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THE REACTION OF NICKELOCENE WITH OCTACHLOROCYCLOHEPTATRIENE

Christina Moberg* and Martin Nilsson**

*Department of Organic Chemistry, Royal Institute of Technology,
S-100 44 Stockholm 70, Sweden

**Department of Organic Chemistry, Chalmers University of Technology and
University of Göteborg, S-402 20 Göteborg 5, Sweden

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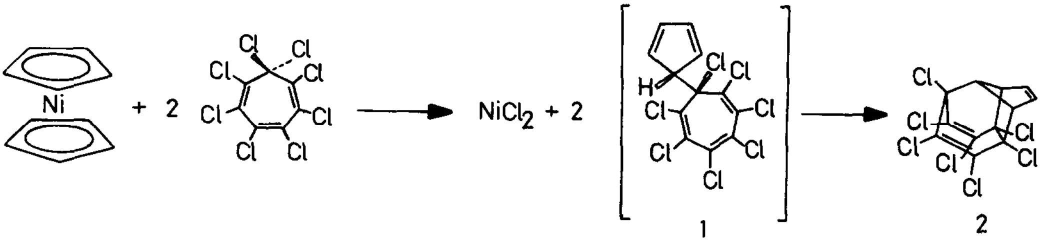
The reactions of nickelocene with tetrachloromethane and with 3-bromopropene in the presence of triphenylphosphine give (trichloromethyl)cyclopentadiene and allylcyclopentadiene, respectively.[1] We have now found that nickelocene reacts with octachlorocycloheptatriene[2] in dry diethyl ether at room temperature.[3] The expected 1,2,3,4,5,6,7-heptachloro-1-(2,4-cyclopentadienyl)-2,4,6-cycloheptatriene (1) could not be isolated but underwent an intramolecular Diels Alder reaction with the double bonds of the cyclopentadienyl ring as the 4 π component and one double bond of the seven-membered ring as the 2 π component to form 2,3,4,5,6,7,8-heptachlorotetracyclo$[7,2,1,0^{2,8},0^{5,12}]$dodeca-3,6,10-triene (2) (mp 167°) in 60 % yield.[4] Nickel chloride precipitates quantitatively. Sodium or lithium cyclopentadienide does not give compound 2 on reaction with octachlorocycloheptatriene.

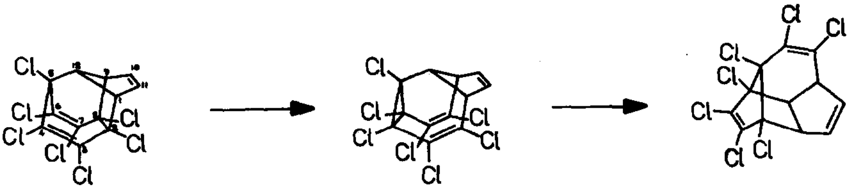


Compound 2 is purified by column chromatography on silica gel with tetrachloromethane and vacuum sublimation (100°, 0.2 mm Hg). The structure is supported by the NMR spectrum (DMSO-d_6), which shows an AA'BXX'-pattern with δ_A 4.09 (C_1H, C_9H), δ_B 3.81 ($C_{12}H$), δ_X 6.22

($C_{10}H$, $C_{11}H$), J_{AB} 7.3 Hz, J_{AX} 1.9 Hz, and J_{BX} 0 Hz. The ^{13}C-NMR spectrum ($CDCl_3$) shows absorptions at δ 47.6, 49.3, and 133.7 (relative intensity 2:1:2). The carbons bearing chlorine are not observed because the relaxation times are too long. The UV spectrum (hexane), with a maximum at λ 224 nm (ε = 0.50 x 10^4 1 mol^{-1} cm^{-1}), indicates a slight interaction of the two double bonds in the seven-membered ring. Over 10 % Pd/C one double bond is hydrogenated in the first step and a compound is formed which shows no absorption in the vinylic region of the NMR spectrum.

