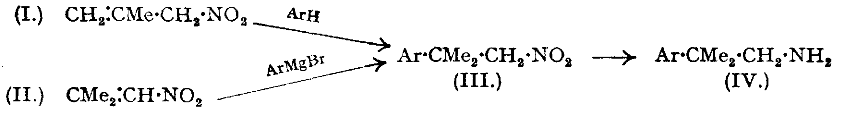
9. *Aliphatic Nitro-compounds. Part XIX. Friedel–Crafts Reactions with α- and β-Nitro-olefins.*

By A. Lambert, J. D. Rose, and B. C. L. Weedon.

1-Nitro-2-methylprop-2-ene (I) and benzene or toluene give a 1-nitro-2-aryl-2-methylpropane. 1-Nitro-2-methylprop-1-ene (II) and toluene in the presence of boron trifluoride give α-p-*tolyl*iso*butyrohydroxamic acid* together with a little 1-nitro-2-*p*-tolyl-2-methylpropane. Benzene and (II) with aluminium chloride give *αβ-dichloro*iso*butyraldoxime*, and *phenyl*iso*butyrohydroxamyl chloride*; the latter is converted into 1-*phenyl*iso*propyl* iso*cyanate* with cold sodium hydrogen carbonate solution. In the presence of aluminium chloride, 1-nitropropan-2-ol and benzene give benzaldoxime and 1 : 1-diphenylethane, whilst nitromethane and benzene give benzaldoxime and benzaldehyde anil.

Reactions of the nitro-paraffins and nitro-olefins have formed the subject of previous papers in this series (see *J.*, **1947**, 1471—1519), but most of the nitro-olefin reactions have been carried out under alkaline conditions; the object of the present work was to investigate the hitherto unknown use of α- and β-nitro-olefins in the Friedel–Crafts reaction with aromatic hydrocarbons.

Reactions of aromatic hydrocarbons with the βγ-unsaturated 1-nitro-2-methylprop-2-ene (I) were normal. With aluminium chloride as catalyst, this nitro-olefin and benzene gave a 56% yield of 1-*nitro*-2-*phenyl*-2-*methylpropane* (III; Ar = Ph) which was reduced catalytically to the *amine*, the identity of which was established by comparison with a specimen prepared unambiguously from 1-nitro-2-methylprop-1-ene (II) and phenylmagnesium bromide (cf. Buckley and Ellery, *J.*, **1947**, 1497), followed by reduction of the product (III) to the amine (IV).



Similarly, toluene and 1-nitro-2-methylprop-2-ene in the presence of boron trifluoride gave 1-*nitro*-2-p-*tolyl*-2-*methylpropane* (III; Ar = p-Me·C_6H_4) which on catalytic hydrogenation gave the corresponding *amine* (IV; Ar = p-Me·C_6H_4).

Reactions with the αβ-unsaturated 1-nitro-2-methylprop-1-ene (II) were more complex. With toluene in the presence of boron trifluoride, a mixture of products containing 1-nitro-2-*p*-tolyl-2-methylpropane (III; Ar = p-Me·C_6H_4), a small amount of an unidentified solid ($C_{11}H_{13}ON$), and a 22% yield of α-p-*tolyl*iso*butyrohydroxamic acid* (V) was obtained. The latter was probably formed by 1 : 4-addition to the nitro-olefin to give the *aci*-nitro-compound (VI) followed by a rearrangement. 1 : 2-Addition, or an alternative rearrangement of (VI), would explain the formation of (III; Ar = p-Me·C_6H_4).

Hydrogenation of (V) gave α-p-*tolyl*iso*butyroamide* (VII), and hydrolysis of either (V) or (VII) gave α-p-*tolyl*iso*butyric* acid (VIII). The structures of (VII) and (VIII) were confirmed (*a*) by oxidation with permanganate to *αα-dimethylhomoterephthalic acid* (IX), and by further oxidation of (IX) with chromic acid to terephthalic acid, and (*b*) by independent and unambiguous synthesis. The structure of the acid previously described in the literature as α-*p*-tolyl*iso*butyric

$$\begin{tikzcd}
p\text{-Me}\cdot\text{C}_6\text{H}_5 + \text{(II)} \arrow[r] & \underset{\text{(VI.)}}{p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_2\cdot\text{CH:NO}\cdot\text{OH}} \arrow[r] & \overset{\text{(V.)}}{p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}} \arrow[d, "\text{HCl}"] \arrow[dr, "\text{H}_2\text{-Ni}"] & \\
\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2(p) & \underset{\text{(IX.)}}{p\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}} \arrow[l] & \underset{\text{(VIII.)}}{p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}} \arrow[l] \arrow[r, leftrightharpoons] & \underset{\text{(VII.)}}{p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}_2}
\end{tikzcd}$$

