

Reaction of Homocyclo-octatetraene Dianion with Oxygen, Potassium Permanganate, and Methyl Iodide in Liquid Ammonia

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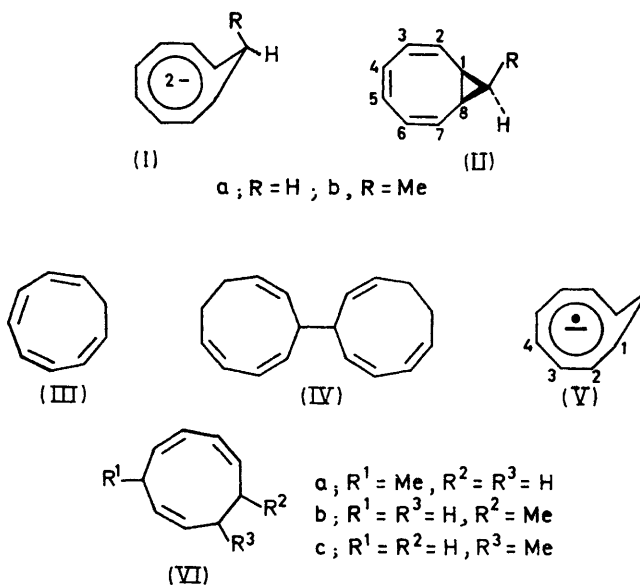
Summary Homocyclo-octatetraene dianion reacts with oxygen, potassium permanganate, and methyl iodide to give 5-substituted cyclonona-*cis,cis,cis*-1,3,6-triene derivatives.

(Ia) by MeI to give (V) plus Me[•] which couple], for it selectively (>95%) produced (VIa)(50%), formally by C(3) or C(4) alkylation then protonation, contaminated by only small amounts (<5%) of (VIb) and (VIc). By

RECENTLY we reported¹ that dilithium homocyclo-octatetraenide (Ia),² prepared by reducing (IIa) in ammonia, reacts with traces of air to give (IIa) (*ca.* 85%). It is interesting that while (IIa) is reformed, cyclonona-*cis,cis,cis,cis*-1,3,5,7-tetraene (III),³ formed by rupture of the C(1)—C(8) bond of (IIa), is not produced. To explore the possibility of actually generating (III) in this way, we investigated the reaction between (Ia) and oxygen in greater detail. We now find that (IIa) is obtained in only small amounts if dilithium-(Ia) is exposed rapidly to larger amounts of oxygen, but that instead, mainly dimer (IV) is obtained.

Oxygen (4 ml) was slowly injected in portions during 1 h through a rubber septum over the surface of the dilithium-(Ia) solution (*ca.* 10⁻² M; 1.5 mmol) at -78° under argon. The initially deep red-orange mixture became nearly colourless after 1 h. After aqueous work up in the usual way, (IIa) contaminated by only traces of (IV) was obtained in up to 85% yield. When oxygen (20 ml) was added at once to a similarly prepared solution of (Ia), a rapid reaction occurred and the mixture became pale yellow. The dimer (IV) was obtained in 51% yield. Under various conditions, disodium-(Ia) could not be oxidized to (IIa) but produced (IV) in up to 48% yield. KMnO₄ oxidation⁴ of (Ia) afforded (IV) in 67% yield while less satisfactory results were obtained using di-*t*-butyl peroxide as oxidant. The dimer might be formed *via* selective coupling [at C(3) or C(4)] of radical anion (V),⁵ the one-electron oxidation product of (Ia), to give a dimeric dianion which is then protonated.

The reaction between (Ia) (Li, Na, or K salts) and MeI (1 or 10 mol) may be of a similar type [*i.e.*, the oxidation of



contrast, the isomers (VIb) and (VIc) [(VIa) was absent] were obtained by reducing (IIb)⁶ as previously described for related compounds.¹ Although the alkylation may be equally well explained as proceeding through a S_N2-type pathway, it is interesting that the reaction between naphthalene dianion and MeBr appears to proceed through the intermediacy of naphthalene radical-anion plus Me[•], which couple.⁷

The structure (IV) m.p. 89—90°, follows from its spectral properties (n.m.r., i.r., u.v., mass), microanalysis, and consumption of *ca.* 6 mol. equiv. of hydrogen to give bicyclononyl. The saturated dimer was identical (n.m.r., i.r., and v.p.c.) to bicyclononyl obtained independently.⁸ The structure (VIa) follows from its spectral data, which show the expected differences from those of the isomeric methyl derivatives (VIb) and (VIc), and the observation that (VIa) reverts to methylcyclononane on absorbing *ca.* 3 mol.

equiv. of hydrogen. The structures (VIb) and (VIc) follow from similar spectral and chemical evidence.†

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† Spectral data are available from the authors. We thank Professor Radlick for comparison spectra of methylcyclononane.

‡ *Added in proof:* The reaction between (Ia) and isopropyl or t-butyl iodide gave results similar to that of the methyl iodide reaction.

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