

242. Addition of Dinitrogen Tetroxide to Olefins. Part III. Propylene.

By NORMAN LEVY and CHARLES W. SCAIFE.

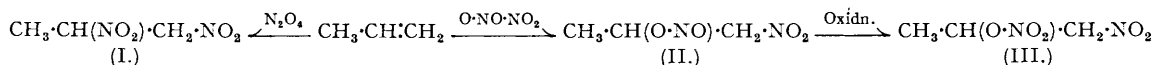
The addition of dinitrogen tetroxide to propylene to give 1 : 2-dinitropropane and β -nitroisopropyl nitrite requires an ether or ester solvent as reaction medium; otherwise, oxidation reactions supervene and the only product isolated is the nitrate ester of lactic acid. When using an excess of the tetroxide in ether, the reaction is at least 3—4 times as fast as that with ethylene, but the modes of addition are similar, *i.e.*, as two nitro-groups and as one nitro- and one nitrite group. With the latter mode of addition, the nitrite group is attached to the carbon with the fewer hydrogen atoms, and the nitro-nitrite so formed is partly oxidised to nitro-nitrate. Like all the lower members of the series, the nitro-nitrite is unstable and should be converted into nitro-alcohol by water treatment for safe and efficient separation of the nitrated products. When oxygen is added to the reaction mixture, the total yield on propylene is about 75% made up of 33% as β -nitroisopropanol, 21% as 1 : 2-dinitropropane, and 21% as β -nitroisopropyl nitrate, and instability and separation difficulties due to addition of dinitrogen trioxide are avoided. In the absence of oxygen, nitro-nitrate formation is small but substantial amounts of 4-nitro-3-methylfurazan oxide are formed, probably *via* nitroacetone oxime, and interfere with separation of the main products. Both 1 : 2-dinitropropane and β -nitroisopropyl nitrate are new, and their reactions are briefly described. Although both 1 : 2-dinitroethane and 1 : 2-dinitroisobutane are solid above room temperature, 1 : 2-dinitropropane is liquid even at -40° , possibly because it is the *dl*-form.

THERE is little previous work on the addition of oxides of nitrogen to propylene and none specifically referring to the tetroxide. Demjanow (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 275) treated propylene with nitrous fumes (from arsenious oxide and nitric acid) in ethereal solution and obtained propylene "nitrosite" as a white solid, m. p. 119—120°, identified by reduction to the propylenediamine. Marshall (U.S.P., 1,473,825, 1921) covered the reaction between propylene and dinitrogen trioxide in ether and other inert solvents to give propylene "nitrosite" for use as a secondary charge in blasting caps and primers. The present work has shown that nitro-nitroso-addition is only of minor importance with the tetroxide and may under appropriate conditions be avoided altogether, while even the trioxide, behaving partly as such and partly as tetroxide, gives less simple products than was thought.

Straightforward addition of the tetroxide to propylene to give 1 : 2-dinitropropane, and β -nitroisopropyl nitrite does not occur unless an ether or ester solvent is used as reaction medium. When propylene is passed into pure liquid dinitrogen tetroxide in the manner described for ethylene (Part II, preceding paper), rapid

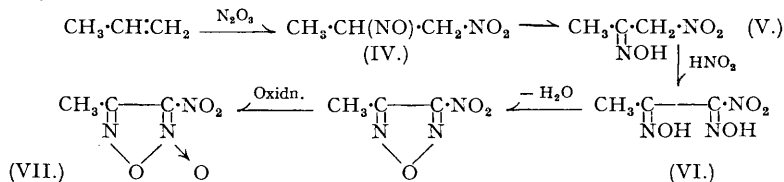
reaction occurs and the mixture soon becomes green owing to reduction of the tetroxide. After removal of unreacted tetroxide, a stable liquid product remains which, since it is completely soluble in water, contains no dinitropropane or nitropropyl nitrate. A clear, almost water-white liquid is obtained by ether extraction and distillation. It deposits needle crystals of the nitrate of lactic acid, $\text{CH}_3\cdot\text{CH}(\text{O}\cdot\text{NO}_2)\cdot\text{CO}_2\text{H}$, on standing. The manner in which this compound is formed has not been investigated, but it is likely to arise from the oxidation of β -nitroisopropyl nitrate. It has previously been prepared by the action of sulphuric and fuming nitric acids on zinc lactate (Duval, *Compt. rend.*, 1903, **137**, 1263).

