Chlorinated Polycyclic Compounds, II. Reactions of 9,10-Dichloroanthracene with 1,1-Dichloroethylene and Related Reactions

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The reaction of 9,10-dichloroanthracene with 1,1-dichloroethylene gave low yields of the Diels-Alder adduct and 1,5-dichlorodibenzobicyclo[3,2,1]octadien-4-one. Convenient syntheses for the latter and several related compounds from the Diels-Alder adduct of 9,10-dichloroanthracene and trans-1,2-dichloroethylene are described.

In the first part of this series it was shown that the Diels-Alder reaction between 9,10-dichloroanthracene (DCA) and cis- or trans-1,2-dichloroethylene gives chloro ketones as side products. As these synthetically interesting ketones can be obtained from the Diels-Alder products, the synthesis of analogous compounds from DCA and chloro olefins was attempted.

The reaction between DCA and 1,1-dichloroethylene failed to give satisfactory yields of the Diels-Alder adduct. At lower temperatures (150 – 200 °C) most of the DCA was recovered and at higher temperatures (200 – 250 °C) extensive polycondensation of dichloroethylene occurred. A small amount of the Diels-Alder adduct 1b was isolated from the reaction mixture. The structure of 1b was confirmed by its spectra and a further structure proof was furnished by the elimination of hydrogen chloride to give the chloro olefin 7. This synthetically versatile compound could be obtained more conveniently by similar elimination from the Diels-Alder adduct of DCA and trans-1,2-dichloroethylene. In addition to 1b, a ketone was isolated, to which the structure 3b was assigned in analogy with the results reported previously. An alternative structure 2b was supported by the fact that the 1H NMR spectrum of the ketone contains only a sharp 2 H singlet besides the aromatic region and that it could also be obtained by acid hydrolysis of 7.

To decide between 3b and 2b a dithioketal was prepared and desulfurized with Raney Ni. Two compounds were obtained, whose 1H NMR spectra showed that neither could be 1a and consequently structures 4a and 4b were assigned to the reduction products. Reduction of 3b with sodium borohydride gave only one alcohol and the synthesis of both epimers via the alcohol-chloride-acetate-alcohol route showed that it was the endo epimer 5d. Dehalogenation with zinc and ethanol caused the removal of one chlorine atom from 3b leading
to the ketone 3a and reduction of the latter gave the endo alcohol 5a as the sole reaction product. If a 1:1 mixture of phosphorus pentachloride and phosphorus oxychloride was used to effect the replacement of hydroxyl by chloride in the alcohols 5a and 5d, the product was 90–95 % exo, while thionyl chloride yielded comparable amounts of both epimers. In the reaction of 5a with thionyl chloride, unlike 5d and other similar cases, the [2,2,2] isomer 5c was formed to a variable extent. The yield of the latter was found to be dependent on the acidity of the reaction mixture and with the use of a large excess of thionyl chloride with added gaseous hydrogen chloride the isomerization was complete. Acetolysis of the chlorides 5c, 6c, 5f and 6f using reaction times of 40

anti-8-protons have different chemical shifts in ¹H NMR and it is possible to correlate the signals with the appropriate protons. In compounds unsubstituted at C-5, the assignment is based on the coupling constants between 5-H and anti-8-H. In the 5-chloro derivatives having an endo-4-substituent, no couplings, except the geminal coupling between the 8-protons, are visible, while all the exo epimers exhibit a long-range splitting of about 1.5 Hz between the endo-4-proton and one of the 8-protons. The proton involved is assumed to be the anti-8-proton in accordance with the concept of W-geometry required for this coupling. When no information based on the coupling constants was available, the chemical shifts were tentatively assigned to the 8-protons making use of the observation that in the compounds discussed above and in other analogous cases, the syn-8-proton absorbs at a higher field than the epimeric anti-8-proton, when the C-4 substituent has endo configuration. In exo-4-substituted compounds the order is reversed. The stereostructure at C-4 is evident from the coupling constants between the 4- and 5-protons, when the latter is present, while in the 5-chloro derivatives it is based on the rule that in the derivatives of dibenzobicyclo[3,2,1]-octadiene, both unsubstituted and those bearing chloro substituents at the 1- and 5-positions, the endo-4-proton absorbs at a higher field than the epimeric exo-4-proton.

EXPERIMENTAL

For general experimental conditions see Ref. 1.

