39. *Catalytic Dehalogenation by Tetrahydronaphthalenes in Presence of Copper.*

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In a number of cases it has been found possible (Gull and Turner, J., 1929, 491; Lesslie and Turner, J., 1930, 1758; 1931, 1188) to prepare unsymmetrically substituted diphenyl derivatives by the action of copper-bronze on mixtures of two dissimilar reactive halogeno-compounds. Definite failure, however, has attended our attempts to effect such syntheses using esters of 2-chloro-3 : 5-dinitrobenzoic acid (or of the corresponding bromo-acid) with *either* 2-*iododiphenyl ether or* 1-*iodotetrahydronaphthalene*, but certain interesting results have been obtained in carrying out these experiments.

2-Iododiphenyl ether itself reacted readily with copper-bronze at 200—220° to give 2 : 2′-*diphenoxydiphenyl*, but when ethyl 2-chloro-3 : 5-dinitrobenzoate was also present an inseparable mixture of products was formed, whilst a mixture of the iodo-ether with ethyl 2-bromo-3 : 5-dinitrobenzoate gave ethyl 4 : 6 : 4′ : 6′-tetranitrodiphenate in good yield as the only isolable product. In agreement with the observation of Ullmann and Engi (*Annalen*, 1909, **366**, 79) and contrary to that of Christie and Kenner (J., 1922, **121**, 614) we found that ethyl tetranitrodiphenate did not separate from benzene solutions with solvent of crystallisation.

When a mixture of ethyl 2-chloro-3 : 5-dinitrobenzoate and 1-iodotetrahydronaphthalene was heated at 200—220° with copper-bronze, the main product was ethyl 3 : 5-dinitrobenzoate. This very interesting result appeared to us to have been brought about by catalytic dehydrogenation, in presence of the copper, of the iodotetrahydronaphthalene, with subsequent dechlorination of the ester. In order to test this explanation, we submitted the chloro-ester to the action of copper in boiling tetrahydronaphthalene, and again ethyl 3 : 5-dinitrobenzoate was obtained in good yield. Under similar conditions, the same ester was obtained both from ethyl 4-chloro-3 : 5-dinitrobenzoate and from ethyl 2-bromo-3 : 5-dinitrobenzoate, and it appeared that a mixture of boiling tetralin and copper-bronze was an effective dehalogenating medium, at any rate for particular types of halogeno-compound.

In order further to substantiate our view as to the processes involved, we heated picryl chloride in tetrahydronaphthalene with copper-bronze, for it was anticipated that *s*-trinitrobenzene would be formed, and might separate during the working-up as its additive compound with naphthalene, produced by the dehydrogenation of the tetrahydronaphthalene. This actually occurred, and the additive compound was isolated in good yield.

It seemed probable that the tetrahydronaphthalene in these dehalogenations could be replaced by other relatively easily dehydrogenated substances. It was found, however, that ethyl 2-chloro-3 : 5-dinitrobenzoate was unaffected when heated in either decahydronaphthalene or *cyclo*hexanol with copper-bronze under conditions similar to those described above.

Although the chlorine atoms in 4 : 4'-*di*(*chloroacetyl*)*diphenyl* are highly reactive towards piperidine, this ketone did not undergo dehalogenation in boiling tetrahydronaphthalene in presence of copper, and it seems possible that when further work can be undertaken it will be found that the copper–tetralin reagent will distinguish between the two known types of reactive halogen atom.

EXPERIMENTAL.

2-*Iododiphenyl Ether*.—2-Aminodiphenyl ether (93 g.) was diazotised in dilute sulphuric acid (preferable to hydrochloric), and the solution was poured on a mixture of potassium iodide and ice. After warming, the ether was extracted with carbon tetrachloride, and the solution washed with alkali, dried, and freed from solvent. Vacuum distillation gave 90—100 g. of 2-*iododiphenyl ether*, b. p. 180—185°/15 mm. This solidified when cold and crystallised from light petroleum (b. p. 40—60°) or from alcohol in parallelepipeds, m. p. 55—55·5° (Found : I, 42·7. $C_{12}H_9OI$ requires I, 42·9%).

