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

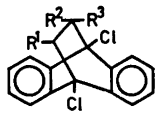
TAPIO MIETTINEN

Department of Chemistry, Helsinki University of Technology, SF-02150 Otaniemi, Finland

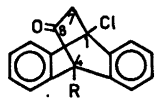
The reaction of 9,10-dichloroanthracene with 1,1-dichloroethylene gave low yields of the Diels-Alder adduct and 1,5-dichlorodibenzobicyclo-[3,2,1]octadien-4-one. Convenient syntheses for the latter and several related compounds from the Diels-Alder adduct of 9,10-dichloroanthracene and *trans*-1,2-dichloroethylene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

In the first part of this series [1] 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.

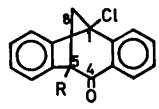
The reaction between DCA and 1,1-dichloroethylene failed to give satisfactory yields of the Diels-Alder adduct. At lower temperatures (150 – 200 °C) most of the DCA was recovered and at higher temperatures (200 – 250 °C) extensive polycondensation of dichloroethylene occurred. A small amount of the Diels-Alder 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.[1] In addition to *1b*, a ketone was isolated, to which the structure *3b* was assigned in analogy with the results reported previously.[1] An alternative structure *2b* was supported by the fact that the ^{1}H 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*.



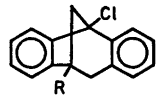
	R^1	R^2	R^3
1a	H	H	H
b	H	Cl	Cl
c	Cl	H	Cl



2a R = H
b R = Cl



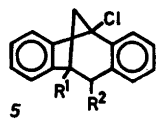
3a R = H
b R = Cl



4a R = H
b R = Cl

To decide between *3b* and *2b* a dithioketal was prepared and desulfurized with Raney Ni. Two compounds were obtained, whose ^{1}H 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 [1] 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,[1] also the [2,2,2] isomer *8c* 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



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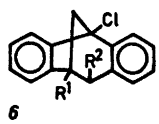

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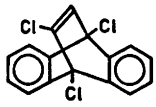
	R^1	R^2
5a, 6a	H	OH
b	H	OAc
c	H	Cl
d	Cl	OH
e	Cl	OAc
f	Cl	Cl



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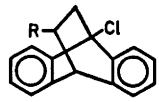

8a	R = OH
b	R = OAc
c	R = Cl

min – 24 h gave 80 – 95 % of the *exo* acetates, but with addition of 10 % of sulfuric acid, only the *endo* acetates were obtained. Treatment of these acetates *5b* and *5e* with 30 % sulfuric acid in acetic acid gave the dibenzobicyclo[2,2,2]octadiene derivatives *8b* and *2a*, respectively. These equilibration results are in good agreement with other observations on the relative thermodynamic stability of the *endo* and *exo* substituted dibenzobicyclo[3,2,1]-octadiene derivatives and the corresponding [2,2,2] isomers.[2]

In most of the dibenzobicyclo[3,2,1]octadiene derivatives discussed here the *syn*- and *anti*-8-protons have different chemical shifts in ^{1}H 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.[3] 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.[4] 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,[3] 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,[3] 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 [3] and those bearing chloro substituents at the 1- and 5-positions,[1] 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 [5] 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-tetrachlorodibenzobicyclo[2,2,2]octadi-

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-dichlorodibenzobicyclo-[3,2,1]octadien-4-one (*3b*), m.p. 155 °C, ν_{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*[1] (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 decolorized by passing it through a silica gel column (20 g). Concentration of the solution gave 6.7 g (75 %) of 1,4,7-trichlorodibenzobicyclo[2,2,2]octatriene (*7*), m.p. 101 °C, δ 6.84 (1 H, s) +8 Ar-H.

