Synthesis of 2-Nitroalkyl Vinyl Ethers[1]

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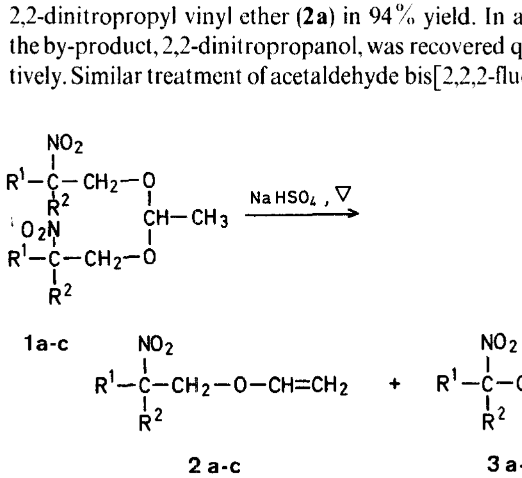
The preparation of 2-nitroalkyl vinyl ethers presents a special problem because 2-nitroalcohols are cleaved in alkaline media to formaldehyde and the alkali metal salt of the resultant nitroalkane. Thus, the most widely used method of preparing alkyl vinyl ethers, the base-catalyzed addition of alcohols to acetylene[2], cannot be employed with 2-nitroalkanols. The mercury(II) acetate-catalyzed vinyl transetherification of ethyl vinyl ether with 2-methyl-2-nitropropanol and 2-nitrobutanol has been reported to give 2-methyl-2-nitropropyl vinyl ether in 32% yield and 2-nitrobutyl vinyl ether in 27% yield, respectively[3]. Three other examples, 2-nitroethyl vinyl ether, 2,2,2-fluorodinitroethyl vinyl ether, and 2,2-dinitropropyl vinyl ether, were obtained in 45–60% yields by treating the nitroalcohols with vinyl acetate in the presence of mercury(II) sulfate[4].

In the present work, other methods[5,6,7] of preparing alkyl vinyl ethers under non-alkaline conditions were evaluated for the application of preparing 2-nitroalkyl vinyl ethers in high yields. The most effective method was found to be the acid-catalyzed pyrolysis of acetals[5]. Acetaldehyde bis[2,2-dinitropropyl] acetal (**1a**) was heated with a catalytic amount of sodium hydrogen sulfate at 140–150° to give 2,2-dinitropropyl vinyl ether (**2a**) in 94% yield. In addition, the by-product, 2,2-dinitropropanol, was recovered quantitatively. Similar treatment of acetaldehyde bis[2,2,2-fluorodinitroethyl] acetal (**1b**) and acetaldehyde bis[2-nitrobutyl] acetal (**1c**) gave an 88% yield of 2,2,2-dinitrofluoroethyl vinyl ether (**2b**) and a 65% yield of 2-nitrobutyl vinyl ether (**2c**), respectively.



1a-c **2a-c** **3a-c**

	R¹	R²
a	CH_3	NO_2
b	F	NO_2
c	C_2H_5	H

Preparation of Acetals:

Acetaldehyde bis[2,2-dinitropropyl] acetal[8] (**1a**), bis[2,2,2-fluorodinitroethyl] acetal[9] (**1b**), and bis[2-nitrobutyl] acetal[10] (**1c**) were prepared according to the following procedure.

A solution of acetaldehyde (10.5 g, 0.24 mol) and the nitroalcohol (0.3 mol) in 1,2-dichloroethane (120 ml) is treated with boron trifluoride etherate (21.3 g, 0.15 mol) dropwise at −10°. The resultant mixture is stirred at −10° for 15 min, then it is poured into water (100 ml). The layers are separated and the organic layer is washed with 5% sodium hydroxide (100 ml), then with water, and dried ($MgSO_4$). The solvent is removed under reduced pressure and the residue is vacuum distilled to yield the pure acetal.

Pyrolysis of Acetals:

The appropriate acetal and anhydrous sodium hydrogen sulfate are heated under the conditions given in the Table in a vacuum distillation apparatus with the receiver cooled in a Dry Ice/acetone bath. Heating is continued until products cease to distill. The distillate is analyzed by ¹H-N.M.R. spectroscopy to give the yields of 2-nitroalkyl vinyl ether and 2-nitroalkanol. In the pyrolysis of **1a**, the 2,2-dinitropropanol solidifies in the distillation column; thus, the distillate contains **2a** with only a trace of the by-product. In contrast, the distillates from the pyrolysis of **1b** and **1c** contain both the ether and the alcohol, which are separated by fractional distillation.

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Table. Pyrolysis of Acetaldehyde Bis[2-nitroalkyl] Acetals

Acetal (mol)	$NaHSO_4$ (g)	Reaction Conditions temp./torr	Product	Yield [%]	b.p./torr (Lit. b.p./torr)	Reference
1a (0.02)	0.06	140–150°/0.06	**2a**	94	45–46°/0.05 (45–48°/0.05)	4
1b (0.02)	0.12	150–170°/0.5	**2b**	88	60–61°/10 (61–62°/13)	4
1c (0.02)	0.06	140–150°/0.1	**2c**	65	72–73°/5 (72–73°/5)	3

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