CII.—*Properties of the β-Chlorovinylarsines and their Interaction with Benzene in the Presence of Aluminium Chloride. Production of* 9 : 10-*Dimethylanthracene.*

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In a recent note (J., 1930, 2785) it was shown that a hydrocarbon of the probable formula $C_{16}H_{14}$ is produced by the interaction of ββ′-dichlorodivinylchloroarsine and benzene in the presence of aluminium chloride. No attempt was made to determine the constitution of the hydrocarbon, but Cook (*Chem. and Ind.*, 1931, **50**, 28) and E. Bergmann (private communication) suggested that it is 9 : 10-dimethylanthracene, which was synthesised by Barnett and Matthews (*Ber.*, 1926, **59**, 1432). The analytical figures of the hydrocarbon isolated in the above reaction showed definitely that it could not be $C_{16}H_{16}$, *i.e.*, the so-called 9 : 10-dimethyl-9 : 10-dihydroanthracene (Davidson and Lowy, *J. Amer. Chem. Soc.*, 1929, **51**, 2978), and we had unfortunately overlooked the prior work of Barnett and Matthews (*loc. cit.*), who, in addition to synthesising 9 : 10-dimethylanthracene, gave conclusive evidence that what had up to 1926 been described as 9 : 10-dimethyl-9 : 10-dihydroanthracene was actually 9 : 10-dimethylanthracene.

Dr. E. de Barry Barnett kindly sent us a pure specimen of 9 : 10-dimethylanthracene so that it might be directly compared with the hydrocarbon isolated by us. Before this could be done, a further quantity of ββ′-dichlorodivinylchloroarsine had to be prepared, and it seemed to be of interest to determine the nature of the product of the interaction of β-chlorovinyldichloroarsine and ββ′β″-trichlorotrivinylarsine respectively and benzene under the same conditions.

ββ′-Dichlorodivinylchloroarsine was prepared by reducing a hot solution of pure ββ′-dichlorodivinylarsonic acid (31·9 g.) in concentrated hydrochloric acid (100 c.c.), containing a little hydriodic acid, with sulphur dioxide. The precipitated oil was extracted with benzene, the extract dried with calcium chloride and evaporated, and the residue distilled twice under reduced pressure. 23·5 G. of the pure compound were obtained in addition to 5·3 g. which had a boiling point 1—2° lower than that of the main product. β-Chlorovinyldichloroarsine was prepared by reducing in a similar manner β-chlorovinylarsonic acid which had been recrystallised from acetone (compare Mann and Pope, J., 1922, **121**, 1755). The product was isolated in the usual way and repeatedly distilled under reduced pressure. ββ′β″-Trichlorotrivinylarsine was purified by repeated fractional distillation under reduced pressure. The following physical properties of these three substances in a high state of purity supplement the data given by previous workers (Green and Price, J., 1921, **119**, 448; Mann and Pope, *loc. cit.*; Burton and Gibson, J., 1926, 464) :

	M. p.	B. p.	$d_{4^\circ}^{t^\circ}$ (vac.).
(*a*) $CHCl{:}CH{\cdot}AsCl_2$	+0·1°	76·1°/10 mm.	1·8754 (26·1°); 1·8648 (30·0°)
(*b*) $(CHCl{:}CH)_2AsCl$	—	115—6/13 mm.	1·6926 (24·1); 1·6884 (27·1)
(*c*) $(CHCl{:}CH)_3As$	+18·0	136·5—7·5/12 mm.	1·5685 (22·0); 1·5631 (26·3)

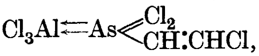
Each of these three substances as isolated may be a mixture of *cis*- and *trans*-isomerides, although the addition of arsenious chloride to acetylene might ordinarily lead to the formation chiefly of the *cis*-modification; compound (*a*) may exist in two, compound (*b*) in three, and compound (*c*) in four isomeric forms. The existence of mixtures of the isomerides, particularly of compound (*c*), may well account for the different melting points recorded for the substance (Green and Price, 3—4°; Mann and Pope, 23°). The three compounds show a strong tendency to remain supercooled in an ordinary freezing mixture but, with the exception of compound (*b*), which solidifies to a glass-like mass, crystallise readily when cooled in solid carbon dioxide–acetone.

