290. *Aliphatic Nitro-compounds. Part XI. Preparation of Nitro-paraffins by* 1 : 4-*Addition of Organometallic Halides to* α-*Nitro-olefins.**

By GERARD D. BUCKLEY and ERIC ELLERY.

A series of hitherto unknown or inaccessible nitro-paraffins has been prepared by 1 : 4-addition of alkyl- or aryl-magnesium halides or alkylzinc halides to α-nitro-olefins. By carrying out the reaction below 10° and avoiding excess of organometallic halide secondary reactions are almost completely suppressed, but the yield of nitro-paraffin never exceeds 65% and is frequently less, apparently owing to the simultaneous occurrence of some 1 : 2-addition.

THE formation of nitro-paraffin derivatives in high yield by the action of Grignard reagents on di- and tri-phenylnitroethylenes has been described by Kohler and Stone (*J. Amer. Chem. Soc.*, 1930, **52**, 761). Under similar conditions simpler nitro-olefins yield a complex mixture of

---

* Cf. B.P. 571,804.

products of which the nitro-paraffin forms only a small proportion (Part X of this series). The nitro-paraffins are formed by 1 : 4-addition of the Grignard reagent to the conjugated system and the by-products arise partly from 1 : 2-addition and partly from the action of excess of Grignard reagent on the initial addition products.

The results described in Part X indicate that the initial addition occurs much more readily than the subsequent reactions, and it has now been found that, by working at low temperatures and avoiding excess of Grignard reagent, secondary reactions are suppressed, and nitro-paraffins are obtained as the main products. The reaction has been carried out on a variety of nitro-olefins and organomagnesium halides (and one alkylzinc halide) and appears to be quite general. The yields are frequently poor, but are probably capable of considerable improvement, since 60—65% yields were obtained consistently in the only two examples in which any attempt was made to determine the optimum conditions of reaction and isolation, *viz.*, the reaction of *n*-butylmagnesium bromide with nitroethylene and of ethylmagnesium bromide with 1-nitro-2-methylprop-1-ene.

In the two cases in which alkylmagnesium iodides were used small amounts of crystalline by-products were formed, but owing to the smallness of the amounts available they were not further investigated; no trace of these compounds was found when the corresponding bromides were used.

EXPERIMENTAL.

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

1-*Nitro*-2 : 2-*dimethylbutane*.—(a) *From ethylmagnesium bromide.* A solution of ethylmagnesium bromide, prepared from ethyl bromide (48 g.) in ether (200 c.c.), was added during 1 hour to a stirred solution of 1-nitro-2-methylprop-1-ene (40 g.; Levy and Scaife, in the press) in pure, dry ether (400 c.c.), the temperature being held at 0—10°. The mixture was refluxed for 1 hour, cooled in ice, and treated cautiously with a solution of acetic acid (20 c.c.) in water (160 c.c.). The ethereal layer was washed with dilute sodium carbonate solution, dried, and distilled, giving 1-nitro-2 : 2-dimethylbutane (30·2 g.; 60% of theory) as a sweet-smelling oil, b. p. 168—170° (cf. Part X).

(b) *From ethylmagnesium iodide.* To an ice-cold, stirred solution of ethylmagnesium iodide, prepared in the usual manner from ethyl iodide (78 g.) in ether (200 c.c.), was added 1-nitro-2-methylprop-1-ene (34 g.) in ether (40 c.c.) during 1 hour at 0—10°. The mixture was stirred at 20° for 2 hours and worked up as before. Distillation of the crude product gave 25·3 g. (57·5% theory) of 1-nitro-2 : 2-dimethylbutane, b. p. 168—170°. The undistilled residue was crystallised from alcohol, giving colourless granules (0·4 g.) of an unidentified product, m. p. 182° (Found : C, 52·25; H, 7·55; N, 14·75. $C_8H_{14}O_3N_2$ requires C, 51·6; H, 7·5; N, 15·05%).

(c) *From ethylzinc iodide.* A solution of ethylzinc iodide in dry toluene, prepared from ethyl iodide (47 g.), was stirred at 0—10° and treated with a solution of 1-nitro-2-methylprop-1-ene (15 g.) in pure, dry ether (15 c.c.) during 1 hour. The mixture was then stirred at 50° for 3 hours, poured into ice, and treated with glacial acetic acid (20 c.c.). The organic layer was separated, dried, and fractionated to give 1-nitro-2 : 2-dimethylbutane (5·6 g.), b. p. 78—80°/30 mm.