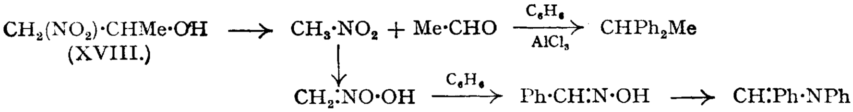
acid is now shown to be wrong; it was prepared by Wallach (*Nachr. Ges. Wiss. Göttingen*, 1899, **2**, 4; *Chem. Zentr.*, 1899, II, 1047) who gave m. p. 72° for the acid (VIII) and m. p. 123—124° for the amide (VII). The preparation was later repeated by Rupe and Burgin (*Ber.*, 1911, **44**, 1222) who gave m. p. 70—71° and 119° for the acid and amide respectively. Further, the nitrile prepared by Wallach (*loc. cit.*) by dehydration of the amide cannot be α-*p*-tolyl*iso*butyronitrile as described, although its constants are very close to those of the authentic nitrile. An independent synthesis has now been carried out by methylation of *p*-tolylacetonitrile with methyl iodide and sodamide in liquid ammonia; the resulting *α-*p*-tolyl*iso*butyronitrile* on hydrolysis with alcoholic potassium hydroxide gave in high yield a mixture of the amide, m. p. 142°, and the acid, m. p. 82°, identical with those obtained from toluene and 1-nitro-2-methylprop-1-ene *via* α-*p*-tolyl*iso*butyrohydroxamic acid. Rupe and Burgin's experiment was also repeated, and the acid, m. p. 68—70°, obtained in very low yield by interaction of toluene and ethyl α-bromo*iso*butyrate, has been shown to depress the m. p. of α-*p*-tolyl*iso*butyric acid (m. p. 82°) to 45—50°. The structures of Wallach's and Rupe and Burgin's compounds are not clear, although from a comparison of the constants it appears plain that the substances handled, at least by Rupe and Burgin, were not pure. It is possible that both these products were impure β-*p*-tolyl*iso*butyric acid formed by dehydrobromination of the ethyl α-bromo*iso*butyrate and addition of the toluene to the ethylenic linkage of the resulting ethyl α-methylacrylate. This is supported by Rupe and Burgin's statement that oxidation of their acid with permanganate gave a good yield of terephthalic acid; we find that, in agreement with the known resistance to oxidation of *gem*-dimethyl groups attached to aromatic nuclei (Smith and Prichard, *J. Amer. Chem. Soc.*, 1940, **62**, 771; Bogert and Davidson, *ibid.*, 1934, **56**, 189; Nazarov and Kuznetsova, *Bull. Acad. Sci. U.R.S.S.*, 1941, 431; cf. *Chem. Abs.*, 1942, **36**, 1296), terephthalic acid could not be obtained directly from (VIII) by treatment with permanganate.

Attempts to cause 1-nitro-2-methylprop-1-ene (II) to react with benzene in the presence of boron trifluoride gave no hydroxamic acid and only very poor yields of products from which a small amount of unidentified solid ($C_{10}H_{11}ON$) was isolated. With aluminium chloride as catalyst, however, reaction occurred readily giving a mixture of *αβ-dichloro*iso*butyraldoxime* (X) (identified by hydrolysis to α-hydroxy*iso*butyric acid) and *α-phenyl*iso*butyrohydroxamyl chloride* (XI). The former, presumably formed initially by the addition to the nitro-olefin of traces of hydrogen chloride present in the mixture (cf. Heath and Rose, *J.*, 1947, 1485), condenses with the benzene and gives (XI), generating more hydrogen chloride for further reaction.

