

Chlorinated Polycyclic Compounds. IV. Reactions of 9,10-Dichloroanthracene with Tri- and Tetrachloroethylene

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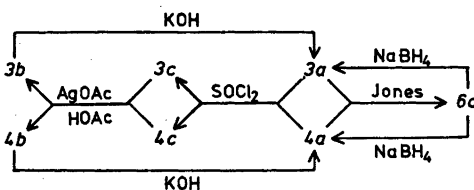
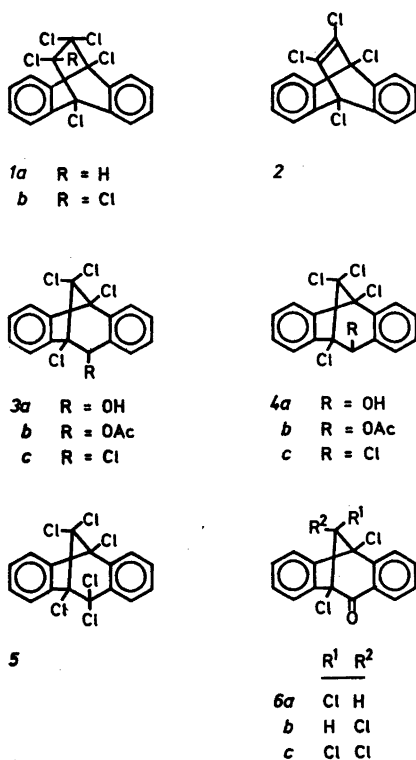
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9,10-Dichloroanthracene gave the Diels-Alder adduct with trichloroethylene in a low yield only. With tetrachloroethylene the adduct was not observed, but some products from other reactions, including 5-dichloromethylene-10,11-dichloro-5*H*-dibenzo[*a,d*]cycloheptene, were identified. Addition of chlorine to 1,4,7,8-tetrachlorodibenzobicyclo[2.2.2]octatriene followed by hydrolysis gave 1,5,8,8-tetrachlorodibenzobicyclo[3.2.1]octadien-4-one in high yield.

Parts I¹ and II² of this series deal with the reactions of 9,10-dichloroanthracene (DCA) with the three isomeric dichloroethylenes. The results from analogous reactions with tri- and tetrachloroethylene are now reported.

The reaction of DCA with trichloroethylene (48 h at 230 °C) occurred more sluggishly and led to a much more complex product mixture than the reactions with *cis*- and *trans*-dichloroethylene. Autocondensation of trichloroethylene occurred to a great extent giving rise to a considerable HCl pressure in the reaction vessel. The condensation products were not separated, but according to the ¹H NMR spectrum, the major component seems to be *cis*-1,1,2,3,4-pentachlorobutadiene.³

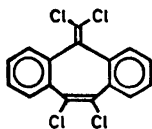
Six compounds were separated from the nonvolatile part of the reaction mixture: the already known chlorides 1*a*⁴ and 2,⁴ ketones 6*a*¹ and 6*b*¹ and two new compounds which were shown to possess the structures 3*c* and 6*c*. The new compounds were interrelated as shown in Scheme 1.



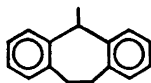
Scheme 1.

The assignment of configuration at C-4 was based on the known fact^{5,1} that the *endo*-H absorbs at a higher field than the *exo*-H in the ¹H NMR spectrum.

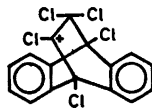
The reaction between DCA and tetrachloroethylene occurred very slowly. After 96 h at 250°C most of the DCA was recovered unchanged. In addition to small amounts of 2 and 6c, a third compound was isolated, to which the structure 7 was assigned, on the basis of mass and UV spectra. Dechlorination of this compound with sodium and isopropyl alcohol gave the hydrocarbon 8.*



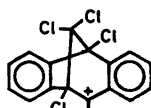
7



8



9



10

The normal Diels-Alder adduct 1b was not found among the reaction products, but it could be obtained by addition of chlorine to 2, although in mixture with its isomer 5. The isomer 1b could be distinguished by the strong base peak at *m/e* 246 in the mass spectrum. A base peak corresponding to an anthracene derivative is a feature common to all dibenzobicyclo[2.2.2]octadiene derivatives examined in connection with these studies. Both 1b and 5 gave the ketone 6c on hydrolysis. The hydrolysis of 1b required the use of 60% sulfuric acid with addition of silver acetate, while 5 was readily hydrolyzed by more dilute acid, without silver acetate.

