292. *Aliphatic Nitro-compounds. Part XIII. Preparation of 3-Nitro-1-arylalkyl Cyanides by Interaction of Arylmethyl Cyanides and α-Nitro-olefins.**

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Arylmethyl cyanides, but not 1-arylethyl cyanides, react with α-nitro-olefins in presence of alkali alkoxides (preferably potassium *tert.*-amyloxide) to give 3-nitro-1-arylalkyl cyanides. 2-Nitroalkyl esters may be used in place of nitro-olefins, *e.g.*, 1-nitro-2-methylprop-1-ene or nitro*tert.*-butyl nitrate reacts with benzyl cyanide to give 3-*nitro*-1-*phenyl*-2 : 2-*dimethylpropyl cyanide* (II).

The use of α-nitro-olefins as the unsaturated component in reactions of the Michael type has been described in earlier parts in this series and elsewhere. Active methylene compounds which have been used successfully in such reactions include primary and secondary nitro-paraffins (Part VIII), ethyl malonate (Kohler *et al.*, *J. Amer. Chem. Soc.*, 1919, **41**, 764; 1926, **48**, 1770), and acetone (Hass and Riley, *Chem. Reviews*, 1943, **32**, 373), and this type of reaction has now been extended to the preparation of 3-nitro-1-arylalkyl cyanides by addition of arylmethyl cyanides to α-nitro-olefins.

$$Ar\cdot CH_2\cdot CN + CH_2{:}CH\cdot NO_2 \longrightarrow NO_2\cdot CH_2\cdot CH_2\cdot CHAr\cdot CN$$

Benzyl cyanide reacted readily with 1-nitro-2-methylprop-1-ene in the presence of sodium methoxide to give 3-*nitro*-1-*phenyl*-2 : 2-*dimethylpropyl cyanide* (II) in 12% yield, but by using potassium *tert.*-amyloxide in place of the methoxide catalyst the yield was raised to 60%. From *p*-bromobenzyl cyanide and 1-naphthylmethyl cyanide, with the amyloxide catalyst, 3-*nitro*-1-p-*bromophenyl*-2 : 2-*dimethylpropyl cyanide* (III) and 3-*nitro*-1-(1-*naphthyl*)-2 : 2-*dimethylpropyl cyanide* (IV) were obtained in 48% and 70% yield respectively.

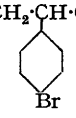
The adducts to 2-nitrobut-2-ene and 1-nitro*cyclo*hexene were obtained as viscous oils from which it was difficult to isolate the pure diastereoisomerides: thus, benzyl cyanide with 2-nitrobut-2-ene gave 3-*nitro*-1-*phenyl*-2-*methyl*-n-*butyl cyanide* (I) and *p*-bromobenzyl cyanide added to 1-nitro*cyclo*hexene to form 2-*nitro*-1-(p-*bromo*-α-*cyanobenzyl*)cyclo*hexane* (V) from which a crystalline isomer was isolated in small yield and with considerable difficulty. An attempt to add 1-phenylethyl cyanide (Meyer, *Annalen*, 1899, **250**, 123) to 1-nitro-2-methylprop-1-ene in the presence of potassium *tert.*-amyloxide failed.

$NO_2\cdot CHMe\cdot CHMe\cdot CHPh\cdot CN$ (I.)

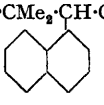
$NO_2\cdot CH_2\cdot CMe_2\cdot CHPh\cdot CN$ (II.)

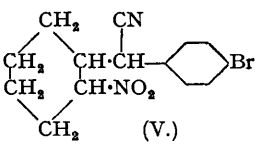
$NO_2\cdot CH_2\cdot CHMe\cdot CHPh\cdot CN$ (VI.)

$NO_2\cdot CH_2\cdot CH_2\cdot CH\cdot CN$ (III.)



$NO_2\cdot CH_2\cdot CMe_2\cdot CH\cdot CN$ (IV.)





(V.)

Esters of 2-nitro-alcohols yield nitro-olefins on treatment with alkalis, and it has been shown that such esters can be used instead of nitro-olefins in addition reactions provided that sufficient alkali is present to neutralise the liberated acid. Nitro-*tert.*-butyl nitrate reacted with 2 mols. of the potassium salt of benzyl cyanide to give 3-nitro-1-phenyl-2 : 2-dimethylpropyl cyanide identical with the product obtained from 1-nitro-2-methylprop-1-ene, and under similar conditions 2-nitro*iso*propyl acetate gave 3-*nitro*-1-*phenyl*-2-*methylpropyl cyanide* (VI).

The reaction is of fairly general application for the preparation of 3-nitro-1-arylalkyl cyanides and is complementary to the method of preparation described in Part XIV of this series. The two methods in conjunction make possible the preparation of a wide variety of these hitherto inaccessible compounds.

Experimental.

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

3-*Nitro*-1-*phenyl*-2-*methyl*-n-*butyl Cyanide* (I).—Benzyl cyanide (60 g.) was run into a solution of sodium methoxide [from sodium (12 g.) in methyl alcohol (200 c.c.)] at 20° and a solution of 2-nitrobut-2-ene (50 g.; this series, Part III) in methyl alcohol (100 c.c.) added dropwise during 1 hour at 5—10°. The mixture was heated at 60° for 18 hours, poured into water, and extracted with ether. The extract was washed with water and discarded, and the combined aqueous solutions were acidified

* Patent application pending.

with acetic acid (50 c.c.) and extracted with ether. The extract was dried and fractionated, giving the *cyanide* as a yellow oil (28·5 g.), b. p. 129—134°/0·2 mm. (Found : N, 13·15. $C_{12}H_{14}O_2N_2$ requires N, 12·85%).