2 : 2'-*Diphenoxydiphenyl*.—2-Iododiphenyl ether was heated at 200—220°, and 1 part of copper-bronze added slowly. A steady reaction took place and after cooling and extraction with chloroform the *phenoxy*-compound was obtained solid. It crystallised from alcohol in needles, m. p. 100—101°. The vapour has a very penetrating odour, combining the peculiarities of diphenyl and diphenyl ether (Found : C, 85·1 ; H, 5·6. $C_{24}H_{18}O_2$ requires C, 85·2 ; H, 5·4%).

Action of Copper on Mixtures of 2-*Iododiphenyl Ether and* 2-*Halogeno*-3 : 5-*dinitrobenzoic Esters*.—(*a*) A mixture of methyl 2-chloro-3 : 5-dinitrobenzoate and iododiphenyl ether (equal parts) reacted with copper-bronze at 155°, but the product consisted of unchanged methyl ester, diphenoxydiphenyl, and iododiphenyl ether. Repetition of this experiment at 215° gave similar results.

(*b*) A mixture of ethyl 2-bromo-3 : 5-dinitrobenzoate (5·5 g.) and 5 g. of the iodo-ether was heated until it began to react with copper-bronze. This occurred at 180°, and the condensation was made to proceed at about this temperature, 5 g. of copper being added in all. *o*-Dichlorobenzene was added, and the copper, etc., removed. Addition of light petroleum and a little acetone to the filtrate gave a solid, m. p. 124—126°, which crystallised from benzene or from alcohol in rosettes of rectangular needles, m. p. 127—129°. After three further crystallisations from benzene the m. p. was 129—130°. The substance showed no signs of premature melting, and contained no benzene of crystallisation (Found : C, 45·1; H, 3·2. Calc. : C, 45·2; H, 2·95%. Calc. for $\frac{1}{2}C_6H_6$ of crystallisation : C, 48·7; H, 3·3%). Hydrolysis of the ester gave the acid, m. p. 288° (decomp.).

The identity of the ethyl ester was established by comparing it with ethyl tetranitrodiphenate prepared by heating ethyl 2-chloro-3 : 5-dinitrobenzoate at 220° and slowly adding copper-bronze as interaction proceeded. The whole was treated with *o*-dichlorobenzene, and the liquid filtered. The cooled filtrate deposited ethyl tetranitrodiphenate, and more was obtained by removing the mother-liquor solvent in steam, and crystallising the residue from alcohol (charcoal).

Since the methyl ester was largely recovered unchanged from the (*a*) experiments, we heated it alone with copper-bronze. No reaction took place below 140°, and the lowest satisfactory temperature for condensation was 155—165°. This temperature is considerably higher than that given by Ullmann and Engi (*loc. cit.*). The product was treated with dichlorobenzene, the solution filtered, and the excess of solvent distilled off. Crystallisation set in on cooling and was completed by addition of light petroleum. The methyl tetranitrodiphenate obtained was crystallised from methyl alcohol and then had m. p. 173—174°, unchanged after crystallisation from benzene.

1-*Iodotetrahydronaphthalene.*—Tetrahydro-α-naphthylamine (Green and Rowe, J., 1918, **113**, 955) was diazotised in hydrochloric acid solution. The filtered diazo-solution reacted smoothly with cold potassium iodide solution, and warming was unnecessary for completing the separation of the iodotetralin. This in carbon tetrachloride was washed with alkali and purified by vacuum distillation. 1-*Iodotetrahydronaphthalene* was obtained as a colourless oil, b. p. 150°/17 mm. or 153°/19 mm. In the same apparatus, 1-iodonaphthalene boiled at 168—169°/21 mm. (Found : I, 48·3. $C_{10}H_{11}I$ requires I, 49·2%). Small quantities of the iodotetralin boiled at 279—280°/765 mm., but large quantities underwent extensive decomposition long before ebullition began. The average yield of iodotetralin was 50 g. from 100 g. of α-naphthylamine.