When, however, propylene is passed into a solution of the tetroxide in ether or dioxan, the oxidising character of the oxide is moderated and the two types of addition usual in this series take place: (a) as two nitro-groups to give I: 2-dinitropropane (I), and (b) as one nitro- and one nitrite group, the latter becoming attached as expected to the carbon with the fewer hydrogen atoms, to give β -nitroisopropyl nitrite (II). Part of the latter is oxidised to the nitro-nitrate (III) in the course of reaction, the amount being sharply increased when oxygen is added with the propylene.



In common with all the lower member of the series, the nitro-nitrite is unstable and it is therefore advisable to treat the crude reaction product with water, after removal of excess tetroxide and solvent, to convert the nitro-nitrite (II) into the stable β -nitroisopropyl alcohol, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NO}_2$. Although the latter had been prepared by Henry (*Bull. Soc. chim.*, 1895, **13**, 999) by condensing nitromethane with acetaldehyde, both (I) and (III) are new. The total yield of separated products on propylene is 70—75%, with 20—30% as dinitropropane, 35—40% as nitro-propanol, and 2—20% as nitroisopropyl nitrate, the proportions depending on the use of oxygen, which not only increases the amount of the nitrate but also prevents interference by dinitrogen trioxide addition, particularly the formation of 4-nitro-3-methylfurazan oxide (VII).

The last substance can be formed to the extent of 5—8% on the propylene consumed, when no oxygen is added to the reaction. It is formed in greater amount when dinitrogen trioxide is used in place of the tetroxide together with dinitropropane and nitropropanol, and only a small amount of nitronitrosopropane can be isolated. For these reasons the following stages in its formation are suggested: (i) addition of trioxide to propylene to give 1-nitro-2-nitrosopropane (IV) which rearranges to nitroacetone oxime (V), and (ii) condensation of the latter with nitrous acid to give the dioxime (VI) followed by dehydration and oxidation to the furazan oxide:



Nitration Procedure.—The apparatus is similar to that described in Part II (see British Patent Application No. 6147/44). Dry propylene is absorbed in a concentrated solution of dinitrogen tetroxide in dry ether or ester solvent. Sodium-dried ethyl ether is the most suitable solvent, and normally the concentration of tetroxide is limited to 40% by weight in order to minimise oxidising side reactions. Reaction temperatures of -10° to 25° can be employed with ether as solvent, $0-10^\circ$ being the preferred range for batch preparations. Still higher temperatures are available with dioxan, since complex formation with the tetroxide then reduces its evaporation. The tendency of the solid complex to separate and also to form in the gas-exit lines makes dioxan a less convenient solvent than ether.

Absorption can be taken to completion (1 mol. of propylene to 1 mol. of dissolved tetroxide) but an excess of the latter is desirable to check formation and addition of trioxide. The absorption rate is at least 3—4 times as fast as that with ethylene, 40% of theoretical being taken up in 3 hours, compared with $10\frac{1}{2}$ hours for ethylene. Still faster rates may be used. Heat is evolved during the reaction and the mixture must be kept cool in an ice-bath. In the absence of oxygen, the mixture soon loses its pale amber colour and turns green, with formation dinitrogen trioxide. Very little oxidation to oxides of carbon occurs, these representing on exit-gas analyses less than 0.1% of the propylene consumed. Addition of oxygen with the propylene gives a product more stable to distillation, much less contaminated with materials arising from addition of trioxide, and richer in nitropropyl nitrate.

