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Chlorinated Polycyclic Compounds. VII. Preparation and Reactions of the Anthracene Adduct of Mucochloric Acid

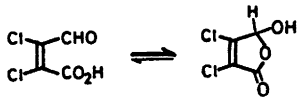
TAPIO MIETTINEN

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

The $AlCl_3$-catalyzed addition of mucochloric acid to anthracene gave the adduct in 40–55 % yields. Like mucochloric acid, the adduct can form normal esters and cyclic pseudo-esters and under suitable reaction conditions products derived from either form can be obtained. Reduction of the adduct gave products at three different oxidation levels. Reaction of the adduct with MeONa in MeOH gave 8-chlorodibenzobicyclo[2.2.2]octatriene-7-carboxylic acid and reaction with aqueous KOH gave 7-hydroxydibenzobicyclo[2.2.2]octadiene-*trans*-7,8-dicarboxylic acid as main products. Treatment with NH_3 or $MeNH_2$ gave nitrogen analogs of the adduct.

In search of new uses for the readily available polyfunctional compound, mucochloric acid (2,3-dichloro-3-formylacrylic acid), the possibility of using it as dienophile in the Diels-Alder reaction was examined.

Mucochloric acid is a mixture of two tautomers, but the equilibrium lies so far to the right that its structure can be best represented by the cyclic formula:[1]



Because the double bond is thus activated[2] by only one carbonyl group, mucochloric acid can be expected to add much slower to anthracene than *e.g.*, dichloromaleic anhydride.[3] Indeed, no adduct formation was observed in boiling xylene. It is known, however, that the Diels-Alder reaction of a double bond conjugated with a carbonyl function is subject to catalysis by Lewis acids.[4,5] Using anhydrous aluminium chloride as catalyst, yields of 40–55 % were obtained, the limiting factor being the formation of high molecular weight side products rather than the reaction velocity.

Like mucochloric acid itself, the anthracene adduct exists almost entirely in the cyclic form. The presence of the open chain tautomer could not be shown spectroscopically, but under suitable reaction conditions products derived from either form could be obtained. Because new asymmetric centers are created in the addition, the compound *1* and its derivatives exist in two epimeric forms, which are in the following referred to as the epimers *a* and *b* with the shown stereostructures. The epimers of the hydroxy compounds *1*, *6*, *24* and *26* could not be separated, whereas chromatographic separation of the corresponding methoxy and acetoxy derivatives gave the pure epimers with epimer ratios between 90:10 and 75:25. Examination of molecular models revealed that the form *a* is considerably less hindered than its epimer *b* and consequently the structure *a* was assigned to the major and *b* to the minor epimer.

a *b*

Two isomeric methyl esters were obtained from the adduct: The normal acid catalyzed esterification gave a mixture of the epimeric pseudo-esters *3*, while the reaction with diazomethane furnished the open chain isomer *4*. The latter is thermodynamically the less stable

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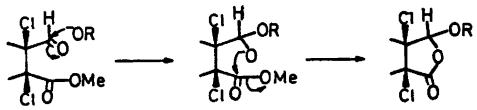
one and was rapidly isomerized to *3* in the presence of methoxide ion. The analogous reaction with hydroxide ion led back to *1*. Also in this respect the adduct bears a close similarity to mucochloric acid.[6,7]



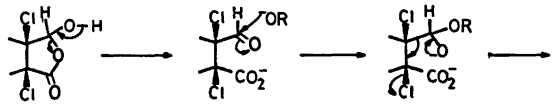
The normal methyl ester *4* reacted with hydride ion as with methoxide or hydroxide ions, the cyclization product being in this case the lactone *5*. If the reduction was performed in an alcohol solvent, a large amount of the corresponding pseudo-ester was obtained as side product. The reduction of *1* required the use of lithium aluminium hydride and the product was the diol *8*. The reductions of both *1* and *4* gave small amounts of the cyclic acetal *6*, a product at an intermediate oxidation level.

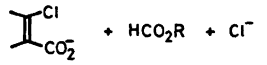
The treatment of *1* with strong bases caused the elimination of one or both chlorine atoms. Reaction of *1* with 5 % aqueous KOH at room temperature gave an almost quantitative yield of the dicarboxylic acid *18*, while a similar reaction mixture refluxed for 20 min led to a mixture of the acids *18*, *22* and *11*. When *1* was refluxed for 20 min with a solution of sodium methoxide in methanol, only *11* was obtained. Prolonged heating gave rise to solvolysis and decarboxylation reactions giving the compounds *13*, *15* and *17*. The acids *11*,[8] *13* [9] and *15* [9] and the ketone *17* [9,10] are known.

