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A NOVEL $S_{RN}1$ SUBSTITUTION: THE REACTION BETWEEN THE ANION OF 2-NITROPROPANE AND 3-BROMO-1-NITROCYCLOHEX-1-ENE

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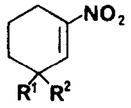
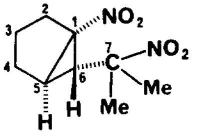
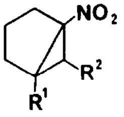
Summary: X-Ray crystallography has been used to determine the unusual cyclopropyl structure for the product of the $S_{RN}1$ *reaction between the anion of 2-nitropropane and 3-bromo-1-nitrocyclohex-1-ene.*

We report an unusual $S_{RN}1$ reaction in our initial studies of the reactions of nitro-olefins substituted in the allylic (γ) position. The anion of 2-nitropropane (10 mmol) and 3-bromo-1-nitrocyclohex-1-ene (1a)[1] (5 mmol) were reacted for 1 h in DMF under nitrogen with light irradiation (2 x 150 W tungsten 'white light' lamps). The reaction yielded one major product with only traces of impurities. Purification by preparative t.l.c. and recrystallisation (hexane) gave a crystalline product (45-55%), m.p. 67-68°C; $C_9H_{14}N_2O_4$; $\nu_{max.}$(nujol) 1550 cm^{-1} (saturated R-NO_2); ^{13}C $\delta(CDCl_3)$, singlets at 87.2 (C_7), 76.9 (C_1), doublets at 36.5, 31.9 (C_5,C_6), triplets at 32.4 (C_2), 26.9, 21.6 (C_3,C_4), quartets at 27.2, 26.9 p.p.m; ^1H $\delta(CDCl_3)$ 1.72, 1.69 ($\underline{Me}_2CNO_2$); m/z 168 (M^+ - NO_2, 100%), 122 (M^+ - $2NO_2$,38%), 121 (M^+ - NO_2 and HNO_2,99%)

(1)


(2)


(3)


1a: R^1 = Br, R^2 = H 1b: R^1 = Me_2CNO_2, R^2 = H

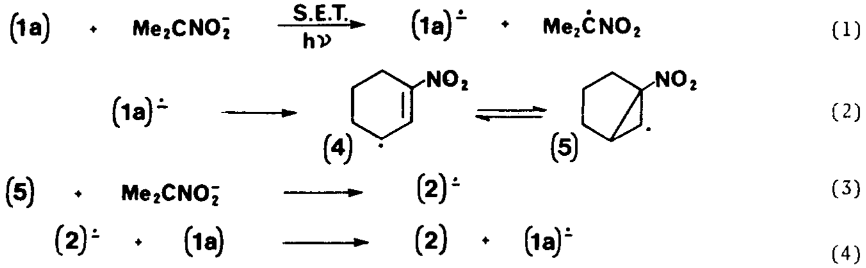
1c, 3c; R^1 = R^2 = Ph 1d, 3d; R^1 = R^2 = H

The absence of nitro-olefin absorption in the i.r. and u.v. spectra and the absence of either a low-field proton in the ^1H n.m.r. spectrum or an olefinic carbon in the ^{13}C n.m.r. spectrum indicated that the expected $S_{RN}1$ product (1b) had not been formed. The ^1H and ^{13}C n.m.r. spectra showed the expected values for the two methyl-groups α to a nitro-group,but not the high-field signals for cyclopropyl carbons and protons because of the effect of the nitro-groups. The data indicated that a substitution had taken place, but with rearrangement/cyclisation. The structure was therefore determined by X-ray crystallography to be the unexpected cyclopropyl compound (2). The X-ray analysis allowed comparison by ^{13}C n.m.r. of a similar structure (3c) reported by Zimmerman.[2] The spectral values fitted closely, confirming the X-ray structure.

Aspects of mechanism: The commonly used diagnostic tests for the $S_{RN}1$ mechanism were carried out.[3] The formation of the cyclopropyl product (2) was completely inhibited when the reaction was repeated under oxygen, in the presence of 30 mol % *p*-dinitrobenzene or 30 mol %

di-t-butylnitroxide, or with the exclusion of light. The reaction is therefore most likely to proceed by a light-catalysed radical radical-anion chain mechanism ($S_{RN}1$).[3] The inhibition reactions yielded unreacted starting material, 2-cyclohexen-1-one, 2,3-dimethyl-2,3-dinitrobutane, and a number of other unidentified decompostion products.

We suggest that the most probable mechanism for the chain susbstitution reaction is as shown in the scheme below:



The scheme conforms to the $S_{RN}1$ chain mechanism with an initiation step (equation 1) and propagation steps (equations 2, 3 and 4). We propose that the intermediate nitro-olefin radical (4), formed by the dissociation of the radical-anion of 3-bromo-1-nitrocyclohex-1-ene, undergoes valence tautomerism to the cyclopropyl radical (5). Rearrangement within the free-radical intermediate of an $S_{RN}1$ reaction to yield a cyclopropyl radical intermediate has been reported for $S_{RN}1$ reactions of β-arylated nitroparaffins.[4] The weakly nucleophilic 2-nitropropane anion could be predicted to react more rapidly with the unstabilised cyclopropyl radical (5) than with the stabilised nitro-olefin radical (4). Tolbert[5] has suggested that the nucleophilic attack by the anion on the intermediate free-radical in $S_{RN}1$ reactions is under kinetic control.

A mechanism involving $S_{RN}1$ substitution to the expected product (1b) and subsequent light-catalysed rearrangement to (2) cannot be discounted. Zimmerman[2] has reported an analogous rearrangement of a diphenyl derivative (1c) to (2c) in 9% yield by photolysis (10 h) with a 450 W medium-pressure mercury arc lamp. Our reaction, in contrast, is rapid, high yielding, and photolysed by a weaker light source. Also, none of the possible intermediate (1c) was observed, and photolysis of 1-nitrocyclohex-1-ene (1d), under the same conditions as for the reaction, for 2h, did not yield any rearranged product (2d) [84% recovery of pure (1d)]. We therefore suggest that the observations indicate that this rearrangement is unlikely.

Another alternative mechanism involving nucleophilic addition of the nitro-anion to the β-position of the nitro-olefin (1a) is possible, but unlikely; firstly due to steric hindrance, and secondly, because the resulting nitro-anion would have to undergo intramolecular $S_{RN}1$ with an unstabilised alkyl bromide ($S_{RN}1$ reaction between anions and unstabliised alkyl halides have not been observed to our knowledge).

References 1. 3-Bromo-1-nitrocyclohex-1-ene was prepared by the method of E.J. Corey and H. Estreicher, *J.Am.Chem.Soc.*, 1978, 100, 6294.
2. H.E. Zimmerman, L.C. Roberts, and R. Arnold, *J.Org.Chem.*, 1977, 42, 621.
3. N. Kornblum in '*Chemistry of amino, nitro, and nitroso compounds and their derivatives*', ed. S. Patai, Wiley, London 1982, Suppl. F, p.361; M. Channon and L. Tobe, *Angew. Chem. Int. Ed. Engl.*, 1982, 21, 1.
4. N. Kornblum, J. Widmer, and S.C. Carlson, *J. Am. Chem. Soc.*, 1979, 101, 658.
5. L.M. Tolbert and S. Siddiqui, *Tetrahedron*, 1982, 38, 1079.

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