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# 6-HALOGENOFULVENES AND ALLYLCYCLOPENTADIENE FROM NICKELOCENE

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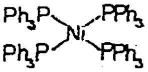
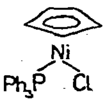
## SUMMARY

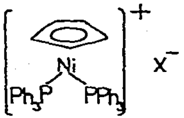
In the presence of triphenylphosphine, nickelocene reacts with tetrachloromethane to give (trichloromethyl)cyclopentadiene, which can be dehydrohalogenated to 6,6-dichlorofulvene. It reacts analogously with tetrabromomethane and (trichloromethyl)benzene. 3-Bromopropene reacts with nickelocene to give allylcyclopentadiene.

## INTRODUCTION

The metal atom in nickelocene has twenty electrons in the outer shells and is therefore prone to undergo reactions in which it attains a noble gas configuration. Typical examples are 1,2-addition to a cyclopentadienyl ring and ligand displacement. Triphenylphosphine displaces both rings of nickelocene to give the complex (I)[1]. Reaction of nickelocene and a phosphine in the presence of tetrachloromethane[2] or an allyl halide[3,4], however, gives compounds (II) or (III), respectively. It has been suggested that bicyclopentadiene is formed together with the complex (I)[5], but in the other cases the fate of the lost cyclopentadienyl ring does not seem to have been investigated.


(I)


(II)


X=Cl,Br,I
(III)

## RESULTS

We have now investigated the reaction of nickelocene with tetrachloromethane and triphenylphosphine and find that, together with the complex (II), (trichloromethyl)cyclopentadiene is formed in good yield, probably as a mixture of the three possible isomers.

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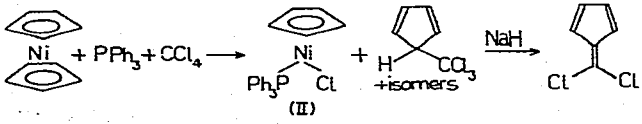
(Trichloromethyl)cyclopentadiene is dehydrohalogenated to the unstable 6,6-dichlorofulvene by sodium hydride, or by heating to temperatures above 200° in the vapor phase.



From the analogous reaction with tetrabromomethane, (tribromomethyl)-cyclopentadiene or dibromofulvene was not isolated; the reaction mixture was treated directly with piperidine to give 6,6-dipiperidinofulvene. In this case two moles of triphenylphosphine are required, probably giving compound (III) (X=Br) (analogous to the compound obtained from nickelocene, 3-bromopropene and tributylphosphine[3]).

The product from nickelocene, (trichloromethyl)benzene and triphenylphosphine on treatment with sodium hydride gives 6-chloro-6-phenylfulvene. Nickelocene and 3-bromopropene, with or without triphenylphosphine, give allylcyclopentadiene, probably as a mixture of the 1- and 2-substituted isomers. This compound has also been obtained from cyclopentadienylmagnesium bromide and 3-bromopropene[6].

We have previously found that cyclopentadienylcopper tributylphosphine reacts with benzoyl chloride to give 6-benzoyloxy-6-phenylfulvene[7]. Preliminary results show that nickelocene reacts with benzoyl chloride in the presence of triphenylphosphine to give the same compound and complex (II).

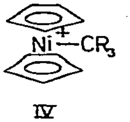
1,3,5-Trinitrobenzene and nickelocene in ethanol solution react immediately to give a Meisenheimer complex, spectroscopically identical to that formed in the reaction of cyclopentadiene with 1,3,5-trinitrobenzene in pyridine[8]. According to the visible spectrum, this is formed in 73% yield, assuming that one cyclopentadienyl ring of nickelocene reacts.

