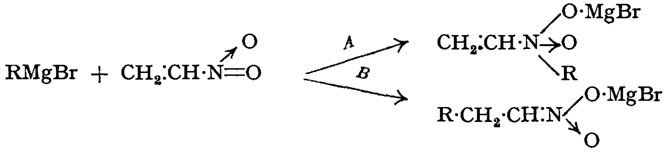
289. *Aliphatic Nitro-compounds. Part X. Action of Grignard Reagents on the α-Nitro-olefins.*

By G. D. Buckley.

The reactions of ethyl- and butyl-magnesium bromides with two primary and one secondary α-nitro-olefins have been studied, and, although most of the reaction products have been identified, several points in the mechanism remain obscure. The initial step is a rapid 1 : 4-addition of the Grignard reagent to the conjugated system C:C·N:O to give a complex which may be decomposed by water to give a nitro-paraffin, or may react with more Grignard reagent to give another complex which on treatment with water yields an oxime. Simultaneously, some 1 : 2-addition to the nitro-olefin occurs, to give a complex which with water gives basic products, probably dialkylhydroxylamines.

Although organo-magnesium halides readily add to the N═O bond of the nitro-group (see Part IX of this series), Kohler and Stone (*J. Amer. Chem. Soc.*, 1930, **52**, 761) have shown that α-nitrostilbene and triphenylnitroethylene react with organo-magnesium halides to give exclusively 1 : 4-addition products. It was therefore of interest to study the reaction of Grignard compounds with aliphatic nitro-olefins to find whether 1 : 2-addition (Type *A*) or 1 : 4-addition (Type *B*) predominated.



$$\mathrm{RMgBr} + \mathrm{CH_2{:}CH{\cdot}N(\to O){=}O} \xrightarrow{A} \mathrm{CH_2{:}CH{\cdot}N(O{\cdot}MgBr)(\to O)R}$$

$$\mathrm{RMgBr} + \mathrm{CH_2{:}CH{\cdot}N(\to O){=}O} \xrightarrow{B} \mathrm{R{\cdot}CH_2{\cdot}CH{:}N(O{\cdot}MgBr)\to O}$$

Addition of ethylmagnesium bromide to an ethereal solution of nitroethylene resulted in immediate polymerisation of the nitro-olefin, but, by reversing the procedure, polymerisation was completely prevented. Slow addition of nitroethylene to 3 mols. of ethylmagnesium bromide at 10—15° resulted in a slow evolution of gas, which was accelerated on boiling the mixture. When 0·66 mol. of gas had been evolved, reaction appeared to be complete, and on treatment of the mixture with water a further 0·75 mol. of gas was evolved, presumably from unreacted Grignard reagent. The acid-insoluble part of the product consisted essentially of two substances, (*a*) 1-nitrobutane (20% yield) identified by its nitrolic acid reaction (Meyer, *Annalen*, 1875, **175**, 120) and by its degradation to *n*-butaldehyde, and (*b*) hexan-3-one oxime (30% yield) which was readily converted into the corresponding 2 : 4-dinitrophenylhydrazone (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2995) and was also reduced to 3-aminohexane. The acid-soluble part of the product was small and boiled over a wide range. It reduced ammoniacal silver nitrate and was hydrogenated to a mixture of non-reducing bases, but no identifiable substance was isolated either before or after hydrogenation. These properties indicated presence of a hydroxylamine.

Nitroethylene reacted similarly with excess of *n*-butylmagnesium bromide to give a 43% yield of 1-nitrohexane, a 27·5% yield of a neutral oil, $C_{10}H_{21}ON$, and a small amount of reducing bases. The compound, $C_{10}H_{21}ON$, was assumed to be *decan-5-one oxime* from its reactions and by analogy with the previous example. It was converted into an oily 2 : 4-dinitrophenylhydrazone which, in agreement with the failure of Bried and Hennion (*J. Amer. Chem. Soc.*, 1938, **60**, 1718) to prepare crystalline derivatives of decan-5-one, could not be obtained solid; catalytic reduction gave 5-*aminodecane*.