The rearranged products from the reactions of DCA with both tri- and tetrachloroethylene seem to have the unsaturated chloride 2 as a common precursor in analogy with the reaction of anthracene and tetrachloroethylene.⁷ This is supported by the fact that the compounds 3c, 7, 6a, 6b and 6c were obtained when 2

* 8 was the only structure to fit reasonably with the ¹H NMR spectrum of the dechlorination product. As, however, the spectrum reported for 8⁶ was markedly different as regards both chemical shifts and coupling constants, 8 was synthesized *via* an independent route. The product thus obtained was in all respects identical with that from 7.

was heated in tetrachloroethylene. As, on the other hand, the presence of a geminal dichloro group in 3c, 7 and 6c clearly indicates the intermediacy of a [2.2.2] species featuring this function, it seems evident that these compounds are formed from 2 *via* the ions 9 and 10. Chloride ion attack on 10 with subsequent hydrolysis of the geminal dichloride^{1,4} leads to 6c, while 7 results from the opening of the five-membered ring with loss of the chlorine atom at C-1. A hydride shift has to be postulated to explain the formation of 3c, but the nature of the reducing agent is not clear. 6a and 6b are derived from 2 in the same way as 6c, with the difference that the first step in the reaction sequence is the protonation of the double bond.

EXPERIMENTAL

For general experimental conditions see Ref. 1. Tri- and tetrachloroethylene were synthetic grade reagents from Merck.

Reaction of DCA with trichloroethylene. A mixture of 24.7 g (0.1 mol) of DCA⁶ and 395 g (3.0 mol) of trichloroethylene was heated for 48 h at 230°C in a 1 l stainless steel pressure vessel. After cooling a pressure of 30 atm due to HCl remained. The reaction mixture was filtered to remove unreacted DCA and the filtrate was distilled with steam to remove all volatile material. Fractionation of the distillate under reduced pressure (12 mmHg) gave 60 g of material boiling up to 80°C, 290 g boiling in the range 80–100°C and a residue of 10 g. The ¹H NMR spectrum of the middle fraction contained a singlet at δ 6.56 having about 90% of the total intensity. The value reported in the literature³ for *cis*-1,1,2,3,4-pentachlorobutadiene is 6.58.

The nonvolatile part of the product mixture was refluxed for 20 min with 5 g of activated charcoal in 100 ml of acetone. The charcoal and acetone were removed and the two distinct groups of reaction products were separated on a silica gel column (100 g). The column was eluted first with light petroleum, then with benzene. The major components of the first fraction were separated by TLC (several elutions with light petroleum) to give in addition to some DCA 0.8 g (2%) of 1,4,7,7,8-pentachlorodibenzobicyclo[2.2.2]octadiene (1a),⁴ 3.5 g (10%) of 1,4,7,8-tetrachlorodibenzobicyclo[2.2.2]octatriene (2)⁴ and 1.4 g (4%) of 1-*endo*-4,5,8,8-pentachlorodibenzobicyclo[3.2.1]-octadiene (3c), m.p. 143°C, δ 5.72 (*exo*-4-H)+8 Ar-H. The components of the second fraction were separated by TLC (elution with a 1:1 mixture of benzene and light petroleum) to give 0.32 g (1%) of 1,5-*syn*-8-trichloro-

dibenzobicyclo[3.2.1]octadien-4-one (6a),¹ 0.28 g (0.9 %) of 1,5-*anti*-8-trichlorodibenzobicyclo[3.2.1]octadien-4-one (6b)¹ and 0.20 g (0.6 %) of 1,5,8,8-tetrachlorodibenzobicyclo[3.2.1]octadien-4-one (6c), m.p. 154°C, ν_{\max} 1705 cm⁻¹, δ only Ar-H, *m/e* 356(15), 321(100).

Reaction of DCA with tetrachloroethylene. A mixture of 24.7 g (0.1 mol) of DCA and 498 g (3.0 mol) of tetrachloroethylene was heated for 96 h at 250°C in a 1 l stainless steel pressure vessel. The reaction mixture was cooled and unreacted DCA was filtered off and washed with acetone. The filtrate was evaporated, the residue stirred for 4 h with 200 ml of light petroleum and the mixture filtered again. In addition to a small amount of DCA, the solution contained three other compounds which were separated by TLC (elution with light petroleum) to give 2.1 g (6 %) of 2, 1.3 g (4 %) of 5-dichloromethylene-10,11-dichloro-5*H*-dibenzo[*a,d*]cycloheptene (7), m.p. 168°C, δ only Ar-H, *m/e* 340(48), 270(100), λ_{\max} 231 (ϵ 68 000), 256 (ϵ 56 000), 271 sh (ϵ 30 000) nm and 0.4 g (1 %) of 6c.