$$\begin{tikzcd}
\text{(II)} \arrow[r, "\text{HCl}"] & \underset{\text{(X.)}}{\text{CMe}_2\text{Cl}\cdot\text{CCl:N}\cdot\text{OH}} \arrow[r, "\text{H}_2\text{O}"] \arrow[d, "\text{C}_6\text{H}_6\text{-AlCl}_3"] & \text{CMe}_2(\text{OH})\cdot\text{CO}_2\text{H} & \\
& \underset{\text{(XI.)}}{\text{CPhMe}_2\cdot\text{CCl:N}\cdot\text{OH}} \arrow[r, "\text{NaHCO}_3", "\text{cold}"'] \arrow[d, "\text{Ph}\cdot\text{NH}_2"] & \underset{\text{(XII.)}}{\text{CPhMe}_2\cdot\text{NCO}} \arrow[r, "\text{NaHCO}_3", "\text{hot}"'] \arrow[d, "\text{H}_2\text{-Ni}"] \arrow[dr, "\text{R}\cdot\text{NH}_2"] & \underset{\text{(XIII.)}}{(\text{CPhMe}_2\cdot\text{NH})_2\text{CO}} \\
& \underset{\text{(XVII.)}}{\text{CPhMe}_2\cdot\text{C(NHPh):N}\cdot\text{OH}} & \underset{\text{(XV.)}}{(\text{CPhMe}_2\cdot\text{NHMe})} \arrow[d] & \underset{\text{(XIV.)}}{\text{CPhMe}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NHR}} \\
& & \text{CPhMe}_2\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CPhMe}_2 \quad \text{(XVI.)} &
\end{tikzcd}$$

Treatment of the hydroxamyl chloride (XI) with sodium hydrogen carbonate solution gave, by loss of hydrogen chloride, *α-phenyl*iso*propyl* iso*cyanate* (XII) which under more drastic conditions was converted into *NN′-di-(α-phenyl*iso*propyl)urea* (XIII). With ethereal ammonia or aniline, the *iso*cyanate (XII) readily gave the corresponding mono- and di-substituted *ureas* (XIV; R = H or Ph). Catalytic hydrogenation of (XII) gave the trisubstituted *urea* (XVI), presumably by reaction of the *iso*cyanate with the secondary amine (XV) formed initially.

Since aliphatic alcohols have frequently been employed in Friedel–Crafts alkylations of aryl compounds, it was hoped that similar use of the readily available nitro-alcohols would provide a convenient means of preparing nitro-alkylated derivatives of aromatic hydrocarbons. Treatment of benzene with 1-nitro-2-propanol (XVIII) in the presence of aluminium chloride gave a mixture of benzaldoxime and 1 : 1-diphenylethane. This surprising result may be explained by assuming an initial dissociation of (XVIII) into nitromethane and acetaldehyde, and subsequent reaction as shown below.



$$\begin{tikzcd} CH_2(NO_2)\cdot CHMe\cdot OH \arrow[r] & CH_3\cdot NO_2 + Me\cdot CHO \arrow[r, "C_6H_6", "AlCl_3"'] \arrow[d] & CHPh_2Me \\ & CH_2{:}NO\cdot OH \arrow[r, "C_6H_6"] & Ph\cdot CH{:}N\cdot OH \arrow[r] & CH{:}Ph\cdot NPh \end{tikzcd}$$

(XVIII.)

Confirmation of this hypothesis was obtained by condensing nitromethane with benzene in the presence of aluminium chloride, when both benzaldoxime and benzaldehyde anil were formed. This reaction of nitromethane with benzene is also of interest in view of recent patents (Universal Oil Products Co., U.S.PP. 2,385,303, 2,393,818) which describe the use of nitro-paraffins as solvents for Friedel–Crafts reactions.

EXPERIMENTAL.

Analyses are by Mr. E. S. Morton. All m. p.s are uncorrected.