Since 1-nitro-2-methylprop-1-ene is not polymerised by Grignard reagents, it was possible to

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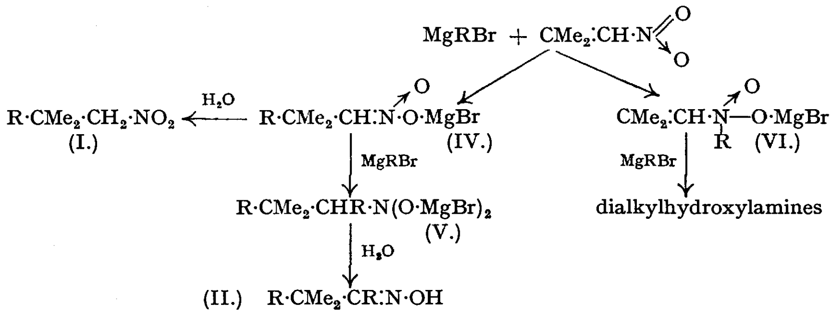
* Cf. B.P. 571,804.

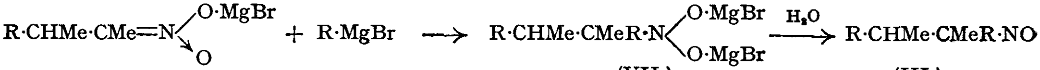
study more closely the course of the reaction of ethylmagnesium bromide with this nitro-olefin. This reaction of the first mol. of Grignard reagent was strongly exothermic and took place readily at 0° without evolution of gas. Further Grignard reagent reacted only slowly at 0°, but more readily at 15—20°. The reaction was mildly exothermic, and 1 mol. of gas was evolved, 3 mols. of Grignard reagent being consumed in all. The gas had the properties of a saturated hydrocarbon, and on combustion was found to be chiefly ethane. The products were 1-*nitro*-2 : 2-*dimethylbutane* (20%) (which gave the characteristic primary nitro-compound reaction and on reduction afforded the known 1-amino-2 : 2-dimethylbutane), and a crystalline solid, $C_8H_{17}ON$ (28%), which failed to react with 2 : 4-dinitrophenylhydrazine or 2 : 4-dinitrophenylsemicarbazide and was hydrogenated only with difficulty to a primary amine, $C_8H_{19}N$; by analogy with the previous examples it is believed to be 3 : 3-*dimethylhexan*-4-*one oxime* (II; R = Et), and the derived amine, 4-*amino*-3 : 3-*dimethylhexane*, the unreactivity of the oxime being attributed to steric factors.

Addition of ethylmagnesium bromide to 2-nitrobut-2-ene gave polymers as in the case of nitroethylene, but this was again overcome by adding the nitro-olefin to excess of the Grignard reagent. Gaseous hydrocarbon (0·75 mol.) was evolved and 2·5 mols. of ethylmagnesium bromide were consumed. An acid-soluble fraction consisting of reducing bases similar to those obtained from the primary nitro-olefin was isolated, and the neutral fraction was separated into an oil, $C_6H_{13}O_2N$ (26%), an oil, $C_8H_{17}ON$ (8%), and a large amount of non-volatile tar. The compound $C_6H_{13}O_2N$, which gave the nitrole reaction characteristic of a secondary nitro-group (Meyer, *loc. cit.*) and yielded a primary amine on reduction, was 2-*nitro*-3-*methylpentane*. The oil, $C_8H_{17}ON$, was colourless and contained one active hydrogen atom (Zerewitinoff); this excluded the possibility that it had the nitroso-structure (III; R = Et). It did not give the Meyer test for a nitro-paraffin, but on reduction it gave an amine, $C_8H_{19}N$. It must therefore be an oxime although, like the isomeric 3 : 3-dimethylhexan-4-one oxime, it failed to react with 2 : 4-dinitrophenylhydrazine or 2 : 4-dinitrophenylsemicarbazide.

