a C–Br distance of 2.06 Å. for this compound. We regard his interpretation as less reliable than ours because his photographs showed fewer maxima and minima than ours and also because he considered only one molecular model (omitting all carbon–hydrogen and bromine hydrogen terms) in making his interpretation.

TABLE III

t-BUTYL BROMIDE

Maximum	Minimum	I	$s_{\text{obsd.}}$	$s_{\text{calcd.}}$	C–Br, Å.
	1		1.856	1.72	1.808
1		20	2.737	2.80	1.995
	2		4.113	3.86	1.829
2		20	4.959	4.97	1.954
	3		6.320	6.07	1.872
3		15	7.176	7.18	1.952
	4		8.522	8.32	1.903
4		11	9.463	9.48	1.954
	5		10.719	10.67	1.940
5		3	11.624	11.69	1.962
	6		12.770	12.60	1.925
6		7	13.751	13.71	1.944
Average (1, 2 min., 1 max. omitted)					1.934

Final results: C_I–Br 1.92 ± 0.03 Å.
C_{II}–Br 2.79 ± 0.03 Å.
C–C–C angle 111° 30′ ± 2°
C–C 1.54 Å. (assumed)
C–H 1.09 Å. (assumed)

The six term radial distribution function, plotted in Fig. 1, shows a large peak at 2.82 Å. This represents the long carbon–bromine distance and some unresolved less important distances.

We wish to express our appreciation to Professor C. P. Smyth for suggesting that the apparatus be built and for his continued interest in the research.

Summary

The molecular structures of isobutane, *t*-butyl chloride and *t*-butyl bromide have been determined by electron diffraction. The C–C–C angles are 113°30′ ± 2°, 111°30′ ± 2° and 111°30′ ± 2° for isobutane, *t*-butyl chloride and *t*-butyl bromide, respectively. The interatomic distances are C–C 1.54 ± 0.02 Å., C–Cl 1.78 ± 0.03 Å. and C–Br 1.92 ± 0.03 Å.

The steric repulsions between hydrogen and halogen are calculated and compared with the electrostatic interactions.

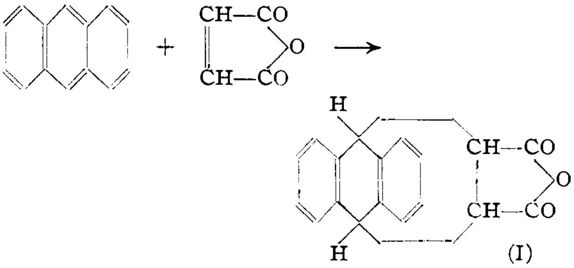
PRINCETON, N. J. RECEIVED DECEMBER 4, 1937

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Reaction between Maleic Anhydride and Polycyclic Hydrocarbons

BY W. E. BACHMANN AND M. C. KLOETZEL[1]

Diels and Alder[2] prepared anthracene-9,10-*endo*-α,β-succinic anhydride (I) by fusing a mixture of anthracene and maleic anhydride just below 260°.



(I)

Clar[3] obtained the adduct by heating a solution of the two compounds in xylene and used this procedure to prepare the adducts of a number of polycyclic hydrocarbons with maleic anhydride. Other investigators have employed either the fusion method or the reaction in a solvent, usually a high-boiling liquid such as xylene, *o*-dichlorobenzene or nitrobenzene. Although the yields of the adducts were not always satisfactory, no systematic study has been made on any of the polycyclic hydrocarbons to determine the conditions for securing the maximum yields of the adducts. The necessity of some such study was brought to our attention in attempting to prepare the adduct (II) from maleic anhydride and 3-methylcholanthrene.

