

384. Condensation of Nitromethane with Aldehydes. Derivatives of 1-Nitropent-3-en-2-ol.

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Alkali-catalysed condensation of nitromethane with crotonaldehyde gave a poor yield of the unsaturated nitro-alcohol, 1-nitropent-3-en-2-ol, which on successive acetylation and dehydroacetylation yielded an unstable liquid, probably 1-nitropenta-1:3-diene. From 1-nitropent-3-en-2-ol, 1-benzamidopentan-2-one was prepared by successive hydrogenation, benzoylation, and chromic acid oxidation. Purification of 1-nitro-2-acetoxypent-3-ene by distillation yielded a residual substance which was not identified.

ALTHOUGH condensation of nitro-paraffins with aldehydes has been the subject of many publications, condensation with unsaturated aliphatic aldehydes was first described by Degering and Sprang (U.S.P. 2,332,482) while the present work was in progress. No yields are quoted by these authors but their results on the condensation of crotonaldehyde and nitromethane show general agreement with those reported in the present paper.

The main object of the present investigation was the preparation of 1-nitropenta-1:3-diene, a substance isomeric with the conjugated nitro-dienes previously prepared by Buckley and Charlsh (J., 1947, 1472) but differing from these in having the nitro-group in the terminal position. An unstable, though distillable, liquid, which was probably the required nitro-diene, was obtained by subjecting 1-nitropent-3-en-2-ol, the primary product of the alkali-catalysed condensation of nitromethane with crotonaldehyde, to successive acetylation with acetyl chloride and dehydroacetylation in presence of a catalytic amount of sodium acetate. The initial reaction of crotonaldehyde with nitromethane gave a maximum yield (on aldehyde) of about 40% and, with high molar ratios of nitromethane to aldehyde, there was evidence that the crotonaldehyde had reacted with more than one mol. of nitro-paraffin. No crystalline derivative for characterisation of the supposed nitro-diene could be obtained by the Diels-Alder reaction or otherwise, but a brittle polymer formed slowly at room temperature without catalyst and more rapidly in presence of sodium methoxide.

1-Nitropent-3-en-2-ol was reduced catalytically, giving poor yields of crude 1-aminopentan-2-ol. Oxidation of the *N*-benzoyl derivative of the latter gave 1-benzamidopentan-2-one.

Purification of 1-nitro-2-acetoxypent-3-ene by distillation gave a residue which yielded a substance, m. p. 102.5–103°, the structure of which was not determined but which was possibly a dimer of 1-nitropent-3-ene-2-ol.

EXPERIMENTAL.

1-Nitropent-3-en-2-ol.—Of a large number of condensations of nitromethane and crotonaldehyde carried out, the following are typical.

(a) Nitromethane (77 g.; 1.25 moles) was added gradually with stirring and cooling to a solution of potassium hydroxide (1.6 g.) in methanol (200 c.c.) followed by crotonaldehyde (70 g.; 1 mole) containing quinol (4 g.). During the addition of aldehyde (30 minutes) the temperature was kept below 30°. The reaction was completed by stirring for a further 25 minutes, the mixture acidified with concentrated hydrochloric acid, and the solution evaporated under reduced pressure (finally at 70°/15 mm.). Removal of potassium chloride by filtration gave a viscous, orange liquid (128 g.; theory 131 g.) which was divided into two parts. (i) 54 G. were distilled in nitrogen with addition of quinol (1 g.), giving nitropentenol (15.1 g.; 27%), b. p. 80°/3 mm.—110°/5 mm., as a yellow liquid; distillation was stopped when the bath temperature reached 170°, since at 190–200° violent decomposition was liable to occur (admission of air initiated violent decomposition at much lower temperatures). (ii) 74 G. were shaken with cold water (2000 c.c.). Three ether extractions of the filtered solution gave a golden liquid (42.7 g.) which on

distillation as in (i) gave nitropentenol (18.2 g.; 24%), b. p. 90°/2.5 mm.—110°/5 mm. For analysis a portion was redistilled (b. p. 91—100°/2 mm.) [Found: C, 45.2; H, 6.5; N, 10.0; *M* (cryoscopic in benzene), 133. Calc. for $C_8H_{11}O_2N$: C, 45.8; H, 6.9; N, 10.7%; *M*, 131].