On the basis of these results it is possible to build up a fairly complete picture of the course of the reaction of a Grignard reagent with a primary nitro-olefin, as shown in the scheme below for the reaction of ethylmagnesium bromide with 1-nitro-2-methylpropene. The initial step is addition (chiefly 1 : 4) of the Grignard reagent to the conjugated system to produce a complex (IV) which on hydrolysis gives the nitro-paraffin (I), but since (IV) contains the system $C{=}N{\rightarrow}O$, addition of a second mol. of Grignard reagent occurs to give the complex (V) which on hydrolysis yields the oxime (II). The formation of reducing bases and of ethane can be explained only by the assumption that part of the nitro-olefin undergoes 1 : 2-addition of Grignard reagent to give a complex (VI) which reacts with more Grignard reagent to give dialkylhydroxylamines; this process is analogous to the formation of dialkylhydroxylamines by the action of Grignard reagents on nitro-paraffins (this series, Part IX; Bevad, *Ber.*, 1907, **40**, 3065). Unfortunately, the nitro-olefin reaction produces mixtures of bases of so complex a nature and in such small amount that it has not been possible to isolate pure products which would establish with certainty the occurrence of 1 : 2-addition.



The secondary nitro-olefin underwent a similar series of reactions. The formation of 2-nitro-3-methylpentane in the reaction of 2-nitrobut-2-ene with ethylmagnesium bromide is clear evidence of 1 : 4-addition, and the isolation of reducing bases and the formation of a hydrocarbon again point to the occurrence of some 1 : 2-addition. The nature of the reaction of the 1 : 4-addition complex of the secondary nitro-olefin with more Grignard reagent is obscure; if it followed the same course as for the primary nitro-olefins the product would be a nitroso-compound (III). However, as stated above, although a product of the same empirical formula as (III) was isolated, it appeared to be an oxime, which may result from a rearrangement of (III) or of its complex (VII). Such a rearrangement might also explain the extensive tar formation, which was observed only in the case of the secondary nitro-olefin.



$$\mathrm{R{\cdot}CHMe{\cdot}CMe{=}N}\begin{matrix}\nearrow \mathrm{O{\cdot}MgBr}\\ \searrow \mathrm{O}\end{matrix} + \mathrm{R{\cdot}MgBr} \longrightarrow \underset{\text{(VII.)}}{\mathrm{R{\cdot}CHMe{\cdot}CMeR{\cdot}N}\begin{matrix}\nearrow \mathrm{O{\cdot}MgBr}\\ \searrow \mathrm{O{\cdot}MgBr}\end{matrix}} \xrightarrow{H_2O} \underset{\text{(III.)}}{\mathrm{R{\cdot}CHMe{\cdot}CMeR{\cdot}NO}}$$

EXPERIMENTAL.

Microanalyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

Nitroethylene and Ethylmagnesium Bromide.—A solution of nitroethylene (Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) (11·2 g.) in dry ether (60 c.c.) was added during 1 hour to a stirred solution of ethylmagesium bromide (from 50 g. ethyl bromide) in ether (250 c.c.) at 10—15°, and the mixture was then stirred and refluxed for 2 hours; gas evolution had then ceased. This gas (2100 c.c. at N.T.P.) did not react with bromine and did not liquefy on cooling to − 80°. The mixture was cooled in ice, and water (100 c.c.) was added dropwise; a further 2300 c.c. of gas were evolved. The mixture was acidified to Congo-red with dilute sulphuric acid, separated, and the aqueous layer, made strongly alkaline with sodium hydroxide, was extracted with ether in a continuous extractor. The extract was dried (NaOH) and distilled, giving a strongly basic oil (4·8 g.) which boiled over a wide range under reduced pressure and reduced ammoniacal silver nitrate. Catalytic hydrogenation in the presence of Raney nickel gave a non-reducing basic oil which distilled over a wide range and from which no crystalline derivative could be prepared.