On heating a mixture of equimolecular proportions of maleic anhydride and 3-methylcholanthrene in xylene at the boiling point of the solution for two hours a 22% yield of the adduct (II) was obtained. In an attempt to improve the yield, we resorted to a higher temperature, using anisole and nitrobenzene as solvents and carrying out the reactions at the boiling points of the solutions, but the yields of the adduct were found to

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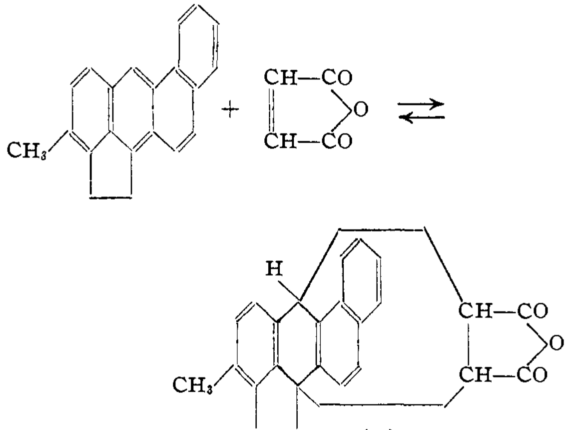
[1] Du Pont Post-Doctorate Fellow.

[2] Diels and Alder, *Ann.*, **486**, 191 (1931).

[3] Clar, *Ber.*, **64**, 2194 (1931).

be lower than that in boiling xylene. A longer time was then allowed for reaction to take place in xylene, but no better yield was obtained. To account for these results it was necessary to postulate the establishment of an equilibrium as shown in the following formulation.



(II)

This explanation proved to be correct when it was found that the identical equilibrium mixture of hydrocarbon, maleic anhydride and adduct was obtained by heating a xylene solution of the adduct.

The investigation of the reaction between maleic anhydride and other polycyclic hydrocarbons containing the anthracene nucleus disclosed similar reversible reactions. In Table I are shown the equilibrium mixtures obtained in boiling xylene, using equimolecular proportions of the hydrocarbon and maleic anhydride. In most cases the equilibrium was checked by heating a solution of the pure adduct. In each instance, 2 cc. of xylene contained 0.1 g. of the hydrocarbon, free or in the form of the adduct, except for 1,2,5,6-dibenzanthracene where 3 cc. of solvent was needed to dissolve the hydrocarbon. It is apparent that for 9,10-diphenylanthracene, 1,2,5,6-dibenzanthracene and 3-methylcholanthrene the equilibrium is decidedly unfavorable for the preparation of the adduct under these conditions.

TABLE I

EQUILIBRIUM MIXTURES

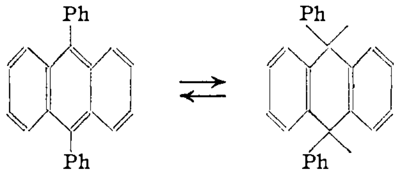
Hydrocarbon	% adduct in equil. mixture
Anthracene	99
9-Methylanthracene	99
9,10-Dimethylanthracene	98
9-Phenylanthracene	75
9,10-Diphenylanthracene	16
1,2-Benzanthracene	84
1,2,5,6-Dibenzanthracene	30
3-Methylcholanthrene	22

It has been observed by others that certain of the adducts can be broken down into the hydrocarbon and maleic anhydride by heating the solids above 200°, and Clar surmised that the low yield of adduct which he obtained from 9,10-dichloroanthracene and maleic anhydride in boiling nitrobenzene was due to a reversible reaction. Others have not appreciated the reversibility of the addition reaction in solvents, for in most cases high-boiling solvents were employed to form the adduct, and we now know that at high temperatures the reverse reaction is favored.

With the recognition of the existence of an equilibrium which was shifted in favor of the hydrocarbon at higher temperatures, two procedures suggested themselves for increasing the yields of the adducts: the use of an excess of maleic anhydride and the employment of a lower temperature for the reaction. Actually, both procedures produced the desired results, so that it became possible to obtain the adducts in excellent yields. By using thirty moles of maleic anhydride to one of the hydrocarbon in the same volume of boiling xylene, the following yields of adducts were obtained: from 9-phenylanthracene, 97%; 9,10-diphenylanthracene, 78%; 1,2-benzanthracene, 99%; 1,2,5,6-dibenzanthracene, 91%; 3-methylcholanthrene, 83%.