## DISCUSSION

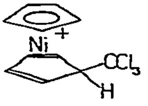
It has been suggested[2] that the initial step in reactions of nickelocene with nucleophiles is the coordination of the nucleophile to the nickel atom followed by, or simultaneous with, $\pi$–$\sigma$ rearrangement of one of the cyclopentadienyl rings. Such $\sigma$-cyclopentadienyl compounds could react with, for example, tetrachloromethane with cleavage of the metal–carbon bond forming a complex of type (II) and (trichloromethyl)cyclopentadiene.

Tetrachloromethane and tetrabromomethane react with triphenylphosphine to give trihalogenomethylphosphonium halides, which react further to the ylids[9,10]. To see if tribromomethylphosphonium bromide could be an intermediate in the reaction between tetrabromomethane, triphenylphosphine and nickelocene, we prepared this salt, but we found that it does not react with nickelocene.

It has recently been shown that nickelocene reacts with triphenylchloromethane to give (triphenylmethyl)cyclopentadiene and nickel(II) chloride[11]. The mechanism has been suggested to involve electrophilic attack of the triphenylmethyl cation on nickelocene, producing the intermediate (IV) (R = Ph). The same kind of intermediate (R = H) has also been suggested in the polymerization of diazomethane with nickelocene as a catalyst[12]. A similar complex (R = Cl) could possibly also be an intermediate in the reaction of nickelocene with tetrachloromethane. This complex could rearrange to complex (V), which would give (trichloromethyl)cyclopentadiene. An alternative path is the direct formation of the complex (V).



IV



V

It should be noted that cobaltocene reacts with tetrachloromethane to π-cyclopentadienyl [(trichloromethyl)cyclopentadiene]cobalt and cobalticinium chloride[13].

Simple 6-halogenofulvenes have been difficult to prepare. 6-Chlorofulvene[14] and 6,6-dichlorofulvene[15] have recently been obtained in poor yields from cyclopentadiene and dichlorocarbene. 6,6-Dichlorofulvene is now available from nickelocene and tetrachloromethane. Preliminary results indicate that *e.g.* dibromo- and tribromomethane react with nickelocene to give, eventually, fulvenes. Halogenofulvenes are promising starting materials, *e.g.* for further fulvenes since the halogens are susceptible to nucleophilic substitution.

On the other hand, according to MS, tetrachloromethane and sodium cyclopentadienide give chlorocyclopentadiene and chlorobenzene. This reaction probably involves dichlorocarbene and is analogous to the reaction of cyclopentadiene with dichlorocarbene[14]. Carbene formation seems to be general in reactions of halogenomethanes with organosodium compounds[16].

## EXPERIMENTAL

Infrared spectra were recorded on a Perkin–Elmer No. 421 spectrometer, ultraviolet spectra with a Beckman DK 2 instrument, NMR spectra on a Varian A 60 A spectrometer (TMS internal standard) and mass spectra on an LKB 9000 instrument. Preparative gas chromatography was performed on a Perkin–Elmer F 21 instrument.

Reactions involving organometallic compounds were performed under purified nitrogen. Diethyl ether was freshly distilled from lithium aluminium hydride. Nickelocene was prepared from sodium cyclopentadienide and hexaamminenickel(II) chloride[17].

