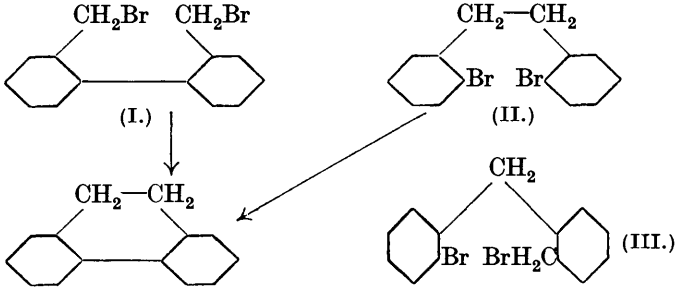
CLI.—*Jackson and White's Synthesis of Phenanthrene.*

By James Kenner and John Wilson.

It was shown some years ago (Kenner and Turner, J., 1911, **109**, 2101) that ωω′-dibromo-2 : 2′-ditolyl (I) is converted by treatment with sodium into a product from which, by oxidation, phenanthraquinone is obtained to the extent of 26% of that theoretically possible. At the same time it was pointed out that the initial material represents one of the possible intermediate products in the conversion of *o*-bromobenzyl bromide into a phenanthrene derivative through the agency of sodium.



The yield of phenanthraquinone obtained by Jackson and White (*Amer. Chem. J.*, 1880, **2**, 383) in this manner amounted, however, to only 2·66%. On the other hand, consideration of the relative reactivities of the two bromine atoms in *o*-bromobenzyl bromide suggests 2 : 2′-dibromodibenzyl (II) as the compound most likely to be produced in the first stages of the reaction. Since, then, anthracene was isolated to the extent of nearly 20% of that theoretically possible, and presumably was derived from 2-bromophenyl-ω-bromo-*o*-tolylmethane (III), it appeared that the action of sodium on 2 : 2′-dibromodibenzyl must furnish as chief product some other compound than dihydrophenanthrene, and it became of interest to investigate this point experimentally.

The dibromo-compound was prepared by the reaction discovered by Busch and Weiss (*Ber.*, 1900, **33**, 2701), consisting in the oxidation of *as*-dibenzylhydrazines by mercuric oxide :

$$(CH_2Ph)_2N\cdot NH_2 + HgO = CH_2Ph\cdot CH_2Ph + N_2 + H_2O + Hg.$$

It was then found that 2 : 2′-*dibromodibenzyl* is converted by treatment with sodium to the extent of more than 50% into dibenzyl, accompanied by other products, including phenanthrene or its dihydro-derivative. By oxidation of the mixture, phenanthraquinone was obtained in a yield of 12% of that theoretically possible, calculated on the weight of the original material. Whilst, therefore, the earlier synthesis connected phenanthrene with ditolyl, the present work, like Pschorr's valuable general synthesis, shows its relationship to dibenzyl.

The formation of dibenzyl, which was also noted by Jackson and White in their experiments, represents a not uncommon type of side reaction in syntheses of this kind (compare Schlubach and Goes, *Ber.*, 1922, **55**, 2889) and is perhaps not surprising in this instance, since Ullmann (*Annalen*, 1904, **332**, 40) found that only a 5% yield of diphenyl is obtained from bromobenzene by the Fittig reaction. In dibromoditolyl, this stage of the synthesis is already achieved, so that a better yield of phenanthrene derivative is obtained from this compound.

By applying the above result to the data supplied by Jackson and White, it is possible to account for almost the whole of their material on the hypothesis that dibromodibenzyl is the source of the phenanthrene derivative obtained by them. Thus their yield of 2·66% involves conversion of 22·2% of the original material into dibromodibenzyl. Their observation that only 75·4% of the total available bromine was eliminated as sodium bromide would correspond to 49·2% of material of which debromination was only half complete. These amounts, together with 19·8% converted into anthracene and 12·5% into products of indeterminate character, account satisfactorily for all the material, and it may therefore be concluded that the phenanthrene derivative obtained by Jackson and White originated for the most part from dibromodibenzyl.

