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

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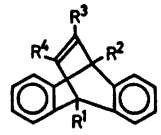
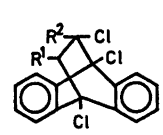
Chloro derivatives of dibenzobicyclo[2,2,2]octatriene on solvolysis in H_2SO_4-HOAc mixtures gave derivatives of dibenzobicyclo[2,2,2]-octadien-7-ol acetate, dibenzobicyclo[2,2,2]octadien-7-one and dibenzobicyclo[3,2,1]octadien-4-one, the ratio of rearranged to unrearranged product being dependent on H_2SO_4 concentration.

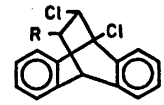
In connection with earlier studies [1] it was shown that the chloro olefin *1f* on hydrolysis in a 60:40 mixture of sulfuric acid and acetic acid gives the rearranged ketone *6c* as the only reaction product. As, however, it was found that in milder acid also the unrearranged hydrolysis product *7d* is formed, the reactions of the chlorides *1a*–*1g* were studied in some more detail. The starting compounds were synthetized by elimination of hydrogen chloride or chlorine from the saturated chlorides. *1f*, *1g* and *1d* were obtained from *2b*, *2c* and *4c*, respectively, by refluxing with 10 % ethanolic potassium hydroxide and *1b* from *5c* with potassium *t*-butoxide in dimethyl sulfoxide. Although *1e* could be prepared from *1f* by hydrogenation and subsequent dehydrochlorination, the reaction with zinc and acetic acid proved a far more convenient method and gave *1e* in a very pure state. Compounds *1a* [2] and *1c* [3] 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 [4] or a stronger base. [2] Similarly, the dechlorination of the latter has been accomplished with sodium in alcohol [4,5] or ether [6] solvents, zinc being almost ineffective. The saturated chlorides result from different reactions: *2b* from the Diels-Alder reaction of 9,10-dichloroanthracene and *trans*-1,2-dichloroethylene,[7] *2c* from the addition of chlorine to *1f*, *5c* from the reaction of 1-chloro-*endo*-4-hydroxydibenzobicyclo[3,2,1] octadiene with thionyl chloride [1] and *4c* from the Diels-Alder reaction of 9-chloroanthracene and *trans*-1,2-dichloroethylene. The last prep-



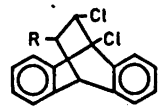
	R^1	R^2	R^3	R^4
1a	H	H	H	Cl
b	Cl	H	H	H
c	H	H	Cl	Cl
d	Cl	H	H	Cl
e	Cl	Cl	H	H
f	Cl	Cl	H	Cl
g	Cl	Cl	Cl	Cl



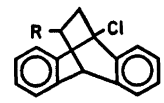
	R^1	R^2
2a	H	H
b	Cl	H
c	Cl	Cl



3a	R = OH
b	R = OAc
c	R = Cl

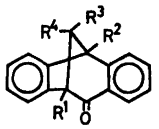


4a	R = OH
b	R = OAc
c	R = Cl

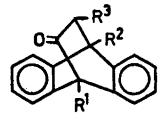


5a	R = OH
b	R = OAc
c	R = Cl

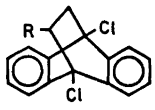
aration was not found to be very convenient, because the yields are only moderate and the purification of the product is rather tedious. However, this method was chosen because the alternative route consisting of addition of chlorine to *1b* gave neither *3c* nor *4c*, but instead, the rearranged chlorides 1-*endo*-4-*syn*-8-trichlorodibenzobicyclo[3,2,1]octadiene and its *exo* epimer.[7] 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*-8-isomers.[7] The alcohol *3a* was obtained by reduction of the ketone *7e* by sodium borohydride. This reduction gave only the *cis* chlorohydrin being still more stereoselective than the reduction of the ketone *7c*.[6] The *trans* chlorohydrin *4a* was prepared by acid catalyzed rearrangement of 1-*anti*-8-dichloro-*endo*-4-hydroxydibenzobicyclo[3,2,1]-octadiene [7] followed by hydrolysis of the acetate.