The structure of the acid *18* is based on the following observations: The configuration of the carboxyl groups is probably *trans*, because no anhydride formation occurred on heating.[11,12] Attempts to acetylate the hydroxyl group of *19* in boiling acetic anhydride caused the elimination of water to give dibenzobicyclo[2.2.2]octatriene-7,8-dicarboxylic acid dimethyl ester, but no acetate was observed. This result shows that the acid *18* has an unchanged carbon skeleton and no rearrangement, frequently encountered in this kind of reaction,[13–15] had occurred. Further proof is provided by the ^{1}H NMR spectrum of the methyl ester *19*, exhibiting coupling constants typical of this ring system [10] and inconsistent with the isomeric [3.2.1] system.[16]

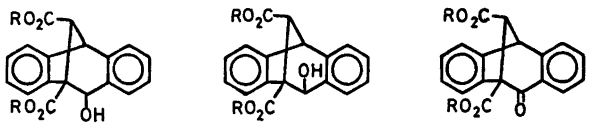
The acid *18* has been described as the main product from the reactions of 7-bromodibenzobicyclo[2.2.2]octadiene-*cis*-7,8-dicarboxylic anhydride with potassium hydroxide [11,17] or silver nitrate.[15] As, however, the reported melting points of both the acid and its dimethyl ester markedly differ from those observed here, the reactions cited above were repeated. It was found that the reaction of the bromo anhydride with silver nitrate gave the two epimeric dicarboxylic acids *33a* and *34a* and the reaction with potassium hydroxide gave *34a* as the major product. In neither case could the presence of *18* be detected. The acids *33a* and *34a* were isolated as their methyl esters. The structures of *33b* and *34b* were confirmed by their spectra [16] and by oxidation to the keto ester *35b*.

The mechanisms leading to both *11* and *18* obviously begin with the opening of the five-membered ring followed by a nucleophilic attack on the aldehyde carbon atom. Elimination of methyl formate (or a formate ion in aqueous solution) and a chloride ion leads to *11:*





The other reaction possibilities of the negative charge on the acetal oxygen atom are the intramolecular reactions with the chlorine atoms. The displacement of the α-chlorine



33a R = H
b R = Me

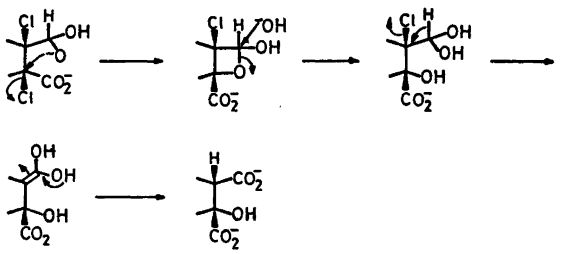
34a R = H
b R = Me

35a R = H
b R = Me

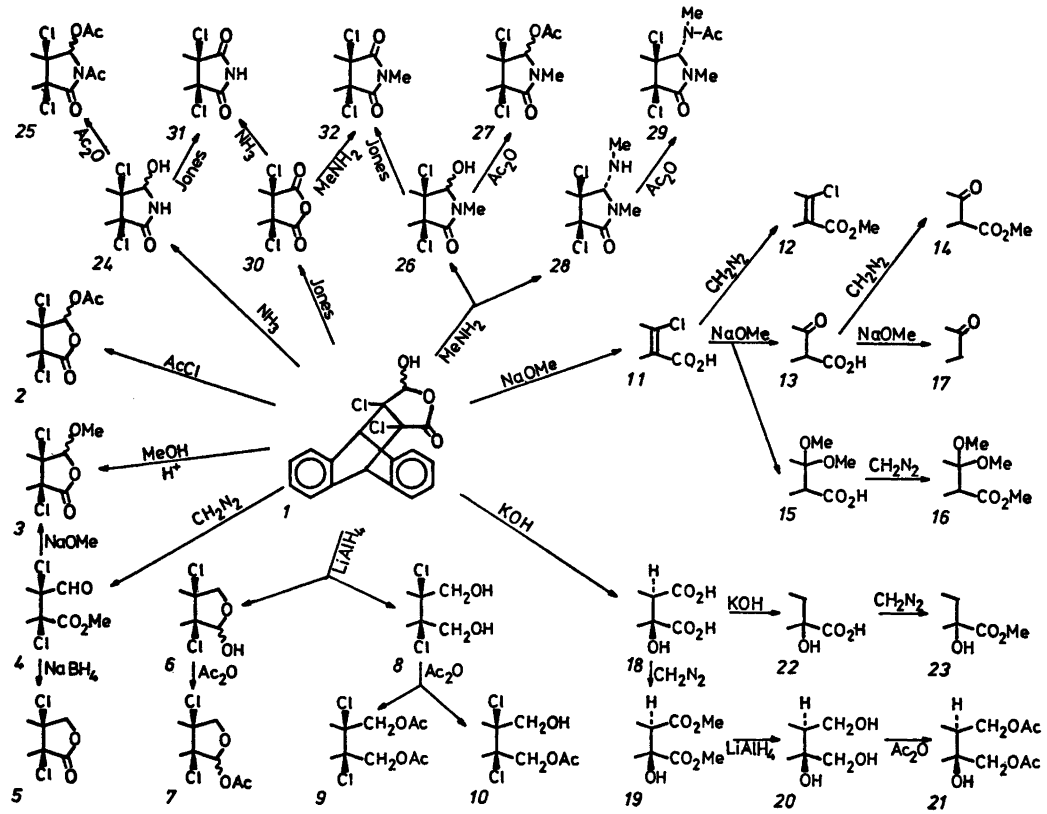
should lead to an α-hydroxy aldehyde *via* an epoxide,[18,19] but the displacement of the other chlorine atom leads to *18*. Another reaction sequence giving the same result starts with the displacement of this chlorine by the carboxylate anion, although the α-lactone thus obtained seems to be a less likely intermediate.