1-*Nitro*-2-*phenyl*-2-*methylpropane* (III; Ar = Ph).—(*a*) 1-Nitro-2-methylprop-2-ene (10 g.; Levy, Scaife, and Wilder-Smith, *J.*, 1948, 52) was added during 15 minutes to a well-stirred suspension of aluminium chloride (16 g.) in benzene (50 c.c.) at 30°. After being stirred at 30—40° for 1 hour, the mixture was cooled and poured on a mixture of concentrated hydrochloric acid and ice. The benzene layer was washed with sodium hydrogen carbonate solution, dried, and distilled, giving 1-*nitro*-2-*phenyl*-2-*methylpropane* (9·55 g.), b. p. 67—70°/0·1 mm., $n_D^{23°}$ 1·5235 (Found: C, 67·0; H, 7·5. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3%).

(*b*) A solution of phenylmagnesium bromide (from 9·6 g. magnesium) in ether (300 c.c.) was added during 1·5 hours to a well-stirred solution of 1-nitro-2-methylprop-1-ene (40 g.) in water (300 c.c.) at −5° to 0°. The mixture was refluxed gently for 0·5 hour and cooled, and the complex decomposed by the gradual addition of acetic acid (24 g.) in water (160 c.c.). Isolation of the product gave 1-nitro-2-phenyl-2-methylpropane (13 g.), b. p. 74—80° (mainly 76—78°)/0·16 mm.

1-*Amino*-2-*phenyl*-2-*methylpropane* (IV; Ar = Ph).—A solution of 1-nitro-2-phenyl-2-methylpropane [4 g. from (*a*) above] in methyl alcohol (50 c.c.) was hydrogenated at ordinary temperature and pressure with Raney nickel as catalyst. After filtration, the solution was acidified and evaporated to dryness. Excess of 2·5N-sodium hydroxide solution was added to the residue, and the precipitated oil extracted with ether. Evaporation of the ethereal solution and distillation of the residue gave 2-*phenyl*-2-*methylpropylamine* (2·5 g.) as a colourless liquid, b. p. 96—98°/14 mm. (Found: equiv., 152. $C_{10}H_{15}N$ requires equiv., 149). The *picrate* formed yellow needles, m. p. 160°, from aqueous methanol (Found: C, 50·8; H, 4·8. $C_{10}H_{15}N,C_6H_3O_7N_3$ requires C, 50·8; H, 4·8%). 2-Phenyl-2-methylpropylurea, from 1-amino-2-phenyl-2-methylpropane and nitrourea, formed colourless needles from water, m. p. 144° (Wallach, *loc. cit.*, gives m. p. 141—142°). Similar reduction of a sample of 1-nitro-2-phenyl-2-methylpropane from (*b*) above gave the same amine, identified by comparison of the derived picrate and urea.

1-*Nitro*-2-p-*tolyl*-2-*methylpropane* (III; Ar = *p*-Me·C_6H_4).—A solution of 1-nitro-2-methylprop-2-ene (10 g.) in toluene (100 c.c.) was saturated with boron trifluoride. After being kept at room temperature overnight, the mixture was heated for 1 hour at 70—80°, cooled, washed with water, and distilled, giving 1-*nitro*-2-p-*tolyl*-2-*methylpropane* (5 g.) as a pale yellow oil, b. p. 145—150°/13 mm., 85—90°/0·05 mm., $n_D^{22°}$ 1·5258 (Found: N, 7·2. $C_{11}H_{15}O_2N$ requires N, 7·3%). The nitro-compound (0·4 g.) was oxidised by boiling it under reflux with aqueous potassium permanganate (3 g. in 25 c.c.) for 4 hours. After treatment with sodium hydrogen sulphite and hydrochloric acid, a white acid (0·3 g.) was collected which crystallised from aqueous alcohol in shining plates, m. p. 236—237°, undepressed by admixture with authentic dimethylhomoterephthalic acid (IX; see later).

2-p-*Tolyl*-2-*methylpropylamine* (IV; Ar = *p*-Me·C_6H_4).—Hydrogenation of a solution of 1-nitro-2-*p*-tolyl-2-methylpropane (3·6 g.) in methyl alcohol (50 c.c.) at ordinary temperature and pressure with Raney nickel as catalyst gave p-*tolyl*-2-*methylpropylamine* (2·5 g.) as a colourless liquid, b. p. 134°/32 mm., 111·5—115°/10 mm., $n_D^{22°}$ 1·5231 (Found: equiv., 164·9. $C_{11}H_{17}N$ requires equiv., 163). The *picrate* formed yellow needles, m. p. 211—213°, from aqueous methyl alcohol (Found: C, 51·9; H, 5·0; N, 14·6. $C_{11}H_{17}N,C_6H_3O_7N_3$ requires C, 52·0; H, 5·1; N, 14·2%).

