

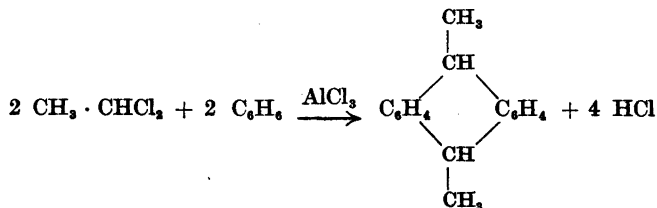
An Unexpected Formation of 9,10-Dimethylantracene

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In an attempt to substitute aromatic hydrogen by the acetic acid residue a mixture of benzene and ethyl monochloroacetate was treated with anhydrous aluminium chloride. The reaction product did not, however, contain any phenylacetic acid but consisted of a mixture of hydrocarbons only. Having removed excess of benzene by distillation a yellow crystalline hydrocarbon $C_{16}H_{14}$ separated from the mixture the liquid part of which was found to contain mainly ethyl-substituted benzenes. The crystalline hydrocarbon, purified by sublimation in a vacuum and subsequent crystallization from methanol, had m.p. 181° . In solution it showed the strong blue to violet fluorescence characteristic of the anthracene hydrocarbons. On treatment with bromine two hydrogen atoms were substituted and as well the hydrocarbon itself as the brominated derivative on oxidation gave anthraquinone. From this it was concluded that the crystalline hydrocarbon was 9,10-dimethylantracene. A preliminary report on this result was given two years ago ¹. Later experiments have shown that it is advantageous by the preparation of the 9,10-dimethylantracene to use ethyl chloroformate instead of the ethyl monochloroacetate.

On treatment of a mixture of 1,1-dichloroethane and benzene with aluminium chloride Anschütz ² obtained a yellow crystalline hydrocarbon with m.p. 181° which he regarded as 9,10-dimethyl-9,10-dihydroanthracene formed by the following reaction:

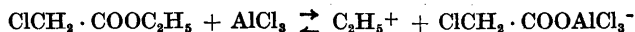


Later Barnett and Matthews ³ showed that the hydrocarbon of Anschütz actually was 9,10-dimethylantracene. They prepared the dihydroderivative

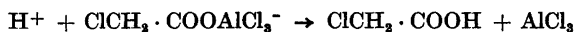
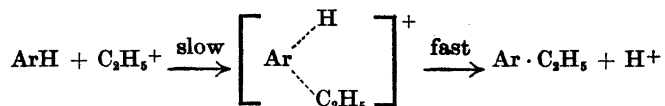
in another way and found that it was easily dehydrogenated to the hydrocarbon with m.p. 181°.

In our experiments the formation of the dimethylantracene must evidently be due to the ethyl group in the chloroacetic ester. This would be in accordance with the results of Kunckell and Ulex⁴ who found that benzene was alkylated by treatment with chloroformic esters and aluminium chloride. Basing on the modern conception of the Friedel-Crafts reaction we therefore consider the formation of the 9,10-dimethylantracene to take place through the following reactions.

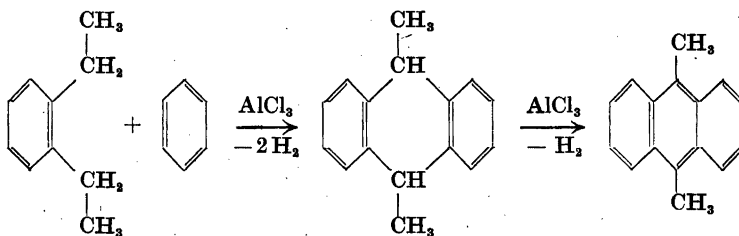
Firstly the presence of aluminium chloride will give rise to the occurrence of the ethyl carbocation:



Secondly the electrophilic carbocation adds by a relatively slow process to the benzene nucleus forming a transition complex which rapidly loses a proton:



By continued alkylation a mixture of higher alkylsubstituted benzenes will be formed, in the first hand, the isomeric diethylbenzenes. It is now suggested that the *ortho*-diethylbenzene in the presence of aluminium chloride condenses with benzene to the dihydroderivative of 9,10-dimethylantracene which is immediately dehydrogenated to the dimethylantracene itself:



This conception is in accordance with the fact that *ortho*-diethylbenzene (or *ortho*-dimethylbenzene) has never been prepared by the Friedel-Crafts reaction. Kunckell and Ulex⁴ and others state explicitly that only the *meta* and *para* derivatives are obtained by this reaction. It would be desirable to test the above scheme by starting with *ortho*-diethylbenzene but as this substance was difficult to obtain a similar reaction was carried out with *ortho*-dimethylbenzene. As expected a small quantity of anthracene could be isolated from the reaction products.

Another explanation of the reaction would be that two molecules of the monoalkylated benzene reacted with each other to give the tricyclic hydrocarbon. However, neither Anschütz² nor we have succeeded in isolating

anthracene or 9,10-dimethylantracene after treating toluene and ethylbenzene respectively with aluminium chloride. On the other hand Anschütz (*l.c.* p. 178) after heating toluene with aluminium chloride isolated another dimethylantracene evidently having none of the methyl groups in the 9 or 10 positions. This result could easily be explained by a primary formation of higher methylated benzenes by the well-known transmethylation and a secondary condensation of one of these containing two methyl groups in *ortho* position with a toluene molecule according to the above scheme.

It should be added that by the reaction between *n*-propyl monochloroacetate and benzene in the presence of aluminium chloride we isolated a crystalline colourless hydrocarbon $C_{18}H_{20}$ which is evidently the 9,9,10,10-tetramethyl-9,10-dihydroanthracene. The fact that 9,10-diethylantracene is not formed by this process must be due to a tautomerization of the primarily formed *n*-propyl ion into the *isopropyl* ion.

As mentioned above the dimethylantracene m.p. 181° was easily substituted by bromine giving a dibromo derivative. Barnett and Matthews³ found that bromination of 9,10-dimethylantracene gave ω,ω' -dibromo-9,10-dimethylantracene. This would be in accordance with our results, *viz.* that the dimethylantracene m.p. 181° as well as the dibromo derivative were oxidized to anthraquinone and that they gave addition compounds with one molecule of maleic anhydride. It is, however, still an open question whether the addition of the maleic anhydride has taken place in 1,4 or 9,10 positions. On the other hand the colourless dihydro derivative of the 9,10-dimethylantracene for which we found the m.p. 90° did not react with maleic anhydride. The dihydro derivative reacted with bromine giving the same dibromo compound as obtained from the 9,10-dimethylantracene which shows that the bromine at the same time acts as a dehydrogenating reagent. A 9,10-dimethyl-9,10-dihydroanthracene has previously been prepared by Badger, Goulder, and Warren⁵ from 9-methylanthrone by a Grignard reaction. They found the m.p. to be $101-102^{\circ}$ and it is therefore possible that our dihydro compound is a geometric isomer.

Added during proof-reading: A new 9,10-dimethyl-9,10-dihydroanthracene with m. p. 130° has been described by K. Sisido, and T. Isida (*J. Amer. Chem. Soc.* **70** (1948) 1289). The same compound has been prepared also by G. M. Badger, M. L. Jones, and R. S. Pearce (*J. Chem. Soc.* **1950** 1700) who regard it as a geometric isomer of the dihydroderivative with m. p. 101° .

EXPERIMENTAL PART

Preparation of 9,10-dimethylantracene

Benzene (200 g), ethyl monochloroacetate (20 g), and anhydrous aluminium chloride (60 g) were mixed and refluxed for 3 days. After cooling sufficient water was added and the benzene layer separated in a funnel and dried with sodium sulphate. The excess of benzene was removed by distillation when a dark liquid remained which partly crystallized on standing for some time. The liquid part was absorbed on a porous plate and the crystalline substance (2 g) was purified by sublimation twice in a vacuum and recrystallization from methanol. The hydrocarbon was then obtained as yellow needles with m.p. 181° . Equivalent quantities of the 9,10-dimethylantracene and picric acid were dissolved

in benzene. On standing the picrate crystallized in dark red needles having m.p. 172—74° (decomp.).

