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Chlorinated Polycyclic Compounds. VI. Alkaline Cleavage of Chloro-substituted Dibenzobicyclo[3.2.1]octadien-4-ones

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Cleavage of chloro-substituted dibenzobicyclo-[3.2.1]octadien-4-ones with bases gave derivatives of 2-(1-indenyl)benzoic acid, 2-(3-indenyl)benzoic acid and spiro[indene-1,1′-isobenzofuran-3′-one] as principal products. Depending on the position of the double bond and of chloro substituents the indenylbenzoic acids gave different types of cyclization products with acid.

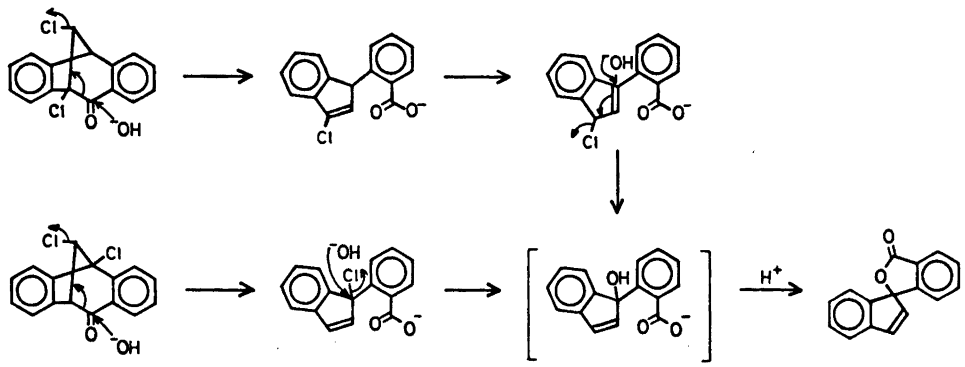
The alkaline cleavage of chloro-substituted dibenzobicyclo[3.2.1]octadien-4-ones was studied as a possible route to indenylbenzoic acids. The results from the reactions of the chloro ketones *5b* – *5p* with ethanolic potassium hydroxide and potassium *tert*-butoxide in dimethyl sulfoxide are shown in Table 1.

The presence of a good leaving group at the *anti*-8-position makes a *trans* elimination possible and consequently all ketones having filled this requisite were readily cleaved with boiling 10 % ethanolic potassium hydroxide. Ketones lacking the *anti*-8-chlorine failed to react or reacted slowly. Competing reactions were in these cases reduction of the 5-chlorine or the carbonyl group. Dechlorinations by base have been encountered earlier within this class of compounds [1] and similar reductions of polycyclic ketones with ethanolic potassium hydroxide are also known.[2] In spite of the relative ease of the initial cleavage reaction the picture is complicated by further reactions so that expected acids of the type *6* were not observed at all under these reaction conditions, the most important of the subsequent reactions being isomerization to acids *7* and formation of spiro

Table 1. Products from the alkaline cleavage of the ketones *5b* – *5p*.

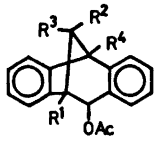
Starting material					Reaction products	Reaction products
No.	R^1	R^2	R^3	R^4	KOH/EtOH	*tert*-BuOK/DMSO
5a	H	H	H	H		
5b	H	H	H	Cl	No reaction	85 % *7a*
5c	H	H	Cl	H	80 % *7a*, 20 % *11a*	75 % *7a*
5d	H	H	Cl	Cl	95 % *8a*, 5 % *11a*	95 % *8a*
5e	H	Cl	H	H	No reaction	75 % *7a*
5f	H	Cl	H	Cl	No reaction	80 % *8a*
5g	H	Cl	Cl	H	50 % *7c*	70 % *7c*
5h	H	Cl	Cl	Cl	100 % *8b*	85 % *8b*
5i	Cl	H	H	H	35 % *3c*, 15 % *5a*, 50 % *5i*	95 % *7a*
5j	Cl	H	H	Cl	50 % *3d*, 50 % *5b*	95 % *6a*, 5 % *7b* [a]
5k	Cl	H	Cl	H	55 % *8a*, 20 % *11a*	65 % *8a*
5l	Cl	H	Cl	Cl	100 % *8c*	95 % *8c*
5m	Cl	Cl	H	H	50 % *8a*, 25 % *11a*, 15 % *5m*	60 % *8a*
5n	Cl	Cl	H	Cl	55 % *8c*, 5 % *3e*, 30 % *5f*	90 % *8c*
5o	Cl	Cl	Cl	H	10 % *7c*, 10 % *8c*, 20 % *13a*	90 % *7d* [a]
5p	Cl	Cl	Cl	Cl	100 % *8d*	90 % *8d*