Separation Procedure.—Ether and excess of tetroxide are removed by careful distillation under reduced pressure. For reasons already stated (Part II), continuous evaporation from a warm, falling film is preferred, with the crude product falling immediately into cold water to convert the β -nitroisopropyl nitrite into nitropropanol (see British Patent Application No. 17,160/45). Two washings with water are usually sufficient and, after being neutralised with calcium carbonate, the bulked aqueous layers are extracted continuously with ether to recover β -nitroisopropanol, which is purified by a single distillation.

The insoluble oil layer is first dried by azeotropic distillation with benzene. Its composition and subsequent treatment vary according to whether or not oxygen is used in the reaction. When oxygen is added, the insoluble

oil consists of a mixture of roughly equal parts of dinitropropane and nitropropyl nitrate which must be separated by fractional distillation under high vacuum, since the former cannot be obtained by freezing as in the case of dinitro-ethane and *-isobutane*. When oxygen is not added, the insoluble oil contains much less nitropropyl nitrate, but may contain as much as 15—20% of 4-nitro-3-methylfuran oxide (VIII). Only part of this can be frozen out by dissolving the oil in twice its volume of methanol and cooling to -70° . The oil is then less stable to distillation, and the solid furazan oxide distils over a wide range, interfering with collection of the main product, *viz.*, 1 : 2-dinitropropane.

Yields.—The combined yield of distilled β -nitroisopropanol and distilled insoluble oil usually accounts for more than 70% of the propylene consumed, but the isolation of pure 1 : 2-dinitropropane, β -nitroisopropyl nitrate, and 4-nitro-3-methylfuran oxide from the insoluble oil occasions some loss, particularly when the last compound is present. Recovery of nitropropanol from the aqueous layer is at best 80%, losses being due to incomplete extraction and to some hydrolytic fission of the nitro-alcohol to nitromethane and acetaldehyde: $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NO}_2 \longrightarrow \text{CH}_3\cdot\text{CHO} + \text{CH}_3\cdot\text{NO}_2$. Yields of distilled nitropropanol and distilled insoluble oil are given below for reaction with and without oxygen. Corrected figures in parentheses make allowance for experimentally determined extraction and distillation losses.

	Yields % on propylene consumed.	
	(a) With oxygen.	(b) Without oxygen.
β -Nitroisopropanol	33.5 (41.9)	41.3 (51.6)
Insoluble oil	42.0 (42.8)	31.2 (36.1)
Totals	75.5 (84.7)	72.5 (87.7)

In case (a), fractional distillation of the insoluble oil gives almost equal molar proportions of 1 : 2-dinitropropane and β -nitroisopropyl nitrate, and in case (b), freezing, followed by rather troublesome fractional distillation, suggests the following proportions, reduced to yields on propylene consumed: 18—20% of dinitropropane, 3—4% of nitroisopropyl nitrate, and 6—8% of 4-nitro-3-methylfuran oxide. The overall yield on tetroxide consumed is about 94%, and the ether recovery 99%.

These results indicate that types of addition other than the two described do not occur to any considerable extent. Addition to form nitropropyl nitrite appears to be markedly favoured in the case of propylene, while oxygen addition assists its conversion to nitropropyl nitrate. A similar effect with oxygen has been found in the case of *isobutylene*.

Properties and Reactions of Products.—1 : 2-Dinitropropane. Unlike 1 : 2-dinitro-ethane and *-isobutane*, 1 : 2-dinitropropane has not been obtained as a solid except at low temperatures. This is possibly associated with its asymmetry, the *d*- and the *l*-form being solid, and the *dl*-form liquid at room temperature. The liquid appears to be more stable than 1 : 2-dinitroethane, distilling under high vacuum to give a practically colourless oil, b. p. $88^{\circ}/\text{ca. } 1 \text{ mm.}$, and developing only a slight yellow tinge in several months' storage. Reaction with aqueous alkali, or even weak bases such as urea, gives polymeric 1-nitropropyl-1-ene (see British Patent Application No. 20,484/44): $\text{CH}_3\cdot\text{CH}(\text{NO}_2)\text{CH}_2\cdot\text{NO}_2 + \text{NaOH} \longrightarrow \text{NaNO}_2 + \text{H}_2\text{O} + \text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{NO}_2 \longrightarrow \text{polymer}$. 1 : 2-Dinitropropane has been further characterised by reduction to 1 : 2-diaminopropane and by acid hydrolysis to hydroxylamine.