In spite of repeated purification, the iodotetralin slowly deposited a crystalline film on being kept, but showed no great tendency to lose iodine, in contrast to iodonaphthalene. It reacted with magnesium in ethereal solution.

Interaction of Iodotetrahydronaphthalene, Ethyl 2-*Chloro*-3 : 5-*dinitrobenzoate and Copper-bronze.*—A mixture of 10 g. of the iodo-compound with 10 g. of the ester was heated at 200°. On addition of copper, an immediate steady reaction set in, which was maintained by addition of copper as required. The temperature range was 210—225°. When no further change was apparent, the mixture was treated with hot *o*-dichlorobenzene, and the liquid filtered. The product was worked up either by distilling off most of the solvent and precipitating the ester from concentrated solution with light petroleum, or by distilling all of it in steam and extracting the residue with alcohol. Either process had to be followed by recrystallisation of tarry first crops from alcohol in presence of charcoal. The product (average yield, 2·5—3 g.) had m. p. 95—96° and was ethyl 3 : 5-dinitrobenzoate (Found : C, 45·3; H, 3·3; N, 11·8; *M*, 232. Calc.: C, 45·0; H, 3·3; N, 11·7%; *M*, 240).

Hydrolysis of the ester gave 3 : 5-dinitrobenzoic acid, m. p. 204—205° (Found : C, 40·0; H, 2·15; N, 13·4. Calc.: C, 39·6; H, 1·9; N, 13·4%).

Dehalogenation of Ethyl 2-*Chloro*-3 : 5-*dinitrobenzoate.*—A solution of 10 g. of the ester in 10 g. of tetrahydronaphthalene was heated at 200—215°, and copper-bronze added so as to give a steady reaction (10 g. were used—a definite excess). The product was treated with tetralin, and the filtered solution steam-distilled; the brownish residue was extracted with boiling alcohol in presence of charcoal. After concentration of the extract to about 60 c.c., needles separated, and these, after recrystallisation from alcohol (charcoal), had m. p. 94—96° and did not depress the m. p. of authentic ethyl 3 : 5-dinitrobenzoate.

Conversion of Picryl Chloride into s-*Trinitrobenzene.*—A solution of 10 g. of picryl chloride in 10 g. of tetralin reacted with copper-bronze at about 195°. Dehalogenation proceeded regularly, the mixture keeping hotter than the bath. When 10 g. of copper had been used, tetralin was added, and the liquid filtered hot. On cooling, a solid separated, m. p. 140—145° with softening at about 120°. This crystallised from alcohol in yellow needles, m. p. 152—153°, alone or mixed with the 1 : 1 additive compound of naphthalene and *s*-trinitrobenzene.

Having thus established the presence of naphthalene in the reaction product, we modified our process of working up the mixture in later experiments : the filtered tetralin extract was poured into alcohol, and naphthalene added. In this way a good yield of the pure additive compound was obtained.

Picryl chloride and decahydronaphthalene do not mix at 180—

200° and the dehalogenation could not therefore be tried in decahydronaphthalene.

4 : 4′-*Di(chloroacetyl)diphenyl.*—Chloroacetyl chloride (94 g.) was gradually added to a mixture of 50 g. of diphenyl, 135 g. of anhydrous aluminium chloride, and 50 c.c. of carbon disulphide. Hydrogen chloride was steadily evolved and a red-brown solid separated. The mixture was eventually heated in warm water for one hour, then cooled, and treated with much dilute hydrochloric acid with vigorous shaking. An ochreous powder separated and the carbon disulphide boiled off. The product crystallised from *cyclo*hexanone in large irregular brownish needles. Small quantities were obtained colourless from phenol or xylene (long needles), and melted at 226—227° (uncorr.) (Found : Cl, 22·4. $C_{16}H_{12}O_2Cl_2$ requires Cl, 23·1%).

The *ketone* reacted vigorously with piperidine, but was recovered unchanged from a mixture of boiling tetrahydronaphthalene and copper-bronze.

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