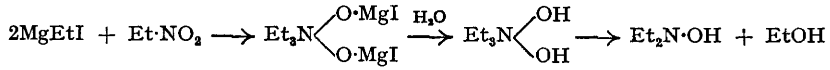
288. *Aliphatic Nitro-compounds. Part IX. Reaction of Nitro-paraffins with Ethylmagnesium Bromide.*

By G. D. Buckley.

In the reaction of nitroethane with ethylmagnesium bromide the first stage is addition of the Grignard reagent to the N=O bond to form a complex (III) which on reduction with zinc and hydrochloric acid gives diethylamine. The complex may react with a second mol. of ethylmagnesium bromide with evolution of 1 mol. of ethane to form a new complex which yields *NN*-diethylhydroxylamine on hydrolysis. Nitromethane, 2-nitropropane, and 2-nitro-2-methylpropane form analogous complexes.

The action of Grignard reagents on nitro-paraffins was first examined by Moureu (*Compt. rend.*, 1901, **132**, 837), who observed that nitroethane reacted with 2 mols. of ethylmagnesium iodide to form *NN*-diethylhydroxylamine. He suggested that the reaction involved the direct addition of both mols. of Grignard reagent to the N=O bonds, followed by breakdown on hydrolysis :

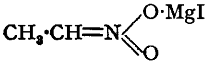


$$\mathrm{2MgEtI + Et{\cdot}NO_2 \longrightarrow Et_3N}\begin{matrix}\mathrm{O{\cdot}MgI}\\ \mathrm{O{\cdot}MgI}\end{matrix} \xrightarrow{\mathrm{H_2O}} \mathrm{Et_3N}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix} \longrightarrow \mathrm{Et_2N{\cdot}OH + EtOH}$$

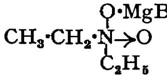
(I.)

Bevad (*Ber.*, 1907, **40**, 3065) studied the reactions of primary and secondary nitro-paraffins with several alkyl-zinc and -magnesium iodides. He found that nitroethane reacted with ethylmagnesium iodide with evolution of ethane and a little ethylene to give a complex which on hydrolysis gave *NN*-diethylhydroxylamine accompanied by smaller amounts of diethylamine and ethyl-*sec.*-butylhydroxylamine. Ethylzinc iodide reacted in a similar manner, but gave ethyl-*sec.*-butylhydroxylamine as the main product. Similar results were obtained with 1- and 2-nitropropanes. As the first stage in the reaction, Bevad postulated reaction of the Grignard reagent with the *aci*-form of the nitro-paraffin to give the complex (II), followed by addition of one or two mols. of Grignard reagent to the double bonds :

(II.)



$$\mathrm{CH_3{\cdot}CH{=}N}\begin{matrix}\mathrm{O{\cdot}MgI}\\ \searrow\mathrm{O}\end{matrix}$$



$$\mathrm{CH_3{\cdot}CH_2{\cdot}}\overset{\mathrm{O{\cdot}MgBr}}{\underset{\mathrm{C_2H_5}}{\mathrm{N}}}\mathrm{{\rightarrow}O}$$

(III.)

It was later shown by Zerewitinoff (*Ber.*, 1910, **43**, 3593) that primary and secondary nitro-paraffins reacted with methylmagnesium iodide to give slightly less than 1 equivalent of methane, and he also considered that this arose from reaction with the *aci*-nitro-paraffin. Finally Wang (*Trans. Sci. Soc. China*, 1933, **7**, 253) made a detailed study of the products obtained by the action of excess of phenylmagnesium bromide on nitromethane. The chief products were phenylmethylhydroxylamine, phenylbenzylhydroxylamine, phenol, and benzene, and a mechanism was formulated, differing in detail from Bevad's theory, but also based on the preliminary formation of a complex of type (II).

All the theories so far advanced are inadmissible since they involve quinquecovalent nitrogen; a complex of type (I) as advocated by Moureu would be expected to yield a trialkylamine oxide and not a dialkylhydroxylamine on hydrolysis. The theories advanced by subsequent authors all postulate the preliminary tautomeric change of the nitro-compound to the *aci*-form, though no evidence has been adduced for the occurrence of this change, which normally requires strongly ionising conditions.

The reaction has therefore been re-examined, particular attention being directed to the initial stages. Treatment of nitroethane with 1 mol. of ethylmagnesium bromide at 0° resulted in a vigorous exothermic reaction to form a solid complex which separated from the solution. No gas was evolved during this reaction, but on addition of a further 2 mols. of Grignard reagent the complex largely redissolved and 1 mol. of gas was evolved; this reaction was relatively slow and required heating to drive it to completion. The gas was not identified, but was assumed to be mainly ethane on the evidence of Bevad (*loc. cit.*). The unreacted Grignard reagent, estimated by treating the mixture with water and collecting the evolved gas, amounted to 1 mol. The main liquid product was diethylhydroxylamine. The initial complex was shown by analysis to be an addition product of equimols. of nitroethane and ethylmagnesium bromide, and on reduction with zinc and hydrochloric acid it gave diethylamine in 60% yield. It must therefore have the structure (III). The analogous complex from nitromethane gave methylethylamine on reduction. Similar addition products were obtained by the action of ethylmagnesium bromide on 2-nitropropane and 2-nitro-2-methylpropane, but attempts to reduce them with zinc and hydrochloric acid failed owing to their instability.

It is evident from these results that the first step in the reaction of a nitro-paraffin with ethylmagnesium bromide is the addition of the Grignard reagent to the N=O bond to form a complex of type (III), which is then reduced by a second mol. of Grignard reagent, by a mechanism which is still obscure, to a product which on hydrolysis yields the dialkylhydroxylamine.

