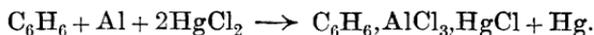


CXLIII.—*Modification and Extension of the Friedel and Crafts' Reaction. Part I.*

By JNANENDRA NATH RÂY.

RADZIEWANOWSKI (*Ber.*, 1895, **28**, 1139) suggested some modifications of the Friedel-Crafts' reaction, in one of which he used a mixture of aluminium powder and mercuric chloride. He prepared ethylbenzene in small yield, but did not obtain any triphenylmethane in the condensation of chloroform and benzene. Von Gulewitsch (*Ber.*, 1904, **37**, 1560) studied the interaction of mercuric chloride and aluminium in benzene, and isolated a compound,  $C_6H_6, AlCl_3, HgCl$ . A similar compound was formed with toluene. It was thought that if this double compound were employed as a catalyst, the secondary changes that rendered Radziewanowski's reaction unsuccessful might disappear. This expectation has been amply realised. Von Gulewitsch showed the course of the reaction to be



The mercury, liberated as above, forms an amalgam with the unchanged aluminium, but when an excess of mercuric chloride is employed, this tendency to amalgamate is reduced, inasmuch as

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the whole of the aluminium is utilised in reducing mercuric to mercurous chloride. The success of the reaction depends on the non-formation of the amalgam, as otherwise it acts concurrently with the double compound.

Some interesting products have been isolated in the condensation of the hydrocarbons with chloroform, carbon tetrachloride, benzylidene chloride, etc. Thianthren has been prepared in an 80 per cent. yield from benzene and sulphur. This compound was obtained in small amount along with phenyl mercaptan, phenyl sulphide, and phenyl disulphide by Friedel and Crafts (*Ann. Chim. Phys.*, 1888, [vi], **14**, 438) in the condensation of benzene and sulphur with aluminium chloride, whilst Genvresse (*Bull. Soc. chim.*, 1897, [iii], **17**, 599) observed the formation of thianthren and isothianthren in the same reaction.

9:10-Diphenyl-9:10-dihydroanthracene is formed by the condensation of benzene and chloroform, whilst in the ordinary Friedel-Crafts' reaction (*Annalen*, 1878, **194**, 254; 1885, **227**, 107), triphenylmethane, chloroarylmethanes, and tetraphenylethane (*Ber.*, 1893, **26**, 1952) are the products. The same compound is obtained by the interaction of benzylidene chloride and benzene.

Carbon tetrachloride and benzene give 9:9:10:10-tetraphenyl-9:10-dihydroanthracene, which is also obtained from benzotrichloride and benzene, whilst in the usual reaction, triphenylmethane, chloroarylmethanes (*Annalen*, 1878, **194**, 254), and tetraphenylethylene (*Ber.*, 1893, **26**, 1952) are obtained.

Similarly, *dimethyl-9:10-ditolyl-9:10-dihydroanthracene* has been obtained from chloroform and toluene. In this condensation, using aluminium chloride, Schwarz (*Ber.*, 1881, **14**, 1530) prepared tetratolyethane, which has the same melting point (215°) and empirical formula, but a mixture of the two melts at 206—208°. Benzylidene chloride and toluene yield *dimethyl-9:10-diphenyl-9:10-dihydroanthracene*.

Finally, chloropicrin and benzene, under the action of the reagent, furnish *ω*-nitrotriphenylmethane, previously obtained by the direct addition of nitrogen peroxide to triphenylmethyl (Schlenk, Mair, and Bornhardt, *Ber.*, 1911, **44**, 1172). Boedtker (*Bull. Soc. chim.*, 1908, [iv], **3**, 726) states, however, that all aliphatic nitro-compounds lose their nitro-groups under the influence of aluminium chloride, and obtained triphenylmethane and some triphenylcarbinol in this reaction.

## EXPERIMENTAL.

To a mixture of 20 c.c. of dry benzene and 20 grams of mercuric chloride contained in a flask with reflux condenser, 1 gram of aluminium powder was added gradually, and the flask vigorously shaken. The heat of the reaction caused the benzene to boil, and the flask was occasionally cooled in an ice-bath. A green, crystalline mass eventually separated, and the reaction was completed by immersing the flask in tepid water for half an hour. The mercury liberated in the reaction was removed, and the preparation of the catalyst was complete.

In all the reactions described below, the components were well agitated by a mechanical stirrer.

*Acetophenone*.—The calculated amount (1 mol.) of acetyl chloride was added through the condenser in small quantities at a time, the mixture allowed to remain for two hours at the ordinary temperature, and then heated to 40° for an hour. On cooling, it was decomposed with water, and the oil extracted with benzene, the benzene solution being dried and finally fractionated. The yield of acetophenone was 60 per cent. of the theoretical, whilst by Friedel and Crafts' method it is 55.5 per cent.

*p-Tolyl Methyl Ketone*.—Following an almost identical method, from 33 c.c. of toluene, 2.5 grams of aluminium, and 45 grams of mercuric chloride, 16.1 grams of this ketone were obtained.

*Thianthren*,  $C_6H_4 \begin{matrix} S \\ \diagup \quad \diagdown \\ S \end{matrix} C_6H_4$ .—The catalyst was prepared from 2.5 grams of aluminium, 45 grams of mercuric chloride, and 30 c.c. of benzene; 10 grams of flowers of sulphur were added, and the mixture was heated on the water-bath until hydrogen sulphide was no longer evolved. The product, on cooling, was decomposed with ice, filtered, and the residue repeatedly extracted with chloroform, from which the substance was obtained on concentration. When crystallised from acetone, it melted at 160°. The yield was 14 grams (Found: C=66.1; H=3.8; S=28.5. Calc.: C=66.6; H=3.7; S=29.6 per cent.).