α-p-*Tolyl*iso*butyrohydroxamic Acid* (V).—A solution of 1-nitro-2-methylprop-1-ene (20 g.) in toluene (100 c.c.) was saturated with boron trifluoride at 50°. Excess of boron trifluoride was removed by blowing air through the solution and by washing with water. α-p-*Tolyl*iso*butyrohydroxamic acid* (8·5 g.) separated from the toluene layer, and when crystallised from benzene formed colourless fibrous needles, m. p. 157° (Found: C, 68·6; H, 7·9; N, 7·3. $C_{11}H_{15}O_2N$ requires C, 68·4; H, 7·8; N, 7·3%). The hydroxamic acid was soluble in dilute sodium hydroxide, but not in sodium hydrogen carbonate, gave a deep red-violet colour with aqueous ferric chloride, and reduced ammoniacal silver nitrate solution. Evaporation of the toluene solution and distillation of the residue gave (i) 1-nitro-2-*p*-tolyl-2-methylpropane (6·0 g.), b. p. 90—96°/0·16 mm. (Found: N, 7·3. Calc. for $C_{11}H_{15}O_2N$: N, 7·3%), which on catalytic reduction gave an amine, the picrate of which had m. p. and mixed m. p. with a specimen prepared as described above, 211—213°, and (ii) a small amount of a unidentified solid which formed colourless leaflets, m. p.

132—134°, from light petroleum (b. p. 60—80°) (Found : C, 75·5; H, 7·6. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·5%.

α-p-*Tolyl*iso*butyramide* (VII).—Catalytic reduction (Raney nickel) of *α*-*p*-tolyl*iso*butyrohydroxamic acid (0·9 g.) in methanol at ordinary temperature and pressure gave *α*-p-*tolyl*iso*butyramide* which crystallised from benzene in colourless plates (0·5 g.), m. p. 143—144° (Found : C, 74·4; H, 8·1; N, 8·3. $C_{11}H_{15}ON$ requires C, 74·6; H, 8·5; N, 7·9%) (Rupe and Burgin, *loc. cit.*, give m. p. 119°; Wallach, *loc. cit.*, gives m. p. 123—124°).

α-p-*Tolyl*iso*butyric Acid* (VIII).—(*a*) *α*-*p*-Tolyl*iso*butyramide (0·2 g.) and dilute sodium hydroxide (15 c.c.; 2N) were heated under reflux until homogeneous (10 hour). The solution was cooled and acidified with hydrochloric acid, and the precipitate obtained was crystallised from light petroleum (b. p. 40—60°), giving *α*-p-*tolyl*iso*butyric acid* (0·17 g.) as colourless prisms, m. p. 82° (Found : C, 74·2; H, 7·9; equiv., 177·4. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%; equiv., 178) (Rupe and Burgin, *loc. cit.*, give m. p. 70—71°; Wallach, *loc. cit.*, gives m. p. 72°). (*b*) *α*-*p*-Tolyl*iso*butyrohydroxamic acid (0·5 g.) and dilute hydrochloric acid (15 c.c.; 2N) were refluxed for 0·5 hour. After cooling, the product was crystallised from light petroleum (b. p. 40—60°), giving *α*-*p*-tolyl*iso*butryic acid, m. p. and mixed m. p. with the specimen described above, 82° (amide, m. p. and mixed m. p. 143—144°).

