281. *Aliphatic Nitro-compounds. Part II. Conjugated Nitro-dienes.*

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Three conjugated nitro-dienes, *viz.*: 3-*nitropenta*-1 : 3-*diene*, 2-*nitro*-3-*methylbuta*-1 : 3-*diene* and 1-(1-*nitrovinyl*)cyclo*hexene* have been synthesised. These compounds are very unstable, and preliminary experiments on their addition reactions have yielded no identifiable products. 1-(1-Nitrovinyl)*cyclo*hexene readily forms a crystalline *dimeride* of unknown constitution.

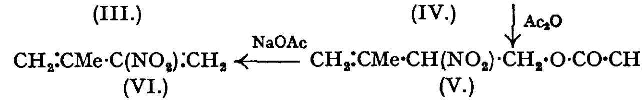
In view of the high reactivity of the α-nitro-olefins, it seemed likely that conjugated nitro-dienes, if they could be prepared, would form a useful starting point for novel synthesis. No attempt to prepare compounds of this type appears to be recorded in the literature, and it was therefore decided to apply to the problem the methods which are successful in the synthesis of the nitro-olefins.

During the preparation of 2-nitro*iso*propyl acetate by acetylation of crude 2-nitro*iso*propyl alcohol formed by interaction of nitromethane and acetaldehyde (Henry, *Bull. Soc. chim.*, 1895, **13**, 999), a large quantity of a high-boiling by-product was accumulated which on fractionation gave a mixture of diastereoisomerides of 3-*nitro*-2 : 4-*diacetoxypentane* (I), one of which was isolated in a pure crystalline state. On being heated with a small amount of sodium acetate, this material readily underwent fission to 3-*nitropenta*-1 : 3-*diene* (II) and acetic acid.

$$\underset{\text{(I.)}}{NO_2\cdot CH(CHMe\cdot O\cdot CO\cdot CH_3)_2} \longrightarrow \underset{\text{(II.)}}{CH_3\cdot CH{:}C(NO_2)\cdot CH{:}CH_2} + CH_3\cdot CO_2H$$

Like the simple nitro-olefins, the nitro-diene was a powerful lachrymator and very unstable. It decomposed to a black tar under the influence of light or heat, even in the presence of quinol, but was apparently unchanged after several weeks in the dark. It did not polymerise on treatment with alkalis but was readily polymerised by peroxides to a dark brown low-melting solid. It failed to react with aqueous sodium hydrogen sulphite and gave only tars on being warmed with maleic anhydride or *cyclo*pentadiene. With bromine in carbon tetrachloride a dark oil was obtained which could not be purified; with piperidine an adduct was formed, but this was not further investigated.

2-*Nitro*-3-*methylbuta*-1 : 3-*diene* was prepared from 1-nitro-2-methylprop-2-ene by the following series of reactions.

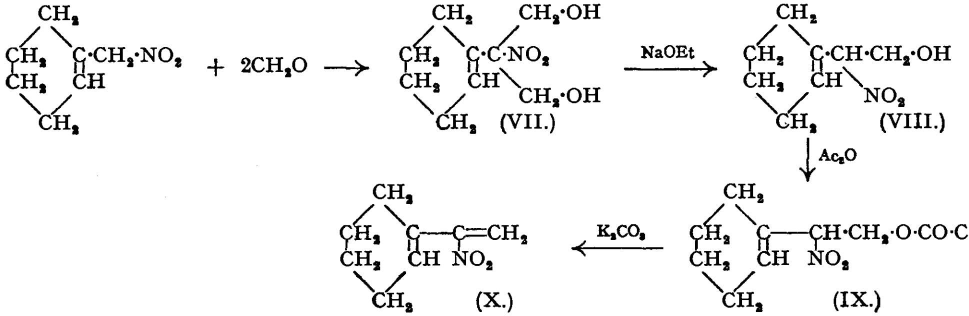


$$CH_2{:}CMe{\cdot}CH_2{\cdot}NO_2 + 2CH_2O \longrightarrow \underset{\text{(III.)}}{CH_2{:}CMe{\cdot}C(NO_2)(CH_2{\cdot}OH)_2} \xrightarrow{NaOEt} \underset{\text{(IV.)}}{CH_2{:}CMe{\cdot}CH(NO_2){\cdot}CH_2{\cdot}OH}$$

$$\xrightarrow{Ac_2O} \underset{\text{(V.)}}{CH_2{:}CMe{\cdot}CH(NO_2){\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_3} \xrightarrow{NaOAc} \underset{\text{(VI.)}}{CH_2{:}CMe{\cdot}C(NO_2){:}CH_2}$$

The *diol* (III) on treatment with sodium ethoxide afforded the *alcohol* (IV) (cf. Schmidt and Wilkendorf, *Ber.*, **1919**, **52**, 389). Both the diol and the alcohol were difficult to purify, but for the preparation of (VI) this was immaterial, provided that the more stable *acetate* (V) was fractionated. The diene (VI) closely resembled the isomeric 3-nitropenta-1 : 3-diene in its properties but was even less stable, decomposing to a black tar on standing for a few days.

