

# The Reaction of Nickelocene with Hexachlorocyclopentadiene

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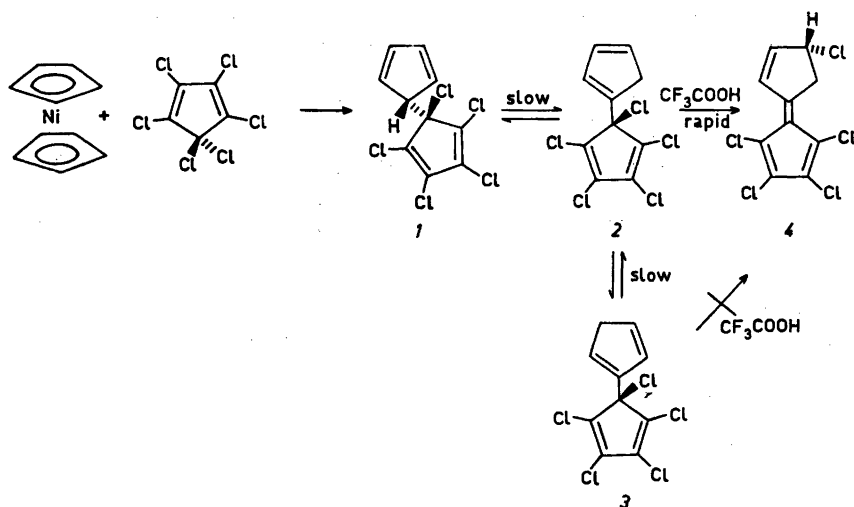
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Nickelocene reacts with hexachlorocyclopentadiene to give 1,2,3,4,5-pentachloro-5-(2,4-cyclopentadienyl)-1,3-cyclopentadiene, which, upon the addition of trifluoroacetic acid, isomerizes to 1,2,3,4-tetrachloro-5-(4-chloro-2-cyclopentenylidene)-1,3-cyclopentadiene. At low temperature a product derived from 5,5'-bicyclopentadiene can be detected in the reaction mixture.

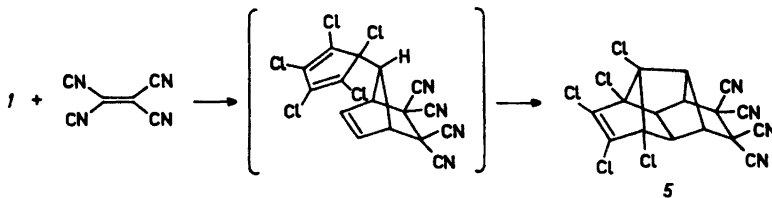
Allylcyclopentadienes are obtained from the reaction of nickelocene with various allylic halides. With simple allylic halides like 3-bromopropene, 3-chloro-1-butene and *trans*-1-chloro-2-butene the yields are low. However, the yields increase considerably when a phosphine is added.<sup>1,2</sup> With octachlorocycloheptatriene the reaction proceeds even in the absence of phosphine.<sup>3</sup> This investigation deals with the reaction of nickelocene with hexachlorocyclopentadiene.

## RESULTS

1,2,3,4,5-Pentachloro-5-(2,4-cyclopentadienyl)-1,3-cyclopentadiene (*1*) was obtained in 45 % yield when 1 mol of nickelocene reacted with 2 mol of hexachlorocyclopentadiene at room temperature. Cyclopentadienes, substituted in the 5-position, are known to rearrange by a [1,5]sigmatropic hydrogen shift to yield mixtures consisting mainly of the 1- and 2-substituted isomers.<sup>4</sup> NMR measurements show that the 5-substituted isomer, in tetrachloromethane, was transformed into the 1-substituted isomer (*2*) in 50 % yield within 25 h, and that after a further six days, about equal amounts of the 1-substituted and the 2-substituted (*3*) isomers were present. However, when trifluoroacetic acid was added to this mixture, the 1-substituted isomer isomerized quantitatively to 1,2,3,4-tetrachloro-



Scheme 1.



Scheme 2.

5-(4-chloro-2-cyclopentenylidene)-1,3-cyclopentadiene (**1**) within a few min, whereas the 2-substituted isomer did so within seven days. When trifluoroacetic acid was added to the isomer **1** in tetrachloromethane, isomers **2** and **3** were never observed but compound **4** was formed quantitatively (half-life 25 h). These observations are consistent with Scheme 1.