Hydrolysis of the unsaturated chloride 7. A mixture of 5.0 g of *7*, 60 g of H_2SO_4 and 40 g of HOAc was refluxed for 80 min. The hot reaction mixture was poured into ice water and the product isolated by ether extraction. TLC and ^{1}H 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-ethanedithiol and 5 ml of BF_3 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 q, 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*-8-H), 2.87 (*anti*-8-H), 2.77 (*endo*-4-H), 3.22 (*exo*-4-H), 3.45 (5-H) +8 Ar-H, $J_{4,5}$=4.5 Hz, $J_{5,8}$=5.0 Hz, $J_{4,4}$=17.2 Hz, $J_{8,8}$= 9.2 Hz, *m/e* 240(49), 205(100) and 0.22 g (35 %) of 1,5-dichlorodibenzobicyclo[3,2,1]octadiene (*4b*), m.p. 72 °C, δ 2.98 (*syn*-8-H), 3.15 (*anti*-8-H), 3.19 (*endo*-4-H), 3.54 (*exo*-4-H) +8 Ar-H, $J_{4,4}$=17.0 Hz, $J_{8,8}$=9.2 Hz, *m/e* 274(37), 239(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]octadien-4-one (*3a*), m.p. 95 °C, ν_{max} 1692 cm^{-1}, δ 3.14 (2 H, d), 3.99 (1 H, tr) +8 Ar-H, $J_{5,8}$=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 $NaBH_4$ 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 ^{1}H NMR examination only one alcohol could be detected in each case; *3a* gave 1-chlorodibenzobicyclo[3,2,1]-octadien-*endo*-4-ol (*5a*), m.p. 143 °C, ν_{max} 3230 cm^{-1}, δ 2.72 (*syn*-8-H), 3.00 (anti-8-H), 4.83 (*exo*-4-H), 3.58 (5-H), 1.30 (OH) +8 Ar-H, $J_{4,5}$=5.3 Hz, $J_{5,8}$=5.3 Hz, $J_{8,8}$=11.0 Hz and *3b* gave 1,5-dichlorodibenzobicyclo[3,2,1]octadien-*endo*-4-ol (*5d*), m.p. 116 °C, ν_{max} 3520 cm^{-1}, δ 3.05 (*syn*-8-H), 3.21 (*anti*-8-H), 4.95 (*exo*-4-H), 2.58 (OH) +8 Ar-H, $J_{8,8}$=10.0 Hz. The analytical samples were crystallized from 80 % aqueous EtOH.

Reactions of the alcohols 5a *and* 5d *with thionyl chloride and phosphorus pentachloride.* The alcohol (1.0 g) was refluxed for 10 min with a mixture of 2.0 g of PCl_5 and 2.0 g of $POCl_3$. 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 ^{1}H 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-dichlorodibenzobicyclo[3,2,1] octadiene (*5c*), m.p. 112 °C, δ 2.73 (*syn*-8-H), 3.00 (*anti*-8-H), 5.50 (*exo*-4-H), 3.74 (5-H) +8 Ar-H, $J_{4,5}$=4.7 Hz, $J_{5,8}$=5.7 Hz, $J_{8,8}$=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, $J_{4,5}$=2.0 Hz, $J_{5,8}$=4.8 Hz, $J_{8,8}$=10.0 Hz. *5d* gave 5 % of 1-*endo*-4,5-trichlorodibenzobicyclo[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), +8 Ar-H, $J_{8,8}$=11.0 Hz and 95 % of the *exo* epimer *6f*, m.p. 134 °C, δ 3.60 (*syn*-8-H), 3.15 (*anti*-8-H), 5.10 (*endo*-4-H) +8 Ar-H, $J_{8,8}$=10.4 Hz, $J_{4,8}$=1.5 Hz. *5d* (1.0 g) refluxed for 20 h with 10 ml of $SOCl_2$ gave 55 % of *5f* and 45 % of *6f*. Similarly *5a* gave 25 % of *5c*, 55 % of *6c* and 20 % of 1,8-dichlorodibenzobicyclo[2,2,2]octadiene (*8c*), m.p. 107 °C, δ 2.20 (*cis*-7-H), 2.68 (*trans*-7-H), 4.14 (8-H), 4.31 (4-H) +8 Ar-H, *cis*$J_{7,8}$=8.6 Hz, *trans*$J_{7,8}$=3.8 Hz, $J_{7,7}$=12.8 Hz, $J_{4,8}$= 2.6 Hz. Only *8c* was obtained, when 1.0 g of *5a* was refluxed with 50 ml of $SOCl_2$ for 8 h and a slow stream of HCl gas was bubbled into the reaction mixture.