Application of these syntheses to 1-nitromethyl*cyclo*hexene gave 1-(1-*nitro*-2-*acetoxyethyl*)-cyclo*hexene* (IX), but attempted distillation of this with sodium acetate resulted in violent decomposition. A similar result was obtained on attempting to dehydrate the *alcohol* (VIII) by distillation with 3-nitrophthalic anhydride.



By treating the nitro-ester (IX) in ether with potassium carbonate in presence of quinol a lachrymatory oil, presumably (X), was obtained, but this could not be purified. On standing it gave a solid which (from analysis and molecular weight) appeared to be a *dimeride* of (X). This product was also obtained directly if the potassium carbonate treatment was carried out in the absence of quinol. The yield was poor, but no other pure compounds were isolated. Although other new products were obtained, these could not be purified. Hydrogenation and addition of bromine to the dimer gave no definite products, and no systematic study of its reactions was attempted.

EXPERIMENTAL.

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

3-*Nitro*-2 : 4-*diacetoxypentane* (I).—The high-boiling residue (700 g.) from a series of preparations of 2-nitro*iso*propyl acetate (prepared by acetylation of the crude nitro-alcohol from acetaldehyde and nitromethane; cf. Schmidt and Rutz, *Ber.*, 1928, **61**, 2142) was fractionated to give a viscous yellow oil (490 g.), b. p. 140—150°/20 mm., which partly crystallised on standing. The solid *compound* was collected and recrystallised from light petroleum (b. p. 100—120°), forming colourless needles (40 g.), m. p. 85—86° (Found : C, 46·6; H, 5·95; N, 6·2. $C_9H_{15}O_6N$ requires C, 46·35; H, 6·4; N, 6·0%). The liquid fraction was apparently essentially a mixture of the two diastereoisomerides (Found : C, 46·05; H, 6·25; N, 6·6%).

3-*Nitropenta*-1 : 3-*diene* (II).—Crude 3-nitro-2 : 4-diacetoxypentane (145 g.) was stirred with anhydrous sodium acetate (1 g.) at 95—100° for 1 hour and distilled under 12 mm. The distillate was washed thrice with saturated brine, dried, and fractionated to give 3-*nitropenta*-1 : 3-*diene* (38 g.; 54% theory) as a pale yellow lachrymatory oil, b. p. 63—65°/13 mm. (Found : C, 53·25; H, 6·3; N, 12·35. $C_5H_7O_2N$ requires C, 53·1; H, 6·2; N, 12·4%). A considerable tarry residue remained after the distillation.

2-*Nitro*-1-*hydroxy*-3-*methyl*-2-*hydroxymethylbut*-3-*ene* (III).—A mixture of 1-nitro-2-methylprop-2-ene (2 g.; Levy and Scaife, in the press), ethyl acetate (6 c.c.), paraformaldehyde (1·3 g.), and 33% aqueous potassium hydroxide (1 drop) was refluxed until all the paraformaldehyde had dissolved. The solution was kept at 0° for several days, and the crystalline precipitate collected and purified by recrystallisation from ethyl acetate, giving colourless rectangular prisms of the *compound*, m. p. 103—104° (Found : C, 44·75; H, 6·55; N, 8·5. $C_6H_{11}O_4N$ requires C, 44·7; H, 6·8; N, 8·7%).

2-*Nitro*-1-*hydroxy*-3-*methylbut*-3-*ene* (IV).—A mixture of 1-nitro-2-methylprop-2-ene (20 g.) *iso*propyl alcohol (60 c.c.), paraformaldehyde (13·2 g.), and 33% aqueous potassium hydroxide (6 drops) was refluxed for 3 hours. After cooling, a solution of sodium ethoxide [from sodium (5 g.) in alcohol (50 c.c.)] was added slowly with stirring below 10°. After 1 hours' stirring at 0—10°, the precipitate was collected, dissolved in a little water, acidified with dilute hydrochloric acid below 15°, saturated with salt, and extracted with ether. The extract was dried and fractionated to give the *compound* as a colourless oil (5·2 g.), b. p. 113—115°/15 mm. (Found : C, 45·55; H, 7·05; N, 10·1. $C_5H_9O_3N$ requires C, 45·8; H, 6·85; N, 10·7%); distillation was stopped at this point owing to incipient decomposition of the residue.

2-*Nitro*-1-*acetoxy*-3-*methylbut*-3-*ene* (V).—1-Nitro-2-methylprop-2-ene (24 g.) was converted into 2-nitro-1-hydroxy-3-methylbut-3-ene as described above. After removal of the ether, the crude product was mixed with acetic anhydride (25·2 g.), heated at 100° for 1 hour, and distilled to give the *compound* as a colourless oil (30·2 g.), b. p. 102—104°/0·5 mm. (Found : C, 49·2; H, 6·3; N, 7·8. $C_7H_{11}O_4N$ requires C, 48·6; H, 6·35; N, 8·1%).

