

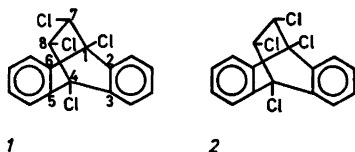
Chlorinated Polycyclic Compounds. I. Reactions of 9,10-Dichloroanthracene with *cis*- and *trans*-1,2-Dichloroethylene

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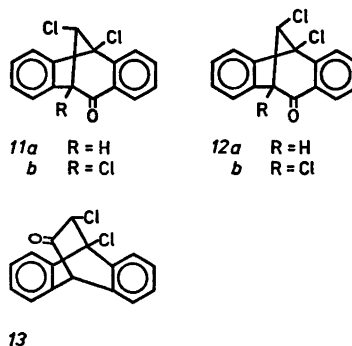
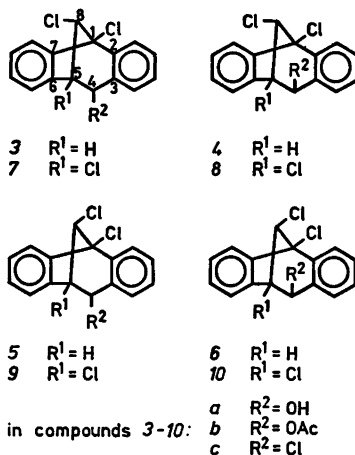
In addition to the normal Diels-Alder reaction product, *syn*- and *anti*-1,8-dichlorodibenzobicyclo[3,2,1]octadien-4-one were formed in the reactions of 9,10-dichloroanthracene with *cis*- and *trans*-1,2-dichloroethylene, respectively. Synthetic routes to several 1,8-dichloro- and 1,5,8-trichlorosubstituted derivatives of dibenzobicyclo[3,2,1]octadiene are described.

Although it is known that substituents at the 9- and 10-positions of anthracene considerably reduce its reactivity towards dienophiles,¹ the reaction between 9,10-dichloroanthracene and *trans*-1,2-dichloroethylene gave good yields of *trans*-1,4,7,8-tetrachlorodibenzobicyclo[2,2,2]-octadiene (**1**), when the starting materials were heated at 210–250 °C for 24–96 h. When



synthetic grade dichloroethylene was used without drying the normal Diels-Alder product was invariably accompanied by a carbonyl compound to which structure **11a** was assigned. In addition to **1** and **11a** some minor components were formed, of which only the rear-ranged tetrachloride **9c** was identified. Similarly, the reaction of 9,10-dichloroanthracene with *cis*-1,2-dichloroethylene gave **2**, **12a** and **7c**. The yield of the normal product was somewhat lower than with the *trans* isomer and more insoluble material, resulting from polycondensation reactions of dichloroethylene, was formed. Although careful drying of the starting materials

considerably reduced the amount of the ketones **11a** and **12a**, they could not be entirely eliminated, the rest being evidently due to moisture in air present in the pressure vessel.



Reduction of ketone **11a** with sodium borohydride gave only the *endo* alcohol **3a** (*exo* hydride attack) whereas ketone **12a** gave

Table 1. Dibenzobicyclo[3,2,1]octadiene derivatives.