β -Nitroisopropyl nitrite. β -Nitroisopropyl nitrite, prepared from the alcohol by reaction with sodium nitrite and dilute acid, is somewhat more stable than the corresponding nitroethyl nitrite. It can be distilled at $28\text{--}30^{\circ}/< 1 \text{ mm.}$, and decomposition with gas evolution on standing is moderately slow. A distilled sample gave N, 20.4 ($\text{C}_3\text{H}_6\text{O}_4\text{N}_2$ requires N, 20.9%). Like β -nitroethyl nitrite, it is hydrolysed by water or methyl alcohol to the nitro-alcohol.

β -Nitroisopropanol is a colourless mobile liquid, b. p. $68^{\circ}/\text{ca. } 1 \text{ mm.}$, $106\text{--}109^{\circ}/20 \text{ mm.}$, $d_4^{20} 1.192$, $n_D^{20} 1.441$. It is not affected by storage and is identical with the nitro-alcohol prepared by condensation of nitromethane and acetaldehyde in the presence of basic catalysts. It is oxidised by aqueous dichromate to nitroacetone, and its acetate on heating affords monomeric 1-nitro-1-propylene: $\text{CH}_3\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{NO}_2 \longrightarrow \text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{NO}_2 + \text{HOAc}$.

β -Nitroisopropyl nitrate, when pure, is a colourless mobile liquid, b. p. $71^{\circ}/\text{ca. } 1 \text{ mm.}$, $d_4^{20} 1.348$, $n_D^{20} 1.447$. It is a powerful explosive, with approximately 75% of the power of blasting gelatin, and is very insensitive to friction and impact. Reaction with alkali readily abstracts nitric acid to form polymeric nitropropylene (British Patent Application No. 24,764/44), and further characterisation has been provided by comparison with synthetic material, using Wieland and Sakellarios's nitration procedure (*Ber.*, 1920, 53, 201) for 2-nitroethanol on β -nitroisopropanol prepared from nitromethane and acetaldehyde.

4-Nitro-3-methylfuran oxide is a white solid identical with the substance prepared by Behrend and Schmitz (*Annalen*, 1893, 277, 310). It crystallises from methanol to give large hexagonal plates, m. p. $67\text{--}69^{\circ}$. The melt is stable to heat, no discernible decomposition (*e.g.*, gas evolution) occurring during 40 hours at 100° . The solid dissolves in warm aqueous alkali and has been catalytically reduced in acetic acid with hydrogen at 100 atm. to give 4-amino-3-methylfuran oxide.

EXPERIMENTAL.

Reagents.—Pure liquid dinitrogen tetroxide was prepared as described in Part II. Propylene was obtained by dehydrating *isopropanol* over active alumina ("Alorco" chips) at $350\text{--}400^{\circ}$. The issuing gases were cooled to condense

water and unchanged isopropanol, washed with water, and dried with calcium chloride before passing directly to the nitration vessel or to catch-pots at -70° for storage as liquid. The alumina catalyst was regenerated at 4-hour intervals by passage of air at 450° , and the purity of the propylene frequently checked by analysis. The ethyl ether used as reaction solvent was washed several times with water to remove any alcohol present, dried over calcium chloride and then metallic sodium, and finally distilled from and stored over sodium.

Nitration Procedure.—The apparatus was similar to that described in Part II, and two typical runs are described: (a) with oxygen added to the propylene before absorption, (b) without oxygen. (a) In the first, 48.5 l. of propylene (85 g.) and 23.5 l. of oxygen were passed into a solution of 435 g. of tetroxide in 1003 g. of ether during 3 hours. Absorption was rapid, and the solution retained its pale amber colour. In (b), 68.0 l. of propylene (119 g.) were passed into a solution of 615 g. of tetroxide in 1540 g. of ether, also during 3 hours, the solution turning a bright green. The external bath temperature was kept at 0° in both cases. The concentrations of tetroxide in ether (30.2% and 28.5% by weight) and the molar percentage absorption of propylene (42.6% and 42.4%) were similar for the two cases.

