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Cycloaddition of Spiro[2.4]hepta-4,6-diene to Tropone

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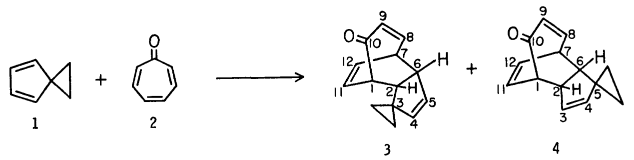
Cycloaddition of cyclopentadiene to tropone leading to *exo*-tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-trien-11-one was reported by Cookson *et al.*[1)] and by Itō *et al.*[2)] as the first example of a thermal [6+4] cycloaddition which had been predicted by Hoffmann and Woodward.[3)] Whereas in [4+2] cycloaddition dimethylfulvene reacts with dienophile in the same way as cyclopentadiene does,[4)] in [6+4] cycloaddition the fulvene was reported to react with tropone as a 6π electron addend due to participation of the exocyclic double bond, the final product being a 2 : 1 adduct of tropone and the fulvene.[5)] From our interest in the alteration of the reaction pattern we carried out cycloaddition of spiro[2.4]hepta-4,6-diene (**1**) to tropone (**2**). Since cyclopentadiene, dimethylfulvene, and **1** all react in a uniform way in the [4+2] cycloaddition, it would be of interest to know the behavior of **1** in the addition reaction with tropone and, particularly, to determine whether or not the cyclopropane ring in **1** takes part displaying its masked unsaturation character.

When a mixture of an equimolar amount of **1** and **2** was heated at 110°C for 6 days in a tube sealed under nitrogen, two major products in a 79 : 16 percent ratio were indicated by vpc, together with two minor products in a total 5%. The vpc peak ratio of the two major products was constant through the reaction period, indicating that they are kinetically-controlled. The 79 and 16% products (**3** and **4**) were isolated by a preparative gas chromatograph (2 m×15 mm) and shown to be both 1 : 1 adducts by elementary analyses and molecular weight determinations (osmometry and mass spectroscopy). Catalytic reduction of the adducts over PtO_2 in ethanol resulted in an uptake of 3 mol of hydrogen and in acetic acid that of 4 mol of hydrogen indicating the presence of three double bonds and one cyclopropane ring. The UV and IR properties indicate the presence of an $\alpha\beta$-unsaturated carbonyl group for both the adducts, and consequently, the absence of a [6+4] cycloaddition type product as observed in the reaction of cyclopentadiene.



Conformatory evidence for the indicated structures **3** and **4** was obtained from the 100 MHz PMR spectra, in which the signal assignments were performed by double resonance technique. The NMR parameters (first-order analyses) are summarized in Table 1. It was concluded that the orientation of the cyclopentene moieties in both the adducts was *endo* by the relatively small vicinal $J_{1,2}$ and $J_{6,7}$ and by the presence of long-range $^4J_{2,11}$ and $^4J_{6,12}$ due to the "W" arrangements of

TABLE 1. NMR DATA OF THE ADDUCTS (**3** AND **4**)

1) Chemical shift, τ

	Solvent	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{11}	H_{12}
3	CCl_4	6.89	7.46	—	4.91	4.72	6.35	6.75	2.99	4.42	4.00	3.76
	C_6D_6	6.73	7.55	—	5.08	4.88	6.64	7.27	3.43	4.26	4.16	3.96
	$\Delta\tau$[a)]	−0.16	0.09	—	0.17	0.16	0.29	0.52	0.44	−0.16	0.16	0.20
4	CCl_4	6.68	6.58	4.58	4.95	—	7.16	7.12	3.12	4.39	4.03	3.70
	C_6D_6	6.55	6.69	4.82	4.14	—	7.47	7.66	3.61	4.26	4.19	3.98
	$\Delta\tau$[a)]	−0.13	0.11	0.24	0.19	—	0.31	0.54	0.49	−0.13	0.16	0.28

a) $\Delta\tau \equiv \tau$ in C_6D_6 − τ in CCl_4.

2) Coupling constant, Hz.

3	$J_{1,2}=2.0$	$J_{1,9}=1.9$	$J_{1,5}=\sim0.2$	$J_{1,11}=7.4$	$J_{1,12}=1.2$	$J_{2,6}=8.8$
	$J_{2,11}=\sim0.6$	$J_{4,5}=5.4$	$J_{4,6}=1.9$	$J_{5,6}=2.1$	$J_{6,7}=2.0$	$J_{6,12}=\sim0.5$
	$J_{7,8}=8.8$	$J_{7,9}=0.9$	$J_{7,11}=1.2$	$J_{7,12}=6.9$	$J_{8,9}=11.0$	$J_{11,12}=8.6$
4	$J_{1,2}=2.1$	$J_{1,9}=1.9$	$J_{1,11}=7.3$	$J_{1,12}=1.2$	$J_{2,3}=2.2$	$J_{2,4}=1.8$
	$J_{2,6}=8.8$	$J_{2,11}=0.7$	$J_{3,4}=5.7$	$J_{3,7}=\sim0.4$	$J_{6,7}=2.2$	$J_{6,12}=0.6$
	$J_{7,8}=8.7$	$J_{7,9}=0.7$	$J_{7,11}=1.2$	$J_{7,12}=6.8$	$J_{8,9}=11.1$	$J_{11,12}=8.7$

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* Née OHTSURU.