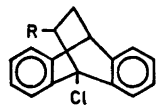
	R^1	R^2	R^3	R^4
6a	H	Cl	H	H
b	Cl	H	H	H
c	Cl	Cl	H	H
d	Cl	Cl	Cl	H
e	Cl	Cl	H	Cl



	R^1	R^2	R^3
7a	H	H	H
b	Cl	H	H
c	H	H	Cl
d	Cl	Cl	H
e	H	Cl	Cl
f	Cl	Cl	Cl



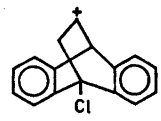
8a	R = OH
b	R = OAc
c	R = H



9a	R = OH
b	R = OAc

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 unrearranged 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. *1f* behaved in the same manner (*Fig. 1*) but with the tetrachloride *1g* the formation of the unrearranged 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 ^{1}H NMR spectra of the alcohols contain typical ABX patterns with coupling constants characteristic of the dibenzobicyclo [2,2,2]octadiene system.[8] The solvolysis of *1a* and *1c* gave the unrearranged ketones *7a* [8,9] and *7c* [6] as the only reaction products. The ketone *6a*, identical with that obtained from *6c* by dechlorination,[1] was formed quantitatively from *1e* and the acetate *5b* [1] was obtained from *1b* as the sole reaction product.

The results show that the features 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



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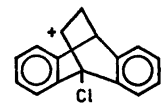

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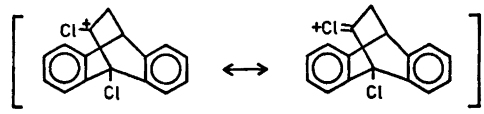

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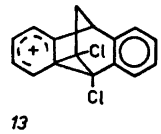

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ion. In the case of *1b* it is *10* because of the inductive effect of the chlorine atom, but when a chlorine is present in the etheno bridge, the unfavorable inductive effect is outweighed by the possibility of resonance stabilization, as in *12*. 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* [10] 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 H_2O/H_3O^+ 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 [11] 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 *4c* amounted to about 55 %. Separation by preparative TLC (several elutions with light petroleum) gave 6.8 g (22 %) of *trans*-1,7,8-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.

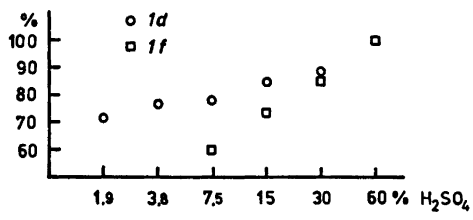

Fig. 1. The percentage of rearranged product as a logarithmic function of H_2SO_4 concentration.

Hydrogenation of 1f. A mixture of 3.0 g of *1f* [1] and 0.4 g of 5 % Pd/C in 50 ml of ethyl acetate was hydrogenated for 5 h under a pressure of 800 mm H_2O 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 (*2a*), m.p. 119 °C, δ 2.37 (*cis*-8-H), 2.80 (*trans*-8-H), 4.17 (7-H) + 8 Ar-H, *cis* $J_{7,8} = 9.0$ Hz, *trans* $J_{7,8} = 3.5$ Hz, $J_{8,8} = 12.7$ Hz and 1.6 g (62 %) of 1,4-dichlorodibenzobicyclo[2,2,2]octadiene (*8c*), m.p. 123 °C (lit.[12] 125 – 127 °C), δ 2.17 (4 H, s) + 8 Ar-H.

Elimination of hydrogen chloride from 2a, 2c, 4c *and* 5c. 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 similarly, but using a reaction time of 160 min, *4c* gave 1,7-dichlorodibenzobicyclo-[2,2,2]octatriene (*1d*), m.p. 95 °C, δ 4.83 (4-H), $J_{4,8} =$ 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, $J_{4,8} = 6.0$ Hz, $J_{4,7} = 2.0$ 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*,[7] 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 acetone 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 CCl_4 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 (*2c*) 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 CCl_4 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 ^{1}H NMR the residue contained about 85 % of 1-*exo*-4-*syn*-8-trichlorodibenzocyclo[3,2,1]octadiene and 15 % of the *endo* epimer.[7]

