

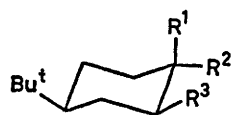
## An Example of Substitution proceeding with Retention in the $S_{RN}1$ Reaction. Trapping of a Pyramidal Benzylic Radical by Benzenethiolate Ion

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**Summary** The  $S_{RN}1$  reaction of *c*-4-*t*-butyl-*c*-2-methyl-*r*-1-nitro-1-*p*-nitrophenylcyclohexane with sodium benzenethiolate in hexamethylphosphoramide, which proceeds with retention of configuration at C-1 at relatively high thiolate concentrations, and with competing inversion and retention at lower thiolate concentrations, implicates the formation and trapping of a pyramidal benzylic radical.

SUBSTITUTION of a nitro-group at a tertiary<sup>1</sup> or neopentyl<sup>2</sup> carbon, bearing a *p*-nitrophenyl group, has been shown to occur by the  $S_{RN}1$  reaction. We have studied the reactions of the cyclohexyl derivatives (**1**) ( $Bu^t$  at  $\delta$  0.90) and (**2**) ( $Bu^t$  at  $\delta$  0.87) with several nucleophiles in dimethyl sulphoxide (DMSO) and hexamethylphosphoramide (HMPA) at 55 °C, under nitrogen with sunlamp irradiation. In HMPA, (**1**) gave an 85% yield of the azide (**3**) ( $Bu^t$  at  $\delta$  0.92) with sodium azide after 1.5 h, a 44% yield of the



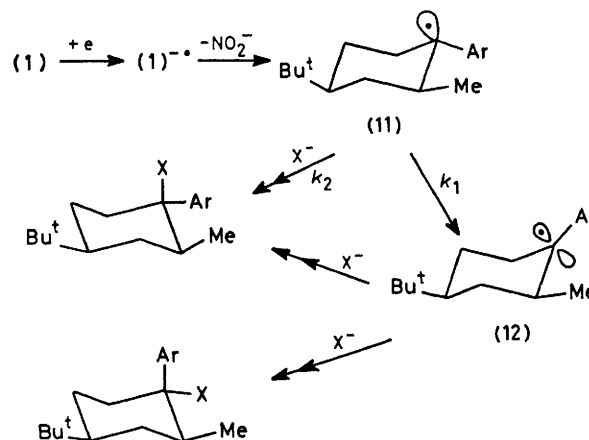
- (1)  $R^1 = \text{NO}_2$ ,  $R^2 = p\text{-O}_2\text{NC}_6\text{H}_4$ ,  $R^3 = \text{Me}$   
 (2)  $R^1 = \text{NO}_2$ ,  $R^2 = p\text{-O}_2\text{NC}_6\text{H}_4$ ,  $R^3 = \text{H}$   
 (3)  $R^1 = \text{N}_3$ ,  $R^2 = p\text{-O}_2\text{NC}_6\text{H}_4$ ,  $R^3 = \text{Me}$   
 (4)  $R^1 = p\text{-O}_2\text{NC}_6\text{H}_4$ ,  $R^2 = p\text{-MeC}_6\text{H}_4\text{SO}_2$ ,  $R^3 = \text{Me}$   
 (5)  $R^1 = p\text{-O}_2\text{NC}_6\text{H}_4$ ,  $R^2 = \text{EtC}(\text{CN})_2$ ,  $R^3 = \text{Me}$   
 (6)  $R^1 = \text{PhS}$ ,  $R^2 = p\text{-O}_2\text{NC}_6\text{H}_4$ ,  $R^3 = \text{Me}$   
 (7)  $R^1 = p\text{-O}_2\text{NC}_6\text{H}_4$ ,  $R^2 = \text{PhS}$ ,  $R^3 = \text{Me}$   
 (8)  $R^1 = \text{PhS}$ ,  $R^2 = p\text{-O}_2\text{NC}_6\text{H}_4$ ,  $R^3 = \text{H}$   
 (9)  $R^1 = p\text{-O}_2\text{NC}_6\text{H}_4$ ,  $R^2 = \text{PhS}$ ,  $R^3 = \text{H}$

sulphone (4) ( $\text{Bu}^t$  at  $\delta$  0.72) after 24 h with sodium *p*-toluenesulphinate and a 50% yield of the substituted malononitrile (5) ( $\text{Bu}^t$  at  $\delta$  0.71) after 20 h with the sodium salt of 2-ethylmalononitrile. The same products, in similar yields, were formed in DMSO. In marked contrast, the reaction of (1) with sodium benzenethiolate (10) gave high



yields (>90%) of the sulphides (6) ( $\text{Bu}^t$  at  $\delta$  0.93) and (7) ( $\text{Bu}^t$  at  $\delta$  0.74), whose proportions in HMPA varied with reactant concentration.<sup>†</sup> For example, (6) containing no more than 2% of (7) was formed from reaction of (1) (0.05 M) with (10) (0.15 M) in a rapid reaction, complete in less than 10 min, whereas (6) and (7) were formed in a 3:2 ratio, after 4.5 h, when (1) ( $8 \times 10^{-3}$  M) reacted with (10) ( $25 \times 10^{-3}$  M). Approximately equal amounts of (6) and (7) were formed in DMSO, even in concentrated solutions. The above substitution reactions were shown to be inhibited by oxygen and *p*-dinitrobenzene, and were found to be accelerated (in the case of the *p*-toluenesulphinate reactions) by entrainment with the lithium salt of 2-nitropropane, clearly demonstrating that the substitutions were occurring by  $S_{\text{RN}}1$  processes.

The above stereochemical results can be interpreted as shown in the Scheme. In the reactions of (1) with higher



SCHEME.  $\text{Ar} = p\text{-O}_2\text{NC}_6\text{H}_4$ .

concentrations of (10) in HMPA the initial pyramidal radical (11) is trapped faster than it collapses to an effectively planar radical<sup>3</sup> (12), i.e.  $k_2 \gg k_1$ . Under other conditions, and with other anions,  $k_1 \gg k_2$ , and products formed from (12) reflect a preference for the less sterically demanding substituent to adopt an axial position.

In the derivative (2), without a methyl group adjacent to the reaction site, the retention phenomenon on reaction with (10) was *not* observed under any conditions, and the same 55:45 mixture of (8) and (9) was produced. Inspection of molecular models reveals that the conversion of (11) into (12) is hindered by the adjacent methyl group. The resultant increase in the life-time of (11) allows this novel, substitution-with-retention to be observed.

To the best of our knowledge, the reaction of (1) with (10) to give (6) is the first demonstration of both the stereochemical course of the  $S_{\text{RN}}1$  reaction and of the trapping of a pyramidal benzylic radical.

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<sup>†</sup> Sulphides (6) and (7) did *not* equilibrate under the reaction conditions.

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