(b) To a stirred solution of crotonaldehyde (105 g.; 1.5 moles) and quinol (6 g.) in methanol (300 c.c.) were added simultaneously nitromethane (91.5 g.; 1.5 moles) and sodium methoxide (0.62 g. sodium in 45 c.c. methanol). Sodium methoxide addition was rapid at first (30 c.c. in 3 minutes) and was complete in 16 minutes, while addition of nitromethane lasted 20 minutes during which the temperature was not permitted to rise above 30°. After reaction had been completed by continuing stirring for 20 minutes at 30°, the calculated amount of hydrochloric acid (2.67 c.c.; d_4^{20} 1.16) was added. Evaporation and filtration gave the crude product (150.2 g.; theory 196.5 g.) which was shaken with water and chloroform. The chloroform layer yielded a yellow liquid (133.7 g.) which, on distillation in nitrogen, gave two fractions: (i) b. p. 90—100°/2 mm. (64.5 g.; 32.8%); (ii) b. p. 100°/2 mm.—120°/10 mm. (27 g.). Redistillation of (ii) gave 12.9 g. (6.6%) of liquid (b. p. 91—100°/2 mm.). Yield of nitropentenol (b. p. 90—100°/2 mm.) 39.4%.

(c) Sodium methoxide (0.4 g. sodium in 40 c.c. methanol) was added with stirring and ice-cooling to a solution of nitromethane (91.5 g.; 1.5 moles) and quinol (0.05 g.) in methanol (50 c.c.). There was then added during 1½ hours at 1—5° with passage of nitrogen a solution of crotonaldehyde (17.5 g.; 0.25 mole) and quinol (0.05 g.) in methanol (20 c.c.). Thereafter, stirring was continued for 1 hour. Acidification with hydrochloric acid, filtration, and removal of methanol and excess of nitromethane below 50° in a stream of nitrogen gave crude nitropentenol (36.7 g.; theory 32.75 g.) which was taken up in chloroform. Washing, drying, and evaporation gave a liquid (27.4 g.) less viscous than the crude product in (a) and (b) above. Distillation up to a bath temp. of 190° in nitrogen into one receiver gave a distillate (23.1 g.) consisting of two main fractions, *viz.*, b. p. 80—95°/0.2 mm. and b. p. 170° (approx.)/0.7 mm. Redistillation of the whole in nitrogen gave nitropentenol (13.4 g.; 41% yield on aldehyde), b. p. 75—80°/0.3 mm. On further distillation a small fraction (1.0 g.), b. p. 80—115°/0.3—0.4 mm., was collected, but violent effervescence and tar formation prevented collection of the high-boiling fraction.

(d) A condensation was effected by using 3 times the theoretical quantity of nitromethane essentially under the conditions described in (c) but allowing the temperature to rise to 23°. On the basis of a small-scale (10 g.) distillation the yield of nitropentenol, b. p. 74°/0.1 mm.—90°/0.2 mm., was 43.5%, but on a larger scale (50 g.) was only 39%.

1-Nitro-2-acetoxypent-3-ene.—Interaction of 1-nitropent-3-en-2-ol and acetic anhydride and pyridine gave a tar, but reaction with acetyl chloride proceeded smoothly. (a) Crude undistilled nitropentenol (17.2 g.) prepared by method (a, ii) was treated with acetyl chloride (18.6 c.c.) at 30—35°. After evolution of hydrogen chloride had ceased the mixture was kept for 2 hours at room temperature, excess acetyl chloride distilled off, and chloroform added. The washed chloroform solution gave a pungent-smelling brown liquid (19.0 g.) which on distillation yielded 1-nitro-2-acetoxypent-3-ene (7.1 g.) as a colourless liquid, b. p. 97—103°/3—3.5 mm. [Violent decomposition at 200° (bath) prevented the distillation of higher-boiling fractions.] Yield 31.2% (on crude nitropentenol). Redistillation of 9.4 g. of the product in nitrogen gave a colourless liquid (6.6 g.) boiling at 96—101°/2 mm. but failing to give satisfactory analyses (Found: C, 47.2; H, 5.8; N, 8.9. Calc. for $C_7H_{11}O_4N$: C, 48.6; H, 6.4; N, 8.1%). (b) Distillation before acetylation gave less efficient conversion of crude nitropentenol into the acetyl derivative. To distilled nitropentenol (4.8 g.) acetyl chloride (10.4 c.c.; 4 times theory) was added gradually with cooling below 35°. The product was isolated as described above. The crude acetyl compound (4.2 g.) gave, on distillation, 3.5 g., b. p. 104—115°/5 mm. Yield 55% (on distilled nitropentenol).