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* [7]) and 0.38 g (10 mmol) of $NaBH_4$ 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-chlorodibenzobicyclo[2,2,2]octadien-7-ol (*9a*), m.p. 70 °C ν_{max} 3250 cm^{-1}, δ 1.52 (*cis*-8-H), 2.33 (*trans*-8-H), 3.94 (7-H), 4.12 (4-H), 2.05 (OH) + 8 Ar-H, *cis* $J_{7,8}$ = 8.8 Hz, *trans* $J_{7,8}$ = 2.3 Hz, $J_{8,8}$ = 12.5 Hz, $J_{4,8}$ = 2.4 Hz and *7d* gave 1,4-dichlorodibenzobicyclo[2,2,2]octadien-7-ol (*8a*), m.p. 101 °C, ν_{max} 3330 cm^{-1}, δ 1.98 (*cis*-8-H), 2.57 (*trans*-8-H), 3.97 (7-H), 2.10 (OH) + 8 Ar-H *cis* $J_{7,8}$ = 8.8 Hz, *trans* $J_{7,8}$ = 2.8 Hz, $J_{8,8}$ = 12.4 Hz. *7e* gave 1,7-dichlorodibenzobicyclo[2,2,2]-octadien-*cis*-8-ol (*3a*), m.p. 171 °C, ν_{max} 3530 cm^{-1}, δ 4.39 (*trans*-7-H), 4.11 (8-H), 4.33 (4-H), 1.83 (OH) + 8 Ar-H, *cis* $J_{7,8}$ = 7.8 Hz, $J_{4,8}$ = 2.4 Hz. By TLC and ^{1}H 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 for 80 min with a mixture of 10 ml of Ac_2O and 1 ml of pyridine, gave the acetate *9b*, m.p. 151 °C, ν_{max} 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* $J_{7,8}$ = 8.6 Hz, *trans* $J_{7,8}$ = 2.6 Hz, $J_{8,8}$ = 12.7 Hz, $J_{4,8}$ = 2.5 Hz. Similarly, *8a* gave *8b*, m.p. 143 °C, ν_{max} 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* $J_{7,8}$ = 8.8 Hz, *trans* $J_{7,8}$ = 2.6 Hz, $J_{8,8}$ = 12.5 Hz and *3a* gave *3b*, m.p. 185 °C, ν_{max} 1738 cm^{-1}, δ 4.41 (*trans*-7-H), 5.09 (8-H), 4.30 (4-H), 1.95 (OAc) + 8 Ar-H, *cis* $J_{7,8}$ = 8.2 Hz, $J_{4,8}$ = 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-dichlorodibenzobicyclo[3,2,1]octadien-*endo*-4-ol,[7] 10 g of H_2SO_4 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 ^{1}H NMR, the reaction yielded almost quantitatively 1,7-dichlorodibenzobicyclo[2,2,2]octadien-*trans*-8-yl acetate (*4b*), m.p. 165 °C, ν_{max} 1737 cm^{-1}, δ 3.98 (*cis*-7-H), 5.05 (8-H), 4.46 (4-H), 1.90 (OAc) + 8 Ar-H, *trans* $J_{7,8}$ = 1.7 Hz, $J_{4,8}$ = 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. 131 °C, ν_{max} 3310 cm^{-1}, δ 3.74 (*cis*-7-H), 4.13 (8-H), 4.13 (4-H), 1.81 (OH) + 8 Ar-H, *trans* $J_{7,8}$ = 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 PCl_5 and 1.0 g of $POCl_3$. Excess reagent was carefully decomposed with water and the product isolated by ether extraction. According to ^{1}H NMR, the product contained 80 % of 1-*exo*-4-*syn*-8-trichlorodibenzobicyclo[3,2,1]octadiene and 20 % of the *endo* epimer. Similar treatment of *4a* gave 95 % of 1-*exo*-4-*anti*-8-trichlorodibenzobicyclo[3,2,1]octadiene and 5 % of the *endo* epimer.[7]

Solvolysis of the unsaturated chlorides 1a – 1g. The general method: A mixture of 1.0 g of the chloride, 6 g of H_2SO_4 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 ^{1}H 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 *1e*; *1f*, 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 H_2SO_4 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*,[7] *6e* [7] and the acetate *5b* [1] were identical with the compounds obtained from other reactions and the spectral properties and melting points of the ketones *7a* [8,9] and *7c* [6] 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, $J_{1,7}$ = 2.7 Hz. The new compounds had the following properties: 5-chlorodibenzobicyclo[3,2,1]octadien-4-one (*6b*), m.p. 159 °C, ν_{max} 1700 cm^{-1}, δ 3.14 (2 H, d), 4.21 (1 H, tr) + 8 Ar-H, $J_{1,8}$ = 2.4 Hz, *m/e* 254(42), 219(100), 1-chlorodibenzobicyclo[2,2,2]-octadien-7-one (*7b*), m.p. 118 °C, ν_{max} 1725 cm^{-1}, δ 2.39 (2 H, d), 4.45 (1 H, tr) + 8 Ar-H, $J_{4,8}$ = 2.5 Hz, *m/e* 254(0.3), 212(100), 1,4-dichlorodibenzobicyclo[2,2,2]octadien-7-one (*7d*), m.p. 117 °C, ν_{max} 1750 cm^{-1}, δ 2.81 (2 H, s) + 8 Ar-H, *m/e* 288(0.9), 246(100).

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