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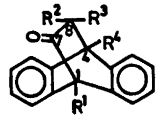
Chlorinated Polycyclic Compounds. IX. Alkaline Cleavage of Chlorosubstituted Dibenzobicyclo[2.2.2]octadien-7-ones

TAPIO MIETTINEN

Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo 15, Finland

Cleavage of chlorosubstituted dibenzobicyclo-[2.2.2]octadien-7-ones with ethanolic potassium hydroxide or potassium *tert*-butoxide in dimethyl sulfoxide gave derivatives of 9-anthraceneacetic acid, 9-anthroic acid and 5*H*-dibenzo[*a*,*d*]cycloheptene-10-carboxylic acid. The reaction mechanisms are discussed.

Part VI of this series [1] dealt with the alkaline cleavage of chlorosubstituted dibenzobicyclo-[3.2.1]octadien-4-ones. This study is now extended to the isomeric [2.2.2] series. Six members of the ketone series *1*, available from previous work,[2–5] were subjected to cleavage by ethanolic potassium hydroxide or potassium *tert*-butoxide in dimethyl sulfoxide. The results are shown in Table 1.



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The structures of the cleavage products were easily determined by spectroscopic means. The only exception was the acid *6*, the structure of which was confirmed by decarboxylation to the known [6] hydrocarbon 5*H*-dibenzo[*a*,*d*]cycloheptene. Of the products examined, *2a* [7] and *6* [8,9] have been described earlier.

As for the reaction mechanisms, the picture is quite involved and several different pathways have to be taken into account to explain the products observed. The cleavage of the ethano bridge is cleanest with the 4-chloro-substituted ketones (*1b*, *1d*, *1f* and *1g*) but the opening can occur at either side of the carbonyl group (pathways A – C). It can be seen that the tendency to bond cleavage between C-7 and C-8 increases with an increasing number of electron-withdrawing chloro substituents on the latter. Thus, the 8-unsubstituted ketones *1b* and *1f* gave only anthraceneacetic acids, the 8-monochloro ketone *1d* gave about equal amounts of anthraceneacetic acid and anthroic acid derivatives and the 8,8-dichloroketone *1g* gave exclusively the anthroic acid derivative *5*.

Table 1. Products from the alkaline cleavage of the ketones *1b* – *1g*.

Starting material No.	R^1	R^2	R^3	R^4	Reaction products KOH/EtOH	Reaction products *tert*-BuOK/DMSO
1a	H	H	H	H		
1b	H	H	H	Cl	100 % *2a*	95 % *2a*
1c	H	H	Cl	H	60 % *2a*	90 % *6*
1d	H	H	Cl	Cl	50 % *3*, 45 % *4*	Complex mixture
1e	H	Cl	Cl	H	60 % *4*	65 % *6*
1f	Cl	H	H	Cl	100 % *2b*	95 % *2b*
1g	H	Cl	Cl	Cl	80 % *5*	High molecular weight products