Reaction of DCA with 1,1-dichloroethylene. A mixture of 24.7 g (0.1 mol) of DCA and 291 g (3.0 mol) of 1,1-dichloroethylene was heated at 210 °C for 24 h in a 1 l stainless steel pressure vessel. After cooling a pressure of 20 atm due to HCl remained. The reaction mixture consisted mainly of hard black porous material that was ground in a mortar and the powder refluxed with 500 ml of acetone for 4 h. The solution was filtered and boiled for 20 min with 10 g of activated charcoal. The solution was filtered and evaporated. The residue was distilled with steam to remove all volatile material and the two major components were separated on a silica gel column (100 g, elution with an 1:1 mixture of benzene and light petroleum) and purified by crystallization from EtOH. The first fraction gave 2.1 g (6.1 %) of 1,4,7,7-tetrachlorodibenzo[bicyclo[2,2,2]octadien.}

ene (1b), m.p. 194 °C, δ 3.33 (2 H, s) + 8 Ar-H, m/e 342(0.2), 246(100) and the second fraction 0.4 g (1.4 %) of 1,5-dichlorobenzobicyclo[3.2.1]octadie-4-one (3b), m.p. 155 °C, v_max 1705 cm⁻¹, δ 3.57 (2 H, s) + 8 Ar-H, m/e 288(17), 218(100).

Elimination of hydrogen chloride from 1c. The chloride 1c (10 g) was added to a solution of 10 g of KOH in 100 ml of EtOH and the mixture refluxed for 40 min. The cooled mixture was acidified with HCl and extracted twice with ether. The ethereal solution was dried and evaporated. The residue was dissolved in 200 ml of light petroleum and deoxygenized by passing it through a silica gel column (20 g). Concentration of the solution gave 6.7 g (75 %) of 1,4,7-trichlorobenzobicyclo[2.2.2]octatetraene (7), m.p. 101 °C, δ 6.84 (1 H, s) + 8 Ar-H.

Hydrolysis of the unsaturated chloride 7. A mixture of 5.9 g of 7, 60 g of H₂SO₄ and 40 g of HOAc was refluxed for 80 min. The hot reaction mixture was cooled, filtered and the precipitate isolated by ether extraction. TLC and ^1¹H NMR examination showed the presence of only one compound. The analytical sample was prepared by crystallization from EtOH and it was identical with the ketone 3b obtained from the Diels-Alder reaction.

Preparation of the dithioketal of 3b and desulfurization with Raney nickel. The ketone 3b (1.0 g) was dissolved in a mixture of 5 ml of 1,2-ethanediethiol and 5 ml of BF₃ etherate. After standing for 20 h at room temperature the mixture was poured into 100 ml of 10 % NaOH solution. The aqueous solution was extracted with ether and the ethereal layer dried and evaporated. The residue crystallized on standing to yield 0.88 g (72 %) of the dithioketal, m.p. 184 °C, δ 3.47 (2 H, AB, J = 11.6 Hz), 3.5—3.9 (4 H, m) + 8 Ar-H.

A mixture of 0.8 g of the dithioketal and 20 g of Raney nickel in 200 ml of EtOH was refluxed until the reduction was complete (as shown by TLC). This took about 10 h. The solution was filtered and evaporated and the residue fractionated by TLC (elution with light petroleum). The two fractions were crystallized from EtOH to give 0.17 g (31 %) of 1-chlorodibenzobicyclo[3.2.1]octadiene (4a), m.p. 102 °C, δ 2.63 (syn-8H), 2.87 (anti-8H), 2.77 (endo-4H), 3.22 (exo-4H), 3.45 (5-H) + 8 Ar-H, J₁₂ ≈ 4.5 Hz, Jₛₛ ≈ 5.0 Hz, Jₛₐ ≈ 17.2 Hz, Hₛ ≈ 9.2 Hz, m/e 240(49), 205(100) and 0.22 g (35 %) of 1,5-dichlorobenzobicyclo[3.2.1]octadiene (4b), m.p. 72 °C, δ 2.98 (syn-8H), 3.15 (anti-8H), 3.19 (endo-4H), 3.54 (exo-4H) + 8 Ar-H, J₁₂ ≈ 17.0 Hz, Jₛₛ ≈ 9.2 Hz, m/e 274(37), 259(100).

Dechlorination of the ketone 3b. A mixture of 2.0 g of 3b, 4.0 g of Zn-powder and 100 ml of EtOH was refluxed for 8 h. The ethanol was removed, the residue dissolved in acetone, the solution filtered and evaporated. Purification by TLC and crystallization from 80 % aqueous EtOH furnished 1.3 g (74 %) of 1-chlorodibenzobicyclo[3.2.1]octadiene-4-one (3a), m.p. 95 °C, v_max 1692 cm⁻¹, δ 3.14 (2 H, d), 3.88 (1 H, s) + 8 Ar-H, Jₛₛ ≈ 2.4 Hz, m/e 254(40), 219(100).