[a] Typical result, reaction difficult to control.

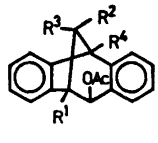


Scheme 1.

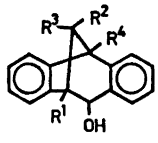
lactones *8*. Lactones were formed from ketones which in addition to the 8-chlorine had another chlorine atom on an adjacent carbon atom, giving 1- or/and 3-chloroindenylbenzoic acids as intermediates (Scheme 1.). It is not clear whether the displacement of the second chlorine is brought about by a hydroxide ion or intramolecularly by the carboxylate anion.



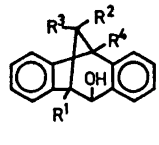
	R^1	R^2	R^3	R^4
1a	H	Cl	Cl	H
b	H	Cl	Cl	Cl
c	Cl	H	Cl	H



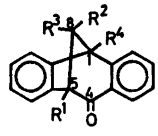
	R^1	R^2	R^3	R^4
2a	H	Cl	Cl	H
b	H	Cl	Cl	Cl
c	Cl	H	Cl	H



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



	R^1	R^2	R^3	R^4
4a	H	Cl	Cl	H
b	H	Cl	Cl	Cl



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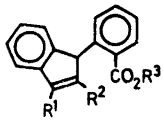
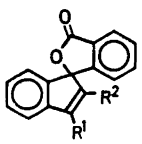
The fulvalene derivatives, which gave an intense red colour to most of the reaction mixtures, form an interesting group of side products. The acid *11a* was obtained in substantial amounts and was the only one to be fully characterized. As shown by experiments conducted under nitrogen, oxidation by atmospheric oxygen is clearly involved in the formation of *11a* from *5c via 7a*, while *5k* and *5m* give the same compound as a product of intermolecular dehydrochlorination of the indenylbenzoic acid *7b*. Cleavage of the five-membered ring of *7d* by base should give a product at the oxidation level of an aldehyde. Hence the diacid *13a* is also an oxidation product. Because in this case the oxidation is not caused by molecular oxygen, a mechanism of the Cannizzaro type has to be postulated.

With the stronger base potassium *tert*-butoxide in dimethyl sulfoxide, all ketones were cleaved irrespective of the substitution pattern and less side reactions occurred than with potassium hydroxide but a serious drawback of this method is the poor reproducibility. Isomerization of the double bond and cyclization to lactones occurred to a variable extent showing no clear dependence of the experimental conditions.

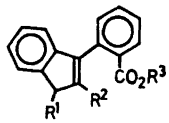
The structures of the new compounds are based on spectroscopic data and chemical reactions. The position of the double bond in the indenylbenzoic acids *7a* and *7c* is evident from the ^{1}H NMR spectra which exhibit 2H singlets corresponding to the 1-protons of the indenyl moiety. The best structure proof for *6a*, *6b* and *7d* is their different behaviour towards acid. When *7d* was heated with a mix-



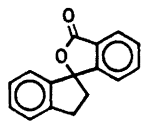
	R^1	R^2	R^3
6a	Cl	H	H
b	Cl	Cl	H
c	Cl	H	Me
d	Cl	Cl	Me



	R^1	R^2
8a	H	H
b	H	Cl
c	Cl	H
d	Cl	Cl



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



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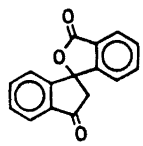