| Compound | No. | M.p./ °C | ν_{\max} / cm ⁻¹ | Chemical shift/ δ | | | | Other | $J_{4,s}$ / Hz | $J_{5,s}$ / Hz |
|-------------------------------------|-----|-------------|------------------------------------|--------------------------|-------------------|-------------|--------------|-------|-------------------|-------------------|
| | | | | endo- 4-H | exo- 4-H | syn- 8-H | anti- 8-H | | | |
| 1-anti-8-Dichloro-4-oxo | 11a | 143 | 1692 | | | 5.04 | | 4.30 | | 4.8 |
| 1-syn-8-Dichloro-4-oxo | 12a | 117 | 1695 | | | | | 4.18 | | |
| 1,5-anti-8-Trichloro-4-oxo | 11b | 168 | 1700 | | | 5.13 | | | | |
| 1,5-syn-8-Trichloro-4-oxo | 12b | 162 | 1703 | | | 5.22 | | | | |
| 1-anti-8-Dichloro-endo-4-hydroxy | 3a | 190 | 3230 | | | 4.70 | | 4.03 | 1.67 (OH) | |
| 1-anti-8-Dichloro-exo-4-hydroxy | 4a | 161 | 3140 | | | 5.03 | | 3.76 | 2.00 | 5.6 |
| 1-syn-8-Dichloro-endo-4-hydroxy | 5a | 142 | 3250 | | 4.71 | 5.07 | | 3.70 | 1.22 | 1.8 |
| 1-syn-8-Dichloro-exo-4-hydroxy | 6a | 130 | 3310 | | 4.43 | 5.07 | | 3.71 | 2.87 | 5.3 |
| 1,5-anti-8-Trichloro-endo-4-hydroxy | 7a | 125 | 3400 | | 4.76 | 5.12 | | | 2.10 | 1.4 |
| 1,5-anti-8-Trichloro-exo-4-hydroxy | 8a | 139 | 3300 | | 4.45 | 5.20 | | | 3.10 | |
| 1,5-syn-8-Trichloro-endo-4-hydroxy | 9a | 121 | 3350 | | 4.76 | 4.77 | | | 2.07 | |
| 1,5-syn-8-Trichloro-exo-4-hydroxy | 10a | 130 | 3460 | | 4.45 | 5.20 | | | 2.80 | |
| 1-anti-8-Dichloro-endo-4-acetoxy | 3b | 155 | 1733 | | 5.87 | 6.18 | | 4.12 | 2.06 (OAc) | 5.6 |
| 1-syn-8-Dichloro-exo-4-acetoxy | 4b | 168 | 1735 | | 5.60 | 6.28 | | 3.78 | 2.13 | 2.0 |
| 1-syn-8-Dichloro-endo-4-acetoxy | 5b | 125 | 1724 | | 5.60 | 6.28 | | 3.97 | 2.06 | 5.5 |
| 1-syn-8-Dichloro-exo-4-acetoxy | 6b | 155 | 1728 | | 6.25 | 6.52 | | 3.75 | 2.13 | 4.7 |
| 1,5-anti-8-Trichloro-endo-4-acetoxy | 7b | 231 | 1750 | | 6.25 | 6.58 | | | 2.15 | |
| 1,5-anti-8-Trichloro-exo-4-acetoxy | 8b | 161 | 1735 | | 6.03 | 6.58 | | | 2.12 | |
| 1,5-syn-8-Trichloro-endo-4-acetoxy | 9b | 176 | 1730 | | 6.03 | 6.58 | | | 2.20 | |
| 1,5-syn-8-Trichloro-exo-4-acetoxy | 10b | 141 | 1732 | | 6.03 | 6.58 | | | | |
| 1-endo-4-anti-8-Trichloro | 3c | 132 | 1732 | | 5.10 | 5.50 | | 4.00 | | 5.2 |
| 1-exo-4-anti-8-Trichloro | 4c | 129 | 1732 | | 5.10 | 5.50 | | 3.98 | | 2.0 |
| 1-endo-4-syn-8-Trichloro | 5c | 94 | 1732 | | 4.92 | 5.07 | | 3.76 | | 4.8 |
| 1-exo-4-syn-8-Trichloro | 6c | 145 | 1732 | | 4.92 | 5.07 | | 3.88 | | 5.0 |
| 1-endo-4,5-anti-8-Tetrachloro | 7c | 113 | 1732 | | 5.35 ^a | 5.53 | | | | |
| 1-exo-4,5-anti-8-Tetrachloro | 8c | 157 | 1732 | | 5.35 ^a | 5.53 | | | | |
| 1-endo-4,5-syn-8-Tetrachloro | 9c | 146 | 1732 | | 5.10 | 5.64 | | | | |
| 1-exo-4,5-syn-8-Tetrachloro | 10c | 159 | 1732 | | 5.10 | 5.64 | | | | |
| 1,4-anti-8-Tetrachloro | 16 | 151 | 1732 | | 5.10 | 5.64 | | 4.41 | | |
| 1,4,4-syn-8-Tetrachloro | 17 | 129 | 1732 | | 5.10 | 5.64 | | 4.19 | | 4.7 |