Unlike the reactions with strong bases, the reactions of *1* with amines did not cause removal of the chlorine atoms. No reaction occurred with triethylamine. Treatment of *1* with 25 % aqueous ammonia gave the compound *24*, the nitrogen analog of *1*. The analogous compound *26* was obtained with 33 % aqueous methylamine, but in this case the major product *28* contained two methylamine units. The structures of these compounds were confirmed by acetylation and oxidation of *24* and *26* to the corresponding imides *31* and *32*. These imides were also prepared from the anhydride *30*.

A probable mechanism for the formation of *24* from *1* consists of the ammonolysis of the lactone ring, giving an amide-aldehyde which



is then recyclized. The reaction leading to *26* is similar, but the formation of *28* requires a reaction of the aldehyde moiety with another methylamine molecule to give an aldimine intermediate. The fact that no product corresponding to *28* was obtained with ammonia, may be due to the lesser stability of the intermediate and/or the end product in this case. Because the ratio *26:28* was independent of the reaction time, it is probable that neither of them is an intermediate in the formation of the other.



EXPERIMENTAL

For general experimental conditions, see also Ref. 20. ^{1}H NMR spectra were recorded with a Varian A-60 spectrometer in CCl_4 solutions, unless otherwise stated. All new compounds gave acceptable analyses, the C, H and N analyses being performed with an F & M 185 CHN analyzer and the Cl analyses in the microanalytical laboratory Alfred Bernhardt, Germany. When isolated yields are not given, the approximative yields are based on ^{1}H NMR.

Reaction of mucochloric acid with anthracene. A solution of 33.8 g (0.2 mol) of mucochloric acid,[21] 35.6 g (0.2 mol) of anthracene and 26.7 g (0.2 mol) of anhydrous $AlCl_3$ in 1600 ml of CH_2Cl_2 was stirred for 10 days at room temperature. The solvent was removed under reduced pressure, the residue dissolved in 100 ml of acetone and the resulting solution mixed with 300 ml of conc. HCl under vigorous stirring. When the strongly exothermic reaction had subsided, water (500 ml) was added and the solution extracted three times with CH_2Cl_2. The organic layer was dried and evaporated. In order to remove the other solvents, 100 ml of benzene was added and the solution evaporated. Another 100 ml of benzene was added and the mixture stirred with heating until all the tarry by-products had dissolved and the sparingly soluble adduct separated as a finely divided precipitate. The mixture was allowed to stand overnight in a refrigerator, then the precipitate was filtered and washed several times with benzene to yield 40 – 55 % of crude adduct. Four recrystallizations from benzene gave the analytical sample of 3,4-dichloro-5-hydroxydibenzobicyclo[2.2.2]octadieno[7,8-*c*] tetrahydrofuran-2-one (*1*), m.p. 250 – 251 °C (dec.), $\bar{\nu}_{max}$ 3390, 1770 cm^{-1}.

