

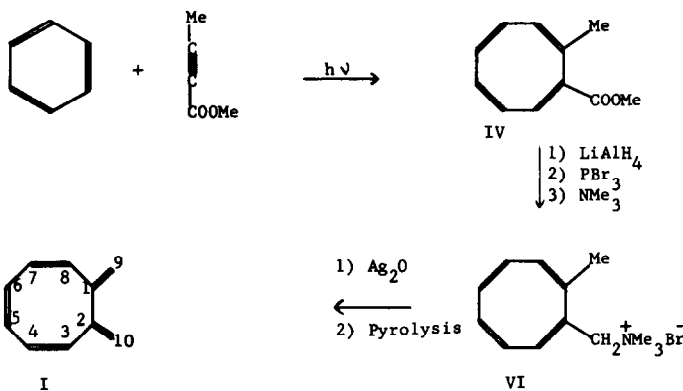
1,2-DIMETHYLENECYCLOOCTATRIENE

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We wish to report the synthesis of 1,2-dimethylenecyclooctatriene (I), a vinylogue of 1,2-dimethylenecyclobutene (II), and 1,2-dimethylenecyclohexadiene (III), by the following sequence of reactions:



Photochemical (low-pressure mercury arc, Corex filter) addition (1) of methyl 2-butynoate to benzene, which was used in large excess, gave a 50% yield of IV. Reduction of IV with lithium aluminum hydride gave a 72% yield of crude alcohol, which was converted by means of phosphorus tribromide in hexane-pyridine to 2-(bromomethyl)-methylcyclooctatetraene (V). Compound V was treated directly with trimethylamine in methanol solution to give VI in 40% yield based on the alcohol. VI formed greenish-yellow needles

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after crystallization from ethanol, m.p. 225-226° (Found: C, 57.64; H, 7.27; N, 5.38. $C_{13}H_{20}BrN$ requires C, 57.78; H, 7.46; N, 5.18). Compounds IV and VI, as well as the intermediates in the preparation of these compounds had the expected spectroscopic properties.

The CH_2 protons of VI were of some interest as their n.m.r. spectra in D_2O consisted of an AB quartet centered on τ 6.06 ($J_{AB} = 13.5$ cps). The AB quartet persisted till at least 100°, showing that inversion of the cyclooctatetraene ring is much slower in this compound than in the monosubstituted derivatives previously studied (2). This slowness was anticipated, as the transition state for inversion has most probably a planar ring and suffers from serious repulsions between the two adjacent ring substituents (2).

Pyrolysis of the dry quarternary hydroxide corresponding to VI in a stream of dry nitrogen at 25mm pressure and collection of the products at dry ice temperatures gave trimethylamine and a volatile, air-sensitive colorless olefin, whose properties are consistent with structure I. The olefin was purified by vapor phase chromatography at 50° on a short silicone SE 30 column, and was obtained in 35% yield. Because of the extreme sensitivity to oxygen, difficulties were encountered in obtaining a correct elementary analysis (Found: C, 91.31; H, 8.04. $C_{10}H_{10}$ requires C, 92.26; H, 7.74%). However, the mass spectrum gave a MW of 130 ($C_{10}H_{10}$ requires MW, 130.2). Furthermore, at low ionization voltages (e.g., 10v), the only significant peaks in the mass spectrum were at m/e 130 (48%), 129 (32%), 128 (4%), and 115 (14%).

The ultraviolet spectrum of I in hexane had two absorption bands, λ max. 272 $m\mu$ ($\log \epsilon$, 3.96) and 228 $m\mu$ ($\log \epsilon$, 4.23). The infrared spectrum of I as a liquid film is shown in Fig. 1. Exposure to air resulted in the loss of the long wavelength fine structure and in the appearance of a strong band in the carbonyl region.

