264. *The Action of Maleic Anhydride upon Some Anthracene Derivatives.*

By E. de Barry Barnett, N. F. Goodway, A. G. Higgins, and C. A. Lawrence.

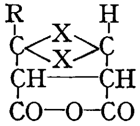
(A) The formation of adjects of the type (I) (I.G. Farben-Ind., E.P. 303,389, 1927; Diels and Alder, *Annalen*, 1931, **486**, 191; Clar, *Ber.*, 1931, **64**, 2194; cf. also Oddy, *J. Amer. Chem. Soc.*, 1923, **45**, 2158, whose product was almost certainly the adject of anthracene and maleic anhydride and not the keto-acid as he stated) is very little influenced by the presence of chlorine atoms or methyl groups in the side rings or, with the exception of dianthranyl, which does not react with maleic anhydride, by a single *meso*-substituent, but may be greatly hindered by two *meso*-substituents, *e.g.*, 9 : 10-diphenylanthracene (Clar, *loc. cit.*) and anthraquinyl diacetate.

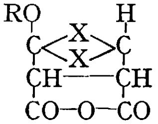
The reactivity in the Friedel–Crafts reaction of the adject obtained from 9 : 10-dichloroanthracene (Clar, *loc. cit.*) suggested easy replacement by hydroxyl of the bromine atom in the adject obtained from 9-bromoanthracene (I; R = Br) since stereochemical considerations render loss (transannular or otherwise) of hydrogen bromide inconceivable. This expectation was not realised, for after boiling the adject with alcoholic caustic potash for 40 minutes, no ionised halogen could be detected, and the adjects of 9 : 10-dichloro- and 9 : 10-dibromo-anthracene behaved in the same way. Indeed, compounds of the expected structure (II; R = H) would seem incapable of existence, since attempts to prepare them by the hydrolysis of the adjects from anthranyl acetates (II; R = Ac) were invariably accompanied by loss of maleic acid and the formation of the anthrone.

The non-existence of these hydroxyl compounds is remarkable in view of the ease with which the formation of their acetates (II; R = Ac) and their methyl ethers (II; R = Me) takes place.

The addition of maleic anhydride to the *meso*-positions of the anthracene complex is not paralleled in the case of heterocyclic compounds of formally similar structure, no

(I.)





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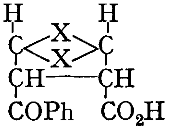
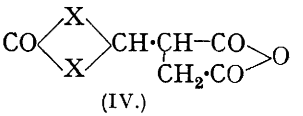


(III.)

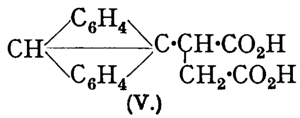
(X = C_6H_4 or substituted C_6H_4.)

adjects having been obtained from acridine, 1 : 2 : 3 : 4-dibenzphenazine, or the azine of indanthrone. Benzaldazine also failed to give such an adject. That of anthracene and maleic anhydride reacted with benzene in the presence of aluminium chloride to give a keto-acid (III), which could not be cyclised, reverted to anthracene on reduction with zinc dust and alkali, and lost the phenyl group on reduction by the Clemmensen method.

(B) Anthrone might be expected to react with maleic anhydride either in the anthranol form to give (II ; R = H), or in the ketonic form to give anthronylsuccinic anhydride (IV) as stated in the patent literature (E.P. 277,342) on inadequate grounds. The latter alternative has proved to be correct, since the product on reduction gives both anthranyl- and dihydroanthranyl-succinic acids (V and VI), both of which on bromination give a bromo-acid (VII), in which the bromine atom is non-reactive, and which gives anthraquinone on oxidation.



(IV.)



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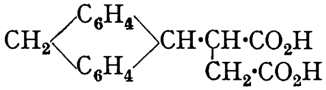
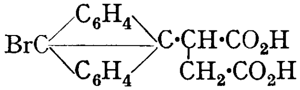


(VI.)



(VII.)

The Bz.-chloro- and Bz.-methyl-anthrones gave similar products, but with the Bz.-chloroanthronylsuccinic acids reduction resulted in quantitative formation of the chloro anthracene when a chlorine atom was in the *peri*-position to the succinic acid residue, whereas in all other cases examined loss of succinic acid on reduction took place only to a very minor extent (about 0·1%).

EXPERIMENTAL.

