149. *The Formation of Carbinols in the Condensation of Aldehydes with Hydrocarbons.*

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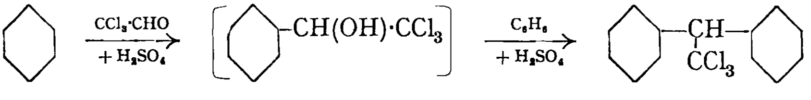
THE condensation of chloral with hydrocarbons under the influence of concentrated sulphuric acid was first observed by Baeyer with benzene (*Ber.*, 1872, **5**, 1089; 1873, **6**, 221; 1874, **7**, 1190) and was extended by his collaborators to toluene (*Ber.*, 1874, **7**, 1191), chloro- and bromo-benzene (*ibid.*, p. 2), and naphthalene (*ibid.*, p. 2), the products being βββ-trichloro-αα-diarylethanes. Probably, aryltrichloromethylcarbinols are intermediate products, but their occurrence in the reactions has not hitherto been observed, although many have been synthesised by other methods.



If benzene, toluene, or ethylbenzene and chloral are shaken with concentrated sulphuric acid, the hydrocarbon being added in such a way that any temporary local excess is avoided, the aryltrichloromethylcarbinol, which is formed in considerable amount, is not further acted upon and, on steam-distillation, comes over in great part before the βββ-trichloro-αα-diarylethane which is also formed; it is then purified by fractional distillation. The phenyl- and the tolyl-trichloromethylcarbinol obtained thus from benzene and toluene are identical with the carbinols obtained by Dinesmann (*Compt. rend.*, 1905, **141**, 201), using aluminium chloride as the condensing agent. The latter was shown by him to be the *p*-derivative, and by analogy the compound obtained from ethylbenzene must be p-*ethylphenyltrichloromethylcarbinol.*

That the carbinols are actually formed in the Baeyer condensation as intermediate compounds is shown by the fact that they themselves, in the presence of concentrated sulphuric acid, condense readily with a further molecule of the original hydrocarbon and yield βββ-trichloro-αα-diarylethanes identical with those obtained by using an excess of hydrocarbon. It seems reasonable to suppose that in these further condensations the position attacked by the $-CH(OH) \cdot CCl_3$ group in the second aryl ring is the same as in the first. Thus the product obtained by the condensation of *p*-tolyltrichloromethylcarbinol with toluene is βββ-trichloro-αα-di-*p*-tolylethane.

When an aryltrichloromethylcarbinol is condensed with a different hydrocarbon, a βββ-trichloro-αα-diarylethane containing two different aryl groups is obtained; *e.g.*, βββ-*trichloro*-α-*phenyl*-α-p-*tolylethane* may be prepared by the condensation either of phenyltrichloromethylcarbinol with toluene or of *p*-tolyltrichloromethylcarbinol with benzene.

Like other monohalogen-substituted benzenes, iodobenzene readily condenses with chloral under the influence of concentrated sulphuric acid with the formation of βββ-*trichloro-αα-di*-p-*iodophenylethane.* Corresponding carbinols have not, however, been isolated from the products of such condensations, although they are undoubtedly formed, the second stage of the reaction appearing to take place extremely readily and the carbinols not being easily separated by steam distillation. The aryltrichloromethylcarbinols themselves readily condense with the monohalogen-substituted hydrocarbons and yield the corresponding mixed ditanes.

When warmed for some time with alcoholic potash, all the βββ-trichloro-αα-diarylethanes lose hydrogen chloride and form ββ-dichloro-αα-diarylethylenes. These are colourless, beautifully crystalline compounds which combine directly with chlorine and with bromine and yield the corresponding substituted benzophenones when oxidised by chromic acid.

EXPERIMENTAL.

78 G. of benzene (1 mol.) were added in 2-g. portions at 5-minute intervals to a vigorously shaken solution of 500 g. of chloral hydrate (3 mols.) in 350 c.c. of concentrated sulphuric acid. Shaking was continued for 2 hours and the dark green emulsion then formed was poured into ice-water, a dark viscid greenish-black liquid separating. This was washed with water and steam-distilled for 36 hours. Phenyltrichloromethylcarbinol, which separated from the distillate in pale yellow, oily drops, was extracted in chloroform, dried, fractionally distilled under diminished pressure, and obtained as a colourless, somewhat viscid liquid, b. p. 145°/15 mm., which solidified on cooling and had m. p. 37° after crystallisation from ether (compare Dinesmann, *loc. cit.*) (Found : C, 42·4; H, 3·0; Cl, 47·3. Calc. for $C_8H_7OCl_3$: C, 42·6; H, 3·1; Cl, 47·2%). The acetate, m. p. 87·5° (Found : Cl, 39·7. Calc. : Cl, 39·8%), and benzoate, m. p. 97·5° (Found : Cl, 32·1. Calc. : Cl, 32·3%), were prepared.