*9:10-Diphenyl-9:10-dihydroanthracene*.—The catalyst was prepared from 1 gram of aluminium, 20 grams of mercuric chloride, and 15 c.c. of benzene. Six c.c. of chloroform were added drop by drop through the condenser, and the flask was allowed to remain at the ordinary temperature for two hours, and then heated for an hour at 40°, and then for another hour at 40–50°. On cooling, the product was decomposed with ice and filtered. There separated from the filtrate a deep red oil, from which some unchanged benzene was evaporated. The residue was extracted with

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boiling acetic acid containing a little water, from which the compound separated on cooling. After being crystallised from dilute alcohol, and then repeatedly from dilute acetone, the compound melted at  $159^{\circ}$  (Linebarger, *Amer. Chem. J.*, 1891, **13**, 556, gives  $164.2^{\circ}$ ) (Found: C=93.2; H=6.7. Calc.: C=93.9; H=6.1 per cent.).

The same compound was obtained by the interaction of 3 c.c. of benzylidene chloride, 8 c.c. of benzene, 0.5 gram of aluminium, and 10 grams of mercuric chloride, the reaction being completed at  $50-55^{\circ}$ . The product was isolated as described above (Found: C=94.0; H=6.39. Calc.: C=93.9; H=6.1 per cent.). A solution of 1 gram of the substance in acetic acid was oxidised with an acetic acid solution of chromium trioxide, and the product poured into water. The resinous mass was dried and then sublimed, and the sublimate was proved to be anthraquinone by the method of mixed melting points.

The *diacetyl* derivative was prepared by heating 1 gram of the substance with 10 c.c. of acetic anhydride and four drops of pyridine under reflux for an hour. The product was poured into water and neutralised with sodium carbonate. The viscous mass solidified, and, after being fractionally crystallised from dilute alcohol, melted at  $92^{\circ}$  (Found: C=85.3; H=7.4.  $C_{28}H_{24}O_2$  requires C=85.7; H=6.8 per cent.).

*Dimethyl-9:10-ditolyl-9:10-dihydroanthracene*.—This condensation was performed as in the preceding case, the catalyst being prepared from 1 gram of aluminium, 20 grams of mercuric chloride, and 15 c.c. of toluene. Chloroform (1 mol. for 2 mols. of toluene) was added through the condenser, and finally the reaction was completed at  $70^{\circ}$ . The oily product obtained after the decomposition of the mixture with ice, after being freed from chloroform and toluene, solidified when kept in a vacuum desiccator, and when crystallised from dilute acetic acid melted at  $215^{\circ}$  (Found: C=92.0; H=7.9.  $C_{30}H_{28}$  requires C=92.7; H=7.3 per cent.).

*Dimethyl-9:10-diphenyl-9:10-dihydroanthracene*.—The catalyst, prepared from 8 c.c. of toluene, 0.5 gram of aluminium, and 10 grams of mercuric chloride, was treated with 4 c.c. of benzylidene chloride, the reaction being completed by heating at  $60-70^{\circ}$  for two hours. The oily product obtained after the usual treatment was dried and distilled under diminished pressure, when some oily matter passed over, and the residue solidified. This was extracted with hot alcohol, and, on concentration, a product was obtained which, after crystallisation from acetic acid, melted at  $185^{\circ}$  (Found: C=92.8; H=7.0.  $C_{28}H_{24}$  requires C=93.3; H=6.7 per cent.).

9:9:10:10-Tetraphenyl-9:10-dihydroanthracene.—Eight c.c. of carbon tetrachloride were added to the catalyst, prepared from 20 c.c. of benzene, 1 gram of aluminium, and 20 grams of mercuric chloride, and the whole was kept at 50—60° for two hours, and then at 70° for an hour. After decomposing the product with ice and filtering, the dried residue was extracted with carbon disulphide, from which some of the tetraphenyl derivative was obtained. The filtrate separated into two layers, and the benzene layer, on evaporation, gave a further quantity of the substance, which, when crystallised from dilute acetone, melted at 159° (Found: C=94·0; H=6·8.  $C_{33}H_{28}$  requires C=94·2; H=5·8 per cent.). The same compound was obtained by adding 5 c.c. of benzotrichloride, in the course of half an hour, to the catalyst, prepared from 15 c.c. of benzene, 1 gram of aluminium, and 20 grams of mercuric chloride. The product, isolated as above, melted at 159° (Found: C=94·02; H=5·1. Calc.: C=94·2; H=5·8 per cent.).

*ω*-Nitrotriphenylmethane.—Five c.c. of chloropicrin were used with 20 c.c. of benzene. The mixture was warmed first in a tepid-water bath and then for a few hours at 45°. The product was decomposed with ice, distilled in a current of steam, and the residue filtered, dried, and extracted with much boiling alcohol. This, on concentration, deposited *ω*-nitrotriphenylmethane, which, on recrystallisation from alcohol, melted and decomposed at 145° (Found: C=78·49; H=5·54; N=4·5. Calc.: C=78·8; H=5·1; N=4·8 per cent.).

In conclusion, I wish to express my best thanks to Sir P. C. Rây for the interest he has taken in the work, and to Mr. M. L. Day for his criticisms and suggestions.

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