$C_{16}H_{14}$ (206.3)	Calc.	C 93.16	H 6.84
	Found	» 93.05, 93.12	» 6.93, 7.12

0.2947 g subst. in 21.83 g benzene, $\Delta = 0.333^\circ$, $M = 207.6$

The liquid part was extracted from the porous plate by means of ether. The material collected from several experiments was fractionated repeatedly in a vacuum, b.p. 78—82° at 15 mm Hg.

$C_{10}H_{14}$ (134.2)	Calc.	C 89.49	H 10.51
	Found	» 89.54, 89.28	» 10.38, 10.24

$n_D^{22} = 1.5020$; *m*-diethylbenzene $n_D^{20} = 1.4955$

Oxidation: To a solution of the 9,10-dimethylantracene (0.32 g) in glacial acetic acid was added CrO_3 (0.94 g) dissolved in the same solvent. After the oxidation had taken place hydrochloric acid and water were added when anthraquinone separated. It was recrystallized from ethanol and obtained as light yellow needles with m.p. 279°, alone and mixed with an authentic sample of anthraquinone. Yield 0.18 g.

$C_{14}H_8O_2$ (208.2)	Calc.	C 80.76	H 3.87
	Found	» 80.61, 80.63	» 3.87, 3.95

The oxidation product gave a positive oxanthranol reaction.

Bromination: To a solution of 9,10-dimethylantracene (0.69 g) in carbon tetrachloride (15 ml) bromine dissolved in carbon tetrachloride was added. On heating very gently hydrogen bromide did evolve and the brominated hydrocarbon (0.98 g) separated. On recrystallization from chloroform it was obtained as yellow needles which had no definite m.p. but decomposed at about 300°.

$C_{18}H_{12}Br_2$ (364.1)	Calc.	C 52.78	H 3.32	Br 43.90
	Found	» 53.05	» 3.40	» 43.72

The brominated product (170 mg) was oxidized in the same way as the hydrocarbon. The recrystallized oxidation product (81 mg) formed light yellow needles with m.p. 279°, alone and mixed with anthraquinone.

Preparation of 9,10-dimethyl-9,10-dihydroanthracene

9,10-Dimethylantracene (1 g) was dissolved in 96 % ethanol and sodium amalgam added in portions. The solution was kept boiling gently and from time to time neutralized with concentrated hydrochloric acid. After 10 hours the solution was poured into water (500 ml) when the 9,10-dimethyl-9,10-dihydroanthracene (0.93 g) separated. It was sublimated in a vacuum and recrystallized from dilute methanol and formed colourless needles, m.p. 90°. Solutions of the dihydro-compound did not show fluorescence.

$C_{18}H_{18}$ (208.3)	Calc.	C 92.26	H 7.74
	Found	» 92.29, 92.15	» 7.91, 7.76

Oxidation: The dihydro-compound, oxidized in the usual way, gave anthraquinone, m.p. 279°.

Bromination: To a solution of the dihydro-compound (205 mg) in carbon tetrachloride bromine was added and the solution refluxed for 10 min. Hydrogen bromide evolved and a crystalline substance (272 mg) separated which was recrystallized from chloroform as yellow needles. The substance was decomposed on heating to about 300°.

$C_{18}H_{18}Br_2$ (364.1)	Calc.	C 52.78	H 3.32
	Found	» 52.66, 52.74	» 3.56, 3.42

Preparation of 9,9,10,10-tetramethyl-9,10-dihydroanthracene

A solution of *n*-propyl monochloroacetate (30 g) in benzene (300 g) to which anhydrous aluminium chloride (90 g) had been added was refluxed for 3 days. After adding ice-water and shaking the benzene layer was dried with sodium sulphate and the benzene distilled off. The remaining brown syrup did not crystallize and it was therefore subjected to fractional distillation in a vacuum. The first fraction formed a yellow mobile liquid

which obviously contained a di-*isopropyl*benzene (see below). The second fraction was a red viscous liquid. On keeping it in a refrigerator for some time it crystallized partly. The crystals were pressed on a porous plate and then recrystallized three times from ethanol. The new hydrocarbon (0.31 g) formed small white needles, m.p. 159°. Dissolved in ethanol it showed a weak fluorescence.