Separation and Purification of Products.—(a) *With oxygen.* Ether and excess of tetroxide were removed at water-pump pressure and collected for re-use in traps cooled to -70° . The total weight recovered was 1265 g., compared with 1252 g. calculated from complete reaction of the propylene absorbed. The pale green reaction product remaining weighed 257 g. (Calc.: 271 g.), and was stirred with 4 vols. of water. The oil was separated, and washed successively with 2 vols. and with 1 vol. of water, the three aqueous layers being bulked for continuous extraction with ether. After the ethereal extract had been dried (Na_2SO_4), the ether was removed under suction, and the 2-nitroisopropanol distilled (71.2 g., 33.5% yield on propylene) (Found: C, 34.1; H, 6.7; N, 13.8. Calc. for $\text{C}_3\text{H}_7\text{O}_3\text{N}$: C, 34.3; H, 6.7; N, 13.3%).

The insoluble oil (130 g.) was mixed with an equal volume of methanol and cooled to -70° , but no solid deposited. Methanol was removed under vacuum, and the residual oil dried by adding 80 ml. of benzene and distilling off the latter with the moisture at about 1 mm. pressure and a bath temperature not exceeding 30° . The remaining oil (123.9 g.) was distilled under high vacuum to give the following fractions: (i) 5.5 g., b. p. 68–79°/1 mm.; (ii) 60.3 g., b. p. 79–86°/1 mm.; (iii) 54.8 g., b. p. 86–92°/1 mm.; residue, 2.1 g. Distillation was smooth throughout and no 4-nitro-3-methylfuran oxide was obtained. The first two fractions were combined and redistilled to give β -nitroisopropyl nitrate (61.7 g.), b. p. 78–80°/1 mm. (Found: C, 25.7; H, 4.5; N, 19.0. $\text{C}_3\text{H}_6\text{O}_5\text{N}_2$ requires C, 24.0; H, 4.0; N, 18.7%). Redistillation of fraction (iii) gave 49.7 g. of 1:2-dinitropropane, b. p. 89–90°/1 mm. (Found: C, 27.3; H, 4.4; N, 20.2. $\text{C}_3\text{H}_6\text{O}_4\text{N}_2$ requires C, 26.8; H, 4.5; N, 20.9%). Fractions (i) and (ii) represent a 21.4% yield of nitropropyl nitrate on propylene consumed, and fraction (iii) a 20.2% yield of dinitropropane.

(b) *Without oxygen.* Ether and excess of tetroxide were removed as before, and the crude product stirred with 1400 ml. of water to give 160 ml. of insoluble oil. This was stirred with 320 ml. of water to give 130 ml. of oil which was reduced by further washing with 250 ml. of water to 128 ml. (158 g.). To this was added a further 15 g. of oil which separated from the bulked aqueous layer. The mixture was extracted with ether and treated as before, giving 122.9 g. of 2-nitroisopropanol, b. p. 68°/ca. 1 mm. (Found: C, 34.1; H, 6.7; N, 13.5. Calc. for $\text{C}_3\text{H}_7\text{O}_3\text{N}$: C, 34.3; H, 6.7; N, 13.3%). The yield on propylene consumed was 41.3%, and there remained 29.2 g. of distillation residue.

The 178 g. of insoluble oil were mixed with an equal volume of methanol and cooled to -70° . Some solid separated, but melted on the filter and passed through. After removal of methanol under suction, the 151 g. of oil remaining were dried by azeotropic distillation with 70 ml. of benzene as above, leaving 148 ml. of oil to be distilled under high vacuum. This gave two fractions: (i) 4.8 g., b. p. 58–86°/3 mm.; (ii) 113.5 g., b. p. 86–108°/2 mm.; residue, 18.6 g. Gas evolution during the beginning and end of distillation necessitated occasional chilling of the boiler with a solid carbon dioxide-methanol bath. Distillation of the first fraction and the early part of the second was accompanied by deposition of solid 4-nitro-3-methylfuran oxide in the receiver. A total of 11.6 g. of this solid was separated from the two fractions by dissolving them in methanol and cooling at -70° overnight. It was recrystallised from methanol to give large hexagonal plates, m. p. 67–69° (Found: C, 25.2; H, 2.2; N, 29.1; *M*, 145. Calc. for $\text{C}_3\text{H}_3\text{O}_4\text{N}_2$: C, 24.8; H, 2.1; N, 29.0%; *M*, 145).