Thermal rearrangement of the chloride 2. A mixture of 40 g of 2 and 500 ml of tetrachloroethylene was heated for 14 days at 250°C. Filtration of the reaction mixture gave a dark liquid and 12 g of black solid that was insoluble in acetone. The solution was evaporated and the residue refluxed for 20 min with 20 g of activated charcoal in 200 ml of acetone. The charcoal and acetone were removed. Upon standing the residue partly crystallized and the separated solid (10.3 g) was identified as the starting material. The remaining mixture was diluted with acetone to 250 ml and 25 ml of this solution was subjected to chromatographic separation. A silica gel column (50 g, elution with a 1:1 mixture of benzene and light petroleum) was used for a rough separation of ketones from non-oxygenated products. The individual ketones were separated by TLC (several elutions with a 1:1 mixture of benzene and light petroleum) to give 0.17 g (5 % based on 2) of 6a, 0.08 g (2 %) of 6b and 0.16 g (4 %) of 6c. The other fraction gave (TLC, several elutions with light petroleum) 0.27 g (7 %) of 2, 0.42 g (11 %) of 7 and 0.47 g (6 %) of 3c.

Dechlorination of the chloride 7 with sodium in isopropyl alcohol. A solution of 0.5 g of 7 in 200 ml of isopropyl alcohol was heated to reflux and 15 g of Na was added over a period of 4 h. When all Na had reacted, the heating mantle was replaced by a magnetic stirrer and water was added, at first drop by drop, until a clear solution was obtained. The solution was made slightly acidic with HCl and extracted three times with ether. The ethereal solution was dried and evaporated and the product purified by TLC (elution with light petroleum) to give 0.22 g (72 %) of 8, m.p. 31–32°C (MeOH), (lit.⁶ m.p. 22–24°C), δ 1.62 (3 H, d, $J=7.3$ Hz), 3.07 (4 H, broad s), 4.23 (1 H, q, $J=7.3$ Hz), 6.7–7.3 (8 H, m).

Synthesis of the hydrocarbon 8. Dibenzobicyclo[3.2.1]octadiene-*exo*-4-*syn*-8-diol diacetate⁹ (10 g) was stirred for 80 min with 100 ml of 10 % ethanolic KOH at room temperature. After the usual work-up and crystallization from 60 % aqueous EtOH, 5.8 g (78 %) of the corresponding diol¹⁰ was obtained.

A mixture of 5.0 g of the diol, 1 g of *p*-toluenesulfonic acid monohydrate and 200 ml of benzene was refluxed for 20 min. The solution was washed with water, sodium bicarbonate and again with water, dried and evaporated. Purification of the product by column chromatography (200 g of silica gel, elution with benzene) and crystallization from EtOH gave 3.1 g (67 %) of 5*H*-dibenzo[*a,d*]cycloheptene-5-carboxaldehyde.¹⁰

A solution of 2.0 g of the aldehyde, 10 ml of 1,2-ethanedithiol and 10 ml of BF₃-etherate was allowed to stand for 20 h. The reaction mixture was added to 100 ml of ether and the solution thoroughly washed with 10 % aqueous KOH, washed with water, dried and evaporated. Crystallization from EtOH gave 2.2 g (82 %) of relatively pure dithioacetal. The analytical sample was crystallized three times from EtOH, m.p. 178°C, δ 3.03 (4 H, broad s), 3.90 (1 H, d, $J=10.2$ Hz), 5.08 (1 H, d, $J=10.2$ Hz), 6.81 (2 H, s) + 8 Ar-H.

The dithioacetal (1.0 g) was desulfurized by refluxing with 20 g of Raney nickel in 100 ml of EtOH for 8 h. The solution was filtered, evaporated and the product purified by TLC (elution with light petroleum) to give 0.64 g (92 %) of 5-methyl-5*H*-dibenzo[*a,d*]cycloheptene,¹¹ which was not obtained in crystalline form. The ¹H NMR spectrum was in agreement with that reported¹¹ (superimposed spectra of two conformers at ordinary temperature).