A portion of the original mother liquor from the crystallization of *1* was run through a silica gel column (elution with benzene) to remove *1* and most of the tar. The major component in the eluate was shown to be the pseudo-ethyl ester of *1*, m.p. 205 – 206 °C, $\bar{\nu}_{max}$ 1780 cm^{-1}, δ ($CDCl_3$) 1.28 (3 H, tr, J = 7.0 Hz), 3.73 (2 H, q, J = 7.0 Hz), 4.75 (1 H, s), 4.82 (1 H, s), 5.71 (1 H, s) + 8 Ar-H, formed from the small amount of ethanol present in the dichloromethane.

Preparation of the pseudo-methyl esters of 1. A mixture of 2.0 g of *1*, 100 ml of MeOH and 0.2 ml of H_2SO_4 was refluxed for 24 h. The solution was neutralized with solid $NaHCO_3$, filtered and evaporated. The residue was dissolved in 20 ml of benzene, unchanged *1* filtered off and the filtrate evaporated. Separation by TLC (elution with benzene) and crystallization from EtOH gave the epimeric pseudo-esters *3a*, m.p. 212 – 213 °C, $\bar{\nu}_{max}$ 1783 cm^{-1}, δ ($CDCl_3$) 3.49 (3 H, s), 4.73 (1 H, s), 4.81 (1 H, s), 5.61 (1 H, s) + 8 Ar-H and *3b*, m.p. 206 – 207 °C, $\bar{\nu}_{max}$ 1776 cm^{-1}, δ ($CDCl_3$) 3.50 (3 H, s), 4.59 (1 H, s), 4.73 (1 H, s) 5.05 (1 H, s) + 8 Ar-H. The yield of the esterification was *ca.* 60 % and the epimer ratio a:b was 75:25.

Preparation of the normal methyl ester of 1. A solution of 5.0 g of *1* in 50 ml of THF was treated with CH_2N_2 until the reaction was complete (according to TLC) and the solution was evaporated. Crystallization of the product from EtOH gave 4.2 g (81 %) of 7,8-dichloro-8-formyldibenzobicyclo[2.2.2]octadiene-*cis*-7-carboxylic acid methyl ester (*4*), m.p. 163 – 164 °C, $\bar{\nu}_{max}$ 1730, 1720 cm^{-1}, δ 3.59 (3 H, s), 4.68 (1 H, s), 4.80 (1 H, s), 9.26 (1 H, s) + 8 Ar-H.

Isomerization of the normal ester to the pseudo-ester. A solution of 0.2 g of *4* in 5 ml of dioxane was added to a methoxide solution prepared from 10 ml of MeOH and 0.1 g of Na and the mixture stirred for 5 min at room temperature. Water and HCl were added and the product isolated by ether extraction. According to ^{1}H NMR, the product was a mixture of the epimeric pseudo-esters *3a* and *3b* with an epimer ratio of 75:25.

Acetylation of 1. The adduct *1* (1.0 g) was dissolved in 20 ml of AcCl and the solution refluxed for 24 h. Excess AcCl was removed under reduced pressure. According to ^{1}H NMR the reaction was complete. Separation by TLC (elution with benzene) and crystallization from EtOH gave the epimeric acetates *2a*, m.p. 200 – 201 °C, $\bar{\nu}_{max}$ 1805, 1767 cm^{-1}, δ ($CDCl_3$) 2.11 (3 H, s), 4.69 (1 H, s), 4.74 (1 H, s), 6.28 (1 H, s) + 8 Ar-H and *2b*, m.p. 208 – 209 °C, $\bar{\nu}_{max}$ 1804, 1765 cm^{-1}, δ ($CDCl_3$) 2.20 (3 H, s), 4.76 (1 H, s), 4.78 (1 H, s), 6.72 (1 H, s) + 8 Ar-H. The epimer ratio was 90:10.

Reduction of 4 *with sodium borohydride.* A mixture of 2.0 g of *4* and 0.4 g of $NaBH_4$ in 80 ml of 1,2-dimethoxyethane was stirred for 10 min at room temperature. Excess hydride was decomposed with cold water and the product isolated by ether extraction. Two recrystallizations from benzene gave 1.50 g (82 %) of 3,4-dichlorodibenzobicyclo[2.2.2]octadieno[7,8-*c*]tetrahydrofuran-2-one (*5*), m.p. 230 – 232 °C, $\bar{\nu}_{max}$ 1786 cm^{-1}, δ ($CDCl_3$) 4.38 (1 H, d, J = 10.5 Hz), 4.50 (1 H, d, J = 10.5 Hz), 4.56 (1 H, s), 4.77 (1 H, s) + 8 Ar-H.