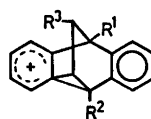
^a Assignment is tentative.

a mixture of both epimers with an *endo-exo* ratio of 30:70. The same behaviour has been observed in the reduction of 8-trichloromethyl derivatives of dibenzobicyclo[3,2,1]octadiene, where obstruction of the C-4 *exo* position by the bulky *syn*-8-trichloromethyl group causes complete *endo* specificity of hydride attack.³ To obtain both epimeric alcohols, **3a** was treated with thionyl chloride to give a mixture of the trichlorides **3c** and **4c** which on acetolysis with acetic acid and silver acetate gave a mixture of the acetates **3b** and **4b**. Hydrolysis of the acetates with ethanolic potassium hydroxide gave the epimeric alcohols **3a** and **4a**.

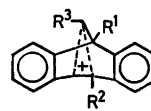
The structure of **9c** was established by the following reaction sequence: Acetolysis of **9c** gave a mixture of two acetates which were hydrolyzed to the corresponding alcohols. On oxidation with Jones reagent both of these alcohols gave the same ketone **12b**. When this ketone was dehalogenated with zinc and ethanol, a quantitative yield of **12a** was obtained. The same reaction sequence applied to **7c** gave another ketone **11b** which furnished about 60 % of **11a** when treated with zinc and ethanol. The fact that in the latter reduction several other compounds are formed, may reflect the greater reactivity of the *anti*-8-chlorine compared with the *syn*-8-chlorine.³⁻⁵

Because of the lack of the 5-proton, the stereostructure at C-4 in the 1,5,8-trichloro-substituted compounds **7-10** cannot be concluded directly from the ¹H NMR spectra, in contrast to the 1,8-dichloro-substituted compounds, **3-6**, where the *endo* and *exo* epimers can easily be distinguished by the coupling constants between the 4- and 5-protons.⁶ In the latter, the *endo*-4-proton absorbs at a higher field than the epimeric *exo*-4-proton by δ 0.33–0.75 which is in good agreement with the results obtained with compounds unsubstituted at the 1-position.⁶ That this rule can be extended to the 1,5,8-trichloroderivatives, was confirmed by equilibration studies. In the dibenzobicyclo[3,2,1]octadiene series the *endo*-substituted derivatives have been shown to be thermodynamically more stable than the corresponding *exo* epimers and in most cases an *exo-endo*-conversion takes place on heating or by acid catalysis.^{7,8} Thus reaction of **7a-10a** with thionyl chloride gave epimeric mixtures which upon further heating slowly shifted towards

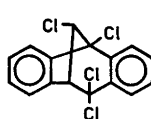
the *endo* chloride. Solvolysis of the tetrachlorides **7c-10c** with acetic acid and silver acetate gave acetate mixtures that did not change on further heating. Only when 5 % of sulfuric acid was added, equilibrium was reached. If stronger acid was used (30 % H₂SO₄ in HOAc) the only product was the dibenzobicyclo[2,2,2]octadiene derivative **13**.



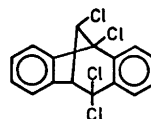
14a R¹ = R² = H, R³ = Cl
b R¹ = R² = R³ = Cl