α-p-*Tolyl*iso*butyronitrile*.—Anhydrous liquid ammonia (1·5 l.) was stirred at −35° with exclusion of moisture, and ferric nitrate hexahydrate (0·2 g.) added. Sodium (36 g.) cut in thin slices was added as rapidly as possible to maintain a steady evolution of hydrogen, the temperature being kept at −35° to −33°. When the blue colour of dissolved sodium had changed to the grey of sodamide, *p*-tolylacetonitrile (98 g.; Atkinson and Thorpe, *J.*, 1907, **91**, 1699) was added dropwise during 10 minutes, and the solution stirred for a further 30 minutes. Methyl iodide (213 g.) was then added dropwise during 1 hour, the solution stirred for 3 hours, anhydrous ether (400 c.c.; previously cooled to −30°) added, and the whole stirred without external cooling for 15 hours, by which time most of the ammonia had evaporated. The mixture was decomposed with iced water (500 c.c.), the product isolated with ether, and the ethereal solution washed successively with water, N-hydrochloric acid and water, dried, and fractionated through a 6-inch column packed with "Monel" metal gauze spirals. The *nitrile* (50 g.; 42%) had b. p. 122—123°/12 mm., 246°/763 mm., $n_D^{22^\circ}$ 1·5106, $d_{22^\circ}^{22^\circ}$ 0·9661 (Wallach, *loc. cit.*, gives b. p. 247—248°, d^{20° 0·955, n_D 1·5057) (Found : C, 82·9; H, 8·0; N, 8·9. $C_{11}H_{13}N$ requires C, 83·0; H, 8·2; N, 8·8%).

The nitrile (8·8 g.) was boiled under reflux for 7½ hours with a solution of potassium hydroxide (10 g.) in alcohol (50 c.c.). There was only slight evolution of ammonia. The cooled solution was poured into water (150 c.c.), and the precipitated solid (8·2 g.) isolated with ether. Crystallisation from light petroleum (b. p. 80—100°) and from light petroleum–benzene gave *α*-*p*-tolyl*iso*butyramide as lustrous, pearly plates, m. p. 142°, undepressed on admixture with the sample obtained by reduction of the hydroxamic acid.

The aqueous alkaline mother liquor was acidified with hydrochloric acid, and the precipitated oil extracted with ether. Evaporation gave an oil (1·05 g.) which rapidly crystallised, and after 2 recrystallisations from light petroleum (b. p. 40—60°) formed colourless prisms, m. p. 82°, not depressed by admixture with the sample prepared above by hydrolysis of *α*-p-tolyl*iso*butyrohydroxamic acid.

Dimethylhomoterephthalic Acid (IX).—A solution of *α*-p-tolyl*iso*butyric acid (4 g.) in aqueous sodium carbonate (40 c.c. of 5%) was refluxed gently, with stirring, and an aqueous solution of potassium permanganate (240 c.c. of 4%) added during 1 hour. After refluxing for a further 2 hours, the mixture was cooled and treated with excess of sulphur dioxide. The precipitate was collected and crystallised from aqueous methanol, giving *αα-dimethylhomoterephthalic* acid (4 g.) as colourless plates, m. p. 236—237° (Found : C, 63·3; H, 5·6; equiv. 102·5. $C_{11}H_{12}O_4$ requires C, 63·4; H, 5·8%; equiv., 104).

Terephthalic Acid.—Dimethylhomoterephthalic acid (0·8 g.) was added to a solution of chromium trioxide in a mixture of water (5 c.c.) and acetic acid (20 c.c.). After being heated on the steam-bath for 4 hours, the mixture was cooled and diluted with water, and the precipitated terephthalic acid (0·4 g.) filtered off and washed thoroughly with boiling water; the dimethyl ester had m. p. and mixed m. p. with an authentic specimen, 141—142°.

Repetition of Rupe and Burgin's Experiment.—Freshly distilled aluminium bromide (40 g.) was dissolved in sodium-dried toluene (160 g.), a few drops of ethyl *α*-bromo*iso*butyrate added, and the mixture warmed on the steam-bath to start the reaction. Ethyl *α*-bromo*iso*butyrate (40 g.) was then added dropwise during 30 minutes, and the mixture refluxed for 5 hours; the evolution of hydrobromic acid had then diminished considerably. The cooled solution was cautiously treated with ice, and the toluene layer separated and boiled under reflux with concentrated hydrochloric acid (200 c.c.) for 4 hours. The toluene layer, after being washed with water, was shaken mechanically with aqueous ammonia (26 c.c. of *d* 0·88 diluted to 200 c.c.) for 1 hour, and the ammonia solution separated, concentrated to half its original volume, acidified with concentrated hydrochloric acid, and extracted with ether. Evaporation of the ethereal solution yielded an oil, which on distillation gave two fractions : (*a*) b. p. 110—120°/12 mm., solidifying on cooling to a crystalline mass (1·5 g.), and (*b*) b. p. 160—170°/12 mm., a yellow oil with a slight blue fluorescence (2 g.).