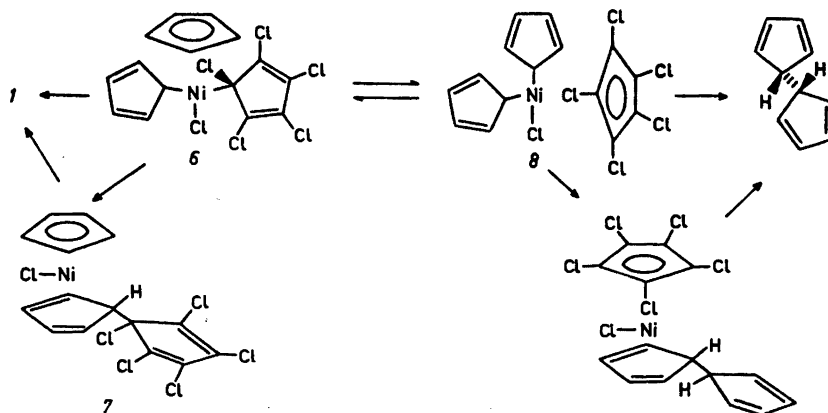
When the reaction of nickelocene with hexachlorocyclopentadiene was run at  $-40^{\circ}\text{C}$  a white crystalline compound (**A**) with the composition  $\text{C}_{10}\text{H}_{10}\text{Cl}_{12}$  was formed in 20% yield, along with compound **1**. The structure of compound **A** is unknown but it is probably a Diels-Alder adduct of one molecule of 5,5'-bicyclopentadiene and two molecules of hexachlorocyclopentadiene. Compound **A** was also formed from authentic 5,5'-bicyclopentadiene and hexachlorocyclopentadiene.

Compound **1** reacted with tetracyanoethylene to give an adduct which, on the basis of spectroscopic data, was assigned structure **5**. This compound was formed by two successive Diels-Alder reactions. Similar adducts have been prepared by Hedaya<sup>5</sup> and Paquette<sup>6</sup> who called this type of reaction a domino Diels-Alder reaction.

## DISCUSSION

We have previously suggested a mechanism involving the oxidative addition of the halide to the nickel atom for the reaction of nickelocene with 3-chloro-1-butene and with *trans*-1-chloro-2-butene.<sup>3</sup> The formation of 5,5'-bicyclopentadiene in the reaction of nickelocene with hexachlorocyclopentadiene provides further evidence for this type of mechanism. The oxidative addition of hexachlorocyclopentadiene to nickel is expected to give complex **6**, which could give compound **1** by reductive elimination or *via* complex **7**. Furthermore, complex **6** could give the isomeric complex **8** by  $\pi$ - $\sigma$  conversions of one substituted and one unsubstituted ring. Subsequent elimination from this complex would give 5,5'-bicyclopentadiene.

A rearrangement somewhat analogous to that of compound **1** to compound **4** has previously been observed for 9,10-dihydrofulvalene, the parent compound of **1**.<sup>7</sup> Normally, this compound isomerizes to 1,5-dihydrofulvalene by two consecutive [1,5] hydrogen shifts. However, in a few cases the rearrangement takes an alternative path in deuteriochloroform, and 1,2-dihydrofulvalene, the parent compound



Scheme 3.

of 4, is formed. This rearrangement is believed to be catalyzed by traces of acid in the solvent.

## EXPERIMENTAL

IR spectra were recorded on a Perkin Elmer No. 421 spectrometer, UV spectra on a Beckman DK 2 instrument, mass spectra on an LKB Model 9000 spectrometer, and NMR spectra on a Jeol MH 100 spectrometer and on a Varian EM 360 spectrometer (TMS internal standard).

Reactions involving organometallic compounds were performed under anhydrous conditions in a purified nitrogen atmosphere. Diethyl ether was freshly distilled from lithium aluminium hydride. Nickelocene was prepared as described earlier.<sup>8</sup> Commercial samples of hexachlorocyclopentadiene were distilled before use.

**Nickelocene and hexachlorocyclopentadiene.** Hexachlorocyclopentadiene (273 mg, 1 mmol) in diethyl ether (20 ml) was added to nickelocene (95 mg, 0.5 mmol) in diethyl ether (40 ml) and the reaction mixture was stirred at room temperature for 5 h. The precipitate was removed by filtration and the solvent was evaporated. The residue was chromatographed on a silica gel column eluted with light petrol. Unreacted hexachlorocyclopentadiene (33%) was eluted first and then compound 1 (45%). MS, *m/e*: 300 ( $M^+$  based on  $^{35}\text{Cl}$ , 5 Cl).  $^1\text{H NMR}$  ( $\text{CCl}_4$ ):  $\delta$  3.62 (1 H, m) and 6.25 (4 H, m) (AA'BB'X-type spectrum).