Methanol was removed under suction from the combined filtrates, the oil dried with benzene as before, and fractional distillation repeated to give: (i) 1.9 g., b. p. 61–76°/1.5 mm.; (ii) 15.7 g., b. p. 76–78°/1.5 mm.; (iii) 77.5 g., b. p. 96–104°/1.5 mm.; residue, 1.0 g. Fraction (ii) gave a further 3.4 g. of the furazan oxide on freezing in methanol, and the early fractions from the redistillation of (iii) in an efficient packed still gave 6.5 g. more, together with a final fraction of 55.8 g. of pure 1:2-dinitropropane. The final result of this complicated combination of freezing out the solid and fractional distillation was: 21.5 g. of pure 4-nitro-3-methylfuran oxide (5.2% on propylene consumed), 55.8 g. of pure 1:2-dinitropropane (14.8%), and 24.6 g. of oil (approximately 6.5%) remaining after solid was frozen out of various fractions and consisting largely of 1:2-dinitropropane with some nitropropyl nitrate and some 4-nitro-3-methylfuran oxide. Distillation residues totalled another 24 g.

Preparation of Derivatives.—*Reduction of 1:2-dinitropropane to propylenediamine.* 0.467 G. of dinitropropane was dissolved in 30 ml. of acetic acid and reduced with electrolytic hydrogen at 85 atm. in the presence of 0.022 g. of Adams's catalyst. The catalyst was then filtered off, the solution saturated with dry hydrogen chloride, and the acetic acid distilled off under reduced pressure, leaving 0.488 g. of crude dihydrochloride (93.5% yield); it was washed with cold alcohol (Found: Cl, 46.6%) and then recrystallised from alcohol, and had m. p. 220–222° (Found: Cl, 47.6. Calc. for $\text{C}_3\text{H}_{10}\text{N}_2 \cdot 2\text{HCl}$: Cl, 48.3%) (lit. m. p. 220°).

The dipicrate had m. p. 237° (lit. 237°) (Found: C, 33.4; H, 3.4; N, 21.3. Calc. for $\text{C}_3\text{H}_{10}\text{N}_2 \cdot 2\text{C}_6\text{H}_5\text{O}_7\text{N}_3$: C, 33.8; H, 3.0; N, 21.1%).

Acid hydrolysis of 1:2-dinitropropane. Reaction for 15 minutes at 150° of 0.300 g. of the dinitropropane with 4.5 ml. of concentrated hydrochloric acid gave, after dilution with 250 ml. of distilled water, 0.0510 g. of hydroxylamine as determined by the procedure outlined in Part II. The yield was 69.1% based on a single primary nitro-group.

Oxidation of β -nitroisopropanol to nitroacetone. A mixture of 24.5 g. of nitropropanol, 37.5 g. of sodium dichromate, and 22.5 ml. of water was vigorously stirred and kept at 20 – 25° while 45 g. of concentrated sulphuric acid in 11.5 ml. of water were added during 2 hours. After a further $2\frac{1}{2}$ hours' stirring, the mixture was diluted with water and extracted three times with 60 ml. of ether. The ether was removed under reduced pressure, leaving 19.8 g. of white crystalline solid (82.5% yield). Two recrystallisations from methanol gave nitroacetone, m. p. 50–51° (Found: C, 35.8; H, 5.2; N, 14.2. Calc. for $\text{C}_3\text{H}_5\text{O}_3\text{N}$: C, 35.0; H, 4.9; N, 13.6%). Henry (*Bull. Acad. roy. Belg.*, 1898, **36**, 149) described nitroacetone as a colourless liquid, b. p. $152^{\circ}/717$ mm., but Harries (*Annalen*, 1901, **319**, 251) obtained it as a white solid, m. p. 50–57°. Its anil, prepared by Harries's method (*loc. cit.*), had m. p. 85–87° after crystallisation from ethyl alcohol (Harries gives m. p. 87°) (Found: C, 60.5; H, 6.1; N, 16.4. Calc. for $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$: C, 60.7; H, 5.6; N, 15.7%).