Fraction (*a*) was recognised as *α*-hydroxy*iso*butyric acid, m. p. 79—80° alone and in admixture with an authentic specimen. Fraction (*b*) on cooling deposited a small amount of crystalline material. This fraction was suspended in water, neutralised to phenolphthalein with 2N-sodium hydroxide, and treated with a solution of strontium nitrate (2·5 g.) in water (10 c.c.). The precipitated strontium salt was collected, pressed dry, and recrystallised from 50% aqueous alcohol, from which it separated slowly as clusters of needles. The salt was collected after 24 hours, suspended in water, and decomposed with 2N-hydrochloric acid. The precipitated semi-solid was collected in ether and distilled (b. p. 165—170°/10 mm.) as a clear oil (0·5 g.). On dilution with light petroleum (b. p. 40—60°) and cooling to −30°, crystals separated which were rapidly collected and repeatedly crystallised from light petroleum (b. p. 40—60°). When no further purification could be effected because of shortage of material, the acid had m. p. 68—70°, and was clearly impure. In admixture with authentic *α*-*p*-tolyl*iso*butyric acid, the m. p. was depressed to 45—50°.

*αβ-Dichloro*iso*butyraldoxime* (*X*) *and α-Phenyl*iso*butyrohydroxamyl Chloride* (XI).—1-Nitro-2-methylprop-1-ene (60 g.) was added during 1 hour to a well-stirred suspension of aluminium chloride (80 g.) in benzene (300 c.c.) at 40°. After being stirred for a further hour at 40°, the mixture was cooled, poured into a mixture of concentrated hydrochloric acid (30 c.c.) and ice, and extracted with benzene. After removal of the benzene, distillation of the residue gave : (i) *αβ-dichloro*iso*butyraldoxime* (25 g.), b. p. 81—85°/14 mm., $n_{\mathrm{D}}^{25^\circ}$ 1·4922 (cf. Heath and Rose, *loc. cit.*) (Found : N, 9·1. C_4H_7ONCl requires N, 9·0%), which was hydrolysed by boiling water to α-hydroxy*iso*butyric acid, m. p. and mixed m. p. with an authentic specimen 78—79°, and (ii) a high-boiling oil which could not be distilled owing to decomposition but which, on crystallisation from light petroleum (b. p. 40—60°), gave *α-phenyl*iso*butyrohydroxamyl chloride* (22 g.) as colourless plates, m. p. 73—74° (Found : C, 60·6; H, 5·8; N, 7·3. $C_{10}H_{12}ONCl$ requires C, 60·7; H, 6·1; N, 7·1%). With an aqueous alcoholic solution of ferric chloride at room temperature the latter was slowly hydrolysed and developed the intense red-violet colour characteristic of hydroxamic acids.

*α-Phenyl*iso*butyrohydroxamanilide* (XVII).—A solution of α-phenyl*iso*butyrohydroxamyl chloride (0·5 g.) and aniline (0·3 g.) in alcohol (6 c.c.) was kept at room temperature for 16 hours. The solid which separated was crystallised from alcohol, giving *α-phenyl*iso*butyrohydroxamanilide* as colourless needles, m. p. 171—172° (Found : C, 75·7; H, 7·1; N, 11·1. $C_{16}H_{18}ON_2$ requires C, 75·6; H, 7·1; N, 11·0%).

*α-Phenyl*iso*propyl* iso*Cyanate* (XII).—α-Phenyl*iso*butyrohydroxamyl chloride (5 g.) was added to a solution of sodium hydrogen carbonate (2·1 g.) in water (100 c.c.), and the mixture shaken until there was no further evolution of gas (0·5 hour). Extraction with ether gave *α-phenyl*iso*propyl* iso*cyanate* (2 g.) as a colourless liquid, b. p. 50—52°/0·16 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·5038 (Found : C, 74·7; H, 6·9. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·9%). The urea, formed with ethereal ammonia, had m. p. 191° [Brander, *Rec. Trav. chim.*, 1917, **37**, 90, gives m. p. 191° (decomp.)].

