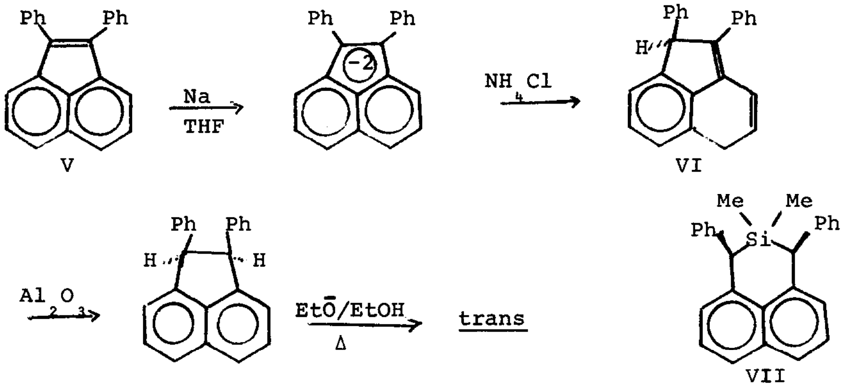
Although the electrocyclic reactions of most radicals, including anion radicals, are not symmetry allowed in either rotatory mode, it has recently been pointed out that the electrocyclic cleavages of benzocyclobutene anion radicals (I$^{\overline{\cdot}}$) to o-xylylene anion radicals (II$^{\overline{\cdot}}$) are allowed in the same (con) rotatory sense as those of the neutral substances.[1] In agreement with this, cis- and



<u>trans</u>-$\mathrm{I}^{\cdot-}$ (R=phenyl) cleave immeasurably rapidly at -78° via conrotatory paths.[1]

We now call attention to the fact that the similar electrocyclic cleavage in the acenaphthene anion radical series ($\mathrm{III}^{\cdot-}$) is also symmetry allowed (disrotatorily), according to orbital correlation diagrams. As is also the case with $\mathrm{I}^{\cdot-}$, the frontier orbital (HOMO) approach yields the opposite prediction (conrotation). Evidently the HOMO approach is, as has been widely suspected, too oversimplified to be generally reliable. For the aforementioned reasons, an experimental study of this theoretically interesting reaction was thought desirable. The cleavage, in addition, would represent the first reported instance of five membered ring cleavage in an anion radical, and would lead to the first stable derivative (a dianion) in the novel 1,8-naphthoquinodimethane series.

A novel synthesis for <u>cis</u>-III (R=phenyl) has developed as follows. 9,10-Diphenylacenaphthene (V) was converted to its dianion by Na/THF (ambient, over night). Quenching of the dianion with saturated aqueous $NH_4Cl$ gave a mixture of dihydro isomers consisting of small quantities of <u>cis</u>- and <u>trans</u>-III (R=phenyl) but predominantly of isomers such as VI in which one naphthalene nucleus has been reduced. However, alumina chromatography converted this mixture into



<u>cis</u>-III (R=phynyl) in overall 62% yield: mp 147-9°; nmr ($CDCl_3$) τ 2.2-3.5 (16H,m), 4.83 (2H,s); mass spectrum (70 ev) <u>m/e</u> 306 (M). This unusual conversion probably reflects adsorption of VI on the alumina surface on the side <u>trans</u> to its protruding phenyl substituent, followed by a suprafacial hydrogen

shift across the trans face of the molecule. Trans- III (R=phenyl) was obtained by base treatment of the cis isomer ($EtO^-$/EtOH, reflux): mp 99-101°; nmr $\tau$ 2.2-3.0 (16H,m), 5.27 (2H,s). The stereochemistry was assigned on the basis of this isomerization, the relative nmr chemical shifts of the saturated methine protons, and mechanistic considerations. Previously, catalytic reduction of V had been reported to give a dihydro isomer of unspecified stereochemistry (evidently the cis isomer, according to the reported mp, 146-7°).[2]

Reaction of cis- and trans-III (R=phenyl) with alkali metals in THF at temperatures from -78° to ambient gave, upon quenching with proton sources ($H_2O$, methanol, $NH_4Cl$) or dimethyldichlorosilane, complex product mixtures appearing to contain little of the desired cleavage trapping products. Surmising that the ultimate cleavage product, a dianion of IV, might not be stable in the presence of the relatively acidic molecules of unreacted III, we tried the lithium salt of biphenyl anion radical as an electron source. Such a soluble species should convert III to its anion radical essentially instantaneously and quantitatively, since the electron affinity of naphthalene is greater than that of biphenyl. This approach succeeded eminently well, but cleavage of the resultant anion radical still did not ensue until about 0°. Quenching of the dianionic product from either cis- or trans-III (R=phenyl) at this temperature gave the cyclic silane VII in good yield: mp 215-17°; nmr ($CDCl_3$) $\tau$ 2.1-2.9 (16H,m), 5.92 (2H,s), 10.00 (3H,s), 10.12 (3H,s). The nmr spectrum, with its nonequivalent silane methyl peaks, is clearly that of the cis isomer and implies the E,E configuration for the dianion (E,E - $IV^{-2}$). The apparently non-specific cleavages can not be construed mechanistically, however, because the Z,E dianion has not been observed, and it is quite conceivable that at 0° any initially formed Z,E dianion could have rapidly isomerized to the E,E isomer. Desiring a lower cleavage temperature [the $II^{-2}$ (R=phenyl) dianions are stable at -78°] we considered emplacing conjugating and/or electron withdrawing substituents at the para positions of the phenyl substituents of III (R=phenyl). Of the possibilities that would still retain the odd electron on the naphthalene nucleus our choice was p-phenyl substituents. Therefore cis- and trans-III (R=p-biphenylyl) were synthesized as previously. The cis isomer has mp 160-1 (EtOH); nmr ($CDCl_3$) $\tau$

2.1-3.0 (20H,m), 3.2 (4H, d, 8Hz), 4.68 (2H,s). Isomerization (t-butoxide/t-butanol) gave the trans-isomer: mp 192-4 (t-butanol); nmr ($CDCl_3$) τ 2.1-3.0 (24H,m), 5.17 (2H,s). Indeed both of these substances cleaved in less than 5 min at -95° (acetone-liquid nitrogen). Quenching at this temperature nevertheless still gave the cis silane from either isomer.

It should be noted that, though E,E-$IV^{-2}$ (R=phenyl) may well be planar or nearly so, the Z,E isomer is probably very highly twisted in its most stable configuration, for steric reasons. Therefore the barrier separating it from the E,E isomer (probably the perpendicular or 0,90 state) may be inordinately small. In order to reach such a twisted state an unsymmetrical disrotatory (lag disrotatory) mechanism of the type proposed for forbidden electrocyclic reactions in bicyclic systems[3] would be required and is proposed.

Finally, we should like to call attention to the enormous rate enhancement for the cleavage reaction engendered by addition of an electron to an antibonding orbital of III. Neutral cis-III (R=phenyl), heated to 275° for 10 hr. in diethylphthalate, with or without added trapping agents such as diphenylisobenzofuran, is recovered substantially unchanged. Its anion radical cleaves rapidly, as noted, at 0°.

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## References

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(3) N. L. Bauld, F. R. Farr, and C.-S. Chang, Tetrahedron Lett., **24**, 2443 (1972).