The condensation of ββ′-dichlorodivinylarsine with benzene in the presence of aluminium chloride was carried out exactly as previously described (Gibson and Johnson, *loc. cit.*). The hydrocarbon obtained in small amount was recrystallised three times from alcohol and had m. p. 180—181°, alone or mixed with 9 : 10-dimethylanthracene. Further proof of the identity of the two substances was obtained by preparing the picrate, of the hydrocarbon now isolated, in benzene solution. After crystallisation, it was obtained in deep brown, soft needles, m. p. 176—177° (decomp.) (compare Barnett and Matthews, *loc. cit.*). This compound was also prepared by Anschütz (*Annalen*, 1886, **235**, 305), who considered it to be the picrate of 9 : 10-dimethyl-9 : 10-dihydroanthracene, $C_{16}H_{16}$; no analysis of the compound is recorded by Barnett and Matthews (Found : C, 60·9; H, 4·1. $C_{22}H_{17}O_7N_3$ requires C, 60·7; H, 3·9%).

β-Chlorovinyldichloroarsine (1 mol.) and ββ′β″-trichlorotrivinylarsine (1 mol.) were allowed respectively to react with benzene in the presence of aluminium chloride (1·1 mols.) in a similar manner and the product was worked up in the usual way. In the case of the trichlorotrivinylarsine, the product remaining after evaporation of the benzene was distilled under reduced pressure, and the hydrocarbon separated from much higher-boiling material. This hydrocarbon was obtained in much smaller yield than in the above case, and, after three crystallisations from alcohol, it had m. p. 180—181° and was identical with 9 : 10-dimethylanthracene (Found : C, 92·8, 92·9; H, 7·1, 7·0. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%).

After evaporation of the benzene solution obtained in the case of β-chlorovinyldichloroarsine, the hydrocarbon solidified without distillation and the amount obtained was much greater proportionally than in either of the other two cases. It was recrystallised from alcohol and finally from benzene. It had m. p. 180—181° and was identical with 9 : 10-dimethylanthracene.

Although 9 : 10-dimethylanthracene is apparently the chief product of the interaction of β-chlorovinyldichloroarsine with benzene in the presence of aluminium chloride, it is accompanied by considerable quantities of higher-boiling material (probably hydrocarbon or hydrocarbons) in the other two cases. In no case was the formation of any heterocyclic organic arsenical observed.

Whatever may be the complete mechanism of the formation of 9 : 10-dimethylanthracene in the reactions now described, it is not unlikely that a co-ordinate compound of the chlorovinylarsine and aluminium chloride, such as, *e.g.*,  $Cl_3Al\leftarrow As{<}\begin{matrix}Cl_2\\ CH:CHCl\end{matrix}$, may be the reactive substance in the first place, since the chlorovinylarsines readily dissolve aluminium chloride; also, it is probable that vinyl chloride may be present at some stage (compare Burton and Gibson, *loc. cit.*).

This work is strong confirmatory evidence that the so-called 9 : 10-dimethyl-9 : 10-dihydroanthracene, whether produced from ethylene bromide, ethylidene chloride, ethylidene bromide (Anschütz, *loc. cit.*), vinyl bromide (Angelbis and Anschütz, *Ber.*, 1884, **17**, 165), or vinyl chloride (Böeseken and Bastet, *Rec. trav. chim.*, 1913, **32**, 184; Davidson and Lowy, *loc. cit.*) and, in each case, benzene and aluminium chloride, is actually 9 : 10-dimethylanthracene (compare Barnett and Matthews, *loc. cit.*).

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