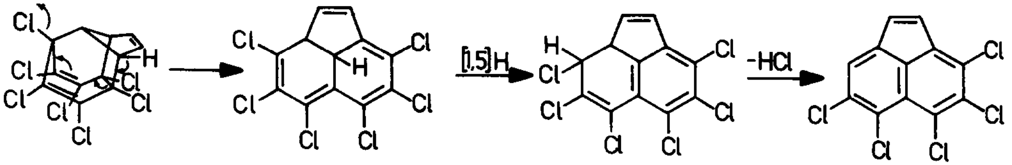
When warmed to 170° in a sealed tube for two minutes, compound 2 rearranges to an isomer which probably is 1,2,3,4,9,10,11-heptachlorotetracyclo[6,3,1,$0^{4,11}$,$0^{5,12}$]dodeca-2,6,9-triene[4,5] (3) (80 %, mp 130-131.5°). (Since some hydrogen chloride is evolved in side reactions, a sodium hydroxide pellet is placed at the top of the tube. One of the products formed from the dehydrochlorination is possibly hexachlorosesquifulvalene (< 5 %, MS)). Compound 3 is purified by column chromatography on silica gel with light petroleum and vacuum sublimation (120°, 0.1 mm Hg). The structure is supported by the NMR spectrum ($CDCl_3$), which shows multiplets centered at δ 3.40 (3 H), 5.70 (d of d, J 8.5 and 1.5 H_3, 1 H) and 6.52 (d of d, J 8.5 and 4.5 H_3, 1 H). As in compound 2, only the carbons bearing hydrogen are observed in the ^{13}C-NMR spectrum. The absorptions ($CDCl_3$) are found at δ 51.3, 52.3, 61.7, 127.9, and 144.3 (equal intensities). No UV maximum above 220 nm is observed.

The rearrangement of compound 2 to 3 could proceed *via* an allylic biradical formed by fission of the C2-C8 bond; the vinylcyclopentene is then formed by bond formation between C2 and C6 (or between C4 and C8). Another possibility is the intermediate formation of a divinylcyclopropane (4) by a Cope rearrangement. Analogously, 1-methyl-2-vinylcyclopropane has been shown to be an intermediate in the thermal isomerization of *cis*-1,4-hexadiene to 4-methylcyclopentene.[6] Stereochemically, the only cyclopentene that can be formed from compound 4 is the isomer from a symmetry-forbidden process. However, even in cases where a concerted reaction is stereochemically possible, the rearrangement has been shown to go *via* a diradical.[7,8]



2 4 3

When compound 2 is treated with potassium hydroxide (3 mol) in ethanol at 45° for 3 h, a yellow product is formed which is probably a mixture of 3,4,5,7,8-pentachloroacenaphthylene and 3,4,5,6,7-pentachloroacenaphthylene (5) (80 %).[4] (Tetrachloroethoxyacenaphthylenes are formed as side products in 10 % yield; with a higher concentration of ethoxide ions and a prolonged reaction time these become the main products.) The pentachloroacenaphthylenes are purified by chromatography on silica gel with tetrachloromethane and vacuum sublimation. Isomers are, however, not separated. The NMR spectrum ($CDCl_3$) shows singlets at δ 6.95 (2 H), 7.42 (ca. 0.4 H) and 7.88 (ca. 0.6 H).[9] Hydrogenation in hexane over 10 % Pd/C gives the corresponding pentachloroacenaphthenes. The UV spectra of the acenaphthylenes and acenaphthenes are similar to those of the parent compounds,[10] though with a bathochromic shift of ca. 20 nm. A possible mechanism for the formation of compound 5 is shown below; the nucleophilic attack of ethoxide ion may be on the intermediate 6 or on the product, which is indeed attacked by the nucleophile.



2 6 5

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2. K. Kusuda, R. West, and V.N. Mallikarjuna Rao, *J. Amer. Chem. Soc.*, 93 (1971) 3627.
3. With 1 mmol octachlorocycloheptatriene and 0.5 mmol nickelocene in 50 ml ether the reaction is complete within 6 h.
4. Elemental analysis is correct and mass spectrum is in accordance with the structure.
5. Molecular weight determination (Rast) shows that the product is not a dimer of compound 2.

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9. No coupling is observed for the corresponding protons in acenaphthylene: M.J.S. Dewar and R.C. Fahey, *J. Amer. Chem. Soc.*, 85 (1963) 2704.

10. R.A. Friedel and M. Orchin, *"Ultraviolet Spectra of Aromatic Compounds"*, John Wiley & Sons, New York (1951), spectra 212 and 234.