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CYCLOADDITION REACTION OF TROPONE WITH 1,1-DIMETHYL-2,5-DIPHENYL-1-SILACYCLOPENTADIENE

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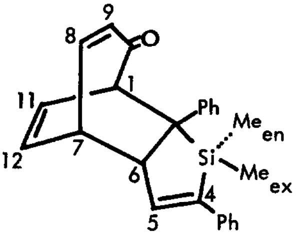
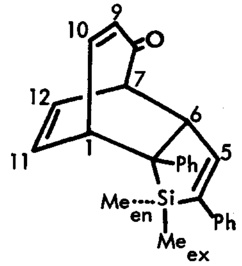
Tropone (I) has been known to react as an electron-defficient 6π, 4π or 2π addend in [$\underline{6}$+4] and [$\underline{4}$+2] and [$\underline{2}$+4] (1) cycloadditions, respectively, when heated with cyclopentadienes (2). The reactions generally proceed with high stereoselectivity, but with poor peri- and regioselectivities. The periselectivity depends largely on the reaction conditions employed, the [6+4] reaction being kinetically controled and the [4+2] reaction controled thermodynamically (2c, 3). Modification of the methylene group of cyclopentadiene also appears to alter the reaction course as was indicated by the reactions of I with 2,5-dimethyl-3,4-diphenylcyclopentadienone (3), spiro[2,4]hepta-4,6-diene (4), 3,4-dimethyl-1-thio-1-phenylphosphole (5), 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene (1d) and isobenzofurane (6). 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene (II) is another modified butadiene with a bulky and electropositive dimethylsilylene group connecting both termini and known to undergo thermal [$\underline{4}$+2] cycloaddition with acetylenes and olefines (7) and [$\underline{2}$+4] addition with 2,3-dimethylbutadiene (8). In order to find out the factors controling these selectivities, the cycloaddition reaction of I with the silole II was carried out (9).

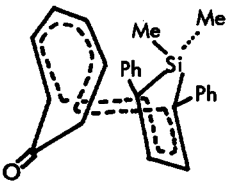
Tropone (I) was heated with 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (II) at 138° for 15 hrs under nitrogen atmosphere in sealed tube to give a mixture of two products in addition to the recovery of II. The preparative TLC (silica gel) resulted in the isolation of II (18%), the major adduct (III), m.p. 183-183.5° (52%), and the impure minor adduct (IV, amorphous, 19%) (10). The almost superimposable mass spectra [m/e 368 (M^+), m/e 262 base peak (II^+)] of III and IV indicate both to be the



III



IV



A

1 : 1 adducts of I and II. Ultraviolet properties of these compounds [λ_{max}^{MeOH} 220 sh (19270), 229 sh (17230), 255 (15480), 284 sh (4060), 292 sh (2370) for III, λ_{max}^{MeOH} 220 sh (16720), 229 sh (14890), 255 (12970), 284 sh (3000), 292 sh (2100) for IV] are also quite similar to each other and to that of 1,8-diphenyl-3,4,9,9-tetramethyl-9-silabicyclo[4,3,0]-nona-3,7-diene (8), suggesting the presence of a stylene chromophore. Both adducts contain an α,β-unsaturated carbonyl system as shown by IR spectra [ν^{KBr} 1656, 1640, 1250, 763 cm^{-1} for III, ν^{KBr} 1664, 1640, 1250, 778 cm^{-1} for IV]. Overall PMR pattern of these compounds is also very similar with each other.

Of the four possible structures having the α,β-unsaturated carbonyl group ([π4s+π2s] adducts), the correct structures were deduced for both adducts from the following observation in the PMR spectral analysis: i) Irradiation of H_5 which is the only vinylic proton with no coupling with the other vinylic protons, allows identification of H_6. Of the other allylic proton in III, H_7 (br.t) couples with H_6 (shown by the irradiation of the former signal). ii) In both compounds, H_1 signal (ddd in III and br.t

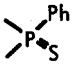
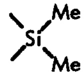
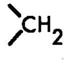
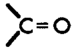
TABLE I. PMR Parameters of III and IV (100 MHz in $CDCl_3$)