Reduction of the ketones 3a and 3b with sodium borohydride. A solution of 10 mmol of the ketone (2.55 g of 3a or 2.89 g of 3b) and 0.38 g (10 mmol) of NaBH₄ in 100 ml of EtOH was stirred for 40 min at room temperature. The solution was poured into water, HCl added and the aqueous solution extracted twice with ether. The ethereal solution was dried and evaporated. By TLC and ^¹H NMR examination only one alcohol could be detected in each case; 3a gave 1-chlorodibenzobicyclo[3.2.1]octadiene-endo-4-ol (5a), m.p. 143 °C, v_max 2320 cm⁻¹, δ 2.72 (syn-8H), 3.00 (anti-8H), 4.83 (exo-4-H), 3.58 (5-H), 1.30 (OH) + 8 Ar-H, Jₛₛ ≈ 5.3 Hz, Jₛₐ ≈ 5.3 Hz, Jₛₐ ≈ 11.0 Hz and 3b gave 1,5-dichlorobenzobicyclo[3.2.1]octadiene-endo-4-ol (5b) was isolated in 78 % yield. m.p. 188 °C, v_max 3.05 (syn-8H), 3.21 (anti-8-H), 4.95 (exo-4-H), 2.58 (OH) + 8 Ar-H, Jₛₛ ≈ 10.0 Hz. The analytical samples were crystallized from 80 % aqueous EtOH.

Reactions of the alcohols 5a and 5d with thiol chloride and phosphorus pentachloride. The alcohol (1.0 g) was refluxed for 10 min with a mixture of 2.0 g of PCl₅ and 2.0 g of POCI₃. The hot mixture was carefully decomposed with water, the aqueous solution extracted twice with ether, the ethereal solution dried and evaporated. Approximate yields estimated from the ^¹H NMR spectra are given. The analytical samples of the chlorides were prepared by TLC (elution with light petroleum) and crystallization from EtOH. 5a gave 10 % of 1-endo-4-dichlorobenzobicyclo[3.2.1]octadiene (5c), m.p. 112 °C, δ 2.73 (syn-8H), 3.00 (anti-8-H), 5.50 (exo-4-H), 3.74 (5-H) + 8 Ar-H, Jₛₛ ≈ 4.7 Hz, Jₛₐ ≈ 5.7 Hz, Jₛₐ ≈ 11.0 Hz and 90 % of the exo epimer 6c, m.p. 89 °C, δ 3.18 (syn-8-H), 2.87 (anti-8-H), 4.97 (endo-4-H), 3.70 (5-H) + 8 Ar-H, Jₛₛ ≈ 2.0 Hz, Jₛₐ ≈ 4.8 Hz, Jₛₐ ≈ 10.0 Hz. 5d gave 5 % of 1-endo-4,5-dichlorobenzobicyclo[3.2.1]octadiene (5f), m.p. 118 °C, δ 3.13 (syn-8-H), 3.38 (anti-8-H), 5.54 (exo-4-H), 4.8 Ar-H, Jₛₛ ≈ 11.0 Hz and 95 % of the exo epimer 6f, m.p. 134 °C, δ 3.60 (syn-8-H), 3.15 (syn-8-H), 3.10 (anti-8-H), 5.10 (endo-4-H) + 8 Ar-H, Jₛₛ ≈ 10.4 Hz, Jₛₐ ≈ 1.5 Hz. 5d (1.0 g) refluxed for 20 h with 10 ml of SOCl₂ gave 55 % of 5f and 45 % of 6f. Similarly 5a gave 25 % of 5c, 55 % of 6c and 20 % of 1,8-dichlorobenzobicyclo[2.2.2]octadiene (6c), m.p. 107 °C, δ 3.20 (cis-7-H), 2.68 (trans-7-H), 4.14 (8-H), 4.31 (4-H) + 8 Ar-H, cis-Jₛₛ ≈ 8.6 Hz, trans-Jₛₛ ≈ 3.8 Hz, Jₛₐ ≈ 12.8 Hz, Jₛₐ ≈ 2.6 Hz. Only 6c was obtained, when 1.0 g of 5a was refluxed with 50 ml of SOCl₂ for 8 h and a slow stream of HCl gas was bubbled into the reaction mixture.

Acetylation of the chlorides 5c, 6c, 5f and 6f. Epimeric mixtures resulting from the reactions

of the corresponding alcohols with thionyl chloride were used as starting material. A mixture of 1.0 mmol of the chloride (0.28 g of dichloride or 0.31 g of trichloride), 0.20 g (1.2 mmol) of AgOAc and 10 g of HOAc was refluxed for 20 h. The acetic acid was removed under reduced pressure, the residue dissolved in acetone, the solution filtered and evaporated. Approximative yields are based on 1H NMR.

