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A NOVEL INTRAMOLECULARLY STABILIZED NITRONIC ACID, 2-ACI-NITRO-1,3-PROPANEDIOL

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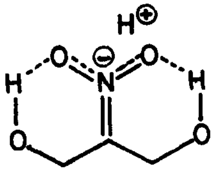
ABSTRACT: A stable nitronic acid, 2-aci-nitro-1,3-propanediol, may be prepared from nitromethane and paraformaldehyde under fluoride ion catalysis.

During attempts to synthesize nitroethanol, we examined a modification using phase transfer catalysis on a known synthesis, devised by Kambe and Yasuda[1]. These workers condensed nitromethane and paraformaldehyde in isopropanol in the presence of a catalytic amount of potassium fluoride, and obtained nitroethanol in 73% yield. In our hands, a mixture of paraformaldehyde (15.0 g, 0.5 mol based on formaldehyde equivalents), nitromethane (14.3 g, 0.250 mol), potassium fluoride (150 mg, 2.50 mmol) and tetra-n-butyl ammonium bromide (80.5 mg, 2.50 mmol) in isopropanol (50 mL) under argon, was stirred for three days. The mixture was filtered through Celite, and the solvent removed, giving 29.0 g of a colourless solid, m.p. 63.2°, whose spectral characteristics[2] correspond to the previously unknown compound 1.



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It is known that the tautomerization of a nitronic acid to the corresponding nitroalkane is slowed if it is a weak acid (subject to inductive effects) or if C-protonation of the nitronate anion is slow (due to resonance stabilization). For example fluorene-9-nitronic acid (or 9-aci-nitro fluorene) protonates slowly[3], while bromomethane nitronic acid tautomerizes much more quickly than the less acidic methane nitronic acid[4]. Tautomerism may also be slowed by the hydrogen bonded stabilization of the nitronate intermediate, in spite of the enhanced acidity[5]. The latter effect increases as the number of hydrogen bonding groups increases[6], the case reported here presenting an extreme.

In our hands this reaction could not be induced to proceed with either paraldehyde or acetaldehyde.

ACKNOWLEDGEMENTS

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REFERENCES

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2) H^1 NMR (200 MHz): 3.97(4H, s, CH_2-OH), 4.38 (2H, s,
CH_2-OH, D_2O exchangeable in the
presence of benzene D6)
IR: 3350 cm^{-1} (OH), 1630 (C=N)
C^{13} NMR: 208.12 (s, aci-nitro carbon), 60.82 (t, CH_2)
Mass Spec.: 121 (1.2%, M^+), 104 (2.9%, loss of OH), 86
(9.9%, loss of H_2O, OH), 73 (28.4%, loss
of CH_2-OH, OH), 57 (100%, loss of NO_2,
H_2O), 45 (56.5%, loss of CH_2OH, NO_2)
High Resolution Mass Spec.: Observed 121.0327; Required
121.0375 (for $C_3H_7NO_4$)
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