scopy 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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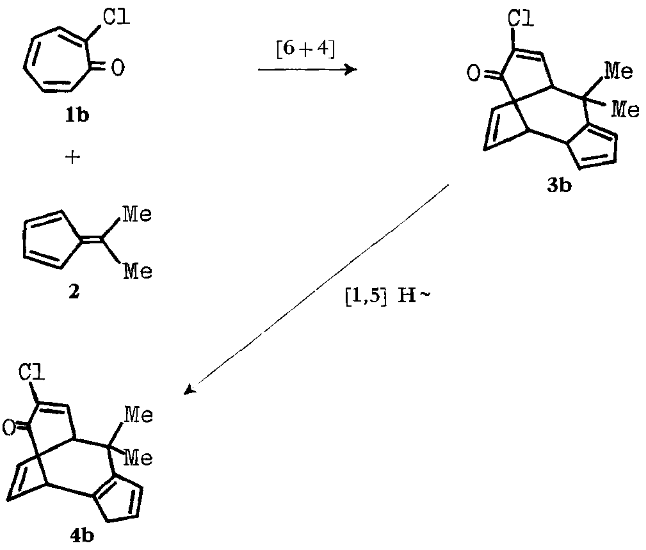
(9. XI. 72)

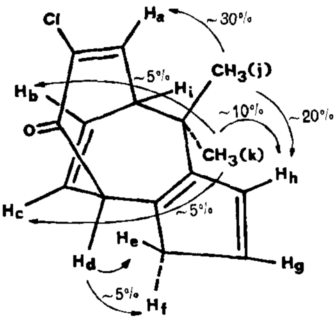
Summary. 2-Chlorotropone reacts with 6,6-dimethylfulvene to form a 1:1 adduct only. From kinetic data as well as from structural evidence the conclusion was drawn that the [6+4] cycloadditions between tropones and cyclopentadiene or fulvenes are highly disfavoured by substituents at the reaction center.

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 ^1H-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



preparative thin layer chromatography, a careful structure elucidation by 100 MHz NMR. spectroscopy including spin-decoupling experiments as well as measurements of the nuclear *Overhauser* effect [3]. The structure of **4b** is shown in Fig. 1. The arrows



4b

Fig. 1

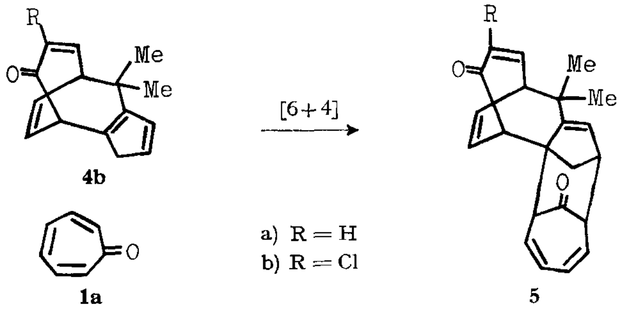
describe the observed NOE enhancements upon double irradiation at three different resonance positions of H_d, H_j, and H_k signals. Further NMR. spectral data are listed in Table 1. The accuracy of chemical shift differences δ is ± 0.02 ppm, that of coupling constants $J = \pm 0.5$ Hz.

Because of the labile nature of the obtained 1:1 adduct **4b**, it was converted, by treatment with excess tropone, into a mixed double [6+4] adduct **5b**, whose NMR. spectrum was very similar to that [2] of the double adduct **5a** obtained from tropone (**1a**) and 6,6-dimethylfulvene (**2**) and, therefore, consistent with structure **5b**.

Table 1. *^{1}H-NMR. spectral data of* (**4b**) *in hexadeuteriobenzene*

	δ (ppm)	Signal multiplicities and coupling constants (Hz)
H_a	6.83	*d*, $J_{ai} = 10$
H_b H_c	5.70 ~ 5.85	*m*
H_d	3.94	*m*
H_e H_f	2.77 and 2.55	AB $q \times t$, $J_{ef} = 23$,[a]) $J_{eg} \sim J_{fg} \sim J_{eh} \sim J_{fh} = 1$
H_g H_h	6.01 and 6.19	AB $q \times t$, $J_{gh} = 5.5$
H_i	~2.38	m
H_j	0.92	*s*
H_k	1.03	*s*

[a]) It must be noted that the geminal coupling between H_e and H_f of 23 Hz is extremely large. This high value is due to the two adjacent double bonds whose π lobes are in a dihedral angle with the methylene group of approximately 30° [4].



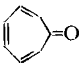
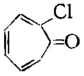
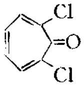
Monitoring the reaction between **1b** and **2** during two half-lives by NMR. spectroscopy revealed no change in resonance shapes during the reaction, indicating that the formation of the original adduct **3b** is much slower than its conversion into **4b** by the [1, 5] hydrogen shift. Thus the rate of the addition step was easily obtained by the technique described in our former publication [1].

In similar experiments with 2,7-dichlorotropone (**1c**) no methyl resonances in the 1.0 ppm region were generated, proving that no [6+4] addition took place. Some minor resonances at 1.8 ppm due to methyls attached to an unsaturated carbon of an adduct were detected after 48 h. Their formation however was considerably slower than those in adduct **4b**.

Table 2 shows the obtained second order rate constants and an earlier reported [1] value.