*Nitro*neo*pentane*.—A solution of methylmagnesium iodide, prepared from methyl iodide (71 g.), was brought into reaction with 1-nitro-2-methylprop-1-ene (34 g.) as described above for ethylmagnesium iodide. After working up in the usual manner, the crude product was distilled, giving *nitro*neo*pentane* (16·2 g.; 42%) as a colourless oil, b. p. 77—78°/65 mm. (Found : C, 51·65; H, 9·35; N, 11·95. $C_5H_{11}O_2N$ requires C, 51·3; H, 9·4; N, 11·95%). The non-volatile residue crystallised on cooling and was purified by recrystallisation from alcohol and benzene, giving colourless prisms, m. p. 144° (Found : C, 46·8; H, 7·8; N, 13·05. $C_4H_8O_2N$ requires C, 47·05; H, 7·85; N, 13·7%).

1-*Nitro*-2 : 2 : 3 : 3-*tetramethylpentane*.—A solution of *tert.*-amylmagnesium chloride, prepared from *tert.*-amyl chloride (21·3 g.) by the method of Whitmore and Badertscher (*J. Amer. Chem. Soc.*, 1933, **55**, 1559), was brought into reaction with 1-nitro-2-methylprop-1-ene (10 g.) as described above for ethylmagnesium iodide. After isolation as before, the crude product was fractionated to give a colourless oil (6·5 g.), b. p. 102—105°/11 mm., having a camphor-like odour (Found : C, 62·55; H, 10·65; N, 8·45. $C_9H_{19}O_2N$ requires C, 62·45; H, 10·95; N, 8·1%).

ααββ-Tetramethylvaleric Acid.—1-Nitro-2 : 2 : 3 : 3-tetramethylpentane (6 g.) was mixed with concentrated aqueous hydrochloric acid (20 c.c.) and heated in a sealed tube at 150° for 6 hours. The product was diluted with water and extracted with ether, and the ethereal solution washed thoroughly with dilute aqueous sodium carbonate. The alkaline extract was acidified with dilute sulphuric acid, extracted with ether, and the dried ethereal solution was distilled, giving *ααββ-tetramethylvaleric acid*, b. p. 122°/15 mm., m. p. 89—90° [from light petroleum (b. p. 40—60°)] (Found : C, 68·8; H, 11·4; equiv., 158. $C_9H_{18}O_2$ requires C, 68·35; H, 11·4%; equiv., 158).

1-*Nitro*-2 : 2-*dimethylpent*-4-*ene*.—Allyl bromide (41 g.) in dry ether (250 c.c.) was converted into the Grignard reagent by the method of Gilman and McGlumphy (*Bull. Soc. chim.*, 1928, **43**, 1322), and the resulting solution filtered through glass wool and cooled to 0°. A solution of 1-nitro-2-methylprop-1-ene (20 g.) in dry ether (50 c.c.) was then added with stirring during 1 hour at 0—10°. After being stirred at 20° for 2 hours the mixture was poured into ice, treated with acetic acid (25 c.c.), and separated. The ethereal solution was dried and distilled under reduced pressure, giving much unchanged 1-nitro-2-methylprop-1-ene and a small yield (6·5 g.) of 1-*nitro*-2 : 2-*dimethylpent*-4-*ene*, b. p. 77°/20 mm. (Found : N, 9·7. $C_7H_{13}O_2N$ requires N, 9·8%). This was a pleasant-smelling oil, which gave the Meyer test for a primary nitro-compound, and reacted with bromine in carbon tetrachloride to give a liquid bromo-derivative.

1-*Nitrohexane.*—Nitroethylene (21 g.) dissolved in dry ether (100 c.c.) was added during 1 hour to a stirred solution of *n*-butylmagnesium bromide (0·4 g. mol.) in ether (250 c.c.). A vigorous exothermic reaction ensued, and the temperature was maintained below 0° with a freezing mixture; when the addition was complete the mixture was stirred for 1 hour at 20° and the complex decomposed by cautious addition of a solution of acetic acid (48 c.c.) in water (240 c.c.). After being stirred for a further 45 minutes, the mixture was steam-distilled, the ethereal layer of distillate separated, dried, and distilled, giving 38·6 g.(65%) of 1-nitrohexane, b. p. 84°/21 mm.; $n_D^{20^\circ}$ 1·4270 (cf. Part X of this series) (Found : N, 10·65. Calc. for $C_6H_{13}O_2N$: N, 10·7%).

2-*Nitro*-3-*methylpentane.*—2-Nitrobut-2-ene (50 g.; this series, Part III) was dissolved in dry ether (250 c.c.) and brought into reaction with a solution of ethylmagnesium bromide (0·75 g. mol.) in ether (375 c.c.) as described above for the preparation of 1-nitrohexane. After working up in the usual way 2-nitro-3-methylpentane (27·7 g.; 42·5%) was obtained as a colourless oil, b. p. 70—73°/20 mm.; $n_D^{20^\circ}$ 1·4320 (cf. Part X of this series) (Found : N, 10·8. Calc. for $C_6H_{13}O_2N$: N, 10·7%).