15a R¹ = R² = H, R³ = D
b R¹ = R² = R³ = Cl



16



17

If *cis*- or *trans*-7,8-dichlorodibenzobicyclo[2,2,2]octadiene is solvolysed with acetic acid and silver acetate, the *syn*- or *anti*-8-chlorodibenzobicyclo[3,2,1]octadienyl-4-acetates are formed, respectively.⁷ This rearrangement is thought to require the intermediacy of carbonium ions of the type **14a**.⁸ In the 1,4,7,8-tetrachloroderivatives it can be expected that the inductive effect of the 1- and 4-chlorine atoms would retard the rate of ionisation. In fact, **1** and **2** were found to be inert in the reaction conditions mentioned above and only when strong acid is used can the ionisation be forced to occur. Thus solvolysis of **1** or **2** in a mixture containing 60 % sulfuric acid in acetic acid and a slight excess of silver acetate gave the rearranged ketones **11a** or **12a** in high yield. As in the rearrangement of **7b-10b** to **13** the normal reaction gives an unstable intermediate that is hydrolyzed to the ketone. Like most rearrangement reactions of the dibenzobicyclo[2,2,2]octadiene system,⁷⁻⁹ these rearrangements are stereospecific: **1** gave only the *anti* compound and **2** only the *syn* compound.

When the ketones **11a** and **12a** are formed in the autoclave the carbonium ion intermediate **14b** can be attacked either by a hydroxyl ion derived from moisture present in the reaction

mixture or by a chloride ion. In the latter case the tetrachlorides *16* and *17* should be formed. The former possibility seems more likely because a ^1H NMR comparison of the mother liquors from the crystallization of *1* and *2* with the tetrachlorides *16* and *17* showed the absence of the latter. *16* and *17* were prepared from the corresponding ketones with phosphorus pentachloride. Even if *16* and *17* are hydrolyzed readily, they should remain when all water in the reaction vessel has been consumed.

The formation of *9c* and *7c*, although in a low yield, is of interest, because it offers a case where intervention of ionic species such as *15b* could be assumed to explain the bond migration from C-5 to C-4. However, chlorine substitution at C-5 makes the intermediates differ essentially from *15a*,¹⁰ making this ion energetically still more unfavorable. Therefore, another reaction pathway consisting of direct chloride ion attack on the three-membered ring in *14b* with consequent bond migration to the adjacent carbon atom should also be considered.

EXPERIMENTAL

^1H NMR spectra were recorded with a JEOL JNM-PMX 60 spectrometer in CCl_4 solution and IR spectra with a Perkin-Elmer 125 spectrometer using KBr pellet technique. All mass spectra (70 eV) exhibited a typical isotope pattern consistent with the number of chlorine atoms present in the molecule. The parent peak based on ^{35}Cl and the base peak are given. *trans*-1,2-Dichloroethylene was synthetic grade reagent from Fluka or Merck, *cis*-1,2-dichloroethylene was obtained by fractional distillation of a commercial isomer mixture. Silica gel used for columns was H & W silica gel M.F.C. and for TLC Merck's Kieselgel 60 PF. Light petroleum refers to the fraction boiling 80–100 °C. Melting points are not corrected.

Reaction of 9,10-dichloroanthracene with trans-1,2-dichloroethylene. In a typical experiment 24.7 g (0.1 mol) of 9,10-dichloroanthracene¹¹ and 291 g (3.0 mol) of *trans*-1,2-dichloroethylene were heated for 24 h at 210 °C in a 1 l steel pressure vessel. After cooling, excess dichloroethylene was removed, 1200 ml of light petroleum was added to the residue and the mixture was stirred overnight. The solution was filtered and the filtrate was passed through a silica gel column (50 g) followed by 2000 ml of light petroleum. After removal of the solvent, the yellow oily residue crystallized on standing to give 22.6 g (66 %) of *1*, m.p. 153 °C (EtOH). δ 4.30 (2 H, s), 7.1–7.4 (4 H, m), 7.5–7.9 (4 H, m).

To obtain the ketone *11a*, the column was eluted with 1500 ml of benzene. The solvent was removed and the residue dissolved in 100 ml of acetone, 5 g of activated charcoal was added and the solution boiled for 20 min. The mixture was filtered and to remove any residual carbon the filtrate was passed through a small (5 g) silica gel column and the column was flushed with 50 ml of acetone. After removal of acetone the product was crystallized from ethanol to give 3.3 g (11 %) of *11a*, *m/e* 288(25), 253(100).

