Chlorinated Polycyclic Compounds. III. Preparation and Solvolysis of Some Chloro Derivatives of Dibenzobicyclo[2,2,2]octatriene

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Chloro derivatives of dibenzobicyclo[2,2,2]octatriene on solvolysis in $\text{H}_2\text{SO}_4$-$\text{HOAc}$ mixtures gave derivatives of dibenzobicyclo[2,2,2]-octadien-7-ol acetate, dibenzobicyclo[2,2,2]octadien-7-one and dibenzobicyclo[3,2,1]octadien-4-one, the ratio of rearranged to unarranged product being dependent on $\text{H}_2\text{SO}_4$ concentration.

In connection with earlier studies it was shown that the chloro olefin $\text{If}$ on hydrolysis in a 60:40 mixture of sulfuric acid and acetic acid gives the rearranged ketone $\text{6c}$ as the only reaction product. As, however, it was found that in milder acid also the unarranged hydrolysis product $\text{7d}$ is formed, the reactions of the chlorides $\text{1a} - \text{1g}$ were studied in some more detail. The starting compounds were synthetized by elimination of hydrogen chloride or chlorine from the saturated chlorides. $\text{If}, \text{Ig}$ and $\text{Id}$ were obtained from $\text{2b}, \text{2c}$ and $\text{4c}$, respectively, by refluxing with 10 % ethanolic potassium hydroxide and $\text{1b}$ from $\text{5c}$ with potassium tert-butoxide in dimethyl sulfoxide. Although $\text{Ie}$ could be prepared from $\text{If}$ by hydrogenation and subsequent dehydrochlorination, the reaction with zinc and acetic acid proved a far more convenient method and gave $\text{Ie}$ in a very pure state. Compounds $\text{1a}$ and $\text{1c}$ are known. It may be pointed out that the reactivity of the bridge chlorine atoms towards bases is greatly enhanced because of the inductive effect of the bridgehead chlorine atoms. The cleavage of hydrogen chloride from the corresponding 1,4-unsubstituted compounds requires the use of elevated temperatures or a stronger base. Similarly, the dechlorination of the latter has been accomplished with sodium in alcohol or ether solvents, zinc being almost ineffective. The saturated chlorides result from different reactions: $\text{2b}$ from the Diels-Alder reaction of 9,10-dichloroanthracene and trans-1,2-dichloroethylene, $\text{2c}$ from the addition of chlorine to $\text{If}$, $\text{5c}$ from the reaction of 1-chloro-endo-4-hydroxydibenzobicyclo[3,2,1] octadiene with thionyl chloride and $\text{4c}$ from the Diels-Alder reaction of 9-chloroanthracene and trans-1,2-dichloroethylene. The last prep.

Solvolysis of Chloro Olefins

Solvolysis was not found to be very convenient, because the yields are only moderate and the purification of the product is rather tedious. However, this method was chosen because the alternative route consisting of addition of chlorine to 1b gave neither 3c nor 4c, but instead, the rearranged chlorides 1-endo-4-syn-8-tri-chlorodibenzocyclo[3,2,1]octadiene and its ezo epimer. Attempts to synthesize the corresponding chlorides from the alcohols 3a and 4a were unsuccessful. Treatment of 3a with phosphorus pentachloride gave a mixture of the same rearranged trichlorides as above while 4a gave a mixture of the anti-isomers. The alcohol 3a was obtained by reduction of the ketone 7e by sodium borohydride. This reduction gave only the cis chlorohydrin being still more stereo-selective than the reduction of the ketone 7e. The trans chlorohydrin 4a was prepared by acid catalyzed rearrangement of 1-anti-8-dichloro-endo-4-hydroxydibenzocyclo[3,2,1]-octadiene followed by hydrolysis of the acetate.

![Diagram](image)