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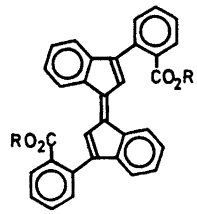
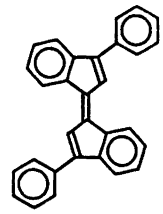
ture containing 30 % sulfuric acid in acetic acid, cyclization to the lactone *8b* occurred. The acids *6a* and *6b* were also cyclized but in a different manner (Scheme 2.). The diketone *16* is a known compound [3,4] which was further characterized by the facile cleavage to the keto acid *14a*. The structures assigned to *6b* and *7d* are supported by the ^{1}H NMR spectra of their methyl esters. The spectrum of the ester *7h*, with signals of two conformers of almost



11a R = H
b R = Me



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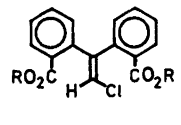
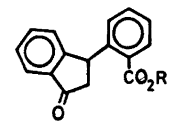
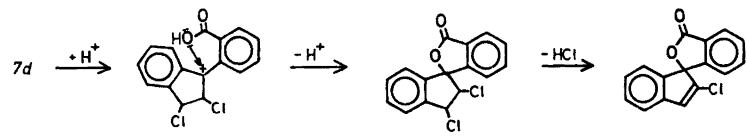


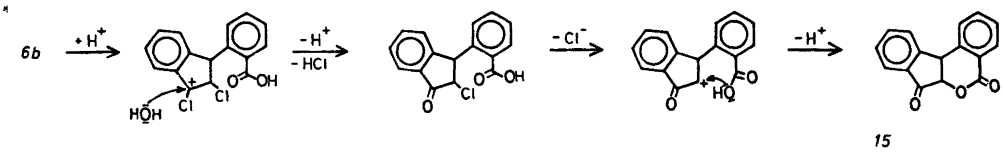
13a R = H
b R = Me



14a R = H
b R = Me



8b



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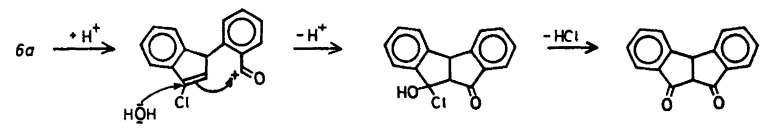

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Scheme 2.

equal intensity, fits better with the more symmetric structure of *7h* compared with the isomeric *6d*. In the corresponding acid *7d* the indenyl proton gives only one singlet reflecting the smaller space requirements of the free carboxyl function.

Treatment of the acid *7a* with sulfuric acid did not give clean results but in dioxane containing aqueous hydrochloric acid it was cyclized to *9*.

The position of the chlorine atom in *8b* and *8c* follows from the substitution pattern of the starting material and was confirmed by acid hydrolysis; *8c* gave the keto lactone *10* but *8b* failed to react under the same conditions.

The fulvalene derivative *11a* and its methyl ester had spectral properties consistent with the given structures and *11a* was further characterized by decarboxylation to the known hydrocarbon *12*.[5]

EXPERIMENTAL

For general experimental conditions see Ref. 6. ^{1}H NMR spectra were measured in CCl_4 solutions unless otherwise stated.

Preparation of the starting materials. The ketones *5b*,[7] *5c*,[8] *5d*,[6] *5e*,[9] *5f*,[6] *5i*,[1,10] *5j*,[7] *5l*,[6] *5n*,[6] and *5p*[11] have been described earlier.