Reduction of 1 *with lithium aluminium hydride and acetylation of the resulting alcohols.* A mixture of 3.47 g (0.01 mol) of *1* and 1.52 g (0.04 mol) of $LiAlH_4$ in 100 ml of anhydrous THF was refluxed for 80 min. Excess hydride was decomposed with ice water, HCl was added and the product isolated by ether extraction. Two recrystallizations from benzene gave 2.70 g (81 %) of 7,8-dichlorodibenzobicyclo[2.2.2]octadiene-*cis*-7,8-dimethanol (*8*), m.p. 192 – 194 °C, $\bar{\nu}_{max}$ 3300 cm^{-1}.

Acetylation of the diol *8* (0.75 g) with 20 ml of Ac_2O and 0.5 g of NaOAc for 24 h at room temperature, followed by TLC separation (elution with chloroform) and crystallization from EtOH, gave 0.33 g (35 %) of the diacetate *9*, m.p. 138 – 139 °C, $\bar{\nu}_{max}$ 1743, 1730 cm^{-1}, δ 2.04 (6 H, s), 3.97 (2 H, d, J = 12.0 Hz), 4.27

(2 H, d, $J = 12.0$ Hz), 4.59 (2 H, s) + 8 Ar-H and 0.28 g (33 %) of the monoacetate *10*, m.p. 170–171 °C, $\bar{\nu}_{max}$ 3480, 1735 cm^{-1}, δ 2.06 (3 H, s), 2.82 (1 H, broad s, exch. with D_2O), 3.31 (1 H, d, $J = 12.0$ Hz), 3.56 (1 H, d, $J = 12.0$ Hz), 3.70 (1 H, d, $J = 12.0$ Hz), 4.37 (1 H, d, $J = 12.0$ Hz), 4.55 (1 H, s), 4.60 (1 H, s) + 8 Ar-H. The protons at δ 3.31 and 3.56 belong to the -CH_2OH group and those at δ 3.70 and 4.37 to the -CH_2OAc group.

To obtain the acetal *6*, a mixture of 6.94 g of *1*, 1.52 g of $LiAlH_4$ and 100 ml of THF was stirred for 20 min at room temperature. The mixture was worked up as above and the product mixture crystallized from benzene to remove most of the diol *8* and unchanged *1*. TLC separation (elution with chloroform) gave 0.40 g (6 %) of 3,4-dichlorodibenzobicyclo-[2.2.2]octadieno[7,8-*c*]tetrahydrofuran-2-ol (*6*), m.p. 182–183 °C (benzene), $\bar{\nu}_{max}$ 3555, 3440 cm^{-1}.

Acetylation of *6* (0.25 g) with 20 ml of Ac_2O and 0.2 g of NaOAc for 24 h at room temperature gave, after TLC separation (elution with benzene-light petroleum 4:1) and crystallization from EtOH, *7a*, m.p. 172–173 °C, $\bar{\nu}_{max}$ 1745 cm^{-1}, δ ($CDCl_3$) 2.02 (3 H, s), 4.04 (1 H, d, $J =$ 9.6 Hz), 4.13 (1 H, d, $J = 9.6$ Hz), 4.40 (1 H, s), 4.57 (1 H, s), 6.07 (1 H, s) + 8 Ar-H and *7b*, m.p. 212–213 °C, $\bar{\nu}_{max}$ 1755 cm^{-1}, δ ($CDCl_3$) 2.20 (3 H, s), 4.02 (2 H, s), 4.44 (1 H, s), 4.65 (1 H, s), 6.11 (1 H, s) + 8 Ar-H. The epimer ratio was 75:25.

Reactions of 1 *with sodium methoxide.* The adduct *1* (1.0 g) was added to a methoxide solution prepared from 2.0 g of Na and 50 ml of MeOH. The mixture was refluxed for 10 min, cooled, acidified with HCl and the product isolated by ether extraction. The residue crystallized on standing and the crystals were washed with hot benzene to give 0.77 g (94 %) of crude 8-chlorodibenzobicyclo[2.2.2]octatriene-7-carboxylic acid (*11*). Three recrystallizations from dioxane–water 1:1 gave the pure acid, m.p. 259–260 °C (lit.[8] m.p. 260–261 °C).

The acid *11*, treated with CH_2N_2, gave the methyl ester *12*, m.p. 136–137 °C, $\bar{\nu}_{max}$ 1695 cm^{-1}, δ 3.69 (3 H, s), 5.04 (1 H, s), 5.70 (1 H, s) + 8 Ar-H.

