Reaction of Tropone with Cyclopentadiene

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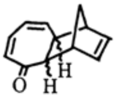
The Diels-Alder reaction of tropone was reported by Nozoe et al.[1] and the structure of the adduct with maleic anhydride was established. However, the nature of the product which results from the reaction of tropone as a dienophile has not been clarified, although a few reactions have been carried out.[2,3] We wish to present evidence for the structure of the adduct obtained from the reaction of tropone and cyclopentadiene; the reaction comprising the first example of a concerted 6+4 cycloaddition.[4]

Heating of tropone and cyclopentadiene at 80°C in benzene for 5 hr. yielded the 1 : 1 adduct I, m. p. 70—71.5°C (Found: C, 83.78; H, 6.98. Calcd. for $C_{12}H_{12}O$: C, 83.68; H, 7.02%. UV λ_{max}^{MeOH} 238 (ε=2840), 248 (3370), 257 (4520), 266 (4630), 300 mμ (480), IR ν_{max}^{KBr} 1715 cm^{-1}, MS *m/e*: 172 (M^+), 107 (base peak), 78, 66, 39. 2, 4-DNP., 185°C (decomp.) (Found: C, 61.32; H, 4.75. Calcd. for $C_{18}H_{16}O_4N_4$: C, 61.36; H, 4.58%. UV λ_{max}^{MeOH} 365 mμ (ε=19100)). These spectral observations confirm the molecular formula and indicate the presence of an isolated carbonyl group and a conjugated diene system. The NMR spectrum of I in benzene exhibited signals at 1.22 (1H, sextet, *J*=11.3, 4.8), 2.12 (1H, d. *J*=11.0), 2.54 (2H, br.s.), 3.03 (2H, m.), and 5.03—5.88 p. p. m. (6H, m.) supporting structure Ib or Ic rather than Ia.



Ia

Ib

Ic

II

III

Although the reduction of I with sodium borohydride or sodium in ethanol failed to take place, reduction with lithium aluminum hydride in tetrahydrofuran yielded an alcohol II, m. p. 32.5—34.5°C (Found: C, 82.88; H, 7.99, Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10%. UV λ_{max}^{MeOH} 243 (ε=4552, sh.), 252(5720), 262 (5668), 273 mμ (3173), IR ν^{KBr} 3490 cm^{-1}. NMR δ^{CDCl_3} 1.49 (1H, m.), 2.21 (1H, d. *J*=10.4), 2.74 (5H, br.m.), 3.90 (1H, br.), 5.83 (4H, m.), 6.21 p. p. m. (2H, br.s.)). From a comparison of the NMR spectra of I and II in deuterochloroform, it is apparent that the methylene protons in I are practically unaffected by the anisotropy of the carbonyl group, a finding in accord with structure Ib but not Ic; an appreciable shift of these protons would be expected in the latter. The fact that the protons on the isolated double bond absorb at appreciably higher field in the case of I (5.99 p. p. m.) than in the case of II (6.27 p.p.m.) is also in accord with structure Ib. Thus the structure Ib was concluded as the correct representation of the structure of I.

Reduction of I with sodium in *n*-butanol yielded the corresponding dihydroalcohol 3, m. p. 95—97°C (Found: C, 81.89; H, 9.10. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15%) which showed only end absorption in its ultraviolet spectrum. NMR δ^{CDCl_3} 1.1—2.6 (11H, br. m.), 3.97 (1H, br.), 5.53 (2H, br.s.), 5.97 (2H, s.). The stereochemistry of the hydroxyl group in II is tentatively assigned by analogy with the cases of norbornyl derivatives.[5] The structure Ib assigned for the adduct is in agreement with the prediction[4] of Hoffmann and Woodward for concerted cycloaddition.[*2]

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[1] T. Nozoe, T. Mukai, T. Nagase and Y. Toyooka This Bulletin, **33**, 1147 (1960).

[2] T. Nozoe, T. Mukai, K. Takase and T. Nagase, *Proc. Japan Acad.*, **28**, 447 (1952).

[3] Reaction of 3,4-benzotropone and tetrachlorocyclopentadiene gives an adduct similar to that obtained here. The structure of the adduct, however, has not been fully established (private communication from Professor Y. Kitahara, Tohoku University).

[4] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046, 4388 (1965).

[5] E. I. Snyder and B. Franzus, ibid., **86**, 1166 (1964); P. Laszlo and P. von Ragué Schleyer, ibid., **86**, 1171 (1964).

[*2] After completion of this work, we became aware of a paper recently published by Cookson et al. (*Chem. Comm.*, 15 (1966)), in which the authors assigned the same structure for the adduct.