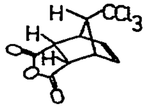
### *(Trichloromethyl)cyclopentadiene*

Nickelocene (4.72 g, 25 mmol) and triphenylphosphine (6.56 g, 25 mmol) were dissolved in ether (50 ml) and tetrachloromethane (3.85 g, 25 mmol) in ether was added. A red colour appeared and a red precipitate formed. After 14 h the precipitate was filtered off and the solvent evaporated. Distillation of the residue gave (trichloromethyl)cyclopentadiene, probably as a mixture of the three possible isomers (2.02 g, 44%, m.p. 7–8°). GLC of the distillate showed one peak corresponding to (trichloromethyl)cyclopentadiene when the temperature of the injector block was ca. 70°. This was replaced by a peak corresponding to 6,6-dichlorofulvene as the temperature was raised to 200°. The yield of (trichloromethyl)cyclopentadiene in the reaction mixture was determined to ca. 70% with GLC (internal standard *o*-dichlorobenzene). (Found: C, 38.7; H, 2.8; Cl, 56.9. $C_6H_5Cl_3$ calcd.: C, 39.3; H, 2.8; Cl, 58.0%.) The mass spectrum showed the parent ion at *m/e* 182, 184, 186, 188 and peaks at *m/e* 147, 149, 151 ($M^+ - Cl$), *m/e* 146, 148, 150 ($M^+ - HCl$), *m/e* 112, 114 ($M^+ - 2Cl$) and *m/e* 111, 113 ($M^+ - HCl_2$) (base peak). The NMR spectrum in $CDCl_3$ showed multiplets at $\delta$ 6.55 and 4.12 ppm (rel. intensity 4.5/1). The UV spectrum in hexane showed an absorption at $\lambda$ 258 nm ($\varepsilon$ 1800 $l \cdot mol^{-1} \cdot cm^{-1}$).

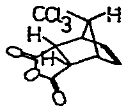
The red precipitate was identified as $\pi$-cyclopentadienyl(triphenylphosphine)-nickel chloride (9.45 g, 90%), decomp. above 140° after recrystallization from benzene/cyclohexane (lit. decomp. 138–139°[2]). (Found: C, 65.4; H, 4.8; Ni, 14.1. $C_{23}H_{20}PNiCl$ calcd.: C, 65.5; H, 4.8; Ni, 13.9%.) The NMR spectrum in $CDCl_3$ showed a multiplet at $\delta$ 7.3–7.8 (15H) and a singlet at 5.02 ppm (5H).

### *Maleic anhydride adduct of (trichloromethyl)cyclopentadiene*

Maleic anhydride (0.49 g, 5 mmol) and (trichloromethyl)cyclopentadiene (0.91 g, 5 mmol) were kept in benzene at room temperature for a week. The solvent was evaporated and the residue chromatographed on silica gel with dichloromethane. The product obtained was identified as *endo*-bicyclo[2.2.1]7-(trichloromethyl)-(5-heptene)-1,3-dicarboxylic anhydride (VI or VII) (0.44 g, 31%, m.p. 173–175° after recrystallization from diisopropyl ether) by comparison of its NMR spectrum in $CDCl_3$ with that of the known adduct from cyclopentadiene and maleic anhydride[18]. (Found: C, 42.6; H, 2.5; Cl, 37.9. $C_{10}H_7O_3Cl_3$ calcd.: C, 42.7; H, 2.5; Cl, 37.8%.) The NMR spectrum in $CDCl_3$ showed multiplets centered at $\delta$ 6.31 (2H), 3.88 (2H), 3.81 (2H) and 3.16 ppm (1H). The mass spectrum showed the parent ion at *m/e* 280, 282, 284, 286. The IR spectrum showed the anhydride carbonyl absorptions at 1860 and 1785 $cm^{-1}$.



(VI)



(VII)

### *6,6-Dichlorofulvene*

6,6-Dichlorofulvene was prepared by the addition of excess sodium hydride to ethereal (trichloromethyl)cyclopentadiene. The reaction was terminated after ca. 30 min. According to the visible spectrum the yield was 67% assuming $\varepsilon$ $3.2 \times 10^2$ $l \cdot mol^{-1} \cdot cm^{-1}$ for the absorption at 379 nm. (Trichloromethyl)cyclopentadiene can also be dehydrohalogenated to 6,6-dichlorofulvene at high temperature (ca 200–250°) in the vapor phase. The fulvene was purified by preparative gas chromatography on an OV 1 column. The NMR spectrum in $CDCl_3$ showed a singlet at $\delta$ 6.42.