In boiling benzene the equilibrium mixture obtained from equimolecular proportions of 3-methylcholanthrene and maleic anhydride contained 94% of the adduct, compared to the 22% present in boiling xylene. It is noteworthy that even at 80° the adduct dissociates into the two compounds. It was found that the adducts obtained from 1,2-benzanthracene and 9-phenylanthracene showed no signs of dissociation in boiling benzene in twenty-four hours. This means that quantitative yields of the adducts should be obtainable using equimolecular proportions of the two components in benzene. However, the reaction of these hydrocarbons with one equivalent of maleic anhydride is extremely slow at this temperature. By using thirty equivalents of maleic anhydride, the reaction in benzene was speeded up and nearly quantitative yields of the adducts were obtained.

The rates of reaction between maleic anhydride and the eight polycyclic hydrocarbons containing the anthracene nucleus varied greatly one from the other. The presence of methyl groups in the *meso*-positions greatly facilitated the reaction (see Table II). Thus, 9-methylanthracene reacts much faster with maleic anhydride than does anthracene. Furthermore, the reaction between maleic anhydride and 9,10-dimethylanthracene takes place rapidly at room temperature; shortly after mixing the two components in benzene, the adduct precipitates from the solution. On the other hand, the presence of phenyl groups in the *meso*-positions slows up the reaction enormously. 9-Phenylanthracene reacts much more slowly than anthracene and the reaction between equimolecular proportions of maleic anhydride and 9,10-diphenylanthracene is incomplete even after days of boiling in benzene. According to Ingold and Marshall[4] 9,10-diphenylanthracene gives rise to a biradical (III) in boiling xylene, and in view of the fact that the free radical triphenylmethyl readily combines with maleic anhydride[5] it might be expected that 9,10-diphenylanthracene would react rapidly with maleic anhydride in boiling xylene. Actually the reaction is slow in this solvent also. The reaction with maleic anhydride is also slow when benzo groups are present in the 1,2- and 5,6-positions. Cook[6] reported that the *meso* additive power of 1,2,5,6-dibenzanthracene is less than that of anthracene and correlated this property with the greater aromaticity of the anthracene molecule containing benzene rings condensed in the angular positions.



(III)

By reaction with potassium hydroxide, the anhydrides which were obtained in the addition reactions were hydrolyzed readily to the salts of the corresponding dicarboxylic acids, from which the free acids were obtained by treatment with an acid. In a number of cases it was found that these dicarboxylic acids were easily converted to the anhydrides; thus, recrystallization of anthracene-9,10-*endo*-α,β-succinic acid and 3-methylcholanthrene-6,12b-*endo*-α,β-succinic acid from ethyl acetate sufficed to give the anhydrides of the acids.

The dicarboxylic acids obtained from the adducts of the carcinogenic hydrocarbons, 1,2,5,6-dibenzanthracene and 3-methylcholanthrene, are of particular interest. The sodium salt of 1,2,5,6-dibenzanthracene-9,10-*endo*-α,β-succinic acid induced tumors when its aqueous solution was injected into mice.[7] By following our procedure this water-soluble carcinogenic substance now can be prepared readily. 3-Methylcholanthrene-6,12b-*endo*-α,β-succinic acid has not been prepared previously, and it will be of interest to determine the carcinogenic activity of its water-soluble salts, since the hydrocarbon is the most potent carcinogenic compound known. We have also prepared the dimethyl esters of these two acids. We are using our procedure to prepare the addition compounds of maleic anhydride and other polycyclic hydrocarbons which are known to be active carcinogenic agents.