The ethereal solution containing the acid-insoluble products was dried and distilled. Two fractions were isolated : (1) b. p. 50—65°/30 mm., and (2) b. p. 90—100°/30 mm. Redistillation of fraction (1) gave 1-nitrobutane (3·2 g.) as a colourless oil, b. p. 150—152°, which gave a positive test for the presence of a primary nitro-group (Meyer, *loc. cit.*). A solution of the nitro-compound in dilute aqueous sodium hydroxide, run into excess of 20% sulphuric acid at 10—15°, gave *n*-butaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. with an authentic specimen, 126°).

Redistillation of fraction (2) gave hexan-3-one oxime (4·7 g.) as a colourless oil, b. p. 98—100°/30 mm. (Found : N, 12·0. Calc. for $C_6H_{13}ON$: N, 12·2%). The oxime, with 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid, gave hexan-3-one 2 : 4-dinitrophenylhydrazone as red needles, m. p. 128—129°; Allen (*loc. cit.*) gives m. p. 129° (Found : C, 50·95; H, 5·5; N, 20·4. Calc. for $C_{12}H_{16}O_4N_4$: C, 51·4; H, 5·7; N, 20·0%).

3-*Aminohexane*. A solution of hexan-3-one oxime (3·5 g.) in methyl alcohol (35 c.c.) was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased. The filtered solution was acidified with hydrochloric acid and evaporated to dryness, and the residue after being washed with acetone afforded 3-aminohexane hydrochloride, m. p. 225—226°. Bevad (*J. pr. Chem.*, 1901, **63**, 230) gives m. p. 227—229° (Found : Cl, 25·2. Calc. for $C_6H_{15}N,HCl$: Cl, 25·9%). The hydrochloride with potassium cyanate in boiling aqueous solution gave 3-*ureidohexane*, m. p. 150—151° (Found : C, 58·65; H, 11·3; N, 18·9. $C_7H_{16}ON_2$ requires C, 58·35; H, 11·1; N, 19·35%).

Nitroethylene and n-*Butylmagnesium Bromide.*—Nitroethylene (14·6 g.) was brought into reaction with a Grignard solution, prepared from *n*-butyl bromide (75·5 g.), as described above for ethylmagnesium bromide. When reaction was complete the mixture was cooled in ice, decomposed by cautious addition of aqueous acetic acid (150 c.c. of 20%), and separated. The ethereal solution was washed with dilute sodium hydrogen carbonate solution, dried, and distilled. This gave two fractions : (1) b. p. 84°/21 mm., and (2) b. p. 120—123°/12 mm. Fraction (1), a colourless, sweet-smelling oil which gave the nitrolic acid reaction, was 1-nitrohexane (Found : C, 55·15; H, 9·85; N, 10·65. Calc. for $C_6H_{13}O_2N$: C, 54·95; H, 9·9; N, 10·7%). Hydrolysis with concentrated hydrochloric acid at 150° in a sealed tube for 12 hours gave hexoic acid, which was characterised as the amide, m. p. 98°, and the anilide, m. p. 95°. Fraction (2) was a colourless oil, *decan-5-one oxime* (Found : C, 70·5; H, 12·45; N, 7·95. $C_{10}H_{21}ON$ requires C, 70·2; H, 12·3; N, 8·2%).

n-*Hexylamine*. A solution of 1-nitrohexane (5·5 g.) in methyl alcohol (80 c.c.) was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased. The filtered solution was acidified with hydrochloric acid and evaporated to dryness, giving the hydrochloride (2·25 g.) which, after being washed with acetone, had m. p. 217—218° (Found : Cl, 25·75. Calc. for $C_6H_{15}N,HCl$: Cl, 25·9%). With potassium cyanate in boiling aqueous solution the hydrochloride gave *n*-hexylurea, m. p. 108° (cf. Norstedt and Wahlforss, *Ber.*, 1892, **25**, ref. 637).