Nickelocene (10 mmol), triphenylphosphine (10 mmol) and tetrachloromethane (10 mmol) were reacted in ether as described above. The precipitate was filtered off and the filtrate treated with excess sodium hydride. When the reaction ceased, the mixture was filtered and the ether solution added to excess piperidine

(40 mmol) in ether. The piperidinium chloride which immediately formed was filtered off. Evaporation of the solvent and recrystallization of the residue from cyclohexane gave 6,6-dipiperidinofulvene (37% based on nickelocene, m.p. 138–143°). (Found: C, 78.6; H, 9.9; N, 11.3. $C_{16}H_{24}N_2$ calcd.: C, 78.6; H, 9.9; N, 11.5%.) The mass spectrum showed the parent ion at *m/e* 244. The NMR spectrum in $CDCl_3$ showed signals at $\delta$ 6.23 (4H, $A_2B_2$ type), 3.40 (8H, broad) and 1.65 ppm (12H). The UV spectrum in n-hexane showed absorptions at $\lambda$ 259 nm ($\varepsilon$ 9190) and $\lambda$ 347 nm ($\varepsilon$= 29600 $l \cdot mol^{-1} \cdot cm^{-1}$).

In the corresponding reaction with dimethylamine the previously known 6,6-bis(dimethylamino)fulvene[19] (m.p. 82–84°, lit. 82–83° [19]) was isolated in a low yield. (Found: C, 72.8; H, 10.0; N, 16.4. $C_{10}H_{16}N_2$ calcd.: C, 73.1; H, 9.8; N, 17.1%.) The NMR and UV spectra agree with those previously reported[19].

### 6,6-*Dibromofulvene*

Nickelocene (1.90 g, 10 mmol) and triphenylphosphine (5.24 g, 20 mmol) were dissolved in ether, tetrabromomethane (3.32 g, 10 mmol) in ether was added and the mixture stirred overnight. The yield of (tribromomethyl)cyclopentadiene and 6,6-dibromofulvene was estimated by GLC to ca. 50% (internal standard *p*-dibromobenzene). The precipitate which formed was filtered off and the ether solution was added to piperidine (40 mmol) in ether. The piperidinium bromide was filtered off and the solvent evaporated. The dark oil formed was crystallized from cyclohexane and vacuum sublimed (100°/0.05 mmHg) to give 6,6-dipiperidinofulvene (13% based on nickelocene, m.p. 139–143°).

The mass spectrum of 6,6-dibromofulvene showed the parent ion at *m/e* 134, 136, 138 and a peak at *m/e* 155, 157 ($M^+ - HBr$) (base peak).

### 6-*Chloro-6-phenylfulvene*

Nickelocene (3.78 g, 20 mmol), triphenylphosphine (5.20 g, 20 mmol) and (trichloromethyl)benzene (3.90 g, 20 mmol) were reacted in ether (50 ml) at room temperature for 16 h. The precipitate formed was filtered off and excess sodium hydride was added. Attempts to separate the products by chromatography failed.

Distillation gave 6-chloro-6-phenylfulvene (16%, b.p. 88–90°/0.3 mmHg) and unchanged (trichloromethyl)benzene (21%). The mass spectrum of 6-chloro-6-phenylfulvene showed the parent ion at *m/e* 188, 190 and the base peak at *m/e* 153 ($M^+ - Cl$).

### *Allylcyclopentadiene*

Nickelocene (0.28 g, 1.5 mmol) and 3-bromopropene (0.36 g, 3 mmol) were reacted in ether (25 ml). According to GLC the yield after 50 h was 37% (internal standard bromobenzene) assuming that both cyclopentadienyl rings react.

Nickelocene (0.57 g, 3 mmol), triphenylphosphine (0.79 g, 3 mmol) and 3-bromopropene (0.36 g, 3 mmol) were reacted in ether (25 ml). According to GLC the yield after 15 h was 95%. The precipitate formed was filtered off, the solvent evaporated and the residue distilled, giving allylcyclopentadiene (53%). The NMR and UV spectra agree with those previously reported[5]. The mass spectrum showed the parent ion at *m/e* 106.

## ACKNOWLEDGEMENTS

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