

The Adduct of Tropone and Cyclopentadiene: A New Type of Cyclic Reaction

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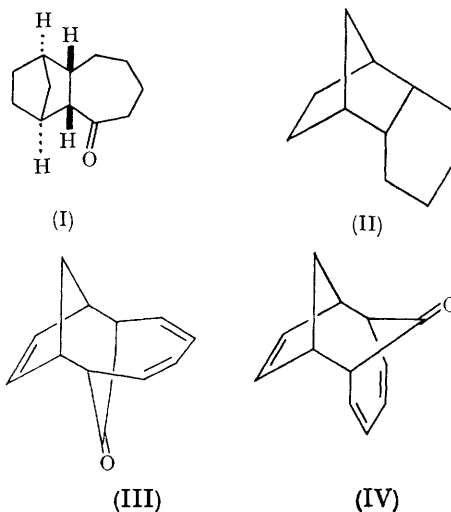
TROPONE and cyclopentadiene form a 1 : 1 adduct,* m.p. 68° (ν_{\max} 1725 cm^{-1} ; λ_{\max} 257 and 267 $\text{m}\mu$, ϵ 7680 and 7870), when left in the dark at room temperature for three days. We have investigated its chemistry in some detail, but now report only the evidence needed to prove the structure.

In boiling xylene the adduct dissociated into its original components, which could be isolated as their respective adducts with maleic anhydride. The dihydro-adduct, m.p. 92° (ν_{\max} 1715 cm^{-1} ; λ_{\max} 258 and 269 $\text{m}\mu$, ϵ 4720 and 4620°), in which only the isolated double bond has been reduced, is stable under those conditions. The saturated (therefore tricyclic) hexahydro-adduct, b.p. 90° at 0.1 mm. (ν_{\max} 1705 cm^{-1}), incorporated no deuterium on treatment with sodium deuterioxide in dioxan and deuterium oxide, under conditions that introduced three atoms of deuterium into the isomer (I). The carbonyl group is therefore in a six-membered ring with both α -hydrogen atoms at bridgeheads. Finally, photolysis of the hexahydro-adduct in hexane (500w medium-pressure mercury arc, through quartz) gave *endo*-tricyclo-[6,2,1,0^{2,7}]undecane (II) identical with a synthetic sample, and different from the *exo*-isomer which was also synthesised. Thus the structure of the adduct must be (III) or (IV).

A tentative decision in favour of (III) is suggested by the n.m.r. spectra. The CH_2 protons

on the methylene bridge should be shielded by the carbonyl group in (IV) but not in (III), so reduction of the carbonyl group in (IV) would be expected to shift the CH_2 resonance to lower field. In fact the peak from the CH_2 group was unchanged in the ketone and the alcohol.

The apparent inversion before cyclisation of the diradical produced on photolysis of the hexahydro-adduct is being investigated further.



* All new compounds gave satisfactory analyses, i.r., u.v., and n.m.r. spectra.

† We have shown that the adduct of tropone and cyclohexa-1,3-diene, mentioned by Nozoe *et al.* (Ref 1) is a homologue of (III).

The reaction of tropone with cyclopentadiene thus represents the first example† of "6 + 4" cyclo-addition² (though it is also a "3 + 4" addition³), which is allowed a concerted course by Hoffmann and Woodward's analysis of the symmetry of the interacting orbitals. The *exo*-configuration corresponding to (III) has just been predicted⁴ for the concerted reaction, in agreement with the experimental indications above. However,

Hoffmann and Woodward's arguments also allow concerted formation of a 1,2-*endo*-adduct, which might then rearrange to the more stable 1,6-*exo*-isomer (III). The adduct is formed much more rapidly from tropone hydrochloride than from free tropone. Signs of a possible intermediate in the latter reaction are now being followed up.

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¹ T. Nozoe, T. Mukai, K. Takase, and T. Nagase, *Proc. Japan. Acad.*, 1952, **28**, 477.

² R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 2046.

³ A. W. Fort, *J. Amer. Chem. Soc.*, 1962, **84**, 4979; R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.*, 1963, 129; R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 1964, 144.

⁴ R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 4388.