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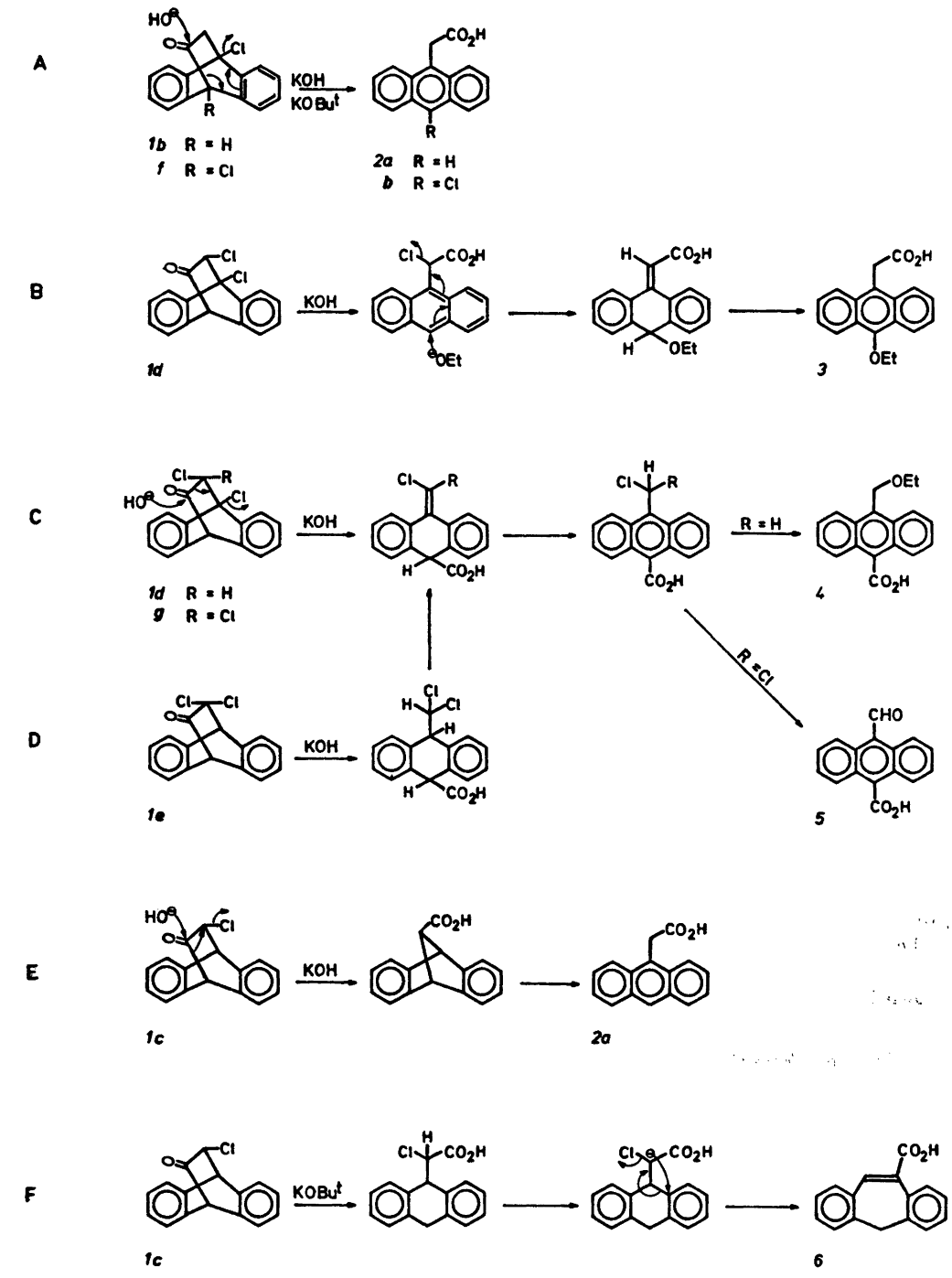

The reaction starting from *1d via* path B leads to removal of both chlorine atoms and incorporation of an ethoxy group in the anthracene ring system. The chlorine atom remaining after the initial cleavage is highly activated, but since direct displacement is prevented by

steric factors, it is displaced by ethoxide ion attack on the opposite face of the anthracene nucleus. This displacement reaction is in good agreement with the concept that the central ring of anthracene in many respects more resembles a 1,3-diene than a benzene ring.

The ketone *1e* behaves similarly with the other 8,8-dichloroketone *1g*, being cleaved predominantly at the 7,8 bond (pathway D). The ketone *1a* is cleaved by boiling 10 % ethanolic potassium hydroxide to 9,10-dihydroanthracene-9-acetic acid.[10] As, however, the reaction occurred only to a small extent under the present reaction conditions, it is probable that the reaction of *1c* starts in another way. As an α-chloro ketone, it can undergo a Favorskii rearrangement giving a bridged acid, which is then isomerized to the more stable anthracene derivative (pathway E).

The results obtained with potassium *tert*-butoxide were more complex, although two of the ketones gave the same products as with potassium hydroxide (pathway A). The formation of the acid *6* is particularly interesting, because it is the only case where the cleavage of the ethano bridge does not lead to regeneration of the thermodynamically favored anthracene structure. As is known from the reaction of ketone *1a*,[11] potassium *tert*-butoxide under these reaction conditions is capable of breaking the 1,7 bond to give a dihydroanthracene intermediate (pathway F). Elimination of hydrogen chloride from this intermediate with subsequent aromatisation of the central ring should give 9-anthraceneacetic acid as the final product even in this case. The higher acidity of the exocyclic hydrogen, compared with the benzhydrylic one, can explain the fact that the former is removed more rapidly by the base. The ion thus formed suffers a rearrangement to be able to expel the chloride ion. Another possible mechanism consists of the formation of a carbene intermediate followed by rearrangement. The fact that the same end product is also obtained from *1e*, must be explained by a dehalogenation occurring prior to the cleavage. Similar reductions of halogen atoms by base have been encountered earlier [1,5,12] but are best known with bromo compounds.[13,14]

EXPERIMENTAL

For general experimental conditions, see Ref. 2. The ketones *1a*,[4,10] *1b*,[3] *1c*,[4,5,15] *1d*,[3] *1e*,[5] *1f* [3] and *1g* [5] have been described earlier.

