The good fractions from the distillation described above (Fig. 1) were combined with similar material from an identical run, and the composite was redistilled at about 20-plate efficiency to obtain the 16 g. of material on which the physical properties in Table I were determined.

Ozonolysis.—Vinylcyclopropane, 3.6 g. (0.053 mole), was ozonized in the apparatus described by Henne and Perilstein.[13] *n*-Pentane was used as the solvent, and the solution was immersed in a Dry Ice-cooled medium.

The ozonide solution was decomposed by the method of Cook and Whitmore[14] in which the ozonide solution is added dropwise to Raney nickel in *n*-pentane with stirring. The pentane was stripped off through a short Vigreux column, and the residue, after heating one and one-half hours on a steam-bath to assure complete decomposition of the ozonide, was extracted with *n*-pentane. The filtered extract was fractionated to remove the pentane but the residue failed to give a derivative with 2,4-dinitrophenylhydrazine, though it should have contained the bulk of the expected cyclopropanecarboxaldehyde. Presumably the aldehyde was hydrogenated or decarbonylated by contact with the hot Raney nickel.

The pentane stripped from the ozonide decomposition was fractionated at about 20-plate efficiency giving a distillate rich in formaldehyde and a residue from which cyclopropanecarboxaldehyde was isolated as the 2,4-dinitrophenylhydrazone (8% yield). This derivative, after recrystallization, melted at 182–185°, and there was no depression when it was mixed with an authentic sample.[15]

Formaldehyde was identified by extracting it from the pentane distillates with small amounts of water, and preparing the dimedone derivative. The crude derivative (3.3 g. or 21% yield) was leached with 10 ml. of hot methyl alcohol, filtered and dried to yield 2.8 g. of crystals with a melting point of 187.5–189.5° (cor.). A mixed melting point with an authentic sample (m. p. 188–189°) showed no depression.

Hydrogenation.—A portion (7.3 g., 0.11 mole) of the vinylcyclopropane on which physical properties were determined was hydrogenated over 0.5 g. of Raney nickel in absolute ethanol at 65 p. s. i. g. and 10 to 20°. Absorption of hydrogen ceased after about six hours. The hydrogenate was steam distilled, washed thoroughly with water and dried by percolation through a small column of silica gel to obtain a 64% yield of material with a refractive index of 1.3724. The infrared absorption spectrum of this product corresponded closely to that of an authentic sample of ethylcyclopropane,[7] but showed minor bands indicating the presence of *n*-pentane (about 30% on the basis of refractive index). Similar results had been obtained in the hydrogenation of isopropenylcyclopropane.[6a]

Infrared Absorption Spectra.—The spectra determined in the course of this work were measured on the Beckman IR-2 Spectrophotometer of the Department of Chemistry at The Ohio State University.

Summary

Vinylcyclopropane has been prepared from methyl cyclopropyl ketone. Additional evidence for the double bond character of the cyclopropane ring has been presented.

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[13] Henne and Perilstein, THIS JOURNAL, **65**, 2183 (1943).

[14] Cook and Whitmore, *ibid.*, **63**, 3540 (1941).

[15] Kindly furnished by Christopher L. Wilson, The Ohio State University.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CARSON-NEWMAN COLLEGE]

Polynitro Paraffins

BY CARL T. BAHNER AND HARVEY T. KITE[1]

Dinitro paraffins in which the nitro groups are in a 1,3-position to each other and the middle carbon atom carries no hydrogen atom have been prepared by Fraser and Kon,[2] Hass and Bourland,[3] and Larrison and Hass[4] by reaction of nitromethane with ketones. Hass[5] has found evidence that the reaction of nitromethane with acetone takes place through the formation of 1-nitro-2-methylpropene which adds nitromethane to form dinitroneopentane. Lambert and Piggott[6] have reported the preparation of dinitro compounds by "heating a primary or secondary nitroparaffin or nitroether or nitrothioether.... with a Δ^{α}-nitro-olefin.... in the presence of a basic substance." Prior to the publications by Hass and Lambert and their associates we had undertaken the preparation of polynitro paraffins by the addition of alkali salts of nitro paraffins to nitro olefins. Our experiments throw light on matters not investigated by them.

Using nitro olefins of the type $R^1C(NO_2)=CHR^2$, where R^1 and R^2 represent H or an alkyl radical, and nitro paraffins containing two or more carbon atoms we have succeeded in obtaining a type of compound which it is inherently impossible to prepare from ketones by the methods of Fraser and Kon, Hass, Larrison and Bourland. We have found that the alkali metal salts of the nitro paraffins give much better results than the use of nitro paraffins together with a basic catalyst. For example, the gradual addition of 2-nitro-1-butene to an alcoholic solution of an equivalent quantity of potassium salt of *aci*-2-nitropropane gave about 90% of the theoretical yield of crude potassium salt of 3,5-dinitro-3-methylhexane, from which the free dinitro compound was recovered readily by treatment with acetic acid. On the other hand, no 3,5-dinitro-3-methylhexane was isolated from a reaction mixture of equimolecular quantities of 2-nitropropane, diethylamine and 2-nitro-1-butene. The use of a quantity of potassium hydroxide sufficient to convert only one-fourth of the 2-nitropropane into the potassium salt resulted in the formation of a viscous high molecular weight product instead of the dinitro paraffin, while the use of a large excess of so-

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[1] Present address: Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee.

[2] Fraser and Kon, *J. Chem. Soc.*, 604–610 (1934).