Experimental

Numerous experiments were carried out in order to determine the effect of concentration, time, and temperature on the yields of adduct. Mixtures of 0.1 g. of the hydrocarbon and either one or thirty mole equivalents of maleic anhydride (freshly sublimed) in 2 cc. of benzene or xylene were heated at the boiling points of the solutions for various periods of time. For 1,2,5,6-dibenzanthracene 3 cc. of xylene was needed to dissolve the hydrocarbon. After evaporation of the solvent by a current of air, the residue was heated for a few minutes on a steam-bath with about 5 cc. of 40% potassium hydroxide solution to hydrolyze the addition product (anhydride) to the corresponding dicarboxylic acid. The potassium salt of the acid, which is usually not very soluble, was dissolved in hot water, benzene was added to dissolve the unreacted hydrocarbon and the two solutions were separated. Evaporation of the benzene solution in a weighed container gave the amount of hydrocarbon that remained; from the aqueous solution the dicarboxylic acid was precipitated by addition of hydrochloric acid. The results of the experiments, which are accurate to a few per cent., are presented in Table I; from them can be determined the conditions to be used for the practical preparation of any of the adducts. Larger yields could be obtained in a shorter time by using smaller amounts of solvent when possible.

Anthracene-9,10-*endo*-α,β-succinic anhydride precipitated in 96% yield as colorless, hexagonal prisms when a mixture of 2 g. of anthracene and 5.6 g. of maleic anhydride in 40 cc. of benzene was refluxed for three hours and then cooled. When the corresponding dicarboxylic acid was recrystallized from ethyl acetate, it was converted completely to the anhydride as was shown by analysis.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.2; H, 4.4. Found: C, 78.1; H, 4.4.

9-Methylanthracene-9,10-*endo*-α,β-succinic anhydride crystallized in 95% yield as colorless needles from a solu-

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[4] Ingold and Marshall, *J. Chem. Soc.*, 3080 (1926).

[5] Conant and Chow, THIS JOURNAL, **55**, 3475 (1933).

[6] Cook, *J. Chem. Soc.*, 3277 (1931).

[7] Barry, Cook, Haslewood, Hewett, Hieger and Kennaway, *Proc. Roy. Soc.* (London), **B117**, 331 (1935).

tion of 0.5 g. of 9-methylanthracene and 0.25 g. of maleic anhydride in 10 cc. of benzene, which had been refluxed for two hours; m. p. 264–266°.

TABLE II

YIELDS OF ADDUCTS OBTAINED UNDER VARIOUS CONDITIONS

Mole ratio MA/RH	Time, hrs.	% adduct Benzene	Xylene
	Anthracene		
1:1	0.08	24	
1:1	2.0	79	
1:1	7.7	96	
1:1	0.5		95
1:1	2.0		99^a
5:1	0.4	93	
5:1	.7	98	
5:1	1.3	100	
30:1	0.25	100	
	9-Methylanthracene		
1:1	0.08	68	
1:1	.6	94	
1:1	1.0	98	
1:1	2.0	99+	
1:1	0.6		99^a
	9,10-Dimethylanthracene		
1:1	0.08	95	
1:1	.33	100	
1:1	.5		98^a
1:1	1.0	89 (25°)	
	9-Phenylanthracene		
1:1	2.0	39	
1:1	2.0		65
1:1	8.5		75^a
30:1	2.0	88	
30:1	8.0	94	
30:1	2.0		97
	9,10-Diphenylanthracene		
1:1	2.0	00	
1:1	2.0		5
1:1	9.0		10
1:1	24.0		16^a
30:1	2.0	6	
30:1	24.0	48	
30:1	48.0	75	
30:1	0.25		35
30:1	2.0		78
	1,2-Benzanthracene		
1:1	2.0	17	
1:1	51.0	78	
1:1	2.0		71
1:1	7.5		84^a
30:1	0.25	37	
30:1	2.0	93	
30:1	18.0	98	
30:1	2.0		100
	1,2,5,6-Dibenzanthracene		
1:1	8.0		30^a
30:1	0.25		60
30:1	1.0		90^a
	3-Methylcholanthrene		
1:1	2.0	20	
1:1	48.0	93^a	
1:1	0.5		22^a
30:1	.5	55	
30:1	2.0	95	
30:1	24.0	98^a	
30:1	0.25		83^a

^{a} Indicates an equilibrium mixture; further heating does not increase the yield of adduct.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.6; H, 4.9. Found: C, 78.7; H, 5.0.