Reactions of the ketones 1b – 1g *with potassium hydroxide in ethanol.* General method: A mixture of 1.0 g of the ketone, 2.5 g of KOH and 25 ml of EtOH was stirred for 40 min at room temperature. The mixture was poured into water, the solution made acidic with HCl and the products were isolated by ether extraction. The carboxylic acids thus obtained were purified by crystallization from EtOH. When mixtures were obtained, the acids were first converted to methyl esters with CH_2N_2 and then separated by TLC (elution with chloroform – light petroleum 1:3). The results are shown in Table 1.

The products had the following physical properties: 9-anthraceneacetic acid (*2a*), m.p. 228 °C (lit.[7] m.p. 229 – 231.4 °C), $\bar{\nu}_{max}$ 3100 – 2500, 1700 cm^{-1}, the methyl ester, m.p. 88 °C (lit.[7] m.p. 87.0 – 88.0 °C), $\bar{\nu}_{max}$ 1735 cm^{-1}, δ 3.53 (3 H, s), 4.46 (2 H, s), 7.2 – 7.6 (4 H, m), 7.7 – 8.1 (4 H, m), 8.22 (1 H, s); 10-chloro-9-anthraceneacetic acid (*2b*), m.p. 268 °C, $\bar{\nu}_{max}$ 3100 – 2500, 1690 cm^{-1}, methyl ester, m.p. 118 °C, $\bar{\nu}_{max}$ 1730 cm^{-1}, δ 3.55 (3 H, s), 4.41 (2 H, s), 7.2 – 7.6 (4 H, m), 8.0 – 8.6 (4 H, m); 10-ethoxy-9-anthraceneacetic acid methyl ester (methyl ester of *3*), m.p. 97 °C, $\bar{\nu}_{max}$ 1735 cm^{-1}, δ 1.59 (3 H, tr, J = 7.0 Hz), 4.17 (2 H, q, J = 7.0 Hz), 3.55 (3 H, s), 4.41 (2 H, s), 7.2 – 7.5 (4 H, m), 8.0 – 8.3 (4 H, m); 10-ethoxymethyl-9-anthroic acid methyl ester (methyl ester of *4*), m.p. 85 °C, ν_{max} 1725 cm^{-1}, δ 1.16 (3 H, tr, J = 7.0 Hz), 3.55 (2 H, q, J = 7.0 Hz), 4.06 (3 H, s), 5.24 (2 H, s), 7.2 – 7.5 (4 H, m), 7.7 – 8.0 (2 H, m), 8.1 – 8.4 (2 H, m); 10-formyl-9-anthroic acid (*5*), m.p. 310 °C (dec.) $\bar{\nu}_{max}$ 3100 – 2600, 1710, 1680, 1640 cm^{-1}, methyl ester, m.p. 170 °C, $\bar{\nu}_{max}$ 1715, 1685 cm^{-1}, δ 4.12 (3 H, s), 7.3 – 8.0 (6 H, m), 8.6 – 8.9 (2 H, m), 11.57 (1 H, s).

Reactions of the ketones 1b – 1g *with potassium* tert-*butoxide in dimethyl sulfoxide.* General method: A mixture of 1.0 g of the ketone, 2.5 g of *tert*-BuOK and 25 ml of DMSO was stirred for 40 min at room temperature. With the ketones *1c* and *1e* a longer reaction time (24 h) was necessary. The mixtures were worked up and the products purified as above. 5*H*-dibenzo[*a*,*d*]cycloheptene-10-carboxylic acid *(6)*, m.p. 196 °C (lit.[8] m.p. 196 – 198 °C), methyl ester, m.p. 85 °C (lit.[9] m.p. 86 °C), $\bar{\nu}_{max}$ 1700 cm^{-1}, δ 3.55 (2 H, s), 3.78 (3 H, s), 6.8 – 7.6 (8 H, m), 8.07 (1 H, s).

Decarboxylation of the acid 6. A mixture of 0.5 g of *6*, 0.2 g of Cu-chromite decarboxylation catalyst (Fluka) and 20 ml of quinoline was refluxed for 20 min. The mixture was cooled, dissolved in 100 ml of ether and washed thoroughly with 2 N HCl. The ethereal solution was dried and evaporated and the residue purified by TLC (elution with light petroleum)

to give 0.31 g (76 %) of 5*H*-dibenzo[*a*,*d*]cycloheptene, which had m.p. and ^{1}H NMR spectrum similar to those reported.[6]

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