The same starting mixture as above heated for 96 h at 250 °C gave 51 g of material insoluble in light petroleum, 6.6 g (19 %) of *1* and 4.1 g (14 %) of *11a*. The mother liquors from the crystallization of both *1* and *11a* were combined and all volatile material was removed by steam distillation. From the spectrum of the residue it was estimated to contain about two thirds of higher molecular weight condensation products of dichloroethylene, the rest being a mixture of *1*, *11a* and some unknown compounds. The most important of the latter group was separated by preparative TLC (several elutions with light petroleum) and two recrystallizations from EtOH. 0.24 g (0.7 %) of pure *9c* was obtained, *m/e* 342(28), 307(100).

Reaction of 9,10-dichloroanthracene with cis-1,2-dichloroethylene. The reaction was carried out in the same manner as with *trans*-dichloroethylene with somewhat different separation of the products. A typical experiment gave 10 g of material insoluble in light petroleum. According to ^1H NMR the solution contained the two principal products in a ratio of 54:46 which corresponds to a yield of about 34 % of *2* and 29 % of *12a*. As the chromatographic separation was much more difficult than with the *trans* adduct, the product mixture, after removal of excess dichloroethylene, was dissolved in 200 ml of acetone and 10 g of activated charcoal was added. The solution was refluxed for 20 min and the charcoal and acetone removed. The residue was crystallized from EtOH to give 7.1 g (21 %) of *2*, m.p. 199 °C, δ 4.54 (2 H, s), 7.1–7.5 (4 H, m), 7.6–8.0 (4 H, m). The mother liquor was evaporated, steam distilled and fractionated on a silica gel column (100 g). Two main components were separated and crystallized from EtOH to give 3.8 g (11 %) of *2* and 6.2 g (21 %) of *12a*. MS of *12a m/e* 288(25), 217(100).

A run for 96 h at 250 °C gave 64 g of material insoluble in light petroleum, 5.3 g (15 %) of *2* and 7.5 g (26 %) of *12a*. 0.35 g (1.0 %) of *7c* was separated from the mother liquor using the same procedure as for *9c*. MS of *7c m/e* 342(28), 202(100).

Reduction of the ketones 11a and 12a. A solution of 2.89 g of the ketone (10 mmol) and 0.38 g of NaBH_4 (10 mmol) in 100 ml of EtOH was refluxed for 20 min. The solution was poured into cold water, acidified with HCl and extracted

twice with ether. The ethereal solution was dried and evaporated. ^1H NMR examination of the reduction product showed that *11a* gave almost pure *endo* alcohol. Crystallization from 80 % aqueous EtOH gave 2.18 g (76 %) of *3a*. The product from *12a* exhibited an *endo-exo* ratio of about 30:70. The epimers were separated by preparative TLC (repeated elutions with a 1:1 mixture of benzene and light petroleum) and purified by crystallization from 80 % aqueous EtOH. 0.40 g (14 %) of the *endo* alcohol *5a* and 1.42 g (49 %) of the *exo* alcohol *6a* were obtained.

Reactions of the alcohols 3a, 5a–10a with thionyl chloride. Epimeric mixtures resulting from reduction of ketones *11a* and *12a* or hydrolysis of acetates *7b–10b* were used as starting material. The alcohol (0.5–1.0 g) was refluxed with 10 ml of SOCl_2 for 20 h. Excess SOCl_2 was removed under reduced pressure, the residue dissolved in ether and the ether solution washed with saturated NaHCO_3 solution. After drying, ether was removed and the residue examined by ^1H NMR. Following mixtures were obtained (starting compounds, *endo-exo* ratio of resulting chloride mixture): *3a*; 60:40, *5a, 6a* 28:72, *7a, 8a* 45:55, *9a, 10a* 65:35. Analytical samples were prepared by chromatographic separation of the epimers (elution with light petroleum) and crystallization from 80 % aqueous EtOH.