$C_{18}H_{20}$ (236.3)	Calc.	C 91.47	H 8.53
	Found	» 91.44, 91.40	» 8.14, 8.30

The first fraction was refractionated several times in a vacuum when a nearly colourless fraction 115–125° at 15 mm Hg was obtained.

$C_6H_4(C_3H_7)_2$ (162.3)	Calc.	C 88.82	H 11.18
	Found	» 87.65	» 10.73

Ortho-xylene and benzene with aluminium chloride

o-Xylene (10 g) and benzene (200 g) to which had been added anhydrous aluminium chloride (60 g) were refluxed for 15 hours. The reaction products isolated as described above were fractionated in a vacuum. The fraction collected between 150 and 200° was kept in a cool place when a small amount of crystalline material separated and was filtered off. After recrystallization several times from glacial acetic acid the colourless substance (20 mg) had m.p. 212–213°, alone and mixed with an authentic sample of anthracene. A small quantity of the hydrocarbon was oxidized with chromic acid. The light yellow oxidation product sublimated above 250° and gave a positive oxanthranol reaction when treated with zinc dust in alkaline solution.

Reactions with maleic anhydride

9,10-Dimethylanthracene: To the hydrocarbon (0.27 g) dissolved in benzene (40 ml) maleic anhydride (0.60 g) was added. The solution at first turned strongly yellow but the colour disappeared after boiling for 15 min. Letting the boiled solution stand for some time at room temperature the adduct (0.32 g) separated. On recrystallization from benzene it was obtained as white needles, m.p. 333° (in a closed tube).

$C_{20}H_{16}O_3$ (304.3)	Calc.	C 78.93	H 5.30
	Found	» 78.85, 78.79	» 5.08, 5.12

The corresponding free acid was obtained by dissolving the adduct in alkali and precipitating with hydrochloric acid.

$C_{20}H_{16}O_4$ (322.3)	Calc.	C 74.52	H 5.63
	Found	» 74.64, 74.52	» 5.69, 5.75

30.68 mg required 1.905 ml N/10 NaOH, $M = 322$

ω, ω' -Dibromo-*9,10-dimethylanthracene*: A mixture of the dibromo-product (0.38 g) and maleic anhydride (1.2 g) was left at 80° for 4 hours when the reaction was finished. In order to remove excess of maleic anhydride the reaction product was spread on a porous plate and again placed at 80°. The adduct was then obtained as a crystalline colourless substance insoluble in organic solvents. It was purified by washing with ether. The yield was quantitative.

$C_{20}H_{14}O_3Br_2$ (462.1)	Calc.	C 51.97	H 3.05
	Found	» 51.62, 51.70	» 3.06, 3.18

SUMMARY

By the reaction of ethyl monochloroacetate or chloroformate with benzene in the presence of aluminium chloride 9,10-dimethylanthracene was obtained besides a mixture of more and less ethylsubstituted benzenes. On using the *n*-propyl ester of monochloroacetic acid a tetramethyldihydroanthracene was obtained which must have all four methyl groups in the middle ring. A small

quantity of anthracene was isolated when *o*-xylene had reacted with benzene in the presence of aluminium chloride. The reduction of 9,10-dimethylantracene led to a dihydro-derivative with m.p. 90° being obviously different from the 9,10-dihydro-derivative described in the literature.

REFERENCES

1. Berner, E., and Gramstad, T. *Tidsskr. Kjemi, Bergv. Metallurgi* **11** (1951) 134.
2. Anschütz, R. *Ann.* **235** (1886) 299.
3. Barnett, E. de B., and Matthews, M. A. *Ber.* **59** (1926) 1429.
4. Kunckell, F., and Ulex, G. *J. prakt. Chem.* [2] **87** (1913) 230.
5. Badger, G. M., Goulden, F., and Warren, F. L. *J. Chem. Soc.* **1941** 18.

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