Similar results were given with nitroacetone prepared from synthetic β -nitroisopropanol (condensation of nitro-methane and acetaldehyde). Nitroacetone crystals tend to become yellow and oily on standing for 2–3 weeks but can be purified by recrystallisation from methanol. They are best stored over potassium hydroxide.

β -Nitroisopropyl acetate and 1-nitropropyl-1-ene. To 170 g. of acetyl chloride were added 90 g. of nitropropanol at a rate just sufficient to maintain reflux, and the mixture was then refluxed for a further hour. The excess of acetyl chloride

and the acetic acid formed were removed under reduced pressure, and the residue distilled to give 118 g. (94%) of acetate, b. p. 76/ca. 1 mm.; this was purified by redistillation (Found: C, 40.5; H, 6.1; N, 10.0. Calc. for $C_5H_9O_2N$: C, 40.9; H, 6.1; N, 9.7%).

The nitro-olefin was prepared from the acetate (50 g.) by heating it with freshly fused and powdered sodium acetate (0.2 g.) at 110–120° for 40 minutes under reflux. The product was then distilled rapidly under 1 mm. pressure into a receiver cooled to –70°. The lachrymatory oil so obtained was washed four times with saturated sodium chloride solution, dissolved in an equal volume of ether, and dried over calcium chloride. The ether was removed and the oil distilled to give 20.5 g. (78%) of 1-nitropropyl-1-ene, b. p. 37–42°/10 mm., and 6.2 g. of unchanged acetate.

Similar results were obtained in both preparations with 2-nitroisopropanol from nitromethane and acetaldehyde.

Polymeric nitropropylene from β -nitroisopropyl nitrate. A solution of 0.266 g. of sodium hydroxide in 20 ml. of water was added dropwise (20 mins.) to a stirred solution of 1 g. of nitropropyl nitrate in 10 ml. of methanol. After a further 30 minutes' stirring, the mixture was acidified with dilute hydrochloric acid, and the solid polymer was filtered off, washed with water and methanol, and dried in a vacuum desiccator over calcium chloride and phosphoric oxide; yield, 0.274 g. (42%) of somewhat moist polymer [Found: C, 40.0; H, 5.6; N, 15.4. Calc. for $(C_3H_5O_2N)_n$: C, 41.4; H, 5.75; N, 16.1%].

Preparation of β -nitroisopropyl nitrate from nitropropanol. Nitropropanol (230 g., prepared from nitromethane and acetaldehyde) was added slowly with stirring to a mixture of 500 g. of nitric acid (98%) and 1000 g. of concentrated sulphuric acid. The mixture was stirred for a further hour, set aside overnight, and the top layer separated and poured into 2 l. of iced water. The mixture was stirred, and the oil separated for a further washing with 350 ml of water; it was then dried by azeotropic distillation with 180 ml. of benzene to give 202.5 g. (61.8%) of the nitrate, b. p. 76°/ < 1 mm. (Found: C, 24.1; H, 4.2; N, 18.6. Calc. for $C_3H_6O_5N_2$: C, 24.0; H, 4.0; N, 18.7%). *4-Amino-3-methylfuran oxide*, formed by reduction of the nitro-compound as described on p. 1103, is a pale yellow solid, m. p. 175° (Found: C, 31.7; H, 4.7; N, 34.8. $C_3H_5O_2N_3$ requires C, 31.3; H, 4.4; N, 36.5%).

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
RESEARCH DEPARTMENT, BILLINGHAM, CO. DURHAM.

[Received, April 2nd, 1946.]