2-*Nitro*-3-*methylbuta*-1 : 3-*diene* (VI).—2-Nitro-1-acetoxy-3-methylbut-3-ene (30 g.) and anhydrous sodium acetate (0·1 g.) were heated under 12 mm. (oil-bath temperature 110—120°). A colourless liquid distilled, but after a short time the residue began to decompose and distillation was stopped. The distillate was washed thrice with saturated brine, dried, and distilled to give 2-*nitro*-3-*methylbuta*-1 : 3-*diene* as a pale yellow lachrymatory oil (4·7 g.), b. p. 54—57°/14 mm. (Found : N, 12·3. $C_5H_7O_2N$ requires N, 12·4%). This closely resembled 3-nitropenta-1 : 3-diene in all its reactions.

1-(1-*Nitro*-2 : 2′-*dihydroxy*iso*propyl*)cyclo*hexene* (VII).—1-Nitromethyl*cyclo*hexene (7 g.; Fraser and Kon, *J.*, 1934, 604), paraformaldehyde (3·3 g.), ethyl acetate (25 c.c.), and 33% aqueous potassium hydroxide (3 drops) were refluxed until homogeneous (2 hours). The mixture was carefully neutralised with N-hydrochloric acid and the solvent removed under reduced pressure. After being kept in a desiccator for several days, the viscous residue crystallised to a white solid, m. p. 58—61°, which was very soluble in all organic solvents except light petroleum. Attempts to purify this material were unsuccessful.

1-(1-*Nitro*-2-*hydroxyethyl*)cyclo*hexene* (VIII).—Crude 1-(1-nitro-2 : 2′-dihydroxy*iso*propyl)*cyclo*hexene (9 g.) was dissolved in alcohol (25 c.c.) and treated with a solution of sodium ethoxide [from sodium (1·25 g.) in alcohol (15 c.c.)] below 15°. The mixture was then cooled to 0°, and the precipitated sodium salt collected, dissolved in water, and acidified with hydrochloric acid below 15°. The product was isolated by extraction with ether, dried, and distilled to give a pale yellow oil (3 g.; 38% theory), b. p. 98—100°/0·5 mm., which solidified to a crystalline mass of 1-(1-*nitro*-2-*hydroxyethyl*)cyclo*hexene*, m. p. 45—46° (Found : C, 56·05; H, 7·25; N, 8·1. $C_8H_{13}O_3N$ requires C, 56·15; H, 7·6; N, 8·2%).

1-(1-*Nitro*-2-*acetoxyethyl*)cyclo*hexene* (IX).—1-Nitromethyl*cyclo*hexene (21 g.), paraformaldehyde (9·9 g.), *iso*propyl alcohol (45 c.c.), and 33% aqueous potassium hydroxide (0·5 c.c.) were refluxed until a clear solution was obtained. After the solution had been cooled to 0°, a solution of sodium ethoxide [from sodium (3·75 g.) in alcohol (40 c.c.)] was added during 30 minutes. After 1 hour at 0—10° with stirring, the sodium salt was collected, dissolved in water (100 c.c.), and acidified with aqueous hydrochloric acid below 10°. The precipitated oil was extracted with ether, the extract dried, and the solvent removed. The crude *product* was cooled in ice, treated with 98% sulphuric acid (2 drops) followed by acetic anhydride (23 g.), and the mixture stirred at 60° for 2 hours. Distillation gave a colourless oil (22·5 g.), b. p. 102—105°/1 mm. (Found : N, 6·5. $C_{10}H_{15}O_4N$ requires N, 6·55%).

1-(1-*Nitrovinyl*)cyclo*hexene* (X).—1-(1-Nitro-2-acetoxyethyl)*cyclo*hexene (15 g.), potassium carbonate (15 g.), ether (50 c.c.), and quinol (0·1 g.) were refluxed with stirring for 4 hours, cooled, and washed with water. The ethereal solution was then treated with a further 0·1 g. of quinol and dried ($CaCl_2$). The ether was removed under reduced pressure at 30°, leaving a pale yellow lachrymatory oil (9·2 g.) which decomposed on attempted distillation under 0·5 mm. (Found : N, 8·8. $C_8H_{11}O_2N$ requires N, 9·15%). The *nitro-diene* did not react with aqueous sodium hydrogen sulphite and did not polymerise on boiling with dilute sodium carbonate solution; on keeping, it slowly dimerised.

1-(1-*Nitrovinyl*)cyclo*hexene Dimer*.—1-(1-Nitro-2-acetoxyethyl)*cyclo*hexene (48 g.), potassium carbonate (48 g.), and ether (150 c.c.) were refluxed with stirring for 4 hours, cooled, washed with water, and dried ($CaCl_2$). The ethereal solution was allowed to evaporate at 20° and the crystals were collected (9·9 g.) and washed with light petroleum (b. p. 100—120°). Recrystallisation from light petroleum and from acetic acid gave large colourless plates of 1-(1-*nitrovinyl*)cyclo*hexene dimer*, m. p. 136—137° (Found : C, 62·6; H, 7·4; N, 9·3; *M* (cryoscopic in benzene), 290. $C_{16}H_{22}O_4N_2$ requires C, 62·75; H, 7·2; N, 9·15%; *M*, 306).

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