9,10-Dimethyl-9,10-*endo*-α,β-succinic Anhydride.—The orange-yellow solution of 1.5 g. of 9,10-dimethylanthracene and 0.72 g. of maleic anhydride in 30 cc. of benzene became colorless after being refluxed for twenty minutes; during this time a large amount of the adduct crystallized from the solution in fine, colorless needles; yield, 96%; m. p. 333–335°.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.9; H, 5.3. Found: C, 78.9; H, 5.2.

The potassium salt of the dicarboxylic acid is only slightly soluble in water; it crystallizes from water in colorless, hexagonal plates. When the aqueous solution of the salt was acidified with hydrochloric acid, the dicarboxylic acid crystallized from the solution in fine, colorless needles. The melting point of the acid was found to be identical with that of the anhydride, which suggested that dehydration occurs during the process. This view was confirmed when it was found that recrystallization from ethyl acetate converted a considerable amount of the acid to the anhydride, as was shown by an analysis of the mixture which was obtained.

9-Phenylanthracene-9,10-*endo*-α,β-succinic Anhydride.—Barnett and co-workers[8] reported the preparation of this compound. When a solution of 139 mg. of the substance in 3 cc. of xylene was refluxed for eight hours, 26 mg. of 9-phenylanthracene was obtained.

9,10-Diphenylanthracene-9,10-*endo*-α,β-succinic Anhydride.—9,10-Diphenyl-9,10-dihydroxy-9,10-dihydroanthracene was prepared readily according to the excellent procedure of Dufraisse and LeBras.[9] The diol can be recrystallized very well from ethyl acetate. The diol was reduced to the hydrocarbon by a mixture of sodium iodide and acetic acid according to the directions of Clar.[10] In order to isolate the adduct a solution of 1 g. of 9,10-diphenylanthracene and 1 g. of maleic anhydride in 10 cc. of benzene was refluxed for one week; during this time 0.3 g. of the adduct had crystallized from the solution in colorless needles. These were filtered from the hot solution and recrystallized from benzene. The anhydride is very little soluble in hot benzene, ethyl acetate or acetone: m. p. 249–250° with decomposition.

Anal. Calcd. for $C_{30}H_{20}O_3$: C, 84.1; H, 4.7. Found: C, 84.3; H, 4.6.

The potassium salt of the dicarboxylic acid obtained by

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[8] Barnett, Goodway, Higgins and Lawrence, *J. Chem. Soc.*, 1224 (1934).

[9] Dufraisse and LeBras, *Bull. soc. chim.*, [5] **4**, 1040 (1937).

[10] Clar, *Ber.*, **63**, 118 (1930).

hydrolysis of the anhydride is very little soluble in hot water.

1,2-Benzanthracene-9,10-endo-α,β-succinic anhydride was isolated by heating a mixture of 0.4 g. of 1,2-benzanthracene and 5 g. of maleic anhydride in 8 cc. of boiling benzene for three hours, evaporating the solution, subliming the maleic anhydride from the mixture at 80° at 0.4 mm. and washing the residue with benzene; yield, 0.26 g. Our product agreed in properties with that reported by Clar.[11]

Dimethyl Ester of 1,2,5,6-Dibenzanthracene-9,10-*endo*-α,β-succinic Acid.—Cook[6] prepared the acid from the adduct obtained by fusing equimolecular proportions of 1,2,5,6-dibenzanthracene and maleic anhydride. He found that most of the hydrocarbon was recovered unchanged when it was heated with half its weight of maleic anhydride in boiling xylene for five hours. As Table II shows, the compound can be obtained in 90% yield in one hour if thirty mole equivalents of maleic anhydride are employed. The dimethyl ester of the dicarboxylic acid was prepared by the action of diazomethane on a suspension of the unrecrystallized acid in acetone. From ethyl acetate the ester crystallized in colorless needles; m. p. 230–231°.

Anal. Calcd. for $C_{26}H_{16}O_3$: C, 79.6; H, 5.3. Found: C, 79.2; H, 5.3.

