3-Nitro-3-methyl-1,2-epoxybutane, a Novel α-Epoxide Synthesis

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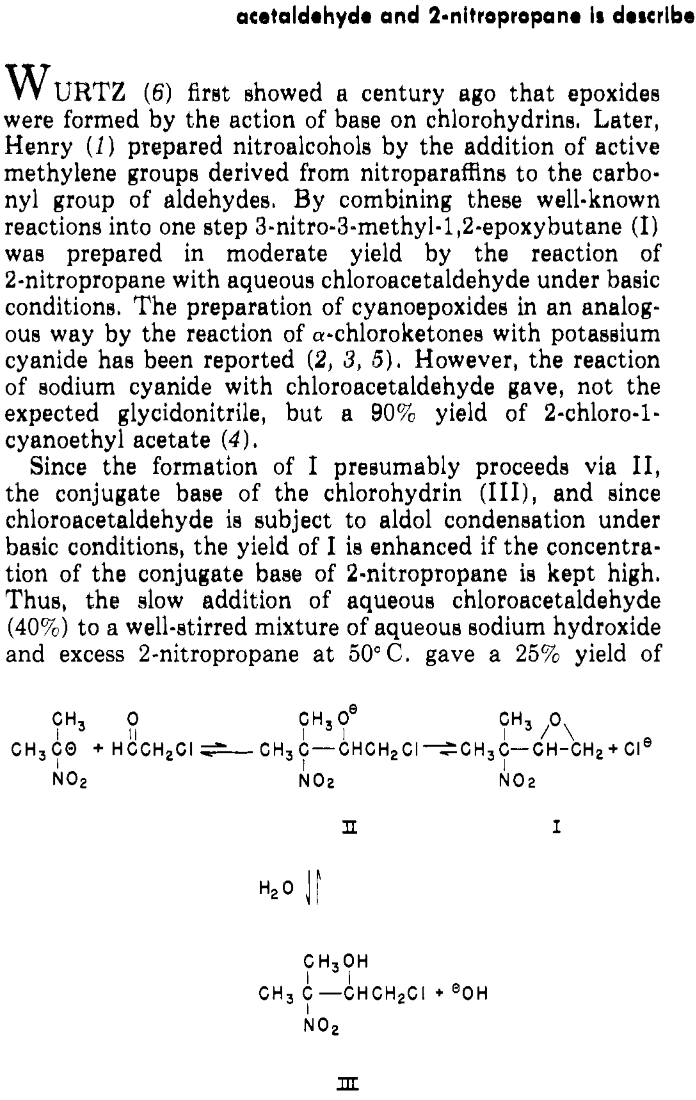
A one-step synthesis of 3-nitro-3-methyl-1,2-epoxybutane from aqueous chloroacetaldehyde and 2-nitropropane is described.

WURTZ (*6*) first showed a century ago that epoxides were formed by the action of base on chlorohydrins. Later, Henry (*1*) prepared nitroalcohols by the addition of active methylene groups derived from nitroparaffins to the carbonyl group of aldehydes. By combining these well-known reactions into one step 3-nitro-3-methyl-1,2-epoxybutane (I) was prepared in moderate yield by the reaction of 2-nitropropane with aqueous chloroacetaldehyde under basic conditions. The preparation of cyanoepoxides in an analogous way by the reaction of α-chloroketones with potassium cyanide has been reported (*2, 3, 5*). However, the reaction of sodium cyanide with chloroacetaldehyde gave, not the expected glycidonitrile, but a 90% yield of 2-chloro-1-cyanoethyl acetate (*4*).

Since the formation of I presumably proceeds via II, the conjugate base of the chlorohydrin (III), and since chloroacetaldehyde is subject to aldol condensation under basic conditions, the yield of I is enhanced if the concentration of the conjugate base of 2-nitropropane is kept high. Thus, the slow addition of aqueous chloroacetaldehyde (40%) to a well-stirred mixture of aqueous sodium hydroxide and excess 2-nitropropane at 50° C. gave a 25% yield of I along with a 13% yield of III. However, a slow addition of aqueous caustic to III led to a lower yield (13%) of I. Under comparable reaction conditions I was found to be stable (93% recovery), and apparently the lower yield obtained from the chlorohydrin resulted from the lack of excess nitropropane (as its conjugate base) to shift the equilibrium in the desired direction. Under these latter conditions much of the chloroacetaldehyde formed was lost to condensation products. The rate of formation of I from II is apparently much slower than rate of cleavage of II to chloroacetaldehyde and the dimethylnitromethide ion.



Presumably, the preparation of α-epoxides by the reaction of chloroacetaldehyde with other active methylene compounds is possible as long as the rate constants for epoxide formation and for cleavage of the intermediate corresponding to II are not too unfavorable. However, an attempt to prepare in a similar way the corresponding epoxide from 1,1-dinitroethane failed, presumably because of the high stability of the dinitroethide ion and the consequent unfavorable equilibrium situation.

EXPERIMENTAL

Materials. Chloroacetaldehyde (40% aqueous solution supplied by the Dow Chemical Co.) and 2-nitropropane (Commercial Solvents Corp.) were used as received.

3-NITRO-3-METHYL-1,2-EPOXYBUTANE, I. A mixture of 500 ml. of water 160 grams (4.0 moles) of sodium hydroxide, and 535 grams (6.0 moles) of 2-nitropropane was stirred at 25° C. for 0.5 hour. The temperature was raised to 50° C. and 660 ml. of aqueous (40%, 4.0 moles) chloroacetaldehyde was added, dropwise, during 3.5 hours. The mixture was stirred at 50° C. for an additional 1.3 hours, cooled, and extracted twice with 250-ml. portions of ether. The combined ethereal solution was shaken with 130 ml. of 1*N* HCl and 150 ml. of saturated aqueous sodium bisulfite and then dried with anhydrous magnesium sulfate. Solvent and excess 2-nitropropane were removed at reduced pressure (20 mm.) and the residue was distilled through a simple head at less than 1-mm. pressure with bath temperature 92° C. Considerable decomposition and gas evolution occurred during this distillation. Redistillation through a 15 × 500 mm. glass helices-packed column at reduced pressure afforded 130 grams (25% yield on chloroacetaldehyde and unrecovered 2-nitropropane) of 3-nitro-3-methyl-1,2-epoxybutane, I (b.p. 29° C./35 microns, n_D^{25} 1.4389, d_4^{25} 1.134), and 86 grams (13% yield on chloroacetaldehyde and unrecovered 2-nitropropane) of 3-nitro-3-methyl-1-chloro-2-butanol, III (b.p. 62° C./35 microns, n_D^{25} 1.4742.

Analyses. Calculated for $C_5H_9NO_3$: C, 45.8; H, 6.9; N, 10.7. Found: C, 45.7; H, 7.0; N, 10.6. Calculated for $C_5H_{10}NO_3Cl$: C, 35.8; H, 6.0; N, 8.4; Cl, 21.2. Found: C, 36.2; H, 6.1; N, 8.4; Cl, 20.3.

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