The analytical samples of the acetates were prepared by TLC (elution with a 1:1 mixture of benzene and light petroleum) and crystallization from EtOH. A mixture of 5e and 6e gave 5% of 1-chlorodibenzo[bicyclo[3,2,1]octadien-endol-4-yl acetate (5b), m.p. 119 °C, $r_{max}$ 1730 cm$^{-1}$, δ 2.76 (syn-8-H), 2.89 (anti-8-H), 6.09 (exo-4-H), 3.80 (5-H), 2.00 (OAc) + 8 Ar-H, $J_{4,5}$ = 5.5 Hz, $J_{5,8}$ = 5.2 Hz, $J_{8,9}$ = 11.0 Hz and 95% of the exo epimer 6b, m.p. 99 °C, $r_{max}$ 1733 cm$^{-1}$, δ 3.02 (syn-8-H), 2.83 (anti-8-H), 5.71 (endo-4-H), 3.56 (5-H), 2.10 (OAc) + 8 Ar-H, $J_{4,5}$ = 2.0 Hz, $J_{5,8}$ = 5.4 Hz, $J_{8,9}$ = 10.8 Hz. A mixture of 5f and 6f gave 15% of 1,5-dichlorodibenzo[bicyclo[3,2,1]octadien-endol-4-yl acetate (5e), m.p. 166 °C, $r_{max}$ 1740 cm$^{-1}$, δ 2.33 (syn- and anti-8-H), 6.50 (exo-4-H), 2.10 (OAc) + 8 Ar-H and 85% of the exo epimer 6e, m.p. 135 °C, $r_{max}$ 1730 cm$^{-1}$, δ 3.47 (syn-8-H), 3.18 (anti-8-H), 6.05 (endo-4-H), 2.13 (OAc) + 8 Ar-H, $J_{4,5}$ = 10.0 Hz, $J_{8,9}$ = 1.5 Hz. When 10% of H$_2$SO$_4$ was added to the reaction mixtures, only the endo acetates were obtained. When 0.2 g of 5b was refluxed for 80 min with a mixture of 3 g of H$_2$SO$_4$ and 7 g of HOAc, the only product was 1-chlorodibenzo[bicyclo[2,2,2]octadien-8-yl acetate (5b), m.p. 98 °C, $r_{max}$ 1732 cm$^{-1}$, δ 1.92 (cis-7-H), 2.61 (trans-7-H), 4.09 (5-H), 4.46 (4-H), 1.82 (OAc) + 8 Ar-H, cis$J_{8,9}$ = 8.6 Hz, trans$J_{8,9}$ = 2.7 Hz, $J_{1,2}$ = 12.8 Hz, $J_{4,5}$ = 2.6 Hz. Similarly, 5e gave 1-chlorodibenzo[bicyclo[2,2,2]octadien-8-one (2a), m.p. 135 °C, $r_{max}$ 1730 cm$^{-1}$, δ 2.63 (7-H), 4.73 (4-H).

Hydrolysis of the acetates 5b, 6b, 5e, 6e and 6b. The acetate (0.5–1.0 g) was stirred with 20 ml of 10% ethanolic KOH for 80 min at room temperature. Water and HCl were added and the alcohol was obtained by ether extraction and purified by crystallization from 80% aqueous EtOH. 6b gave 1-chlorodibenzo[bicyclo[3,2,1]octadien-exo-4-ol, (6a), m.p. 138 °C, $r_{max}$ 3320 cm$^{-1}$, δ 2.94 (syn-8-H), 2.74 (anti-8-H), 4.46 (endo-4-H), 3.40 (5-H), 2.27 (OH) + 8 Ar-H, $J_{4,5}$ = 2.0 Hz, $J_{5,8}$ = 4.8 Hz, $J_{8,9}$ = 10.5 Hz, 6e gave 1,5-dichlorodibenzo[bicyclo[3,2,1]octadien-exo-4-ol (6d), m.p. 171 °C, $r_{max}$ 3260 cm$^{-1}$, δ 3.45 (syn-8-H), 3.10 (anti-8-H), 4.54 (endo-4-H), 2.82 (OH) + 8 Ar-H, $J_{5,8}$ = 10.0 Hz, $J_{4,5}$ = 1.5 Hz and 6b gave 1-chlorodibenzo[bicyclo[2,2,2]octadien-8-ol (8a), m.p. 104 °C, $r_{max}$ 3270 cm$^{-1}$, δ 1.61 (cis-7-H), 2.40 (trans-7-H), 3.76 (5-H), 4.02 (4-H), 2.38 (OH) + 8 Ar-H, cis$J_{8,9}$ = 8.6 Hz, trans$J_{8,9}$ = 2.4 Hz, $J_{1,2}$ = 12.8 Hz, $J_{4,5}$ = 2.6 Hz, 5b and 5e gave the alcohols 5a and 6a, respectively, which were identical with those obtained from the reduction of the ketones 3a and 3b.

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REFERENCES


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