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2) S. Itō, Y. Fujise, T. Okuda, and Y. Inoue, This Bulletin, **39**, 1351 (1966).

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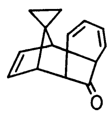
5) a) K. N. Houk, L. J. Luskus, and N, S. Bhacca, *J. Amer. Chem. Soc.*, **92**, 6392 (1970). b) N. S. Bhacca, L. J. Luskus, and K. N. Houk, *Chem. Commun.*, **1971**, 109.

related protons. The values of $J_{1,2}$ and $J_{6,7}$ are of nearly the same magnitude as the corresponding coupling constants reported for the major [4+2] adduct of cyclopentadiene with 2-chlorotropone, 1-chlorotricyclo-[5.3.2.0$^{2,6(exo)}$]dodeca-3,8,11-trien-10-one.[6] Relative configuration (*anti* or *syn*) of the cyclopropane ring and the carbonyl group in **3** and **4** was determined by the following observations: the presence of spin-couplings between H_6 (or H_2) and the olefinic protons in **3** (or in **4**) (determinable by double resonance experiments); the relatively higher-field positions of H_1 and H_2 signals in **3** and those of H_6 and H_7 in **4** arising from the long-range anisotropy effect of the cyclopropane ring; and the presence of long-range couplings between H_1 and H_5 in **3** ($^5J_{1,5}$) and H_3 and H_7 in **4** ($^5J_{3,7}$) located in the zigzag paths.



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Thus it is found that, with tropone, cyclopentadiene reacts as a 4π electron addend, dimethylfulvene as a 6π addend, and the present **1** as a 2π addend. In comparison to the reaction conditions reported for cyclopentadiene and dimethylfulvene,[1,2,5] the occurrence of reaction of **1** seems to require the severest conditions. A molecular model suggests that the [6+4] cycloadduct from **1** and **2** (**5**), if formed, would have severe steric compression around the cyclopropane ring and the butadiene bridge, so that this cycloaddition process would be strongly retarded and the cyclopentadiene moiety in **1** compelled to react as a 2π addend toward the 4π electron system in **2**, despite the higher activation energy required.

Experimental

Melting points were taken in capillary tubes and are corrected. Infrared spectra were determined with a Nippon Bunko IR-S spectrometer, ultraviolet spectra with a Hitachi EPS-3T spectrometer, and NMR spectra with a Varian A-60A and HA-100. VPC analysis was carried out on a Hitachi gas chromatograph K-53 equipped with a hydrogen flame ionization detector, using a 1 m×3 mm glass column packed with 5% XE 60 on Chromosorb W.

Reaction of 1 with 2. Diene **1** was prepared by the reported method.[7] A mixture of 1.5 g of **1** and 1.6 g of **2** was placed in a tube, sealed under nitrogen, and heated at 110°C for 6 days. VPC analysis of the reaction mixture revealed two major products (**3** and **4**) in a 79: 16 percent ratio, with two minor products in a total 5%. Isolation of **3** and **4** was carried out by a Yanagimoto gas chromatograph GCG-3 equipped with 2 m×15 mm glass column packed with 5% XE 60 on Chromosorb W. With a column temperature 180°C and helium carrier gas 300 m*l*/min, the retention times were 25 min for **3** and 31 min for **4**. Recrystalliaztion of the **3** fraction thus isolated from *n*-pentane gave colorless crystals, mp 66—66.5°; mass spectrum (70 eV) *m/e* 198 (parent peak); molecular weight by osmometry 192; UV λ_{max} (95% EtOH): 225 mμ (shoulder, ε 7000), 265 (1800); IR ($CHCl_3$): 1660 cm^{-1} (CO). Found: C, 84.76; H, 7.17%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%. Recrystallization of the **4** fraction from *n*-pentane gave colorless crystals, mp 96.3—97.0°C; mass spectrum (70 eV) *m/e* 198 (parent peak); UV λ_{max} (95% EtOH): 230 mμ (shoulder, ε 5370), 260 (2000); IR ($CHCl_3$): 1656 cm^{-1} (CO). Found: C, 85.10; H, 7.14%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%. NMR data for **3** and **4** are summarized in Table 1.

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[6] S. Itō, K. Sakan, and Y. Fujise, *Tetrahedron Lett.*, **1969**, 775.

[7] C. F. Wilcox, Jr., and R. R. Craig, *J. Amer. Chem. Soc.*, **83**, 3866 (1961) and references cited therein.