6a H Cl H H
b Cl H H H
c Cl Cl H H
d Cl Cl Cl H
e Cl H Cl H
f H Cl Cl H

7a H H H
b Cl H H
c H H Cl
d Cl Cl H
e H Cl Cl
f Cl Cl Cl

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

9a R = OH
b R = OAc

10

11

12

13

To study the solvolysis of 1a – 1g the chlorides were refluxed with sulfuric acid-acetic acid mixtures of varying concentration. 1d gave mixtures of the isomeric ketones 6b and 7b, the former being the major component. The ratio of rearranged to unarranged product was found to be dependent on the sulfuric acid concentration but not on the reaction time. On the other hand, the reaction time necessary for complete conversion of the starting material increased rapidly with decreasing acid concentration. If behaved in the same manner (Fig. 1) but with the tetrachloride 1g the formation of the unarranged ketone 7f was not observed. Obviously, to obtain 7f, long reaction times are necessary to allow for lower acidity, for the reaction of 1g with 30% sulfuric acid for 96 h gave only 4% of 6d and 4% of 6e in addition to unchanged starting material. The structures of 7b and 7d were confirmed by their spectra and by reduction to the alcohols 9a and 8a. The 1H NMR spectra of the alcohols contain typical ABX patterns with coupling constants characteristic of the dibenzobicyclo[2,2,2]octadiene system. The solvolysis of 1a and 1c gave the unarranged ketones 7a and 7c as the only reaction products. The ketone 6a, identical with that obtained from 6c by dechlorination, was formed quantitatively from 1e and the acetate 5b was obtained from 1b as the sole reaction product. The results show that the factors governing the solvolysis are the site of protonation of the double bond and the possible chloro substituent at the bridgehead carbon atom adjacent to the positive charge. The protonation occurs in a direction to give the more stable carbonium
ion. In the case of 1b it is 10 because of the inductive effect of the chlorine atom, but when a chlorine is present in the etheno bridge, the unfavorable inductive effect is outweighed by the possibility of resonance stabilization, as in 12. Rearranged products are obtained only when the bridgehead carbon atom next to the positive charge is chloro substituted (compounds 1d – 1g). The intermediate ion 13 has a chlorine atom in the three-membered ring and attack by a nucleophile leads to a ketone via an irreversible reaction step. Unlike 12 and 13, the ions 10 and 11 are not interconvertible.

The fact that the 1,7-dichlorosubstituted compounds give both of the isomeric ketones, can be ascribed to a competition between hydrolysis and rearrangement of the ion 12. Increased acidity causes a decrease in the H2O/H3O+ ratio and consequently a lower rate of direct hydrolysis (Fig. 1).

EXPERIMENTAL

For general experimental conditions see Ref. 7. Sulfuric acid (95–98 %) and acetic acid (99–100 %) used for the solvolysis reactions were of commercial quality.

Reaction of 9-chloroanthracene with trans-1,2-dichloroethylene. A mixture of 21.2 g (0.1 mol) of 9-chloroanthracene and 291 g (3.0 mol) of trans-1,2-dichloroethylene were heated at 210 °C for 24 h in a 1 l stainless steel pressure vessel. Excess dichloroethylene was removed under reduced pressure, the residue dissolved in 300 ml of light petroleum and the solution filtered. After drying the insoluble part weighed 10.5 g and removal of the solvent from the filtrate left 12.5 g of heavy brown oil. TLC and 1H NMR examination revealed the presence of several components, among which the expected normal adduct 4e amounted to about 55 %. Separation by preparative TLC (several elutions with light petroleum) gave 6.8 g (22 %) of trans-1,7,8-trichlorodibenzobicyclo-

![Graph]

**Fig. 1.** The percentage of rearranged product as a logarithmic function of H2SO4 concentration.

Hydrogenation of 1f. A mixture of 3.0 g of 1f and 0.4 g of 5 % Pt/C in 50 ml of ethyl acetate was hydrogenated for 5 h under a pressure of 800 mm H2O over the atmospheric pressure. The solution was filtered and evaporated and the two major components separated by TLC (elution with light petroleum) and purified by crystallization from MeOH. There were obtained 0.7 g (24 %) of 1,4,7-trichlorodibenzobicyclo-

[2,2,2]octadiene (4c), m.p. 135 °C, δ 4.23 (3 H, m, +8 Ar-H, m/e 308(0.3), 212(100). Other components were not isolated.

Elimination of hydrogen chloride from 2a, 2c, 4e and 6c. The chloride (0.4 g of 2a or 2c) was added to a solution of 1.0 g of KOH in 10 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 product was essentially pure in each case. 2a gave 1,4-dichlorodibenzobicyclo[2,2,2]octatriene (1e), m.p. 92 °C, δ 6.72 (2 H, s) + 8 Ar-H and 2c gave 1,4,7,8-tetrachlorodibenzobicyclo[2,2,2]-octatriene (1g), m.p. 200 °C, only Ar-H. Otherwise similar, but using a reaction time of 160 min, 4e gave 1,7-dichlorodibenzobicyclo-

[2,2,2]octatriene (1d), m.p. 95 °C, δ 4.83 (4 H), J4= a= 6.6 Hz, 8-H in the aromatic multiplet. To eliminate HCl from 5c, 1.0 g of the chloride and 1.0 g of t-BuOK were dissolved in 20 ml of DMSO and the mixture stirred for 4 h at room temperature. Water and HCl were added and the reaction product isolated by ether extraction to give 1-chlorodibenzobicyclo[2,2,2]-octatriene (1b), m.p. 116 °C, δ 4.90 (4-H), 7- and 8-H in the aromatic multiplet, J4= a= 6.0 Hz, J4= b= 2.0 Hz. Analytical samples of the unsaturated chlorides were prepared by TLC (elution in light petroleum) and crystallization from EtOH.