The colourless solid remaining after the steam-distillation was crystallised from alcohol, and βββ-trichloro-αα-diphenylethane obtained as colourless leaflets, m. p. 64° (compare Baeyer, *Ber.*, 1872, **5**, 1098) (Found : Cl, 37·1. Calc. for $C_{14}H_{11}Cl_3$: Cl, 37·3%).

p-*Tolyltrichloromethylcarbinol* (compare Dinesmann, *loc. cit.*), prepared in exactly the same way, was obtained as a colourless viscid liquid, b. p. 155°/13·5 mm., which solidified; m. p. 63° (Found : C, 44·6; H, 3·7; Cl, 44·8. Calc. for $C_9H_9OCl_3$: C, 44·5; H, 3·8; Cl, 44·5%); the acetate, m. p. 107·5° (Found : Cl, 38·2. Calc. : Cl, 37·8%), and benzoate, m. p. 100·5° (Found : Cl, 31·2. Calc. : Cl, 31·0%), were prepared. βββ-*Trichloro-αα-di*-p-*tolylethane* formed colourless shining plates, m. p. 89°, from alcohol (compare Fischer, *Ber.*, 1874, **7**, 1191) (Found : Cl, 34·1. Calc. : Cl, 34·0%).

p-*Ethylphenyltrichloromethylcarbinol,* prepared in the same way from ethylbenzene, distilled in steam as a colourless viscid liquid, b. p. 175°/25 mm. (Found : Cl, 42·2. $C_{10}H_{11}OCl_3$ requires Cl, 42·0%).

Iodobenzene, when condensed with chloral, yielded βββ-*trichloro-αα-di*-p-*iodophenylethane,* colourless compact prisms, m. p. 172° (Found : Cl, 19·5; I, 47·1. $C_{14}H_9Cl_3I_2$ requires Cl, 19·8; I, 47·2%).

βββ-*Trichloro-α-phenyl-α*-p-*tolylethane.*—7·5 G. of phenyltrichloromethylcarbinol were dissolved in 3 g. of toluene (1 mol. + slight excess), and an equal volume of concentrated sulphuric acid added with vigorous shaking. The temperature rose to about 60° and a thick emulsion was formed, which was poured into ice-water, a thick, dark green liquid separating. This was washed with warm water until the washings were no longer acid and then dissolved in boiling alcohol. βββ-*Trichloro-α-phenyl-α*-p-*tolylethane,* which separated after several days, crystallised from alcohol in colourless shining plates, m. p. 72·5° (Found : Cl, 35·4. $C_{15}H_{13}Cl_3$ requires Cl, 35·6%). An identical compound was obtained from the condensation of benzene with *p*-tolyltrichloromethylcarbinol.

The following mixed βββ-trichloro-αα-diarylethanes were prepared in a similar way and crystallised from alcohol : βββ-*Trichloro-α-phenyl-α*-p-*chlorophenylethane,* compact colourless prisms, m. p. 74° (Found : Cl, 45·6. $C_{14}H_{10}Cl_4$ requires Cl, 45·8%). βββ-*Trichloro-α-phenyl-α*-p-*bromophenylethane,* long, slender, colourless prisms, m. p. 96° (Found : Cl, 29·0; Br, 21·7. $C_{14}H_{10}Cl_3Br$ requires Cl, 29·2; Br, 21·9%). βββ-*Trichloro-α-phenyl-α*-p-*iodophenylethane,* long, slender, colourless prisms, m. p. 119·5° (Found : Cl, 25·6; I, 30·4. $C_{14}H_{10}Cl_3I$ requires Cl, 25·9; I, 30·9%). βββ-*Trichloro-α*-p-*chlorophenyl-α*-p-*tolylethane,* colourless prisms, m. p. 81° (Found : Cl, 42·2. $C_{15}H_{12}Cl_4$ requires Cl, 42·5%). βββ-*Trichloro-α*-p-*bromophenyl-α*-p-*tolylethane,* compact colourless prisms, m. p. 102° (Found : Cl, 28·0; Br, 20·9. $C_{15}H_{12}Cl_3Br$ requires Cl, 28·1;

Br, 21·1%). βββ-*Trichloro*-α-p-*iodophenyl*-α-p-*tolylethane*, long, slender, colourless prisms, m. p. 117° (Found : Cl, 24·6; I, 29·5. $C_{15}H_{12}Cl_3I$ requires Cl, 25·0; I, 29·8%).

ββ-*Dichloro*-α-*phenyl*-α-p-*tolylethylene*.—10 G. of βββ-trichloro-α-phenyl-α-*p*-tolylethane were boiled under reflux for an hour with excess of a concentrated solution of alcoholic potash. On cooling, and addition of water, ββ-*dichloro*-α-*phenyl*-α-p-*tolylethylene* separated as a colourless solid. It crystallised from alcohol in slender prisms, m. p. 87·5° (Found : Cl, 27·3. $C_{15}H_{12}Cl_2$ requires Cl, 27·0%).

The following mixed ββ-dichloro-αα-diarylethylenes were prepared similarly and crystallised from alcohol : ββ-*Dichloro*-α-*phenyl*-α-p-*chlorophenylethylene*, long colourless prisms, m. p. 93° (Found : Cl, 37·8. $C_{14}H_9Cl_3$ requires Cl, 37·6%). ββ-*Dichloro*-α-*phenyl*-α-p-*bromophenylethylene*, long colourless needles, m. p. 113° (Found : Cl, 21·2; Br, 24·1. $C_{14}H_9Cl_2Br$ requires Cl, 21·6; Br, 24·4%). ββ-*Dichloro*-α-*phenyl*-α-p-*iodophenylethylene*, long colourless prisms, m. p. 108° (Found : Cl, 19·0; I, 34·1. $C_{14}H_9Cl_2I$ requires Cl, 18·9; I, 33·8%). ββ-*Dichloro*-α-p-*iodophenyl*-α-p-*tolylethylene*, short slender prisms, m. p. 90° (Found : Cl, 17·9; I, 32·3. $C_{15}H_{11}Cl_2I$ requires Cl, 18·2; I, 32·6%).

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