N-*Phenyl*-N′-*α-phenyl*iso*propylurea* was prepared from the *iso*cyanate (0·2 g.) and aniline (0·12 g.) in ether. The precipitate was crystallised from aqueous alcohol giving colourless needles (0·25 g.), m. p. 193—194° (Found : C, 75·6; H, 7·3; N, 10·9. $C_{16}H_{18}ON_2$ requires C, 75·6; H, 7·2; N, 11·0%).

NN′-*Di-α-phenyl*iso*propylurea* (XIII).—α-Phenyl*iso*propyl *iso*cyanate (0·6 g.) was added to a solution of sodium hydrogen carbonate (0·8 g.) in water (15 c.c.) and the mixture refluxed for 3 hours. The resulting solid was filtered off and crystallised from alcohol to give NN′-*di-α-phenyl*iso*propylurea* (0·4 g.) as colourless needles, m. p. 226—227° (Found : C, 76·7; H, 8·3; N, 9·5. $C_{19}H_{24}ON_2$ requires C, 77·0; H, 8·2; N, 9·5%).

N-*Methyl*-NN′-*di*-(*α-phenyl*iso*propyl*)*urea* (XVI).—Hydrogenation of α-phenyl*iso*propyl *iso*cyanate (4 g.) in methyl alcohol (40 c.c.) over Raney nickel at ordinary temperature and pressure gave N-*methyl*-NN′-*di*-(*α-phenyl*iso*propyl*)*urea* (1·6 g.) as colourless needles, m. p. 171—172°, from aqueous methanol (Found : C, 77·4; H, 8·8; N, 8·9. $C_{20}H_{26}ON_2$ requires C, 77·4; H, 8·5; N, 9·0%).

Reaction between 1-*Nitro*-2-*propanol and Benzene*.—1-Nitro-2-propanol (50 g.) was added during 0·5 hour to a well-stirred suspension of aluminium chloride (190 g.) in benzene (210 c.c.). The mixture was refluxed gently for 4 hours and set aside overnight. Decomposition of the complex and isolation of the product gave a mixture of (i) benzaldoxime (23 g.), b. p. 130°/30 mm., the identity of which was proved by (*a*) formation of benzaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. with an authentic specimen 234°, on treatment with a methanolic solution of 2 : 4-dinitrophenylhydrazine sulphate, (*b*) formation of hydroxylamine hydrochloride on hydrolysis with concentrated (1 : 1) hydrochloric acid, and (*c*) formation on hydrogenation (Raney nickel) in methanol solution of benzylamine (picrate, m. p. and mixed m. p. with an authentic specimen 195—197°) and dibenzylamine, the hydrochloride of which crystallised as colourless leaflets from alcohol, m. p. 260—261° (decomp.) (Found : C, 71·8; H, 6·9; N, 6·0; Cl, 15·6. Calc. for $C_{14}H_{16}NCl$: C, 71·9; H, 6·9; N, 6·0; Cl, 15·2%) (Limpricht, *Annalen*, 1867, **144**, 314, gives m. p. 256°), and (ii) 1 : 1-Diphenylethane (9·0 g.), b. p. 68—71°/0·12 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·5768 (Boeseken and Bastet, *Rec. Trav. chim.*, 1913, **32**, 1892, give b. p. 136°/12 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5761) which on oxidation with chromic acid in acetic acid at 100° gave benzophenone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. with an authentic specimen 232°) in 55% yield.

Reaction between Nitromethane and Benzene.—A well-stirred suspension of aluminium chloride (134 g.) in benzene (100 c.c.) and nitromethane (20 g.) was refluxed gently for 4 hours and set aside overnight. Decomposition of the complex and isolation gave (i) benzaldoxime (4 g.) and (ii) a mixture, b. p. 130—170°/1 mm. (6 g.), which readily gave benzaldehyde 2 : 4-dinitrophenylhydrazone on addition of 2 : 4-dinitrophenylhydrazine sulphate in methanol, and on being heated with dilute (1 : 1) hydrochloric acid gave aniline (as its hydrochloride) in *ca.* 30% yield.

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