The reaction mixture from 2.0 g of *1*, 5.0 g of Na and 100 ml of MeOH was refluxed for 8 h, worked up as above and the resulting acid mixture treated with CH_2N_2. Separation by TLC (elution with benzene) gave the ester *12* and the known compounds dibenzobicyclo-[2.2.2]octadien-7-one (*17*),[10] 8-oxodibenzobicyclo[2.2.2]octadiene-7-carboxylic acid methyl ester (*14*),[9] δ 3.17 (1 H, d, $J = 2.3$ Hz), 3.44 (3 H, s), 4.71 (1 H, d, $J = 2.3$ Hz), 4.77 (1 H, s) + 8 Ar-H and 8,8-dimethoxydibenzobicyclo[2.2.2]-octadiene-7-carboxylic acid methyl ester (16),[9] δ 2.85 (1 H, d, $J = 2.2$ Hz), 3.20 (6 H, s), 3.50 (3 H, s), 4.32 (1 H, d, $J = 2.2$ Hz), 4.42 (1 H, s) + 8 Ar-H. Approximate yields were 55 %, 10 %, 25 % and 5 %, respectively.

Reactions of 1 *with potassium hydroxide.* The adduct *1* (5.0 g) was dissolved in 250 ml of 5 % aqueous KOH and the solution allowed to stand for 24 h at room temperature. The solution was acidified with HCl and extracted with ether to give the crude product which was shown to contain only one compound (TLC and ^{1}H NMR after treatment with CH_2N_2). Three recrystallizations from MeOH–H_2O 1:1 gave the pure sample of 7-hydroxydibenzobicyclo-[2.2.2]octadiene-*trans*-7,8-dicarboxylic acid (*18*), m.p. 187–188 °C, $\bar{\nu}_{max}$ 3500–2500, 1720–1690 cm^{-1}.

Treatment of the acid *18* with CH_2N_2 and two recrystallizations from MeOH gave the dimethyl ester *19*, m.p. 145–146 °C, $\bar{\nu}_{max}$ 3560, 1735 cm^{-1}, δ 3.47 (3 H, s), 3.50 (3 H, s), 3.59 (1 H, d, $J = 2.0$ Hz), 4.03 (1 H, broad s, exch. with D_2O), 4.45 (1 H, s), 4.56 (1 H, d, $J = 2.0$ Hz) + 8 Ar-H.

The above reaction mixture refluxed for 20 min, gave after similar work-up, treatment with CH_2N_2 and TLC separation (several elutions with benzene-light petroleum 1:1) 55 % of *19*, 25 % of *12* and 25 % of 7-hydroxydibenzobicyclo[2.2.2]octadiene-7-carboxylic acid methyl ester (*23*), m.p. 134–136 °C (MeOH), $\bar{\nu}_{max}$ 3490, 1723 cm^{-1}, δ ($CDCl_3$) 1.64 (1 H, dd, $J = 13.2$ & 2.8 Hz), 2.67 (1 H, dd, $J = 13.2$ & 2.8 Hz), 2.8 (1 H, broad s, exch. with D_2O), 3.43 (3 H, s), 4.27 (1 H, tr, $J = 2.8$ Hz), 4.31 (1 H, s) + 8 Ar-H.

The ester *23* (0.5 g) was dissolved in 25 ml of dioxane, 50 ml of 5 % aqueous NaOH was added and the mixture refluxed for 40 min. The solution was acidified with HCl and the hydrolysis product isolated by ether extraction. Two recrystallizations from MeOH–H_2O 1:1 gave the pure acid *22*, m.p. 185–186 °C, $\bar{\nu}_{max}$ 3500–2500, 1700 cm^{-1}.

Reaction of 19 *with acetic anhydride.* The dimethylester *19* (0.5 g) was refluxed for 8 h with a mixture of 50 ml of Ac_2O and 0.5 g of NaOAc. Acetic anhydride was removed under reduced pressure, the residue dissolved in ether, the mixture filtered and the filtrate evaporated. TLC fractionation gave, in addition to unchanged starting material, a small amount of anthracene and 0.07 g (15 %) of dibenzobicyclo-[2.2.2]octatriene-7,8-dicarboxylic acid dimethyl ester, identical with a sample prepared from anthracene and dimethyl acetylenedicarboxylate.[22] The acetate of *19* was not observed.

Reduction of 19 *with lithium aluminium hydride and acetylation of the resulting alcohol.* A mixture of 1.69 g (0.005 mol) of *19* and 0.76 g (0.02 mol) of $LiAlH_4$ in 25 ml of anhydrous THF was refluxed for 40 min. Excess hydride was decomposed by careful addition of water, the solution acidified with HCl and the alcohol isolated by ether extraction. Two recrystallizations from benzene gave 1.0 g (71 %) of 7-hydroxydibenzobicyclo[2.2.2]octadiene-*trans*-7,8-dimethanol (*20*), m.p. 160–161 °C, $\bar{\nu}_{max}$ 3400, 3280 cm^{-1}.