2-*Nitropentane.*—2-Nitroprop-1-ene (17·4 g.; this series, Part I) dissolved in dry ether (60 c.c.) was brought into reaction with ethylmagnesium bromide (from 22 g. of ethyl bromide) in ether (100 c.c.) as described above for the preparation of 1-nitrohexane. After working up in the usual way the crude distillate (b. p. 40—60°/12 mm.) was washed with aqueous sodium hydrogen sulphite to remove unchanged 2-nitroprop-1-ene, dried, and fractionated, giving a colourless oil, b. p. 148—150°. 2-*Nitropentane* is a pleasant-smelling oil, soluble in dilute aqueous sodium hydroxide, which gives the Meyer test for a secondary nitro-compound (Found : C, 51·65; H, 9·7; N, 11·8. $C_5H_{11}O_2N$ requires C, 51·3; H, 9·4; N, 11·95%). Reduction of 2-nitropentane (3·5 g.) in methyl alcohol with hydrogen in the presence of Raney nickel in the usual way gave 2-aminopentane, isolated as the hydrochloride (3·4 g.). Reaction of the base with phenyl *iso*cyanate gave the phenylurea, m. p. 119—120°, colourless plates from aqueous alcohol. Mailhe (*Bull. Soc. chim.*, 1905, **33**, 966) gives m. p. 120° for *N*-phenyl-*N'*-α-methylbutylurea (Found : N, 13·6. Calc. for $C_{12}H_{18}ON_2$: N, 13·6%).

2-*Nitro*-3-*methylpentadecane.*—A solution of dodecylmagnesium bromide (from 55 g. of dodecyl bromide) in dry ether (250 c.c.) was added during 1 hour to a stirred solution of 2-nitrobut-2-ene (30 g.) in dry ether (150 c.c.) at 0—5°. The mixture was refluxed for 1 hour, cooled, and treated cautiously with aqueous acetic acid (120 c.c. of 20%). The mixture was stirred until all the magnesium salts had dissolved, and the ethereal layer was dried, concentrated, and the residue repeatedly fractionated in a vacuum to give the nitro-compound (20 g.) as a pale yellow oil, b. p. 111—115°/0·06 mm. (Found : C, 71·0; H, 12·1; N, 5·85. $C_{16}H_{33}O_2N$ requires C, 70·85; H, 12·2; N, 5·2%). This gave the Meyer test for a secondary nitro-compound and formed a crystalline sodium salt on treatment with alcoholic sodium hydroxide.

2-*Amino*-3-*methylpentadecane.*—The nitro-compound (10 g.) was catalytically reduced in methyl alcohol in the presence of Raney nickel at ordinary temperature and pressure. Distillation of the filtered solution gave the *amine* (5·5 g.) as a colourless oil, b. p. 158—160°/11 mm. (Found : equiv., 237. $C_{16}H_{35}N$ requires equiv., 241). An aqueous solution of the hydrochloride, on being boiled with excess potassium cyanate, deposited colourless crystals of 2-*ureido*-3-*methylpentadecane*, m. p. 122—123° (from alcohol) (Found : C, 71·4; H, 12·4; N, 9·9. $C_{17}H_{36}ON_2$ requires C, 71·8; H, 12·7; N, 9·9%).

2-*Nitro*iso*propyl*cyclo*hexane.*—*cyclo*Hexylmagnesium bromide (from 81·5 g. of *cyclo*hexyl bromide) was brought into reaction with 1-nitroprop-1-ene (29 g.; this series, Part I) as described above for the preparation of 1-nitrohexane. After decomposition of the complex the ethereal layer was concentrated and the residue dissolved in alcohol (200 c.c.), treated with aqueous sodium hydroxide (35 c.c. of 32%) at 0—5°, the solution diluted with water (400 c.c.), and washed with ether. The aqueous solution was made acid to Congo-red with concentrated hydrochloric acid at 0—5° and extracted with ether. The extract was dried and distilled, giving 2-*nitro*iso*propyl*cyclo*hexane* as a pale yellow oil, b. p. 122°/16 mm. (Found : C, 63·4; H, 9·7; N, 8·2. $C_9H_{17}O_2N$ requires C, 63·15; H, 9·95; N, 8·2%).