When the reaction between *o*-bromobenzyl bromide and hydrazine hydrate in alcoholic solution was carried out either at the ordinary temperature or at 100°, the desired product was accompanied by a considerable proportion of *tri*-o-*bromobenzylhydrazine*,

$$(C_6H_4Br{\cdot}CH_2)_2N{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4Br \text{ (IV)},$$

and of non-basic material, corresponding in composition to o-*bromobenzylidenedi*-o-*bromobenzylhydrazone*,

$$(C_6H_4Br{\cdot}CH_2)_2N{\cdot}N{:}CH{\cdot}C_6H_4Br \text{ (V)}.$$

In their analogous preparation of dibenzylhydrazine, Busch and Weiss (*loc. cit.*) had similarly noted the formation of benzylidenebenzylhydrazone, and tentatively explained it by the equation :

$$2(CH_2Ph)_2N{\cdot}NH_2 = (CH_2Ph)_2N{\cdot}N{:}CHPh + CH_2Ph{\cdot}NH{\cdot}NH_2.$$

Although, in support of this view, they described the isolation of the hydrazone as a product of the reduction of dibenzylnitrosoamine, Busch and Weiss were unable to detect the benzylhydrazine formulated as the second product, and it will also be seen that the two sides of the equation do not balance. In our experiment, it seemed simpler to attribute the formation of (V) to oxidation of (IV), and in fact this reaction was shown to occur rapidly and quantitatively when the hydrochloride of (IV) was boiled in alcoholic solution with a little cupric oxide. Busch and Weiss observed the formation of tribenzylhydrazine in their experiment, whilst Franzen and Kraft (*J. pr. Chem.*, 1911, **84**, 157) showed that it could be obtained by direct benzylation of hydrazine, and also prepared it from benzylidenedibenzylhydrazone by reduction.

A further study of the reaction between benzyl chloride and hydrazine showed that some tribenzylhydrazine is produced even when the amount of hydrazine used is twice that required for dibenzylation, whilst when the reactants in equimolecular proportion were heated in alcoholic solution, the tribenzylhydrazine, which constituted the main product, was accompanied by some tetrabenzylhydrazine. This compound had previously been prepared by Wieland and Schomberg by treating tribenzylhydrazine with benzyl bromide (*Ber.*, 1920, **53**, 1329).

Finally, it was shown that tribenzylhydrazine hydrochloride could be oxidised to benzylidenedibenzylhydrazone by atmospheric oxygen in hot dilute alcoholic solution.

EXPERIMENTAL.

Comparative experiments showed decomposition of a solution of *o*-toluenediazonium bromide with Naturkupfer C, first at 0° and ultimately at 40°, to be the best method of preparing *o*-bromotoluene. Its monobromination was achieved very satisfactorily at 135° by adding 75% of the calculated quantity of bromine. *o*-Bromobenzyl bromide, separated by fractionation, boiled at 129°/19 mm.

Interaction of o*-Bromobenzyl Bromide and Hydrazine.*—When a cooled solution of the bromide (10 g.) in alcohol (15 c.c.) was treated with hydrazine hydrate (2·5 g.), a vigorous reaction occurred with evolution of heat and separation of an oily layer of aqueous hydrazine hydrochloride. This salt separated in needles after the mixture had been boiled for 1 hour and concentrated to one-third of the original bulk and the residue cooled. The other products were isolated by extracting the supernatant liquor with ether, after dilution with water (1 l.). When the dried ethereal solution was treated with an alcoholic solution of hydrogen chloride, *di-*o*-bromobenzylhydrazine hydrochloride* (3·5 g.), m. p. 205°, was precipitated. After purification by solution in alcohol (35 c.c.) and precipitation by ether (70 c.c.), it was obtained in matted, colourless needles, m. p. 214° (Found: N, 7·1; equiv., 406. $C_{14}H_{14}N_2Br_2$,HC2 requires N, 6·9%; equiv., 406·5). Its *benzylidene* derivative forms white plates, m. p. 116° (Found: N, 6·2. $C_{21}H_{18}N_2Br_2$ requires N, 6·1%).