The reaction of nickelocene with hexachlorocyclopentadiene was also performed at  $-40^\circ\text{C}$ . After stirring at  $-40^\circ\text{C}$  for 1 h, the reaction mixture was allowed to reach room temperature over a period of 12 h and was then worked up as described above. Preparative thin-layer chromatography on silica gel yielded unreacted hexachlorocyclopentadiene ( $R_F$  0.68) and compound 1 ( $R_F$  0.61) together with a compound with molecular formula  $\text{C}_{20}\text{H}_{10}\text{Cl}_{12}$  ( $R_F$  0.13) (20%). An analytical sample of the latter compound was obtained by vacuum sublimation at  $190^\circ\text{C}/0.04$  mmHg. Anal.  $\text{C}_{20}\text{H}_{10}\text{Cl}_{12}$ : C, H, Cl. MS, *m/e*: 670 ( $M^+$ ), 400 ( $M^+ - \text{C}_2\text{Cl}_6$ ), 365, 130 ( $M^+ - 2\text{C}_2\text{Cl}_6$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.50 (4 H, m), 3.42 (2 H, m), 3.82 (2 H, m) and 5.40 (2 H, m). IR,  $\nu_{\text{max}}$  (KBr): 1602 (m) and 1448 (m)  $\text{cm}^{-1}$ . UV,  $\lambda_{\text{max}}$  (hexane) ( $\epsilon$ ): 237 ( $2.14 \times 10^4$ ), 246 ( $2.27 \times 10^4$ ) and 225 ( $1.65 \times 10^4$ ) nm ( $1 \text{ mol}^{-1} \text{ cm}^{-1}$ ).

**Rearrangement of 1,2,3,4,5-pentachloro-5-(2,4-cyclopentadienyl)-1,3-cyclopentadiene to 1,2,3,4-tetrachloro-5-(4-chloro-2-cyclopentenylidene)-1,3-cyclopentadiene.** The rearrangement of compound 1 was followed by NMR techniques, using ca. 0.1 M solutions of compound 1 in  $\text{CCl}_4$ . After seven days a mixture of about equal amounts of the 1-substituted (2) and the 2-substituted (3) isomers were present. NMR

( $\text{CCl}_4$ ): Methylene protons of isomer 2 at  $\delta$  3.00 (2 H, m) and of isomer 3 at  $\delta$  3.05 (2 H, m), the vinylic protons of both isomers centered at  $\delta$  6.3 (3 H, m). Addition of trifluoroacetic acid gave 1,2,3,4-tetrachloro-5-(4-chloro-2-cyclopentenylidene)-1,3-cyclopentadiene (4), m.p.  $125-126^\circ\text{C}$ . Found: C 39.6; H 1.9; Cl 56.1–57.3. Calc. for  $\text{C}_{10}\text{H}_5\text{Cl}_5$ : C 39.7; H 1.7; Cl 58.6. MS, *m/e*: 300 ( $M^+$ ).  $^1\text{H NMR}$  ( $\text{CCl}_4$ ): ABMPX-spectrum,  $\delta$  3.47 ( $\text{H}_A$ ), 3.79 ( $\text{H}_B$ ), 5.06 ( $\text{H}_X$ ), 6.80 ( $\text{H}_M$ ), and 7.85 ( $\text{H}_P$ ),  $J_{AB}$  20.5,  $J_{AX}$  1.1,  $J_{BX}$  6.4,  $J_{XM}$  3.0,  $J_{XP}$  1.0, and  $J_{PM}$  6.0 Hz. UV,  $\lambda_{\text{max}}$  (hexane) ( $\epsilon$ ): 350 ( $2.44 \times 10^4$ , sh.), 327 ( $3.17 \times 10^4$ ), 341 ( $2.77 \times 10^4$ ) 356 ( $1.27 \times 10^4$ , sh.) and 450 ( $4.01 \times 10^3$ ) nm ( $1 \text{ mol}^{-1} \text{ cm}^{-1}$ ). IR,  $\nu_{\text{max}}$  (KBr): 1540, 1560 and  $1590 \text{ cm}^{-1}$ .

**Preparation of the Diels Alder adduct of compound 1 and tetracyanoethylene.** Compound 1 was prepared from nickelocene (1 mmol) and hexachlorocyclopentadiene (2 mmol) as described above. The crude reaction mixture was filtered and tetracyanoethylene (2 mmol) was added to the filtrate. The mixture was stirred at room temperature overnight. A precipitate formed and was assigned structure 5. The crude product (45% yield based on hexachlorocyclopentadiene) was purified by vacuum sublimation. Anal.  $\text{C}_{10}\text{H}_5\text{Cl}_5\text{N}_4$ : C, H, Cl, N. MS, *m/e*: 428 ( $M^+$ ), 493, 366, 300, 265, 230.  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ ):  $\delta$  3.27 (2 H, d,  $J$  3.2 Hz), 3.52 (1 H, tt) and 4.70 (2 H, d,  $J$  2.5 Hz), IR,  $\nu_{\text{max}}$  (KBr): 3020, 2260 and  $1620 \text{ cm}^{-1}$ . UV: no absorption above 220 nm.

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