To reduce the double bond, the unsaturated hydrocarbon (0.64 g) was dissolved in 100 ml of isopropyl alcohol and 10 g of Na was added to the boiling solution over a period of 4 h. The reaction mixture was worked up as described above (dechlorination of 7) and the product purified by TLC (elution with light petroleum) to give 0.51 g (79 %) of 5-methyl-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (8).⁶ This product was in all respects identical with that obtained from the dechlorination of 7.

Addition of chlorine to 2. A solution of 100 g of 2 in 500 ml of dry 1,1,2,2-tetrachloroethane was saturated with chlorine at room temperature. The solution was slowly heated to reflux and the refluxing was continued for 8 h while a slow stream of chlorine was bubbled into the mixture. The reaction was stopped when most of 2 had reacted (according to TLC). Attempts to push the reaction to completion led to the appearance of a group of several byproducts, possibly due to ring chlorination. The solution was cooled and the solvent removed under reduced pressure. The residue crystallized rapidly to give 62 g (51 %) of 1,4,7,7,8,8-hexachlorodibenzobicyclo[2.2.2]octadiene (1b).

The analytical sample of *1b* was prepared by three recrystallizations from benzene and had m.p. 234°C, δ only Ar-H, m/e 410(0.07), 246(100). Chromatographic separation from the residue (TLC, elution with light petroleum) and four recrystallizations from EtOH gave the analytical sample of 1,4,4,5,8,8-hexachlorodibenzobicyclo[3.2.1]octadiene (*5*), m.p. 166°C, δ only Ar-H, m/e 410(10), 375(100). The amount of *5* in the product mixture was estimated to correspond to a yield of about 25%.

Acetolysis of the hexachlorides 1b and 5. A mixture of 4.13 g (0.01 mol) of *1b*, 5.00 g (0.03 mol) of AgOAc, 60 g of H₂SO₄ and 40 g of HOAc was refluxed for 20 h. The mixture was cooled and poured into ice water. The aqueous solution was extracted with chloroform, and to facilitate the separation of the layers, the whole mixture was filtered through silica gel. The chloroform solution was dried and evaporated. Crystallization of the residue from EtOH gave 2.6 g (73%) of *6c*. When mixtures of *1b* and *5* were used as starting material, less AgOAc was required, because *5* is readily hydrolyzed by acid alone.

Reactions leading from the chloride 3c to the ketone 6c and vice versa. The acetolysis, hydrolysis, oxidation, reduction and replacement reactions were conducted as previously in analogous cases.^{1,2} Approximative yields are based on ¹H NMR. The analytical samples were prepared by TLC (elution of alcohols and acetates with a 1:1 mixture of benzene and light petroleum and of chlorides with light petroleum) and crystallization from EtOH.

Acetolysis of *3c* gave 50% of 1,5,8,8-tetrachlorodibenzobicyclo[3.2.1]octadien-*endo*-4-yl acetate (*3b*), m.p. 174°C, ν_{\max} 1753 cm⁻¹, δ 6.63 (*exo*-4-H), 2.13 (OAc) + 8 Ar-H and 50% of the *exo* epimer *4b*, m.p. 120°C, ν_{\max} 1740 cm⁻¹, δ 6.23 (*endo*-4-H), 2.20 (OAc) + 8 Ar-H. Hydrolysis of *3b* gave 1,5,8,8-tetrachlorodibenzobicyclo[3.2.1]octadien-*endo*-4-ol (*3a*), m.p. 155°C, ν_{\max} 3540, 3580 cm⁻¹, δ 5.15 (*exo*-4-H), 2.12 (OH) + 8 Ar-H and *4b* gave the *exo* epimer *4a*, m.p. 171°C, ν_{\max} 3440, 3570 cm⁻¹, δ 4.70 (*endo*-4-H), 2.88 (OH) + 8 Ar-H. Oxidation of both *3a* and *4a* gave *6c*. Reduction of *6c* gave 25% of *3a* and 75% of *4a*. Reaction of the mixture of *3a* and *4a* with SOCl₂ gave 50% of *3c* and 50% of 1-*exo*-4,5,8,8-pentachlorodibenzobicyclo[3.2.1]octadiene (*4c*), m.p. 195°C, δ 5.30 (*endo*-4-H) + 8 Ar-H.

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