Acetolysis 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 ^{1}H 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 *5c* and *6c* gave 5 % of 1-chlorodibenzobicyclo[3,2,1]octadien-*endo*-4-yl acetate (*5b*), m.p. 119 °C, ν_{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, $J_{8,8}=11.0$ Hz and 95 % of the *exo* epimer *6b*, m.p. 99 °C, ν_{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, $J_{8,8}=$ 10.8 Hz. A mixture of *5f* and *6f* gave 15 % of 1,5-dichlorodibenzobicyclo[3,2,1]octadien-*endo*-4-yl acetate (*5e*), m.p. 166 °C, ν_{max} 1740 cm^{-1}, δ 3.23 (*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, ν_{max} 1730 cm^{-1}, δ 3.47 (syn-8-H), 3.13 (anti-8-H), 6.05 (endo-4-H), 2.13 (OAc) +8 Ar-H, $J_{8,8}=10.0$ Hz, $J_{4,8}=$ 1.5 Hz. When 10 % of H_2SO_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_2SO_4 and 7 g of HOAc, the only product was 1-chlorodibenzobicyclo[2,2,2]octadien-8-yl acetate (*8b*), m.p. 98 °C, ν_{max} 1732 cm^{-1}, δ 1.92 (*cis*-7-H), 2.61 (*trans*-7-H), 4.98 (8-H), 4.46 (4-H), 1.82 (OAc) +8 Ar-H, *cis*$J_{7,8}=8.6$ Hz, *trans*$J_{7,8}=2.7$ Hz, $J_{7,7}=12.8$ Hz, $J_{4,8}=2.6$ Hz. Similarly, *5e* gave 1-chlorodibenzobicyclo[2,2,2]octadien-8-one (*2a*), m.p. 135 °C, ν_{max} 1730 cm^{-1}, δ 2.63 (7-H), 4.73 (4-H).

Hydrolysis of the acetates 5b, 6b, 5e, 6e *and* 8b. 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 was added and the alcohol was obtained by ether extraction and purified by crystallization from 80 % aqueous EtOH. *6b* gave 1-chlorodibenzobicyclo-[3,2,1]octadien-*exo*-4-ol, (*6a*), m.p. 138 °C, ν_{max} 3320 cm^{-1}, δ 2.94 (*syn*-8-H), 2.74 (*anti*-8-H), 4.45 (*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, $J_{8,8}=10.5$ Hz, *6e* gave 1,5-dichlorodibenzobicyclo[3,2,1]octadien-*exo*-4-ol (*6d*), m.p. 171 °C, ν_{max} 3260 cm^{-1}, δ 3.45 (*syn*-8-H), 3.10 (*anti*-8-H), 4.54 (endo-4-H), 2.83 (OH) +8 Ar-H, $J_{8,8}=10.0$ Hz, $J_{4,8}=1.5$ Hz and *8b* gave 1-chlorodibenzobicyclo[2,2,2]octadien-8-ol (*8a*), m.p. 104 °C, ν_{max} 3270 cm^{-1}, δ 1.61 (*cis*-7-H), 2.40 (*trans*-7-H), 3.76 (8-H), 4.02 (4-H), 2.38 (OH) +8 Ar-H, *cis*$J_{7,8}=8.6$ Hz, *trans*$J_{7,8}=2.4$ Hz, $J_{7,7}=$ 12.8 Hz, $J_{4,8}=2.6$ Hz. *5b* and *5e* gave the alcohols *5a* and *5d*, respectively, which were identical with those obtained from the reduction of the ketones *3a* and *3b*.

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