[3] Hass and Bourland, U. S. Patent 2,343,256, March 7, 1944.

[4] Larrison and Hass, U. S. Patent 2,383,603, Aug. 28, 1945.

[5] Hass, *Ind. Eng. Chem.*, **35**, 1151 (1943).

[6] Lambert and Piggott, *J. Chem. Soc.*, 1489–1492 (1947); British Patent 584,789, July 24, 1944.

dium ethylate over the amount necessary to produce the sodium salt of the 2-nitropropane led to the conversion of a large portion of the nitro olefin into a nitro ether.[7] Metallic sodium added to an equimolecular mixture of 2-nitro-1-butene and 2-nitropropane at 8° did not appear to react immediately, but within a few minutes produced a violent reaction terminating in a mild explosion. For best yields it is desirable that the nitro olefin be added in small quantities with vigorous stirring to a solution of the alkali salt of the nitro paraffin at near or below room temperature and that the reaction mixture be acidified with a weak acid as soon as the addition reaction is complete.

Distillation of the dinitro compounds which we prepared was made more difficult by a tendency toward decomposition at high temperature. However we succeeded in purifying 3,5-dinitroheptane, 3,5-dinitro-3-methylhexane and 1,3-dinitro-2,2-ethyl-3-methylbutane by crystallization from methanol solution at Dry-Ice temperature.

Our chemical process is not limited to the preparation of dinitro paraffins, since the alkali metal salt of the dinitro compound obtained in the first step can be allowed to react in the same manner with one or more additional molecules of nitro olefin to form high molecular weight polynitro compounds.

Experimental

Nitro Paraffins.—The nitro paraffins used in these experiments were supplied by the Commercial Solvents Corporation.

Nitro Olefins.—The nitro olefins used were prepared by heating the acetates of the corresponding nitro alcohols with sodium acetate, by a modification of the method of Schwarz and Nelles.[8] The nitro ester mixed with about 5% by weight of anhydrous sodium acetate in a flask attached to a Vigreux column and condenser was heated in an oil-bath at 110–135° at a pressure of 20–50 mm., thus distilling off the decomposition products as they were formed. This procedure prevented the violent decomposition sometimes encountered when the heating was done at a higher pressure. The distillate was treated with a saturated solution of sodium carbonate to remove the acetic acid, washed with water, dried over calcium chloride, and used at once to avoid polymerization.

3,5-Dinitro-3-methylhexane.—Forty-five grams (0.5 mole) of 2-nitropropane was added to 221 ml. of 2.259 *N* alcoholic potassium hydroxide (0.5 mole) to form the potassium salt. This solution was chilled in an ice-bath and 50.2 g. (0.497 mole) of fresh 2-nitro-1-butene added in small portions with vigorous stirring over a period of thirty minutes, keeping the temperature at 18–20°. At the end of this time the reaction mixture suddenly deposited a large quantity of white crystals of the potassium salt of *aci*-3,5-dinitro-3-methylhexane. After dilution with water to approximately 500 ml. the salt was converted to 3,5-dinitro-3-methylhexane by acidifying with acetic acid, a 90% yield of crude product being obtained. Repeated recrystallization from chilled methanol yielded an analytically pure product in the form of white crystals which could be kept indefinitely in an ice-chest at 4° but melted below 21° to a liquid n^{25}_D 1.451. *Anal.* Calcd. for $C_7H_{14}N_2O_4$: C, 44.20; H, 7.42. Found: C, 43.93; H, 7.22.[9]

1,3-Dinitro-2-ethyl-3-methylbutane.—An 85% yield of crude 1,3-dinitro-2-ethyl-3-methylbutane was obtained from 1-nitro-1-butene and potassium 2-nitropropane. A sample was crystallized repeatedly from redistilled methanol by chilling with Dry Ice–acetone mixture and the white needle-shaped crystals were washed quickly with chilled methanol. Since the moist crystals melted below 5°, the operation was carried out in a cold storage room. After removal of remaining traces of solvent by warming the melted crystalline material to 50° at 1 mm. it had the following properties: n^{25}_D 1.463; d^{25}_4 1.152. MR_D predicted: 45.77. Found: 45.49. *Anal.* Calcd. for $C_7H_{14}N_2O_4$: C, 44.20; H, 7.42. Found: C, 43.99; H, 7.34.

3,5-Dinitroheptane.—This compound was prepared from potassium 1-nitropropane and 2-nitro-1-butene in a similar manner, but the yield was not as good as the yields of the two compounds described above, possibly because of its structure. The symmetrical structure resulted in its melting point being above room temperature. The long white needle-shaped crystals, m. p. 33°, have a mild menthol like odor and can be kept for years. *Anal.* Calcd. for $C_7H_{14}N_2O_4$: C, 44.20; H, 7.42. Found: C, 44.53; H, 7.26.

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Summary

New polynitro compounds having the nitro groups in a beta position to one another have been synthesized by the addition of an alkali salt of a nitro paraffin to a nitro olefin and treatment of the resulting salt with a weak acid.

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[7] *Cf.* Bahner, U. S. Patent 2,391,815, Dec. 25, 1945; *J. Tenn. Acad. Sci.*, **23**, 281–282 (1948).

[8] Schwarz and Nelles, U. S. Patent 2,257,980, Oct. 7, 1941.

[9] Analyses were carried by Dr. Carl Tiedcke, 705 George St., Teaneck, N. J.