8,8-Dichlorodibenzobicyclo[3.2.1]octadien-4-one (*5g*). A mixture of 6.16 g (20 mmol) of 4,8,8-trichlorodibenzobicyclo[3.2.1]octadiene,[1] 4.00 g (24 mmol) of AgOAc and 200 ml of HOAc was refluxed for 24 h. Acetic acid was removed under reduced pressure, the residue dissolved in acetone, the solution filtered and evaporated. The product contained *ca.* 20 % of 8,8-dichlorodibenzobicyclo[3.2.1]octadien-*endo*-4-yl acetate (*1a*), m.p. 189 °C, $\bar{\nu}_{max}$ 1735 cm^{-1}, δ 6.27 (*exo*-4-H), 4.33 (1-H), 4.19 (5-H), 2.08 (OAc)+8 Ar-H, $J_{4,5}$=5.5 Hz, and 80 % of the *exo* epimer *2a*, m.p. 178 °C, $\bar{\nu}_{max}$ 1728 cm^{-1}, δ 5.84 (*endo*-4-H), 4.39 (1-H), 3.97 (5-H), 2.17 (OAc)+8 Ar-H, $J_{4,5}$=1.2 Hz. The epimers were separated by TLC (elution with a 3:1 mixture of light petroleum and chloroform) and crystallized from EtOH. A mixture of the epimeric acetates *1a* and *2a* (5.0 g) was stirred for 80 min with 50 ml of 10 % ethanolic KOH at room temperature. Water and HCl was added and the alcohol mixture was isolated by ether extraction. Analytical samples of the pure epimers were prepared by hydrolysis of pure acetates and crystallized from 80 % aqueous EtOH. The acetate *1a* gave the alcohol *3a*, m.p. 178 °C, $\bar{\nu}_{max}$ 3180 cm^{-1}, δ 5.09 (*exo*-4-H), 4.30 (1-H), 3.95 (5-H), 2.00 (OH)+8 Ar-H, $J_{4,5}$=5.5 Hz and the acetate *2a* gave the alcohol *4a*, m.p. 178 °C, $\bar{\nu}_{max}$ 3340 cm^{-1}, δ 4.65 (*endo*-4-H), 4.30 (1-H), 3.92 (5-H), 2.67 (OH)+8 Ar-H, $J_{4,5}$<1 Hz. A mixture of the alcohols *3a* and *4a* (5.0 g) dissolved in 50 ml of acetone was treated with Jones reagent until the reaction was complete (as shown by TLC). Water was added and the product isolated by ether extraction and crystallized from EtOH to give 8,8-dichlorodibenzobicyclo[3.2.1]octadien-4-one (*5g*), m.p. 132 °C, $\bar{\nu}_{max}$ 1695 cm^{-1}, δ 4.42 (1-H), 4.59 (5-H)+8 Ar-H.

1,8,8-Trichlorodibenzobicyclo[3.2.1]octadien-4-one (*5h*). Acetolysis of 1,4,8,8-tetrachlorodibenzobicyclo[3.2.1]octadiene[1] as described above gave *ca.* 15 % of 1,8,8-trichlorodibenzobicyclo[3.2.1]octadien-*endo*-4-yl acetate (*1b*), m.p. 140 °C, $\bar{\nu}_{max}$ 1733 cm^{-1}, δ 6.32 (*exo*-4-H), 4.37 (5-H), 2.09 (OAc)+8 Ar-H, $J_{4,5}$=5.5 Hz and 85 % of the *exo* epimer *2b*, m.p. 154 °C, $\bar{\nu}_{max}$ 1732 cm^{-1}, δ 5.77 (*endo*-4-H), 4.12 (5-H), 2.18 (OAc)+8 Ar-H, $J_{4,5}$=1.0 Hz. Hydrolysis of the acetate *1b* gave the alcohol *3b*, m.p. 173 °C, $\bar{\nu}_{max}$ 3225 cm^{-1}, δ 5.17 (*exo*-4-H), 4.17 (5-H), 1.37 (OH)+8 Ar-H, $J_{4,5}$=5.5 Hz and the acetate *2b* gave the alcohol *4b*, m.p. 171 °C, $\bar{\nu}_{max}$ 3300 cm^{-1}, δ 4.63 (*endo*-4-H), 4.13 (5-H), 2.89 (OH)+8 Ar-H, $J_{4,5}$<1 Hz. Oxidation of the alcohols *3b* and *4b* gave 1,8,8-trichlorodibenzobicyclo[3.2.1]octadien-4-one (*5h*), m.p. 113 °C, $\bar{\nu}_{max}$ 1695 cm^{-1}, δ 4.62 (5-H)+8 Ar-H, *m/e* 322(16), 287(100).