2-*Nitro*-3-*phenylbutane.*—Phenylmagnesium bromide (from 51 g. of bromobenzene) was brought into reaction with 2-nitrobut-2-ene (20 g.) as described above for the preparation of 1-nitrohexane. After isolation in the usual manner the product was distilled under reduced pressure, giving impure 2-nitro-3-phenylbutane (22·5 g.), b. p. 118—120°/13 mm. This material, which appeared to contain some diphenyl, was not further purified but was reduced with hydrogen in methyl alcohol in the presence of Raney nickel at ordinary temperature and pressure. The filtered solution was acidified with hydrochloric acid and evaporated to dryness on the steam-bath, the residue dissolved in water, and washed with ether. The aqueous solution was then basified with concentrated sodium hydroxide and extracted with ether. The extract was dried (KOH) and distilled, giving the *amine* as a colourless oil (10·7 g.), b. p. 87°/12 mm. (Found : equiv., 147. $C_{10}H_{15}N$ requires equiv., 149). Reaction with picryl chloride gave 2-*picrylamino*-3-*phenylbutane*, m. p. 119—120°, yellow plates from alcohol (Found : N, 15·65. $C_{16}H_{16}O_6N_4$ requires N, 15·55%).

2-*Nitro*-3-*phenylheptane.*—2-Nitro-1-phenylprop-1-ene (32 g.; Alles, *J. Amer. Chem. Soc.*, 1932, **54**, 272) dissolved in dioxan (120 c.c.) was added during 1 hour to a stirred ethereal solution (150 c.c.) of butylmagnesium bromide (prepared from 42 g. of butyl bromide) at 0—5°. The mixture was stirred at 20° for 1 hour and the product isolated in the usual way. Distillation gave impure 2-nitro-3-phenylheptane (29 g.), b. p. 62—90°/0·02 mm., which was not further purified, but was reduced with hydrogen and Raney nickel in methyl alcohol. The filtered solution was acidified with hydrochloric acid and evaporated to dryness on the steam-bath; the residue was dissolved in water and washed with ether. The aqueous solution was basified with sodium hydroxide and the amine isolated with ether. Distillation gave 2-*amino*-3-*phenylheptane* as a colourless oil, b. p. 114—115°/9 mm. (Found : equiv., 191. $C_{13}H_{21}N$ requires equiv., 191). This material, apparently a mixture of stereoisomerides, gave a *hydrochloride* of indefinite m. p. (Found : Cl, 15·5. $C_{13}H_{21}N,HCl$ requires Cl, 15·6%). Attempts to prepare crystalline derivatives with benzoyl chloride, phenyl *iso*cyanate, picryl chloride, and nitrourea failed.

1-*Nitro*-2-(2-*furyl*)*hexane.*—A solution of 1-nitro-2-(2-furyl)ethylene (14 g.; Thiele and Landers, *Annalen*, 1909, **369**, 303) in dioxan (70 c.c.) was added during 1 hour at 0—10° to a stirred solution (150 c.c.) of *n*-butylmagnesium bromide prepared from *n*-butyl bromide (34·5 g.). The solution was stirred at 20° for 18 hours, poured on ice, and the product isolated in the usual way, giving 1-*nitro*-2-(2-*furyl*)-*hexane* as a pale yellow oil (6·5 g.), b. p. 78—82°/0·4 mm. (Found : N, 7·2. $C_{10}H_{15}O_3N$ requires N, 7·1%).

1-*Nitro*-2-*benzyl*cyclo*hexane*.—An ethereal solution of benzylmagnesium chloride (prepared from 34 g. of benzyl chloride) was brought into reaction with 1-nitro*cyclo*hexene (32 g.; Wieland *et al.*, *Annalen*, 1921, **424**, 71) as described above for the preparation of 1-nitrohexane. Distillation of the product gave impure 1-nitro-2-benzyl*cyclo*hexane (23·5 g.), b. p. 91—115°/0·04 mm. This material, apparently containing 1 : 2-diphenylethane, was hydrogenated in the usual way over Raney nickel without further purification. The resulting amine was purified through its hydrochloride and finally distilled, giving a colourless oil (12·5 g.), b. p. 138—140°/11 mm. (Found : equiv., 191. Calc. for $C_{13}H_{19}N$: equiv., 189). This base, apparently a mixture of isomerides, was dissolved in benzene (50 c.c.) and shaken with 2N-hydrochloric acid (70 c.c.). After 45 minutes, the precipitated hydrochloride was collected; this appeared to be still a mixture, and no pure derivatives could be isolated from it. On standing overnight the mother liquor deposited a second precipitate which was collected and crystallised repeatedly from 2N-hydrochloric acid to give pure *cis*-2-benzyl*cyclo*hexylamine hydrochloride, m. p. 224°. This formed an acetyl derivative, m. p. 116°, and a benzoyl derivative, m. p. 155° (Found : C, 82·5; H, 8·25; N, 4·7. Calc. for $C_{20}H_{23}ON$: C, 81·9; H, 7·85; N, 4·8%). No m. p. depression was observed on admixture of these derivatives with authentic specimens prepared according to Schöpf and Boettcher (*Annalen*, 1926, **448**, 1).

The authors thank Dr. H. A. Piggott and Mr. J. D. Rose for their interest and encouragement in this work.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, RESEARCH LABORATORIES,
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9.

[*Received, January 23rd,* 1947.]