αβ-endo-9 : 10-*Dihydroanthraquinyl*-9 : 10-*succinic Anhydrides* (I).—These were prepared by boiling the anthracene derivative with a slight excess of maleic anhydride in *o*-dichlorobenzene (10 c.c. per g. of anhydride) for an hour. The crystals which separated on cooling were recrystallised from *o*-dichlorobenzene and then from the solvent given in the table below. The *products* were all colourless and well crystallised, and showed no fluorescence when examined in the light of the arc lamp. In most cases they melted with some decomposition.

			Analysis, %.			
			Found.		Calc.	
Substituent.	M. p.	Solvent.	C.	H.	C.	H.
9-Ph	252°	o-$C_6H_4Cl_2$	81·8	4·7	81·8	4·5
9-CH_2Ph	223	Xylene	82·0	5·1	82·0	4·9
9-Br	255	Anisole	61·0	3·1	60·8	3·1
9-OAc	240	Xylene	71·8	4·3	71·9	4·2
9 : 10-$(OMe)_2$	259	Anisole	71·4	5·0	71·4	4·8
1 : 5-Cl_2-9-OAc	244	Toluene	59·6	3·3	59·6	3·0
1 : 8-Cl_2-9-OAc	227	Xylene	59·6	3·2	,,	,,
4 : 5-Cl_2-9-OAc	249	Xylene	59·5	3·1	,,	,,

The hydrolysis of the four acetoxy-compounds was effected by boiling 3 g. with a solution of 3 g. of caustic potash in 30 c.c. of alcohol for 30 minutes. In each case the resulting anthrone was identified both as such and as its anthranyl acetate by the method of mixed m. p.

β-*Benzoyl*-αβ-endo-9 : 10-*dihydroanthraquinylpropionic Acid* (III).—Anthracene–maleic anhydride adject (10 g.), benzene (100 c.c.), and aluminium chloride (11 g.) were boiled for an hour, and the resulting very dark solution worked up in the usual way. The *product* after repeated recrystallisation from xylene was almost colourless and melted to an orange liquid at 234° (Found : C, 81·5; H, 5·3. $C_{20}H_{18}O_3$ requires C, 81·4; H, 5·1%).

Anthronylsuccinic Anhydrides.—These were prepared by boiling molecular quantities of the anthrone and maleic anhydride in *p*-tolyl ethyl ether (5·5 c.c. per g. of anhydride) for 3 hours. The yields were almost quantitative, but the 1 : 3-dimethyl compound was very difficult to purify, and the yield of pure material very small. A similar but much less pronounced difficulty was experienced in the purification of the 1 : 4-dimethyl compound. The *anthronylsuccinic anhydrides* were all colourless or very slightly yellow, and in most cases decomposed at or about their m. p. Their solutions in caustic soda were orange or red, but that of the 1 : 4-dimethyl compound was only slightly coloured. Attempts to prepare an anthranyl acetate from anthronylsuccinic anhydride were not successful, for treatment with acetic anhydride with or without the addition of pyridine always resulted in resinous products.

			Analysis, %.			
			Found.		Calc.	
Substituent.	M. p.	Solvent.	C.	H.	C.	H.
(None)	215°	Anisole	73·8	4·4	74·0	4·1
1 : 5-Cl_2	212	Xylene	59·9	3·0	59·8	2·8
1 : 8-Cl_2	215	Xylene	59·9	3·0	,,	,,
4 : 5-Cl_2	237	Xylene	59·8	2·9	,,	,,
1 : 3-Me_2	197	EtOAc	75·1	5·3	75·0	5·0
1 : 4-Me_2	210	Xylene	74·7	5·0	,,	,,
2 : 3-Me_2	240—260	Anisole	75·1	5·3	,,	,,
2 : 4-Me_2	230—235	Anisole	75·0	5·2	,,	,,

Anthranylsuccinic Acids and Anhydrides.—The anthronylsuccinic anhydride (10 g.) was boiled with 250 c.c. of sodium hydroxide solution (8%) and 30 g. of zinc dust (activated with copper sulphate) until the orange colour had vanished (about 4 hours). The period of reduction should not be unduly prolonged as the anthronylsuccinic acids differ from other anthrones by being easily reduced by zinc dust and alkali to the dihydro-stage, and this tendency was so strongly marked in the case of the 1 : 8-dichloro-compound that in spite of several attempts no pure product was isolated. The behaviour of anthronylsuccinic acid itself was also erratic, and in spite of numerous experiments, conditions could not be established which would lead with certainty to either product. For instance, in one experiment, in which the reduction had been prolonged for 26 hours, the product was pure anthranylsuccinic acid, whereas in another experiment under almost identical conditions, pure dihydroanthranylsuccinic acid was obtained after 7 hours. The tendency to form the dihydro-acid can be minimised by omitting to activate the zinc, and by stopping the reduction as soon as a filtered sample of the solution is yellow.

