51. Steric Effect in [6+4] Cycloaddition Reactions. Part I

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Summary. Kinetics of cycloaddition of tropone to 6-methylfulvene and 6,6-dimethylfulvene were determined. It was concluded that steric effects play a role in [6+4] cycloadditions.

Most of the [6 + 4] cycloaddition reactions so far carried out have used tropone (**1**) as one addend. As cycloadditions are known to occur easily if the electron densities of the addends are very different [1], the reason for the high reactivity of tropone must be seen to lie in its low electron density. It is therefore understandable why tropone (**1**) does not dimerize thermally even in concentrated solutions at up to 100° [2] but easily undergoes reactions with such electron rich compounds as cyclopentadiene [3] and cyclohexadiene [3], [4]. Though electronic effects do certainly play an important role in [6 + 4] additions too, we report here about a steric effect in a reaction of this type.

One of the few examples of [6 + 4] additions is the double addition of tropone (**1**) to 6,6-dimethylfulvene (**2a**) [5]. *Houk et al.* [5] found that tropone (**1**) is first added at the 6 and 2 positions of **2a** to form **3a**, which immediately undergoes a [1,5] hydrogen shift to yield the rearranged 1:1 adduct **4a**. A second molecule of tropone (**1**) is then added to **4a** similarly[1]. A concurring [4+2] addition was found to be more than 18 times slower than the [6+4] addition. As this reaction proceeds at room temperature and in high yields of **5a**, and as the Authors [7] found that the same reaction takes place with 6-methylfulvene (**2b**), we were prompted to compare the reactivities of the two [6+4] cycloadditions. In an extended ^{1}H-NMR. investigation in hexadeuteriobenzene at 40°, during the early stage of the reaction, only resonances due to an intermediate with methyls attached to a saturated carbon could be observed, even when **1** was used in excess. Therefore the reactivity of the first addition step was easily investigated during one half-live of the total reaction. Towards the end of the reaction only resonances due to the 2:1 adducts **5** remained. Approximate reaction rates were obtained in a ^{1}H-NMR. spectroscopic study using tetramethylsilane as internal standard. By plotting the logarithm of the ratio of the peaks due to the fulvene methyl resonances and those due to tetramethylsilane against time during one half-live, straight lines were obtained from whose slopes pseudo first order rate constants were calculated. Dividing these rates by the molar concentration of **1** gave the corresponding second order rate constants.

Similar investigations at 100° showed a clean reaction of **2b** with a second order rate constant of ca. $5.0 \cdot 10^{-4}$ $l \cdot mol^{-1} \cdot s^{-1}$, though the ^{1}H-NMR.-data on reaction of

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[1] A similar reaction between tropone and 8,8-dimethylisobenzofulvene [6] furnished only a 1:1 [6+4] adduct. To this adduct a further addition of tropone cannot be expected because of the aromatic character of its incorporated indene moiety.

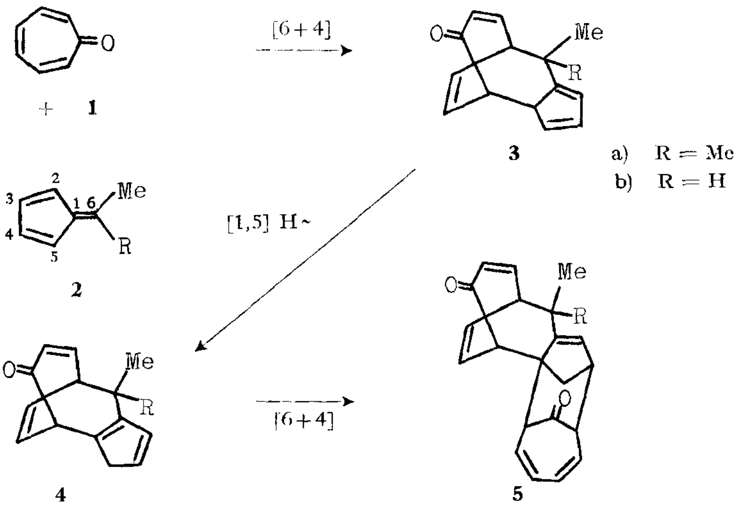
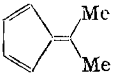
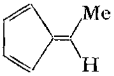