3-Methylcholanthrene-6,12b-*endo*-α,β-succinic Anhydride.—This compound is best prepared in benzene since some decomposition occurs in boiling xylene. A bright-red color, presumably of a molecular complex, is formed on mixing 3-methylcholanthrene and maleic anhydride in a solvent; as the addition reaction proceeds, the red color disappears. When a mixture of 1 g. of 3-methylcholanthrene and 0.5 g. of maleic anhydride in 10 cc. of benzene was refluxed for two days and then cooled, 0.8 g. of the adduct crystallized from the solution in large, transparent prisms. From ethyl acetate the anhydride crystallized in colorless needles; m. p. 209–210° with decomposition.

Anal. Calcd. for $C_{25}H_{18}O_3$: C, 81.9; H, 4.9. Found: C, 81.6; H, 4.9.

The dicarboxylic acid which was obtained from the anhydride by hydrolysis with potassium hydroxide followed by treatment of the salt with hydrochloric acid dissolved readily in cold ethyl acetate; no crystallization took place when the solution was allowed to evaporate. When, however, the solution was heated at the boiling point for a few minutes and then cooled, immediate crystallization of colorless needles of the anhydride took place.

When a solution of 135 mg. of 3-methylcholanthrene-6,12b-*endo*-α,β-succinic anhydride in 2 cc. of xylene was refluxed for thirty minutes, a 78% yield of 3-methylcholanthrene was formed. By employing a larger volume of solvent it should be possible to effect nearly complete dissociation of the adduct and the procedure offers a method of purifying methylcholanthrene. The regenerated methylcholanthrene possessed a pale yellow color. By heating a solution of 135 mg. of the adduct in 2 cc. of benzene for twenty-four hours, a 6% yield of 3-methylcholanthrene was obtained.

The **dimethyl ester** of 3-methylcholanthrene-6,12b-*endo*-α,β-succinic acid was prepared by the action of diazomethane on an acetone solution of the dicarboxylic acid freshly precipitated from the aqueous solution of its potassium salt. From ethyl acetate the ester crystallized in colorless needles; m. p. 165.5–166.5°.

Anal. Calcd. for $C_{27}H_{24}O_4$: C, 78.6; H, 5.9. Found: C, 78.6; H, 5.8.

Summary

The effect of concentration, time and temperature on the yields of adduct formed in the Diels–Alder reaction between maleic anhydride and eight polycyclic hydrocarbons containing the anthracene nucleus has been determined.

It has been established that in boiling xylene an equilibrium is established in virtue of the reversible reaction. Procedures have been worked out for securing excellent yields of the adducts.

ANN ARBOR, MICHIGAN RECEIVED DECEMBER 27, 1937

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[11] Clar, *Ber.*, **65**, 519 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A New Synthesis of 3,4-Benzphenanthrene

BY MELVIN S. NEWMAN AND LLOYD M. JOSHEL[1]

Of the four possible tetracyclic aromatic hydrocarbons of the formula $C_{18}H_{12}$, namely, 1,2-benzanthracene I, 3,4-benzphenanthrene II, chrysene III, naphthacene IV, and triphenylene V, only the first has been much studied from the point of view of the effect of chemical constitution on carcinogenic activity. Itself inactive, the latent carcinogenic properties of the 1,2-benzanthracene nucleus are developed to a remarkable degree in certain of its derivatives. For example, methylcholanthrene, which may be considered as a 5,6,10-trisubstituted 1,2-benzanthracene, is the most potent carcinogenic hydrocarbon known, and certain other derivatives, all containing groups on the *meso*-positions, approach methylcholanthrene in their ability to induce sarcoma (cancer of connective tissue) in mice.[2]

Since certain derivatives of I are potent cancer-

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[1] Ohio State University Fellow.

[2] For reviews on the subject of carcinogenic activity see: (a) Barry, Cook, *et al.*, *Proc. Roy. Soc.* (London), **B117**, 318 (1935); (b) Bachmann, Cook, *et al.*, *ibid.*, **B123**, 343 (1937); (c) Fieser, *et al.*, *Am. J. Cancer*, **29**, 260 (1937).