The listed data show similar rates in the additions of tropone (**1a**) and 2-chlorotropone (**1b**) toward fulvene (**2**). As cycloaddition to **1b** is restricted to the unsubstituted 4- and 7-positions, however, it may be considered that the introduction of

Table 2. *Second order rate constants of [6+4] cycloadditions of tropones* (**1**) *to 6,6-dimethylfulvene* (**2**) *in hexadeuteriobenzene at 40°*

		k ($l \cdot mol^{-1} \cdot sec^{-1}$)
	(**1a**)	ca. $2.9 \cdot 10^{-6}$ [a]
	(**1b**)	$2.8 \cdot 10^{-6}$
	(**1c**)	no reaction [b]

[a] Refer to [1].

[b] Containing heptadeuterio-N,N-dimethylformamide for solubility reasons.

Cl into tropone slightly increases the relative reaction rate. As the electron density hereby is decreased, such rate increase can be expected assuming that the fulvene is an electron donor and tropone an electron acceptor. In fact, it has been found [6] that the reactivities of 2-substituted tropones toward cyclopentadiene increase in the order: OMe < H < Cl < F.

A double [6+4] adduct, similar to that found with unsubstituted tropone (**1a**) [2] cannot be expected with 2-chlorotropone (**1b**), because for its formation a large steric interaction at the Cl-substituted reaction center had to be overcome in the second addition step. A usual addition of the *Diels-Alder* type at this stage would not proceed by an addition to the Cl-substituted carbon but is probably, as can be expected from earlier findings [1] [2] [5], too slow to form a double [6+4], [4+2] adduct in considerable amount at the mild reaction conditions (3 days, 50°).

The formation of a double [6+4] adduct was possible, however, by an addition of the 1:1 adduct **4b** to unsubstituted tropone (**1a**). No large steric interactions are involved in this reaction. The isolation of the compound **5b** in an overall yield of 42% proves that the additions can be carried out stepwise, and that **4b** does not undergo a second addition with **1b**.

Steric reasons must also be considered as the reason why 2,7-dichlorotropone (**1c**) does not undergo a [6+4] addition to fulvene **2**. In this example the discussed steric interaction of the chlorine already arises at the first stage.

The observed steric interactions are also compatible with the findings of *Ito et al.* in the cycloaddition of 2-chlorotropone to unsubstituted cyclopentadiene itself in which a variety of adducts have been found, the [6+4] adduct only being a minor product [7].

It must be pointed out that in [6+4] cycloadditions between tropones and fulvenes as well as between tropones and cyclopentadienes steric influence is of considerable importance. Unlike usual *Diels-Alder* reactions in which change in reactivity but not in structure of product arises from steric interactions, [6+4] additions, because of the complicated structures of their addends, will be overcome easily by other allowed processes, if their steric requirements are not met.

Experimental Part

Melting points are corrected. NMR. spectra were taken on a 100 MHz *Varian* HA-100, IR. spectra on a *Jasco* IR.-S, UV. spectra on a *Beckmann* DK-2A and Mass spectra on a *Hitachi* RMU-6 spectrometer. Kinetic experiments were carried out as described in our former publication [1].

Preparation of the mixed double adduct **5b** *of 6,6-dimethylfulvene, tropone and 2-chlorotropone.* 140.5 mg (1 mmol) 2-chlorotropone and 138 mg (1.3 mmol) 6,6-dimethylfulvene were kept in a sealed tube under nitrogen at 50°. After 3 days IR. spectroscopy indicated only traces of left 2-chlorotropone. Excess of fulvene was removed carefully at high vacuum and the remaining material was kept with 318 mg (3 mmol) tropone under nitrogen at 50° for 3 days. Separation by preparative thin layer chromatography (benzene/methylisopropylketone 9:1) yielded 146 mg (42% based on 2-chlorotropone) of mixed double adduct **5b** which easily crystallized. Recrystallisation from hot methanol yielded pure material m.p. 161–162°. UV. (cyclohexane): λ_{max} 203 nm (ε = 11000), 260 nm (ε = 3800), 270 nm (ε = 2900).

IR. ($CHCl_3$): 1715 (saturated C=O), 1675 cm^{-1} (C=CCl–C=O). Mass spectrum: 352 (M^+), *246* ($C_{15}H_{15}ClO$), *107*, 106 (C_7H_6O). The NMR. spectrum in C_6D_6 is very similar to that of compound **5a** [2]. The ClC=CH resonance appears as one doublet (J = 9.5) however.

$C_{22}H_{21}ClO_2$ (352.84) Calc. C 74.88 H 5.99 Cl 10.04% Found C 74.84 H 6.04 Cl 10.08%

We thank Dr. *K. Tori* and Miss *Y. Yoshimura* for their NMR. spectroscopic investigations.

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53. Eine kinetische Studie über Ligandenverdrängungsreaktionen von π-Allyl-π-cyclopentadienyl-Metallkomplexen[1]

von **Viktor Harder** und **Helmut Werner**

Anorganisch-chemisches Institut der Universität Zürich

Herrn Professor *Max Viscontini* zum 60. Geburtstag gewidmet

(30. XII. 72)

Summary. The kinetics of the reactions of the complexes $C_3H_5MC_5H_5$ (M = Ni, Pd) with tertiary phosphites $P(OR)_3$ to give $M[P(OR)_3]_4$ have been investigated. For M = Ni and R = C_2H_5, there results a third-order rate law whereas for M = Pd and R = C_6H_5 a second-order rate law is observed. Possible mechanistic implications of the kinetic data will be discussed.

Vor einiger Zeit hatten wir über kinetische Untersuchungen der Reaktion von Di-π-cyclopentadienylnickel mit Trialkylphosphiten berichtet [2]. Die Bildung der

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[1] 14. Mitteilung der Reihe «Kinetische Untersuchungen der Reaktionen von Metallkomplexen»; 13. Mitteilung siehe [1].