The crude acids were resinous, but after recrystallisation from very dilute methyl alcohol were easily purified by recrystallisation from anisole. They were all pale yellow, crystalline solids which decomposed on melting, and were all strongly fluorescent.

The *anhydrides* were obtained from the acids by boiling for 4 hours with *o*-dichlorobenzene (4 c.c. per g.) or for ½ hour with acetic anhydride (3 c.c. per g.). The 2 : 3-dimethyl compound was recrystallised from toluene; all the others from anisole. The anhydrides were somewhat darker than the free acids.

		Acid. Analysis, %.					Anhydride. Analysis, %.			
		Found.		Calc.			Found.		Calc.	
Substituent.	M. p.	C.	H.	C.	H.	M. p.	C.	H.	C.	H.
(None)	219°	73·3	4·8	73·5	4·8	200°	78·1	4·4	78·3	4·4
1 : 4-Me_2	228	74·3	5·7	74·5	5·6	235	79·1	5·4	79·0	5·3
2 : 4-Me_2	235	74·7	5·8	,,	,,	240	78·9	5·5	,,	,,
2 : 3-Me_2	235	74·6	5·9	,,	,,	192—194	78·9	5·4	,,	,,

9 : 10-*Dihydroanthranylsuccinic Acid* (VI).—As stated above, this was frequently obtained by the zinc dust–alkali reduction of anthronylsuccinic anhydride, although the exact conditions cannot be defined. After recrystallisation from very dilute methyl alcohol, it separated from anisole in colourless crystals, m. p. 211° (decomp.) (Found : C, 73·0; H, 5·6. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%). On boiling for 3 hours with *o*-dichlorobenzene or for 10 minutes

with acetic anhydride, it passed into its *anhydride*, which after recrystallisation from toluene was colourless and had m. p. 169° (Found : C, 77·7; H, 5·3. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%).

10-*Bromoanthranylsuccinic Acid* (VII).—This was obtained when either anthranylsuccinic acid (3 g.) or its dihydro-compound was brominated with a slight excess of bromine in boiling glacial acetic acid (50 c.c.). It was isolated by diluting with water and cooling, and after recrystallisation from anisole was yellow; m. p. 255° (decomp.) (Found : C, 58·2; H, 3·8. $C_{18}H_{13}O_3Br$ requires C, 57·9; H, 3·5%). When 3·5 g. were boiled for 8 hours with 25 c.c. of *o*-dichlorobenzene, it slowly dissolved, and on cooling the *anhydride* crystallised; recrystallised from toluene it was yellow, m. p. 247° (decomp.) (Found : C, 60·8; H, 3·1. $C_{18}H_{11}O_3Br$ requires C, 61·0; H, 3·5%).

Anthraquinyl Dimethyl Ether.—The preparation of this by Meyer's method (*Annalen*, 1911, **379**, 68) is very inconvenient, but it was readily obtained when methyl *p*-toluenesulphonate and aqueous potassium hydroxide (30%) were added alternately in small amounts to a boiling alcoholic solution of 10-methoxyanthrone (Barnett, J., 1931, 3340).

Anthraquinyl Diacetate.—Both the method of Liebermann (*Ber.*, 1888, **21**, 1172) and that of Eckert and Pollak (*Monatsh.*, 1917, **38**, 11) for the preparation of this compound are troublesome, but it was extremely easily obtained in almost quantitative yield when zinc dust (10 g.) was slowly added to a boiling solution of 21 g. of anthraquinone in 100 c.c. of pyridine and 40 c.c. of acetic anhydride. After recrystallisation from glacial acetic acid, it had m. p. 270° (lit., 260°, decomp.). In exactly the same way 1 : 5-*dichloroanthraquinyl diacetate* (pale yellow crystals from anisole; m. p. 310°, decomp.) was obtained from 1 : 5-dichloroanthraquinone (Found : C, 59·5; H, 3·6. $C_{18}H_{12}O_4Cl_2$ requires C, 59·5; H, 3·3%), and the 1 : 8-*isomeride* (pale yellow crystals from xylene; m. p. 249°) was obtained from 1 : 8-dichloroanthraquinone (Found : C, 59·5; H, 3·4%). The method was also convenient for the preparation of phenanthraquinyl diacetate from phenanthraquinone.

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