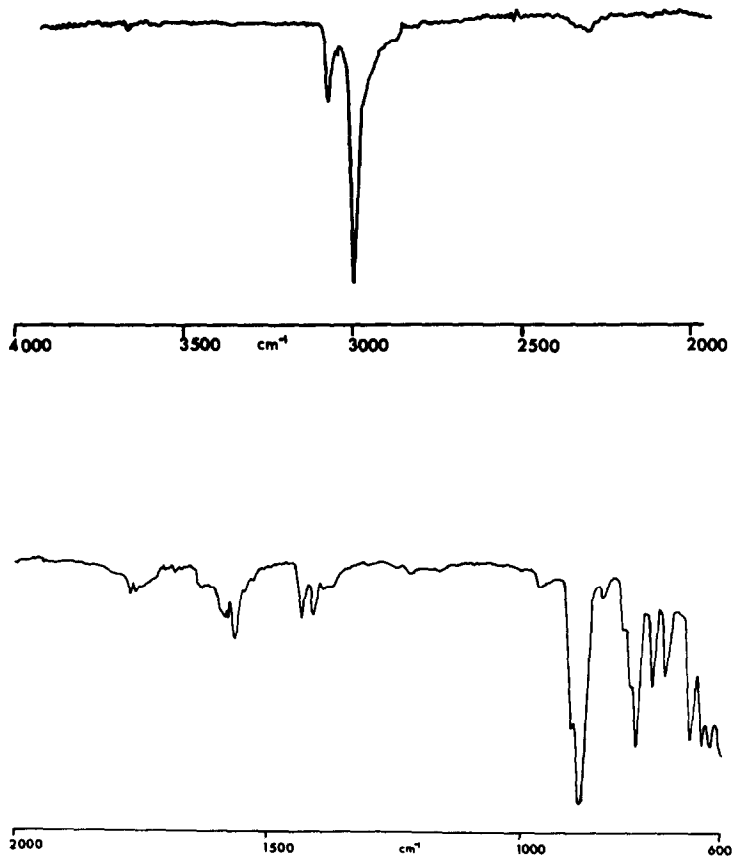


FIG. 1 Infrared Spectrum of I (Beckman IR-8)

The n.m.r. spectrum (Fig. 2) showed the absence of protons attached to saturated or aromatic carbons, and clearly showed the presence of terminal olefinic protons (τ 5.00 and 5.25). Protons 3 and 4 (and also 8 and 7) form a recognizable AB quartet (with further small splittings) having $J_{AB} = 12$ cps, as expected for pairs of cis-olefinic protons. The band at τ 4.3, which partially obscures the high-field band of the AB quartet, is relatively narrow and can be assigned to protons 5 and 6, which have the same chemical shifts. Also, these protons appear to show only small couplings to protons 4 and 7, a fact best explained in terms of a non-planar tub form for I. The chemical shifts of the ring protons would be expected to be at lower field in a planar or near-planar structure, because such a structure would exist only because of strong resonance stabilization. Molecular orbital (Hückel) calculations (3) gave a delocalization energy (DE) of 2.397β (cf. DE for II, 1.21β ; DE for III, 1.954β) and free valence values of 0.915 at C_9 and C_{10} (cf. 0.86 and 0.957 for analogous carbons in II and III, respectively) for a planar structure. The calculated DE of planar I is probably too high, even if a low β (-17 kcal/mole) is used, as the strain energy of the planar form is probably only about 25 kcal/mole (4), and thus a nearly planar molecule would be predicted.

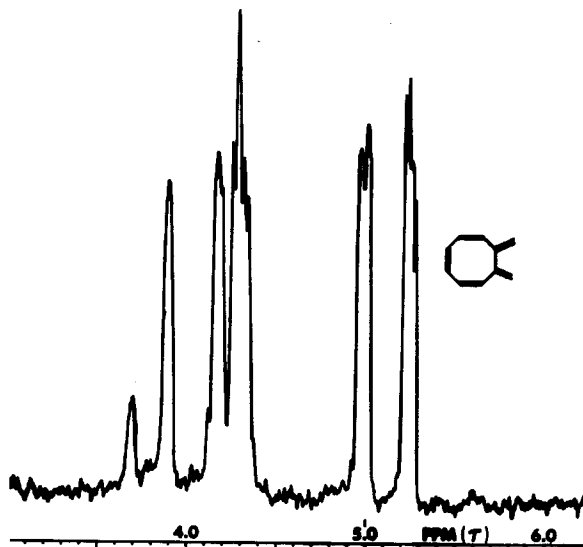
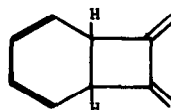


FIG. 2 Nmr Spectrum of I in CS_2 Solution, with TMS as an internal standard (Varian A60).

Both the n.m.r. and infrared spectra exclude structures Ia and Ib, which possess saturated CH or CH₂ groups. The ions formed in the mass



Ia

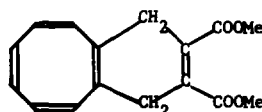


Ib

spectrometer from I, however, may well cyclize to give ions derived from Ia or Ib by the loss of one or two hydrogens. The ion at m/e 115 is formed at least in part by the loss of CH₂ from the m/e 129 ion (metastable peak at m/e 102.6) and may have structure VII. The same structure has been suggested by LeGoff and LaCount (5) for an ion obtained from cycloocta[c]furan,



VII, m/e 115



VIII

a compound closely related to I.

Tetracyanoethylene reacted extremely rapidly with I, but the compound formed appeared to be air-sensitive and was not completely characterized. Dimethyl acetylenedicarboxylate also reacted rapidly with I, with the complete disappearance of terminal olefinic protons, and the appearance of a new band (τ7.1) which can be assigned to the methylene protons in VIII. Although these experiments are still in a preliminary stage, there seems to be no tendency for 1,2-addition of dienophiles to I, such as occurs with II.

In the case of 1,4-addition of dienophiles (6) (Diels-Alder reaction), the reactivity sequence is III > I > II, which reflects the reactivity sequence, benzene < cyclooctatetraene (non-planar) << cyclobutadiene.

Acknowledgements

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