Table 1. *Second order rate constants of [6+4] addition of tropone to 6,6-dimethylfulvene* (**2a**) *and 6-methylfulvene* (**2b**) *at 40° in hexadeuteriobenzene*

		k [$l \cdot mol^{-1} \cdot s^{-1}$]
	(**2a**)	*ca.* $2.9 \cdot 10^{-6}$
	(**2b**)	*ca.* $7.7 \cdot 10^{-6}$

2a at this temperature indicated the formation of by-products in addition to the expected **5a**.

The rates obtained are of the same magnitude as those of the [6+4] addition between tropone (**1**) and cyclopentadiene [2], so the rate at 100° of [6+4] addition of 6-methylfulvene (**2b**) is approximately 900 times faster than that of [4+2] cycloaddition of norbornene to tropone [8]. In both cases tropone reacts as 4 π attendant.

The difference in reactivity between the two fulvenes **2a** and **2b** at 40°, a factor of 2.7, is most easily explained by a steric effect at one reaction center. As dimethylfulvene **2a** is more electron rich than the monomethyl compound **2b** and since we found that tropone tends to react preferably with electron-rich compounds [8] the results obtained show that steric demands may even overcome electronic effects in [6+4] cycloadditions.

Experimental Part

Melting points are corrected. Kinetic ^1H-NMR.-studies were carried out on a *Varian* T-60 spectrometer.

Preparation of adduct **5b**. A mixture of 2.65 g (25 mmol) tropone and 0.92 g (10 mmol) 6-methylfulvene was left at room temperature. After two days the mixture crystallized and NMR. spectroscopy indicated no remaining fulvene material. The mixture was crystallized twice from hot methanol to give 2.00 g (65%) white crystals, m.p. 159–60°. For spectral data refer to [7].

$C_{21}H_{20}O_2$ (304.4) Calc. C 82.86 H 6.62% Found C 82.82 H 6.66%

Kinetic NMR. investigations. 0.5 ml of a solution of 0.2M of fulvene **2a** or **2b** and 2.0M of tropone in C_6D_6 containing about 1% tetramethylsilane was kept under nitrogen in a sealed NMR. sample tube in a constant temperature bath at 40°. After appropriate time intervals the tube was removed from the bath, the NMR. spectrum immediately taken at 40°, and the tube immediately put into the bath again. This procedure was repeated seven times during one half-live. By plotting the logarithm of the ratios of the peak erea of the fulvene methyl resonance to that of tetramethylsilane first order rate constants were obtained. These constants divided by the molar concentration of tropone gave the corresponding second order rate constants.

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52. Steric Effect in [6+4] Cycloadditions. Part II

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Summary. 2-Chlorotropone reacts with 6,6-dimethylfulvene to form a 1:1 adduct only. From kinetic data as well as from structural evidence the conclusion was drawn that the [6+4] cycloadditions between tropones and cyclopentadiene or fulvenes are highly disfavoured by substituents at the reaction center.

In our recent publication [1] we reported a steric effect in the [6+4] addition between tropone and methylfulvenes. This reaction easily led to a double [6+4] adduct in high yield [1] [2]. In order to get information about effects of substitution at the tropone moiety we have now investigated the cycloaddition between 2-chlorotropone (**1b**) and 6,6-dimethylfulvene (**2**).

Leaving a mixture of the two addends **1b** and **2** at 50° for three days led to a clean reaction. A single carbonyl absorption (in CCl_4) at 1685 cm^{-1} in the IR. spectrum of the reaction mixture indicated the formation of a 1:1 adduct only. Two singlet resonances (in C_6D_6) in the ^{1}H-NMR.-spectrum at δ 0.92 and 1.01 were consistent with methyls attached to a saturated carbon and therefore with a [6+4] type addition of **1b** to **2**. Although the obtained adduct **4b** was resinous upon standing and exposure to air, it was stable enough in solution to allow, after separation by