EXPERIMENTAL.

The nitro-paraffins used were purified by repeated distillation over phosphoric oxide, followed by thorough washing with water, drying ($CaCl_2$), and fractionation through a Widmer column. An ethereal solution of ethylmagnesium bromide was filtered through glass wool; the ethylmagnesium bromide content was determined by the method of Gilman *et al.* (*J. Amer. Chem. Soc.*, 1923, **45**, 150), and the solution was then diluted with dry ether to a concentration of 2 g.-mols. per l.

Nitroethane.—(*a*) A solution of nitroethane (7·5 g.) in pure dry ether (25 c.c.) was placed in a flask cooled in ice–salt and fitted with a mercury-sealed stirrer, reflux condenser, dropping funnel, and system for collecting evolved gases. Ethylmagnesium bromide solution (50 c.c.) was added dropwise to the stirred solution during 1 hour at − 5° to 0°. A strongly exothermic reaction took place and a heavy white precipitate was formed, but no gas was evolved. A further 100 c.c. of the Grignard solution was added during 1 hour, by which time the precipitate had largely redissolved and 1400 c.c. of gas had been evolved. The mixture was then refluxed for 1 hour (resulting in the evolution of a further 800 c.c. of gas), cooled in ice, and treated with water (50 c.c.) dropwise at 0—10°. During the addition of the water, 2200 c.c. of gas were evolved.

(*b*) Ethylmagnesium bromide solution (50 c.c.) was added dropwise during 1 hour to a stirred solution of nitroethane (7·5 g.) in pure dry ether (100 c.c.) at − 5° to 0°. The mixture was then refluxed for 1 hour; no gas was evolved. After cooling, the precipitate was collected, washed with pure dry ether, and dried in a vacuum at 20°, giving a hygroscopic white powder (17·4 g.) which appeared to decompose on treatment with water (Found: Br, 37·25; Mg, 11·65. $C_4H_{10}O_2NBrMg$ requires Br, 38·45; Mg, 11·54%).

This *complex* (15 g.) was dissolved in 19% hydrochloric acid (200 c.c.) with ice-cooling, and granulated zinc (30 g.) was added. The reduction was completed by heating on the steam-bath for a short time and the mixture was then cooled in ice, basified with excess of 32% sodium hydroxide solution, and steam-distilled into N-hydrochloric acid (100 c.c.); back-titration of the distillate with N-sodium hydroxide showed that base equivalent to 45·3 c.c. of N-acid (60% theory) had distilled. The neutralised solution was evaporated to dryness and the crude hydrochloride treated with concentrated sodium hydroxide solution. The base, which separated as a volatile oil, reacted with picryl chloride to give a picramide, m. p. 164—165°, not depressed on admixture with diethyl picramide, m. p. 165° (Found: N, 19·8. Calc. for $C_{10}H_{12}O_6N_4$: N, 19·7%). With phenyl *iso*cyanate the base gave a urea, m. p. 83—84°, not depressed on admixture with *N′*-phenyl-*NN*-diethylurea, m. p. 84°.

(*c*) Ethylmagnesium bromide solution (750 c.c.) was added during 2 hours to a stirred solution of nitroethane (37·5 g.) in dry ether (100 c.c.) at 0—10°. The mixture was refluxed for 4 hours, cooled, poured into ice, and steam-distilled until the distillate was only faintly alkaline to brilliant-yellow paper. The distillate was acidified with hydrochloric acid, and the ethereal layer was separated, washed with water, and discarded. The combined aqueous layer and washings were concentrated under reduced pressure, cooled, treated with a large excess of sodium hydroxide, and extracted with ether. The extract was dried (KOH) and fractionated to give diethylhydroxylamine as a colourless oil (20·4 g.), b. p. 50—52°/18 mm. (Found: equiv., 88·3. Calc. for $C_4H_{11}ON$: equiv., 89), together with small amounts of a volatile base, probably diethylamine, and a high-boiling residue which was not further examined.

Nitromethane.—Nitromethane (6·1 g.) was brought into reaction with ethylmagnesium bromide solution (50 c.c.) by the method (*b*) described above for nitroethane. This gave the *complex* (14·5 g.) as a hygroscopic white powder (Found: Br, 41·75; Mg, 12·65. $C_3H_8O_2NBrMg$ requires Br, 41·25; Mg, 12·4%). Reduction with zinc and hydrochloric acid gave methylethylamine (63% yield), characterised as the picrate, m. p. 96°, and the hydrobromide, m. p. 87—88° (Found: Br, 57·2. Calc. for C_3H_9N,HBr: Br, 57·15%).

2-*Nitropropane.*—2-Nitropropane (8·9 g.) was brought into reaction with ethylmagnesium bromide solution (50 c.c.) by the method (*b*) described above for nitroethane to give the *complex* (17·2 g.) as a hygroscopic white powder (Found: Br, 35·3; Mg, 10·65. $C_5H_{12}O_2NBrMg$ requires Br, 36·05; Mg, 10·8%).

Nitro-tert.-*butane*.—Nitro-*tert*.-butane (10·3 g.) was brought into reaction with ethylmagnesium bromide solution (50 c.c.) by the method (*b*) described above for nitroethane. This gave a hygroscopic white *complex* (10 g.) (Found: Br, 34·2; Mg, 10·3. $C_6H_{14}O_2NBrMg$ requires Br, 33·9; Mg, 10·15%).

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