5-*syn*-8-Dichlorodibenzobicyclo[3.2.1]octadien-4-one (*5m*) and 5,8,8-trichlorodibenzobicyclo-[3.2.1]octadien-4-one (*5o*). The above route (the intermediate alcohols and acetates were not separated) was also used to give *5m*, m.p. 152 °C, $\bar{\nu}_{max}$ 1715 cm^{-1}, δ 5.08 (*anti*-8-H), 4.37 (1-H)+8 Ar-H, $J_{1,8}$=4.8 Hz from 4,5-*syn*-8-trichlorodibenzobicyclo[3.2.1]octadiene[1] and *5o*, m.p. 159 °C, $\bar{\nu}_{max}$ 1705 cm^{-1}, δ 4.77 (1-H)+8 Ar-H from 4,5,8,8-tetrachlorodibenzobicyclo-[3.2.1]octadiene.[1]

5-*anti*-8-Dichlorodibenzobicyclo[3.2.1]octadien-4-one (*5k*), m.p. 158 °C, $\bar{\nu}_{max}$ 1710 cm^{-1}, δ 4.93 (*syn*-8-H), 4.51 (1-H)+8 Ar-H, was obtained by hydrolysis of 5-*anti*-8-dichlorodibenzobicyclo[3.2.1]octadien-4-yl acetate (a mixture of *1c* and *2c*)[12] and oxidation of the resulting alcohol mixture.

Reactions of the ketones 5b – 5p *with potassium hydroxide in ethanol.* General method: A solution of 1.0 g of the ketone and 3.0 g of KOH in 30 ml of EtOH was refluxed for 40 min. The reaction mixture was poured into water and the aqueous solution was extracted twice with diethyl ether. The combined ether extracts were washed with water, dried and evaporated. The aqueous solution was made slightly acidic with HCl, extracted twice with ether and the combined extracts were dried and evaporated. The two fractions thus obtained were examined separately. The first fraction contained the unreacted starting ketones *5b*, *5e*, *5f*, *5i* and *5m* and reaction products which had not undergone ring cleavage, *viz.* the ketones *5a*[8] and *5b* and the alcohols *3c*,[1] *3d*[7] and *3e*.[6] These com-

pounds were identified by comparison with authentic samples. The carboxylic acids *7a*, *7c*, *11a* and *13a* and the lactones *8a* – *8d* were found in the second fraction. In most cases the isolation and purification of the products were straightforward and consisted of preparative TLC (elution with 3:1 or 1:1 mixtures of light petroleum and chloroform) and crystallization from EtOH. In more complex cases detailed information is given. Approximative yields are based on ^{1}H NMR.

The lactones *8* had the following properties: Spiro[indene-1,1′-isobenzofuran-3′-one] (*8a*), m.p. 115 °C, $\bar{\nu}_{max}$ 1755 cm^{-1}, δ 6.08 (1 H, d, J = 5.5 Hz), 6.6 – 7.7 (8 H, m), 7.7 – 8.1 (1 H, m), *m/e* 234(100), 206(19), 205(17), 189(17), 178(81), 176(17); spiro[2-chloroindene-1,1′-isobenzofuran-3′-one] (*8b*), m.p. 118 °C, $\bar{\nu}_{max}$ 1768 cm^{-1}, δ 6.7 – 7.7 (8 H, m), 7.8 – 8.1 (1 H, m), *m/e* 268(39), 233(100), 212(20), 205(19), 189(19), 176 (21); spiro[3-chloroindene-1,1′-isobenzofuran-3′-one] (*8c*), m.p. 135 °C, $\bar{\nu}_{max}$ 1760 cm^{-1}, δ 6.10 (1 H, s), 6.7 – 7.7 (7 H, m), 7.7 – 8.0 (1 H, m), *m/e* 268(84), 233(100), 212(33), 205(62), 189(69), 176(48); spiro[2,3-dichloroindene-1,1′-isobenzofuran-3′-one] (*8d*), m.p. 132 °C, $\bar{\nu}_{max}$ 1770 cm^{-1}, δ 6.7 – 7.7 (7H, m), 7.7 – 8.1 (1 H, m), *m/e* 302(17), 267(100), 239(13), 223(11), 187(11), 176(20).