1-Nitro-2-(3:5-dinitrobenzoxypent-3-ene.—This was prepared by heating the nitro-alcohol with 3:5-dinitrobenzoyl chloride until hydrogen chloride evolution ceased, and recrystallising the product twice from ethanol—light petroleum and once from aqueous methanol. The compound (needles) melted at 75.5—77° (Found: C, 43.3; H, 2.02; N, 12.5. $C_{12}H_{11}O_6N_3$ requires C, 44.3; H, 3.4; N, 12.9%).

1-Nitropenta-1:3-diene.—(a) Powdered anhydrous sodium acetate (0.3 g.) and quinol (0.2 g.) were added to 1-nitro-2-acetoxypent-3-ene (13.0 g.) and the mixture distilled in a stream of nitrogen. Three fractions were collected: (i) <130° (bath)/10 mm., (ii) 84—94°/9 mm. (6.2 g.), and (iii) 85—90°/5 mm. (1.8 g.). Fraction (i) was largely acetic acid, and (ii) was a highly refractive yellow liquid of penetrating odour consisting of crude nitropentadiene (yield 73%).

(b) In another preparation the acetic acid and nitropentadiene were collected as one fraction and the former removed by addition of chloroform and washing in turn with water and sodium hydrogen carbonate. Fractionation gave a product boiling at 85—100°/5—8 mm., yielding on redistillation nitropentadiene, b. p. 88—90°/8 mm. A sample of the substance was analysed but, in absence of quinol, it had decomposed appreciably before the analysis could be completed (Found: C, 51.3; H, 6.2; N, 10.4. Calc. for $C_5H_7O_2N$: C, 53.1; H, 6.2; N, 12.4%). On standing at room temperature 1-nitropenta-1:3-diene formed a brittle, amber resin in a few days, or, in presence of quinol, in a few weeks. Polymerisation was catalysed by sodium methoxide. A solution of nitropentadiene (2.17 g.) in dioxan (5.7 c.c.) was cooled in ice, and sodium methoxide (0.025 g. of sodium in 1.5 c.c. methanol) was added during 2 minutes with stirring at 0°. After being stirred for 1 hour at room temperature the mixture was poured into dilute acetic acid. The precipitated gum which still contained some monomer was washed repeatedly with water and dried in a vacuum desiccator (yield 0.84 g.; 39%). The product was almost completely soluble in acetone.

Attempted Cyanoethylation of 1-Nitropent-3-en-2-ol.—The method was essentially that of Bruson and Riener (*J. Amer. Chem. Soc.*, 1943, 65, 23). The nitro-alcohol (15 g.) was dissolved in dioxan (30 c.c.) and Triton B (40% aqueous benzyltrimethylammonium hydroxide; 2 g.) was added, followed during 40 minutes below 28° by acrylonitrile (18.2 g.; 3 mols.). After 6 hours at room temperature the product was isolated by extraction with chloroform and crystallised partly on addition of methanol (1.7 g.; washed with methanol). Tris-2-cyanoethylnitromethane was recrystallised thrice from methanol and formed needles, m. p. 112.5—113° (Found: C, 54.8; H, 5.4; N, 24.4. Calc. for $C_{10}H_{12}O_2N_4$: C, 54.6; H, 5.5; N, 25.4%).