Acetylation of *20* (0.4 g) with 50 ml of Ac_2O and 0.5 g of NaOAc for 24 h at room temperature and crystallization of the acetate from EtOH gave 0.42 g (81 %) of the diacetate *21*, m.p. 101 – 103 °C, $\bar{\nu}_{max}$ 3450, 1730 cm^{-1}, δ 1.95 (7 H, broad s), 2.40 (1 H, s, exch. with D_2O), 3.4 – 4.1 (4 H, m), 4.17 (1 H, d, $J = 2.0$ Hz), 4.21 (1 H, s) + 8 Ar-H.

Reaction of 7-bromodibenzobicyclo[2.2.2]octadiene-cis-*7,8-dicarboxylic anhydride with silver nitrate and potassium hydroxide and oxidation of the products.* The reported procedure [15] was followed with the difference that instead of fractional crystallization the reaction products were converted to methyl esters, separated by TLC (elution with chloroform) and crystallized from MeOH to give *endo*-4-hydroxydibenzobicyclo[3.2.1]octadiene-5-*anti*-8-dicarboxylic acid dimethyl ester (*33b*), m.p. 157 – 159 °C (lit.[15] m.p. 160.5 – 161.8 °C), $\bar{\nu}_{max}$ 3470, 1750, 1723 cm^{-1}, δ ($CDCl_3$) 2.01 (1 H, broad s, exch. with D_2O), 3.53 (3 H, s), 3.55 (1 H, s), 3.82 (3 H, s), 4.24 (1 H, s) 5.40 (1 H, broad s) + 8 Ar-H and the *exo* epimer (*34b*), m.p. 200 – 201 °C (lit.[15] m.p. 199.0 – 199.6 °C), $\bar{\nu}_{max}$ 3480, 1733, 1710 cm^{-1}, δ ($CDCl_3$) 2.64 (1 H, broad s, exch. with D_2O), 3.62 (3 H, s), 3.80 (1 H, s), 3.87 (3 H, s), 4.18 (1 H, s), 4.94 (1 H, s) + 8 Ar-H. The *endo*-*exo* ratio was 35:65; other compounds were not detected.

Reaction of the bromoanhydride with KOH [17] gave *ca.* 80 % of *34a* but no *33a* was observed. The other compounds were not identified.

On oxidation with Jones reagent both *33b* and *34b* gave the same compound, 4-oxodibenzobicyclo[3.2.1]octadiene-5-*anti*-8-dicarboxylic acid dimethyl ester (*35b*), m.p. 184 – 185 °C (EtOH), $\bar{\nu}_{max}$ 1750, 1733, 1686 cm^{-1}, δ 3.56 (3 H, s), 3.80 (3 H, s), 4.00 (1 H, s), 4.43 (1 H, s) + 8 Ar-H.

Reaction of 1 *with ammonia and acetylation of the products.* The adduct *1* (8.0 g) was dissolved in 250 ml of 25 % aqueous NH_3 and the solution allowed to stand for 48 h at room temperature. The precipitate was then filtered, washed with water and dried to give 7.45 g (93 %) of crude product. Two recrystallizations from dioxane gave the analytical sample of 3,4-dichloro-5-hydroxydibenzobicyclo[2.2.2]octadieno[7,8-*c*]-tetrahydropyrrol-2-one (*24*), m.p. 258 – 259 °C (dec.), $\bar{\nu}_{max}$ 3360 – 3200, 1690 cm^{-1}.

A solution of *24* (2.0 g) in 50 ml of DMF was mixed with 100 ml of Ac_2O and 0.5 g of NaOAc and the mixture stirred for 24 h at room temperature. Acetic anhydride was removed under reduced pressure, water was added and the products isolated by ether extraction. Separation of the epimeric acetates by TLC (elution with chloroform – benzene 1:1) and crystallization from EtOH gave the epimer *25a*, m.p. 216 – 217 °C, $\bar{\nu}_{max}$ 1758, 1728 cm^{-1}, δ ($CDCl_3$) 2.20 (3 H, s), 2.22 (3 H, s), 4.62 (1 H, s), 4.80 (1 H, s), 7.04 (1 H, s) + 8 Ar-H and the epimer *25b*, m.p. 244 – 245 °C, $\bar{\nu}_{max}$ 1753, 1724 cm^{-1}, δ ($CDCl_3$) 2.07 (3 H, s), 2.09 (3 H, s), 4.75 (2 H, s), 6.50 (1 H, s) + 8 Ar-H. The epimer ratio was 80:20.