The reaction mixture from the ketone *5c* had an intense red colour and upon acidification a red compound began to crystallize. It was separated by filtration and washed with acetone. The amount corresponded to a yield of about 20 %. Crystallization from dioxane gave the pure sample of 3,3′-di(2-carboxyphenyl)-$\Delta^{1,1'}$-biindene (*11a*), m.p. 295 °C, $\bar{\nu}_{max}$ 3100 – 2500, 1670 cm^{-1}, λ_{max} 402(ε 15 000), 385(ε 13 000), 307(ε 9000) nm. The acid *11a* was treated with CH_2N_2 and the product crystallized from dioxane to give the methyl ester *11b*, m.p. 260 °C, $\bar{\nu}_{max}$ 1722 cm^{-1}, δ ($CDCl_3$) 3.57 (6 H, s), 7.0 – 8.1 (18 H, m), λ_{max} 402(ε 8 700), 385(ε 8 100), 308(5 200) nm, *m/e* 496 (100), 434(9), 406(9), 405(7), 378(8), 377(15), 375(8), 227(20), 189(16). After the separation of *11a* the aqueous solution was extracted with ether, the ether solution dried and evaporated. Separation by preparative TLC (elution with chloroform) and crystallization from light petroleum gave 2-(3-indenyl)benzoic acid (*7a*), m.p. 136 °C, $\bar{\nu}_{max}$ 3100 – 2500, 1690, 1670 cm^{-1}, δ 3.38 (2 H, d, J = 1.8 Hz), 6.27 (1 H, tr, J = 1.8 Hz), 6.8 – 7.6 (7 H, m), 7.7 – 8.0 (1 H, m), 9.5 (1 H, br s). The acid *7a* was treated with CH_2N_2 and the product crystallized from light petroleum to give the methyl ester *7e*, m.p. 80 °C, $\bar{\nu}_{max}$ 1718 cm^{-1}, δ 3.33 (5 H, s), 6.29 (1 H, tr, J = 1.8 Hz), 6.9 – 7.5 (7 H, m), 7.7 – 8.0 (1 H, m).

The ketones *5g* and *5o* gave highly coloured and complex product mixtures. Among the products from *5g* only the major component (*ca.* 50 % yield) was isolated by preparative TLC (elution with chloroform) and crystallized from MeOH to give 2-[3-(2-chloroindenyl)]-benzoic acid (*7c*), m.p. 207 °C, $\bar{\nu}_{max}$ 3100 – 2500, 1680 cm^{-1}. Treatment with CH_2N_2 and crystallization from EtOH gave the methyl ester *7g*, m.p. 100 °C, $\bar{\nu}_{max}$ 1715 cm^{-1}, δ 3.52 (3 H, s), 3.65 (2 H, s), 6.7 – 7.5 (7 H, m), 7.8 – 8.0 (1 H, m).

The product mixture from *5o* was first treated with CH_2N_2 and then fractionated by preparative TLC (several elutions with a 3:1 mixture of light petroleum and chloroform) to give *ca.* 10 % of *7g*, 10 % of *8c* and 20 % of chloromethylenediphenylmethane-2,2′-dicarboxylic acid dimethyl ester (*13b*), m.p. 114 °C, $\bar{\nu}_{max}$ 1720 cm^{-1}, δ 3.69 (6 H, s), 6.15 (1 H, s), 7.0 – 7.9 (8 H, m), *m/e* 295(M-35,100), 263(8), 248(35), 220(6), 193(7), 176(7), 165(8), 132(6).