5-*Aminodecane*. 5-Decanone oxime (3 g.) was dissolved in methyl alcohol and hydrogenated over Raney nickel at 20°/1 atm. After filtration and evaporation, 5-aminodecane was obtained as an oil which on treatment with phenyl *iso*cyanate gave 5-*phenylureidodecane*, m. p. 129—130°, colourless needles from acetic acid (Found : C, 73·85; H, 10·1; N, 10·15. $C_{17}H_{28}ON_2$ requires C, 73·9; H, 10·15; N, 10·15%).

1-*Nitro*-2-*methylprop*-1-*ene and Ethylmagnesium Bromide.*—1-Nitro-2-methylprop-1-ene (25 g.; Levy and Scaife, in the press) was dissolved in dry ether (25 c.c.) and cooled to 0°. A solution of ethylmagnesium bromide (125 c.c.) was added during 1 hour with stirring at 0—5°; no gas was evolved. The temperature was raised to 15° and a further 475 c.c. of the Grignard solution were added during 1 hour at 15—25°; 5·5 l. of ethane were evolved. The mixture was refluxed for 12 hours, cooled and treated dropwise with water (125 c.c.) which liberated a further 5·5 l. of ethane. After acidification with dilute hydrochloric acid, the mixture was separated and the aqueous portion was made strongly alkaline with sodium hydroxide and steam-distilled. From the distillate was obtained by isolation with ether a small amount of a strongly basic oil which reduced ammoniacal silver nitrate.

The ethereal solution, containing the acid-insoluble products, was dried and distilled, giving two fractions. Fraction (1) (6·2 g.), a colourless, sweet-smelling oil, b. p. 70°/25 mm., which gave the nitrolic acid reaction, was 1-*nitro*-2 : 2-*dimethylbutane* (I; R = Et) (Found: C, 54·75; H, 9·8; N, 10·8. $C_6H_{13}O_2N$ requires C, 54·95; H, 9·9; N, 10·7%). Fraction (2) (10·1 g.), a colourless crystalline solid, b. p. 100°/25 mm., was 3 : 3-*dimethylhexan*-4-*one oxime* (II; R = Et), m. p. 42—43°, from light petroleum (b. p. 40—60°) (Found: C, 67·55; H, 12·1; N, 9·65. $C_8H_{17}ON$ requires C, 67·15; H, 11·9; N, 9·8%).

1-*Amino*-2 : 2-*dimethylbutane*. A solution of the nitro-compound (4·3 g.) in methyl alcohol (50 c.c.) was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased. The filtered solution was fractionally distilled, giving the amine as a colourless oil (2·3 g.), b. p. 110—115° (Found: equiv., 99·9. Calc. for $C_6H_{15}N$: equiv. 101). The picramide, yellow needles from alcohol, had m. p. 89° (Found: C, 46·25; H, 5·25; N, 17·85. Calc. for $C_{12}H_{16}O_6N_4$: C, 46·15; H, 5·1; N, 18·0%). The benzenesulphonyl derivative had m. p. 59° (Found: N, 6·05. Calc. for $C_{12}H_{19}O_2NS$: N, 5·8%). Drake, Kline, and Rose (*J. Amer. Chem. Soc.*, 1934, **56**, 2079) give m. p. 88—88·5° for the picramide and m. p. 59—59·5° for the benzenesulphonyl derivative of 1-amino-2 : 2-dimethylbutane.