Crystalline Substance from Purification of 1-Nitro-2-acetoxypent-3-ene.—Crude distilled acetyl compound [b. p. <150° (bath)/3 mm.] was redistilled up to 105—110°/3 mm. (bath 150°). The dark, viscous residual liquid crystallised to a small extent on standing. (Redistillation of the twice distilled acetyl compound gave a further, small, partly crystalline residue, so that the crystalline substance was apparently derived from the acetyl compound.) The viscous mother liquor was removed and the crystals washed and recrystallised; m. p. 98·5—100·5° (from methanol). From several hundred g. of crude acetyl compound about 10 g. of crystals were obtained. Five more recrystallisations from ethanol raised the m. p. to 102·5—103°, and from benzene this was unaltered [Found (averages of 3 determinations): C, 45·9; H, 6·9; N, 10·2; *M* (Rast), 230—400. (C₅H₉O₃N)_n requires C, 45·8; H, 6·9; N, 10·7%]. The following qualitative results were obtained. (a) Tests with bromine in chloroform and permanganate in acetone revealed no unsaturation. (b) The substance was recovered unchanged after attempted dehydroacetylation by refluxing it with sodium acetate in acetic acid or with potassium hydrogen carbonate in benzene. (c) After treatment for 4 days at room temperature with benzoyl chloride (50% excess on basis of one HO-group per C₅H₉O₃N unit) in pyridine, 64% of starting material was recovered. (d) After treatment for 4 days at room temperature and 1 hour at 45° in acetic acid with chromium trioxide (75% excess on basis of one HO-group per C₅H₉O₃N unit), 43% of the starting material was recovered unchanged. (e) The substance was recovered after being shaken for 6 hours at room temperature with hydrogen and platinum dioxide in acetic acid-acetic anhydride. With a large quantity of palladium black (prepared by method of Heilbron, Sexton, and Spring, *J.*, 1929, 929) in ethanol at room temperature, absorption of hydrogen ceased after 8 hours and was approximately that calculated for reduction of one nitro-group per C₅H₉O₃N unit. The product was a strongly basic liquid with an odour resembling that of 1-aminopentan-2-ol (see below), and gave a picrate, m. p. 265—270° (decomp.), after recrystallisation from ethanol-ether. With benzoyl chloride in pyridine and with nitrourea the crude base gave non-crystalline products.

1-Aminopentan-2-ol.—1-Nitropent-3-en-2-ol (13·4 g.; b. p. 75—80°/0·3 mm.) in ethanol (200 c.c.) was hydrogenated at 80 atmospheres (initial pressure) for 5 hours at 35—40°, using Raney nickel catalyst (3 g.). Charcoal treatment and evaporation gave a brown syrup (7·15 g.; theory 10·5 g.), which, on distillation, yielded a pale-yellow liquid (3·98 g.; 38%), b. p. 75° (approx.)/3·5 mm.; a redistilled sample, b. p. 75—80°/3·5—4 mm., gave unsatisfactory analyses (Found: C, 56·0; H, 10·0; N, 12·0. Calc. for C₅H₁₃ON: C, 58·2; H, 12·6; N, 13·6%). Interaction of the base and picric acid gave a tar, and nitrourea gave fibrous needles, m. p. 240° (decomp.) which were not the derived urea.

1-Benzamidopentan-2-ol.—Benzoyl chloride (1 mole) was added gradually during 1½ hours to a stirred suspension of sodium carbonate in a benzene solution of the amino-alcohol (1 mole) at 10°, and the mixture stirred until all benzoyl chloride had reacted (4 hours). Hot filtration and cooling gave plates (56% yield), m. p. 111—113°. Concentration of the benzene mother liquor and addition of light petroleum gave a further small quantity of crystals (total yield 61%). Recrystallised twice from benzene the compound melted at 112—113·5° (Found: C, 69·6; H, 8·1; N, 7·5. C₁₂H₁₇O₂N requires C, 69·5; H, 8·2; N, 6·8%).

1-Benzamidopentan-2-one.—1-Benzamidopentan-2-ol (3·10 g.) in acetic acid (20 c.c.) was added to a solution of chromium trioxide (1·05 g.) in water (2 c.c.). After 2 days at room temperature and 1 hour at 45° a semi-crystalline product was isolated by ether extraction. Addition of benzene and filtration gave unchanged 1-benzamidopentan-2-ol. The benzene solution on concentration gave a semi-crystalline, sticky mass, which, on prolonged filtration, yielded crystals, m. p. ca. 55°. Four recrystallisations from light petroleum (b. p. 40—60°) gave the compound as plates, m. p. 61·5—62·5 (Found: C, 70·3; H, 7·3; N, 6·8. C₁₂H₁₅O₂N requires C, 70·3; H, 7·3; N, 6·8%).

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