Dechlorination of 2b with zinc and acetic acid. A mixture of 30 g of 2b, 20 g of Zn-powder and 200 ml of acetic acid was refluxed for 20 h. The solution was filtered hot, evaporated, the residue dissolved in acetic acid and filtered through 10 g of silica gel. The acetone was removed and the residue dissolved in 50 ml of 80 % aqueous EtOH, from which the product soon crystallized to yield 18.6 g (78 %) of 1e.

Addition of chlorine to 1f. A solution of 10 g of 1f in 100 ml of dry CCl4 was saturated with chlorine at room temperature. The reaction took place rapidly with evolution of heat. To complete the reaction, the solution was allowed to stand overnight. After removal of the solvent a quantitative yield of 1,4,7,7,8-pentachlorodibenzobicyclo[2,2,2]octadiene (2e) was obtained. M.p. 156 °C δ 4.81 (8-H) + 8 Ar-H.

Addition of chlorine to 1b. A solution of 0.1 g of 1b in 10 ml of dry CCl₄ was saturated with chlorine at 0 °C and the solution allowed to stand for 40 min. The solvent was removed under reduced pressure. According to ¹H NMR, the residue contained about 85 % of 1-endo-4-8-chlorodibenzocyclo[3,2,1]octadiene and 15 % of the endo epimer.¹

Reduction of the ketones 7b, 7d and 7e with sodium borohydride. A solution of 10 mmol of the ketone (2.55 g of 7b, 2.89 g of 7d or 7e) and 0.38 g (10 mmol) of NaBH₄ in 100 ml of EtOH was stirred for 40 min at room temperature. Water and HCl were added and the product isolated by ether extraction. The analytical samples were crystallized from 80 % aqueous EtOH. 7b gave 1-chlorodibenzocyclo[2,2,2]octadec-7-ol (9a), m.p. 70 °C, vmax 3250 cm⁻¹, δ 1.62 (cis-8-H), 2.33 (trans-8-H), 3.94 (7-H), 4.12 (4-H), 2.05 (OH)+8 Ar-H, cis J₈₉ = 5.8 Hz, J₉₈ = 2.3 Hz, J₈₉ = 12.5 Hz, J₉₈ = 2.4 Hz and 7d gave 1,4-dichlorodibenzocyclo[2,2,2]octadec-7-ol (8a), m.p. 101 °C, vmax 3350 cm⁻¹, δ 1.98 (cis-8-H), 2.57 (trans-8-H), 3.97 (7-H), 2.10 (OH) + 8 Ar-H, cis J₈₉ = 8.8 Hz, trans J₉₈ = 2.8 Hz, J₉₈ = 12.4 Hz. 7e gave 1,7-dichlorodibenzocyclo[2,2,2]octadec-8-ol (3a), m.p. 171 °C, vmax 3530 cm⁻¹, δ 4.39 (trans-7-H), 4.11 (8-H), 4.33 (4-H), 1.93 (OH)+8 Ar-H, cis J₈₉ = 7.8 Hz, J₉₈ = 2.4 Hz. By TLC and ¹H NMR examination, the presence of the trans isomer was not detected.

Acetylation of the alcohols 9a, 8a and 3a. The alcohol 9a (0.5 g) refluxed with 80 ml of a mixture of 10 ml of Ac₂O and 1 ml of pyridine, gave the acetal 9b, m.p. 151 °C, vmax 1735 cm⁻¹, δ 1.53 (cis-8-H), 2.47 (trans-8-H), 5.07 (7-H), 4.19 (4-H), 1.89 (OAc)+8 Ar-H, cis J₈₉ = 8.6 Hz, trans J₉₈ = 2.6 Hz, J₉₈ = 12.7 Hz, J₈₉ = 2.5 Hz. Similarly, 8a gave 8b, m.p. 143 °C, vmax 1750 cm⁻¹, δ 1.97 (cis-8-H), 2.82 (trans-8-H), 5.09 (7-H), 1.87 (OAc)+8 Ar-H, cis J₈₉ = 8.8 Hz, trans J₉₈ = 2.6 Hz, J₉₈ = 12.5 Hz and 3a gave 3b, m.p. 183 °C, vmax 1738 cm⁻¹, δ 4.41 (trans-7-H), 5.09 (8-H), 4.30 (4-H), 1.95 (OAc)+8 Ar-H, cis J₈₉ = 8.2 Hz, J₉₈ = 2.5 Hz. The analytical samples were crystallized from 80 % aqueous EtOH.