Acetolysis of the chlorides 3c–10c. A mixture of 1 mmol of the chloride (0.31 g of trichloride or 0.34 g of tetrachloride), 0.20 g (1.2 mmol) of AgOAc and 10 ml of HOAc was refluxed for 20 h. Acetic acid was removed under reduced pressure, the residue dissolved in acetone, the solution filtered and evaporated. Following mixtures were obtained (starting compounds, *endo-exo* ratio of resulting acetate mixture): *3c, 4c* 19:81, *5c, 6c* 24:76, *7c, 8c* 22:78, *9c, 10c* 52:48. Analytical samples were prepared by chromatographic separation of the epimers (elution with a 1:1 mixture of benzene and light petroleum) and crystallization from EtOH.

When 0.05 g of the *exo* acetate *8b* was refluxed for 20 h with a mixture of 1 ml of H_2SO_4 and 9 ml of HOAc, complete epimerization to the *endo* acetate *7b* occurred. Similarly *10b* gave *9b*. 0.4 g of *10b* refluxed for 20 h with a mixture of 2 ml of H_2SO_4 and 8 ml of HOAc gave, after the usual work-up and crystallization from EtOH, 0.24 g (76 %) of *13*. The same product was obtained from *8b*, m.p. 131 °C, δ 4.13 (1 H, s), 4.79 (1 H, s), 7.1–7.5 (6 H, m), 7.6–7.9 (2 H, m). ν_{max} 1740 cm^{-1} .

Hydrolysis of the acetates 3b–10b. The acetate (1 mmol; 0.33 g of a dichloro compound or 0.37 g of a trichloro compound) was stirred with 10 ml of 10 % KOH in EtOH for 80 min at room temperature. Water and HCl was added and the product was obtained by ether extraction and purified by crystallization from 80 % aqueous EtOH.

Oxidation of the alcohols 7a–10a. The alcohol (0.1–0.5 g), dissolved in acetone, was treated with Jones reagent until the oxidation was complete (as shown by TLC). After the usual work-up the pure ketones were obtained by crystallization from EtOH. MS of *11b m/e* 322(15), 251(100), *12b m/e* 322(16), 251(100).

Dechlorination of the ketones 11b and 12b with zinc and ethanol. A mixture of 0.2 g of *12b*, 0.4 g of Zn-powder and 10 ml of EtOH was refluxed for 8 h. Ethanol was removed, the residue dissolved in acetone, the solution filtered and evaporated. According to ^1H NMR the product was almost pure *12a*. Two recrystallizations from EtOH gave 0.11 g (62 %) of pure ketone, m.p. 116 °C. It showed no melting point depression when mixed with a sample of *12a* obtained from the reaction of 9,10-dichloroanthracene and *cis*-1,2-dichloroethylene.

When the same procedure was used for the dechlorination of the *anti*-8-chloro ketone *11b* (0.2 g), a mixture of several compounds was obtained, the major component being the expected ketone *11a*. Separation by TLC (elution with a 1:1 mixture of benzene and light petroleum) and crystallization from EtOH gave 0.07 g (39 %) of pure product, identical with *11a* from the Diels-Alder reaction. The other products were not identified.

Acetolysis of the tetrachlorides 1 and 2. A mixture of 3.44 g (0.01 mol) of *1*, 3.50 g (0.021 mol) of AgOAc , 40 ml of H_2SO_4 and 60 ml of HOAc was refluxed for 20 h. The mixture was cooled and poured into cold water. The aqueous solution was extracted three times with ether, the ether solution dried and evaporated. The residue was crystallized from EtOH to give 2.3 g (81 %) of *11a*. Similarly 3.44 g of *2* gave 1.90 g (66 %) of *12a*.

Synthesis of the tetrachlorides 16 and 17. *11a* (0.5 g) was refluxed for 80 min with a mixture of 5 g of PCl_5 and 5 g POCl_3 . The hot mixture was carefully poured into vigorously stirred ice water. When excess reagent was completely decomposed, the aqueous solution was extracted twice with ether, the ethereal solution dried and evaporated. The crude product was purified by TLC (elution with light petroleum) followed by crystallization from EtOH to give 0.49 g (82 %) of *16*. Similarly, the ketone *12a* gave 0.41 g (69 %) of *17*.

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