*Tri-*o*-bromobenzylhydrazine hydrochloride*, which crystallises in hexagonal prisms, m. p. 194° (Found: N, 4·9. $C_{24}H_{19}N_2Br_3$,HCl requires N, 4·9%), is soluble in a mixture of alcohol and ether. It separated from the mother-liquor after precipitation of dibromobenzylhydrazine hydrochloride in the manner just described. Both were, however, precipitated when dry hydrogen chloride was passed directly into the above dried ethereal solution. The tribromobenzyl derivative was rapidly oxidised in boiling alcoholic solution by cupric oxide, and gradually by atmospheric oxygen during recrystallisation, to o*-bromobenzylidenedi-*o*-bromobenzylhydrazine*, which formed prisms, m. p. 108° (Found: N, 5·4; Br, 44·9. $C_{21}H_{17}N_2Br_3$ requires N, 5·2; Br, 44·7%).

Synthesis of Phenanthraquinone.—2 : 2′*-Dibromodibenzyl* was obtained in almost quantitative yield by adding yellow mercuric oxide to a solution of dibromodibenzylhydrazine, prepared by shaking the hydrochloride with dilute sodium hydroxide solution and chloroform. It separated from alcohol in plates, m. p. 84·5° (Found: Br, 47·15. $C_{14}H_{12}Br_2$ requires Br, 47·1%).

When the dibromo-derivative (5 g.) was boiled under reflux with a suspension of sodium powder (5 g.) in dry ether for 14 days, 96·6% of the bromine was obtained in the ionic condition. On evaporation, the ethereal solution furnished an oil (2·60 g.), from which dibenzyl (1·42 g.) crystallised. This was purified by steam distillation and identified by comparison with an authentic specimen. In two concordant experiments, oxidation of the oil by a solution of chromic acid in glacial acetic acid, followed by the usual procedure for purification, yielded phenanthraquinone corresponding to 12% of that theoretically possible.

Interaction of Benzyl Chloride with Hydrazine.—(a) The observation that dibromodibenzylhydrazine yields a monohydrochloride rendered it necessary to examine the product described by Busch and Weiss as the dihydrochloride of dibenzylhydrazine. Analysis showed the salt, m. p. 202° (Busch and Weiss give m. p. 200°), to be a *monohydrochloride* (Found : N, 11·5; equiv., 249·5. $C_{14}H_{16}N_2$,HCl requires N, 11·3%; equiv., 248·5).

(b) In order to study its tendency to oxidise, tribenzylhydrazine was prepared by boiling benzyl chloride (22 g.), hydrazine hydrate (8·7 g.), and alcohol (25 c.c.) together for 1 hour and finally concentrating the mixture to one-third of its original bulk. Hydrazine hydrochloride separated on cooling; the filtrate was then diluted and extracted with ether. From the dried ethereal solution tribenzylhydrazine hydrochloride (22 g.), m. p. 181° (Found : N, 4·9%; equiv., 336), was obtained by treatment with alcoholic hydrogen chloride. Tetrabenzylhydrazine, m. p. 139° (Found : N, 7·3%), was isolated in small amount from the liquor.

When air was passed through a boiling solution of tribenzylhydrazine hydrochloride (1 g.) in alcohol (100 c.c.) for 8 hours, 0·25 g. of pure benzylidenedibenzylhydrazine, m. p. 87°, was obtained, whereas a quantitative yield was obtained after a few minutes in presence of cupric oxide. Dibenzylhydrazine hydrochloride, on the other hand, did not undergo atmospheric oxidation.

A series of experiments in which benzyl chloride was similarly treated with variously excessive proportions of hydrazine hydrate showed that the formation of tribenzylhydrazine and the corresponding hydrazone to a greater or less extent always accompanies that of dibenzylhydrazine. The formation of the hydrazone observed by Busch and Weiss may therefore safely be ascribed to oxidation of tribenzylhydrazine. Separation of the two hydrazine hydrochlorides was effected by taking advantage of the smaller solubility of the dibenzyl derivative in ether and by crystallising the tribenzyl derivative from alcohol.

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