	δ_1	δ_5	δ_6	δ_7	δ_8	δ_9	δ_{10}	δ_{11}	δ_{12}	Ph	Me_{ex}	Me_{en}
III	4.34 ddd	6.84 d	4.09 dd	3.53 br.t	7.01 dd	5.52 ddd	—	6.23 ddd	6.43 ddd	7.15-7.35	-0.42	0.40
IV	4.21 br.t	6.95 d	3.75 dd	3.65 br.d	—	5.59 ddd	7.15-7.40*	6.62 ddd	6.05 ddd	7.15-7.40	-0.45	0.41

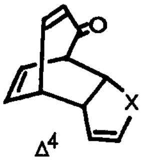
	$J_{1,9}$	$J_{1,10}$	$J_{1,11}$	$J_{1,12}$	$J_{5,6}$	$J_{6,7}$	$J_{7,8}$	$J_{7,9}$	$J_{7,11}$	$J_{7,12}$	$J_{8,9}$	$J_{9,10}$	$J_{11,12}$
III	1.9	—	7.6	1.2	3.0	1.6	8.5	0.7	1.0	7.6	11.0	—	7.6
IV	0.7	6.5	7.5	1.0	3.2	1.1	—	2.1	1.2	7.8	—	11.6	8.5

*Overlaps with phenyl signals.

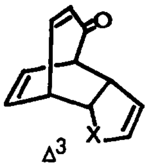
TABLE II. Thermal [4+2] Cycloadditions of Tropone with Cyclopentadienes

X	conditions	peri-selectivity	[4+2] addition stereo-selectivity	 regioselectivity $\Delta^4 : \Delta^{3*}$	references
	100°, 4-6 days	[4+2]	endo	1 : 0.6	5
	110°, 6 days	[4+2]	endo	1 : 0.2	4
	138°, 15 hrs	[4+2]	endo	1 : 0.37	present study
	127°, 36 hrs	[6+4] [4+2]	endo/exo 83 : 13	major minor	1c also cf. 1e
	100°	[6+4] [8+2] [4+2]	endo	sole prod.	3

* Δ^4 and Δ^3 refer to the following partial structures.



Δ^4



Δ^3

in IV) appears in the low field than H_7 signal (br.t in III and br.d in IV), the phenomenon attributed to the paramagnetic anisotropy of phenyl group on the adjacent carbon atom. iii) The detection of the nuclear Overhauser effect at H_1 signal (8% in III and 3% in IV) on irradiation of the endo methyl group verifies the presence of H_1 in the vicinity of the methyl group and allows the unequivocal assignment of methyl signals. iv) Small coupling constants ($J_{6,7}$) of H_6 in III and IV reveal the endo configuration of the silacyclopentene moiety in both adducts (11). The PMR parameters determined are listed in the TABLE I.

Peri-, stereo- and regioselectivities found in the present reaction have common features, as shown in TABLE II, with those previously observed in the reaction of I with the various cyclopentadiene derivatives. Although tropone tends to afford [4+2] adducts at higher temperature (1c, 6), the [6+4] adduct was completely absent in the present reaction as in the cases of spiro[4,2]heptadiene (4) and the phosphole (5). One possible and probably main factor for this perispecificity is, as was pointed out by Tanida for spiro[4,2]heptadiene (4), a severe steric hindrance between X and carbon bridge in the transition state (shown in A) of the symmetrically allowed [6+4] reaction. It is remarkable that regioselectivity, Δ^4 adducts predominating over Δ^3 isomers (TABLE II), was kept in all cases examined, regardless of the electronic properties of X. Both stereo- and regioselectivity observed in these reactions follow the result of the calculation of stabilization energy (2c) for the reaction of I and cyclopentadiene, suggesting various substituents studied so far on cisoid butadiene have too small effect to upset the stabilization due to the π-π interaction.

References and Footnotes

* To whom all the correspondences should be addressed.

1) An underline is used here to indicate the mode of addition of the subject compound (tropone in this sentence).

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9) If the reaction had afforded [6+4] adduct, it was also our intention to investigate its possibility as a dimethyl sililene generator.

10) IV was obtained only as a mixture with III (III:IV=5:6). Because of the instability of IV, further purification was abandoned. The spectral data for IV described in this paper were obtained by subtracting absorptions due to III from those of the mixture. The yields are corrected accordingly.

11) For coupling constant in the similar situation, see S. Itô, K. Sakan and Y. Fujise, Tetrahedron Letters, 775 (1969).