Reactions of the ketones 5b – 5p *with potassium tert-butoxide in dimethyl sulfoxide.* General method: 0.2 g of the ketone and 0.2 g of potassium *tert*-butoxide were dissolved in 10 ml of dimethyl sulfoxide and the solution was allowed to stand for 2 h at room temperature. The solution was poured into water, the mixture made slightly acid with HCl and extracted twice with ether. The ether solution was washed with water, dried and evaporated. To facilitate the TLC and ^{1}H NMR analysis, the reaction mixtures were treated with CH_2N_2 to convert all carboxylic acids to their methyl esters. Approximative yields are based on ^{1}H NMR. The results are shown in Table 1.

In the cases where a part of the starting material had remained unreacted or the reaction resulted in a complex mixture, a higher concentration of base was used. Thus, 0.2 g of the ketone and 0.5 g of *tert*-butoxide were dissolved in 5 ml of dimethyl sulfoxide, the solution allowed to stand for 2 h at room temperature and worked up as above. The ketone *5j* gave mixtures of the isomeric acids *6a* and *7b*, the former being the major component. Sometimes the only product was *8a*. Because of the facile isomerization the acid *7b* could not be isolated, but the ^{1}H NMR spectrum of its methyl ester was obtained from the acid mixture treated with CH_2N_2. 2-[1-(3-Chloroindenyl)]benzoic acid (*6a*) was crystallized three times from EtOH and had m.p. 187 °C, $\bar{\nu}_{max}$ 3100 – 2500, 1680 cm^{-1}, δ ($CDCl_3$) 5.88 (1 H, d, J = 2.0 Hz), 6.44 (1 H, d, J = 2.0 Hz), 6.6 – 6.8 (1 H, m), 6.9 – 7.6 (6 H, m), 7.9 – 8.1 (1 H, m), 10.3 (1 H, br s). The methyl ester *6c* was crystallized from EtOH and had m.p. 75 °C, $\bar{\nu}_{max}$ 1710 cm^{-1}, δ 3.85 (3 H, s), 5.76 (1 H, d, J = 2.0 Hz), 6.45 (1 H, d, J = 2.0 Hz), 6.6 – 6.8 (1 H, m), 7.0 – 7.5 (6 H, m), 7.7 – 8.0 (1 H, m). The isomeric ester *7f* had δ 3.43 (3 H, s), 5.29 (1 H, d, J = 2.0 Hz), 6.12 (1 H, d, J = 2.0 Hz) + 8 Ar-H. The major cleavage product from *5o* was 2-[3-(1,2-dichloroindenyl)]benzoic acid (*7d*), m.p. 204 °C, $\bar{\nu}_{max}$ 3100 – 2500, 1680 cm^{-1}, δ ($CDCl_3$) 5.23 (1 H, s), 6.7 – 7.0 (1 H, m), 7.0 – 7.7 (6 H, m), 8.0 – 8.2 (1 H, m), 8.6 (1 H, br s). The acid was purified by TLC (elution

with chloroform) and crystallized from EtOH. The methyl ester *7h* had m.p. 89 °C, $\bar{\nu}_{max}$ 1720 cm^{-1}, δ 3.48 and 3.54 (à 1.5 H, s), 5.20 and 5.26 (à 0.5 H, s), 6.7–6.9 (1 H, m), 7.0–7.6 (6 H, m), 7.9–8.1 (1 H, m), *m/e* 318(5), 283(100), 251(15), 248(15), 233(35), 189(24). Although the reaction normally gave *7d* only, the isomeric 2-[1-(2,3-dichloroindenyl)]benzoic acid (*6b*) was once obtained in about 70 % yield, but attempts to repeat this synthesis were unsuccessful. The acid *6b* was purified as *7d* and had m.p. 241 °C $\bar{\nu}_{max}$ 3100–2500 cm^{-1}, solubility too low for ^{1}H NMR. The methyl ester *6d* had m.p. 85 °C, $\bar{\nu}_{max}$ 1720 cm^{-1}, δ 3.95 (3 H, s), 6.08 (1 H, s), 6.5–6.8 (1 H, m), 7.0–7.6 (6 H, m), 7.9–8.1 (1 H, m).