4-*Amino*-3 : 3-*dimethylhexane*. A solution of 3 : 3-dimethylhexan-4-one oxime (6·8 g.) in methyl alcohol (70 c.c.) was stirred in an autoclave with Raney nickel and hydrogen at 100°/100 atm. until absorption ceased. The filtered solution was acidified with hydrochloric acid and evaporated to dryness. The product was dissolved in a little water, washed with ether, basified with sodium hydroxide, extracted with ether, and the extract dried (KOH). Distillation gave 4-*amino*-3 : 3-*dimethylhexane* (3·3 g.) as a colourless oil, b. p. 152° (Found: equiv., 130·7. $C_8H_{19}N$ requires equiv., 129). Reaction with phenyl *iso*cyanate in dry ether gave 4-*phenylureido*-3 : 3-*dimethylhexane*, m. p. 157—158°, colourless needles from acetic acid (Found: C, 72·45; H, 9·65; N, 11·35. $C_{15}H_{24}ON_2$ requires C, 72·6; H, 9·7; N, 11·3%). With picryl chloride in alcohol the base gave 4-*picrylamino*-3 : 3-*dimethylhexane*, m. p. 60°, orange plates from alcohol (Found: C, 49·6; H, 5·5; N, 16·65. $C_{14}H_{20}O_6N_4$ requires C, 49·4; H, 5·9; N, 16·45%).

2-*Nitrobut*-2-*ene and Ethylmagnesium Bromide*.—2-Nitrobut-2-ene (62 g.; this series, Part III) was brought into reaction, under the conditions described above for nitroethylene, with a Grignard solution prepared from ethyl bromide (218 g.); 10 l. of ethane were evolved. Distillation of the acid-insoluble portion of the product under reduced pressure left a large non-volatile tarry residue, and repeated fractionation separated the distillate into two fractions. The acid-soluble portion (12 g.), fraction (3), was isolated by treatment of the aqueous solution with sodium hydroxide, followed by extraction with ether in a continuous extractor. Fraction (1) (20·3 g.), a colourless oil, b. p. 68—70°/25 mm., which gave the ψ-nitrole reaction (Meyer, *loc. cit.*), was 2-*nitro*-3-*methylpentane* (Found: C, 54·75; H, 9·6; N, 10·8. $C_6H_{13}O_2N$ requires C, 54·95; H, 9·9; N, 10·7%). Fraction (2) (7 g.) was a colourless oil, b. p. 98—100°/20 mm., which did not give the Meyer nitro-paraffin test and did not react with 2 : 4-dinitrophenylhydrazine in acid solution (Found: C, 67·8; H, 11·8; N, 10·1; active H (Zerewitinoff) 0·63. $C_8H_{17}ON$ requires C, 67·15; H, 11·9; N, 9·8; 1 active H, 0·7%). On reduction with Raney nickel and hydrogen in methyl alcohol at 100°/100 atm. fraction (2) gave a colourless basic oil, b. p. 157—158° (Found: equiv., 130·2. $C_8H_{19}N$ requires equiv., 129), which gave a hydrochloride of indefinite m. p., readily soluble in alcohol, acetone, and ether (Found: Cl, 21·65. $C_8H_{19}N,HCl$ requires Cl, 21·45%).

Fraction (3) was a strongly basic oil, boiling over a wide range (40—110°/10 mm.); it reduced ammoniacal silver nitrate and absorbed hydrogen in the presence of a nickel catalyst, but no crystalline derivatives could be obtained from the resulting mixture of amines.

2-*Amino*-3-*methylpentane*. A solution of 2-nitro-3-methylpentane (10 g.) in methyl alcohol (100 c.c.) was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased. The filtered solution was distilled, giving 2-*amino*-3-*methylpentane* as a colourless oil, b. p. 105—107° (Found: equiv., 102·7. $C_6H_{15}N$ requires equiv., 101). With picryl chloride it gave a *picramide*, m. p. 58—59° (Found: C, 46·3; H, 5·1; N, 17·7. $C_{12}H_{16}O_6N_4$ requires C, 46·15; H, 5·1; N, 18·0%).

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