Synthesis of 4a and 4b. A solution of 1.0 g of 1-anti-8-chlorodibenzocyclo[3,2,1]octadien-endo-4-ol,¹ 10 g of H₂SO₄ and 40 g of HOAc was refluxed for 20 h. The solution was diluted with water and the product isolated by ether extraction. According to ¹H NMR, the reaction yielded almost quantitatively 1,7-dichlorodibenzocyclo[2,2,2]octadec-8-yl acetate (4b), m.p. 165 °C, vmax 1737 cm⁻¹, δ 3.98 (cis-7-H), 5.05 (8-H), 4.46 (4-H), 1.90 (OAc)+8 Ar-H, trans J₈₉ = 1.7 Hz, J₉₈ = 3.0 Hz.

The acetate 4b (0.5 g) hydrolyzed with 20 ml of 10 % ethanolic KOH for 80 min at room temperature gave the alcohol 4a, m.p. 112 °C, vmax 3310 cm⁻¹, δ 3.74 (cis-7-H), 4.13 (8-H), 4.13 (4-H), 1.81 (OH)+8 Ar-H, trans J₈₉ = 1.2 Hz. The analytical samples of 4a and 4b were crystallized from 80 % aqueous EtOH.

Reactions of 3a and 4a with phosphorus pentachloride. The alcohol 3a (0.2 g) was refluxed for 10 min with a mixture of 1.0 g of PCl₅ and 1.0 g of POCl₃. Excess reagent was carefully decomposed with water and the product isolated by ether extraction. According to ¹H NMR, the product contained 80 % of 1-endo-4-anti-8-chlorodibenzocyclo[3,2,1]octadiene and 20 % of the endo epimer. Similar treatment of 4a gave 95 % of 1-endo-4-anti-8-chlorodibenzocyclo[3,2,1]octadiene and 5 % of the endo epimer.²

Solvolysis of the unsaturated chlorides 1a-1g.

The general method: A mixture of 1.0 g of the chloride, 6 g of H₂SO₄ and 14 g of HOAc was refluxed for 80 min. The hot reaction mixture was poured into ice water and the product isolated by ether extraction. The yields were estimated from the ¹H NMR spectra. Following compounds were obtained (starting material, percentage of products): 1a, 100 % of 7a; 1b, 100 % of 5b; 1c, 100 % of 7c; 1d, 89 % of 6b and 11 % of 7b; 1e, 90 % of 6a and 10 % of 1c; If, 85 % of 6c and 15 % of 7d; 1g, 100 % of 1g. In the cases where a part of the starting material was recovered, longer reaction times were used. Thus 1e refluxed for 24 h gave 100 % of 6a, but 1g refluxed for 96 h gave only 4 % of 6d and 4 % of 6e, in addition to unchanged 1g. A solution of 1.0 g of 1g, 12 g of H₂SO₄ and 8 g of HOAc refluxed for 24 h gave 47 % of 6d and 53 % of 6e. The solvolysis of 1d and 1f was studied in different acid concentrations (Fig. 1) using reaction times sufficient for complete conversion of the starting material (up to 96 h). Further heating did not affect the product ratios. The analytical samples were prepared by TLC (elution with a 1:1 mixture of benzene and light petroleum) and crystallization from EtOH. The ketones 6a,¹ 6c,¹ 6d,¹ 6e and the acetate 5b were identical with the compounds obtained from other reactions and the spectral properties and melting points of the ketones 7a,¹ 7b and 7e were in agreement with the values reported in literature. The ketone 7c had δ 4.04 (7-H), 4.71 (4-H), 4.55 (1-H)+8 Ar-H, J₈₉ = 2.7 Hz. The new compounds had the following properties: 5-chlorodibenzocyclo[3,2,1]octadien-4-one (5b), m.p. 159 °C, vmax 1700 cm⁻¹, δ 3.14 (2 H, d), 4.21 (1 H, tr)+8 Ar-H, cis J₈₉ = 2.4 Hz, m/e 254(42), 219(100), 1-chlorodibenzocyclo[2,2,2]octadec-7-one (7b), m.p. 115 °C, vmax 1725 cm⁻¹, δ 2.30 (2 H, d), 4.45 (1 H, tr)+8 Ar-H, J₈₉ = 2.5 Hz, m/e 254(0.3), 219(100), 1,4-dichlorodibenzocyclo[2,2,2]octadec-7-one (7d), m.p. 117 °C, vmax 1750 cm⁻¹, δ 2.81 (2 H, s)+8 Ar-H, m/e 288(0.9), 246(100).

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REFERENCES


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