Hydrolysis of the compound 8c. The lactone *8c* (1.0 g) was refluxed for 80 min with a mixture of 3.0 g of H_2SO_4 and 7.0 g of HOAc. The mixture was poured into water and the product isolated by ether extraction. According to TLC and ^{1}H NMR only one compound was formed. Crystallization from EtOH gave the pure sample of spiro[indan-3-one-1,1′-isobenzofuran-3′-one (*10*), m.p. 146 °C, $\bar{\nu}_{max}$ 1758, 1720 cm^{-1}, δ ($CDCl_3$) 3.27 (1 H, d, J = 18.0 Hz), 3.35 (1 H, d, J = 18.0 Hz), 7.0–7.4 (2 H, m), 7.4–8.1 (6 H, m). The isomeric lactone *8b* failed to react under these reaction conditions.

Decarboxylation of the acid 11a. A mixture of 1.0 g of the acid *11a*, 0.2 g of copper chromite decarboxylation catalyst (FLUKA) and 20 ml of quinoline was refluxed for 2 h. The reaction mixture was poured into water, the solution acidified with HCl and extracted twice with chloroform. The chloroform solution was washed with HCl and water, dried and evaporated. The yield was almost quantitative. After two recrystallizations from benzene the hydrocarbon *12* had m.p. 206–207 °C (lit.[5] 208 °C).

Cyclization of the acids 6a, 6b, 7a *and* 7d. The acid *6a* (1.0 g) was refluxed for 80 min with a mixture of 3.0 g of H_2SO_4 and 7.0 g of HOAc. The mixture was poured into water and extracted twice with chloroform. The chloroform solution was dried and evaporated. Purification by preparative TLC (elution with chloroform) and crystallization from EtOH gave 0.64 g (83 %) of dibenzobicyclo[3.3.0]octadiene-2,8-dione (*16*), which had a melting point (241 °C) and spectral properties in agreement with those reported in literature.[3,4] Similarly, the acid *6b* (0.2 g) gave 0.11 g (67 %) of dibenzo-2-oxabicyclo[4.3.0]nonadiene-3,9-dione (*15*), m.p. 232 °C, $\bar{\nu}_{max}$ 1720 cm^{-1}, δ ($CDCl_3$) 4.83 (1 H, d, J = 7.2 Hz), 5.37 (1 H, d, J = 7.2 Hz), 7.1–7.9 (7 H, m), 8.0–8.2 (1 H, m), *m/e* 250(81), 222(58), 206(47), 194(89), 193(86), 178(21), 165(100) and *7d* gave a nearly quantitative yield of *8b*, identical with that obtained from the alkaline cleavage reactions.

A mixture of 1.0 g of the acid *7a*, 5.0 ml of conc. HCl and 50 ml of dioxane was refluxed for 80 min. The reaction mixture was worked up as above and the product crystallized from EtOH to give 0.75 g (75 %) of spiro[indane-1,1′-isobenzofuran-3′-one] (*9*), m.p. 141 °C, $\bar{\nu}_{max}$ 1742 cm^{-1}, δ 2.4–2.8 (2 H, m), 3.1–3.5 (2 H, m), 6.6–6.8 (1 H, m), 6.9–7.6 (6 H, m), 7.7–7.9 (1 H, m). The other acids of the types *6* and *7* failed to react under these conditions.

Alkaline cleavage of the diketone 16. A mixture of 1.0 g of *16* and 20 ml of 10 % ethanolic KOH was refluxed for 5 min, water and HCl were added and the product isolated by ether extraction. Crystallization from EtOH gave 0.81 g (75 %) of 2-[3-(1-oxoindanyl)]benzoic acid (*14a*), m.p. 242 °C, $\bar{\nu}_{max}$ 3200–2500, 1710, 1670 cm^{-1}. The methyl ester *14b* had m.p. 116 °C, $\bar{\nu}_{max}$ 1710 cm^{-1}, δ 2.43 (1 H, dd, J = 19.0, 4.0 Hz), 3.18 (1 H, dd, J = 19.0, 8.0 Hz), 3.83 (3 H, s), 5.49 (1 H, dd, J = 8.0, 4.0 Hz), 6.7–8.0 (8 H, m).

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