3-*Nitro*-1-*phenyl*-2 : 2-*dimethylpropyl Cyanide* (II).—(a) *From* 1-*nitro*-2-*methylprop*-1-*ene*. To a stirred, ice-cooled solution of potassium *tert.*-amyloxide (from 8 g. of potassium), benzyl cyanide (23·5 g.) was added at 5—10°. 1-Nitro-2-methylprop-1-ene (20 g.; Levy and Scaife, in the press) was then added dropwise during 1 hour at 5—10°, and the reaction was completed by stirring at 60° for 2 hours. After cooling, the mixture was diluted with water and extracted with ether. The ethereal extract was washed with water and discarded, and the combined aqueous solutions were acidified with acetic acid (13 c.c.) and extracted with ether. The extract was washed with sodium hydrogen carbonate solution, dried, evaporated, and the residue (25 g.; 60% yield), consisting of almost pure 3-*nitro*-1-*phenyl*-2 : 2-*dimethylpropyl cyanide*, was left in a desiccator until completely solid. Crystallisation from a little methyl alcohol gave colourless needles, m. p. 59° (Found : C, 66·15; H, 5·95; N, 12·9. $C_{12}H_{14}O_2N_2$ requires C, 66·05; H, 6·4; N, 12·85%).

(b) *From nitro*-tert.-*butyl nitrate*. A solution of potassium *tert.*-amyloxide [from potassium (2 g.) in *tert.*-amyl alcohol (40 c.c.)] was treated with benzyl cyanide (5·85 g.) as before. Nitro-*tert.*-butyl nitrate (4·1 g.; Levy and Scaife, in the press) in *tert.*-amyl alcohol (5 c.c.) was added during 1 hour at 5—10°, and the mixture was then stirred at 60° for 2 hours and worked up as before. The product, m. p. 59°, was identical with that prepared above from 1-nitro-2-methylprop-1-ene.

3-*Nitro*-1-p-*bromophenyl*-2 : 2-*dimethylpropyl Cyanide* (III).—*p*-Bromobenzyl cyanide (9·8 g.) was brought into reaction with 1-nitro-2-methylprop-1-ene (5·05 g.) as described for benzyl cyanide. After several days in a desiccator the product solidified (7·1 g.; 48% yield), and crystallisation from methyl alcohol gave colourless needles of 3-*nitro*-1-p-*bromophenyl*-2 : 2-*dimethylpropyl cyanide*, m. p. 72—74° (Found : N, 9·4; Br, 27·55. $C_{12}H_{13}O_2N_2Br$ requires N, 9·4; Br, 26·9%).

3-*Nitro*-1-(1-*naphthyl*)-2 : 2-*dimethylpropyl Cyanide* (IV).—1-Naphthylmethyl cyanide (5 g.) was brought into reaction with 1-nitro-2-methylprop-1-ene (3 g.) as described for benzyl cyanide. The product (5·5 g.; 70% yield), isolated as before, solidified on removal of the ether. After two recrystallisations from alcohol (charcoal) the *cyanide* was obtained as long, colourless needles, m. p. 116° (Found : C, 71·7; H, 6·0; N, 10·4. $C_{16}H_{16}O_2N_2$ requires C, 71·65; H, 6·0; N, 10·4%).

3-*Nitro*-1-*phenyl*-2-*methylpropyl Cyanide* (VI).—A solution of potassium *tert.*-amyloxide [from potassium (8 g.) in *tert.*-amyl alcohol (160 c.c.)] was treated with benzyl cyanide (23·5 g.) as before. 2-Nitro*iso*propyl acetate (14·6 g.; Schmidt and Rutz, *Ber.*, 1928, **61**, 2142) was then added during 1 hour at 5—10°, and the resulting solution was stirred at 60° for 2 hours, cooled to 20°, and diluted with water. Isolation in the usual way yielded 3-*nitro*-1-*phenyl*-2-*methylpropyl cyanide* as a pale yellow oil (6·7 g.; 25% yield), b. p. 122—126°/0·15 mm. (Found : C, 65·3; H, 5·55; N, 14·2. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9; N, 13·75%).

2-*Nitro*-1-(p-*bromo*-α-*cyanobenzyl*)cyclo*hexane* (V).—1-Nitro*cyclo*hexene (14 g.; Wieland *et al.*, *Annalen*, 1921, **424**, 71) was brought into reaction with *p*-bromobenzyl cyanide (21·6 g.) in presence of potassium *tert.*-amyloxide as previously described. The crude product, isolated as before, was a viscous oil (10·7 g.), apparently a mixture of diastereoisomers. After several days in a desiccator, it partly crystallised, and was then treated with a little alcohol and the crystals were collected (2·9 g.). Recrystallisation from methyl alcohol gave the *compound* as colourless granules, m. p. 103—104° (Found : N, 8·75: Br, 25·2. $C_{14}H_{15}O_2N_2Br$ requires N, 8·65; Br, 24·75%).

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