Reaction of 1 *with methylamine and acetylation of the products.* The reaction starting with 7.5 g of *1* and 150 ml of 33 % aqueous $MeNH_2$ was conducted as with NH_3. Filtration of the precipitate gave 5.2 g (65 %) of crude product. Three recrystallizations from benzene gave the analytical sample of 3,4-dichloro-5-methylamino-1-methyldibenzobicyclo[2.2.2]octadieno-[7,8-*c*]tetrahydropyrrol-2-one (*28*), m.p. 234 – 235 °C, $\bar{\nu}_{max}$ 3370, 1710 cm^{-1}, δ ($CDCl_3$) 1.77 (1 H, broad s, exch. with D_2O), 2.33 (3 H, s), 2.46 (3 H, s), 3.85 (1 H, s), 4.44 (1 H, s), 4.74 (1 H, s) + 8 Ar-H. The filtrate was evaporated on a steam bath to give 2.70 g (35 %) of crude 3,4-dichloro-5-hydroxy-1-methyldibenzobicyclo-[2.2.2]octadieno[7,8-*c*]tetrahydropyrrol-2-one (*26*). Two recrystallizations from dioxane gave the analytical sample, m.p. 246 – 248 °C (dec.), $\bar{\nu}_{max}$ 3230, 1680 cm^{-1}.

The amine *28*, acetylated as *24*, gave the acetate *29*, m.p. 229 – 230 °C (EtOH), $\bar{\nu}_{max}$ 1715, 1650 cm^{-1}, δ ($CDCl_3$) 2.14 (3 H, s), 2.17 (3 H, s), 2.67 (3 H, s), 4.74 (2 H, s), 5.84 (1 H, s) + 8 Ar-H. The other epimer was not observed. The compound *26* gave the epimeric acetates *27a*, m.p. 208 – 209 °C (EtOH), $\bar{\nu}_{max}$ 1753, 1720 cm^{-1}, δ ($CDCl_3$) 2.13 (3 H, s), 2.30 (3 H, s), 4.66 (1 H, s), 4.71 (1 H, s), 5.67 (1 H, s) + 8 Ar-H and the epimer *27b*, m.p. 231 – 232 °C (EtOH), $\bar{\nu}_{max}$ 1755, 1725 cm^{-1}, δ ($CDCl_3$) 2.32 (3 H, s), 2.43 (3 H, s), 4.64 (1 H, s), 4.77 (1 H, s), 6.51 (1 H, s) + 8 Ar-H. The epimer ratio was 75:25.

Oxidation of the compounds 1, 24 *and* 26 *with Jones reagent.* The compound to be oxidized (1.0 g) was dissolved in 100 ml of acetone and Jones reagent was added to the stirred solution until the reaction was complete (according to TLC), then water was added and the oxidation product isolated by ether extraction. According to TLC, only one compound was obtained in each case. Oxidation of *1* gave 7,8-dichlorodibenzobicyclo[2.2.2]octadiene-*cis*-7,8-dicarboxylic anhydride (*30*), m.p. 238 – 240 °C (EtOH) (lit.[3] m.p. 238 – 243 °C), $\bar{\nu}_{max}$ 1874, 1857, 1797 cm^{-1}, δ ($CDCl_3$) 4.87 (2 H, s) + 8 Ar-H, *24* gave 7,8-dichlorodibenzobicyclo[2.2.2]octadiene-*cis*-7,8-dicarboximide (*31*), m.p. 258 – 259 °C (EtOH-dioxane 1:1), $\bar{\nu}_{max}$ 3180, 3080, 1795, 1730 cm^{-1} and *26* gave *N*-methyl-7,8-dichlorodibenzobicyclo[2.2.2]octadiene-*cis*-7,8-dicarboximide (*32*), m.p. 297 – 298 °C (EtOH-dioxane 1:1) (lit.[3] m.p. 293 – 294.5 °C), $\bar{\nu}_{max}$ 1796, 1720, 1711 cm^{-1}, δ ($CDCl_3$) 2.59 (3 H, s), 4.82 (2 H, s) + 8 Ar-H.

Reactions of 30 *with ammonia and methylamine.* A solution of 0.2 g of *30* in 10 ml of dioxane was mixed with 20 ml of 25 % aqueous NH_3 and the solution allowed to stand for 24 h at room temperature. The solution was evaporated to dryness on a steam bath and the residue crystallized from EtOH-dioxane 1:1 to give *31*, identical with that obtained by oxidation. Similarly, the use of 33 % aqueous $MeNH_2$ gave *32*.

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