Rearrangement of an *o*-Substituted Phenyl Radical by 1,7-Hydrogen Atom Migration

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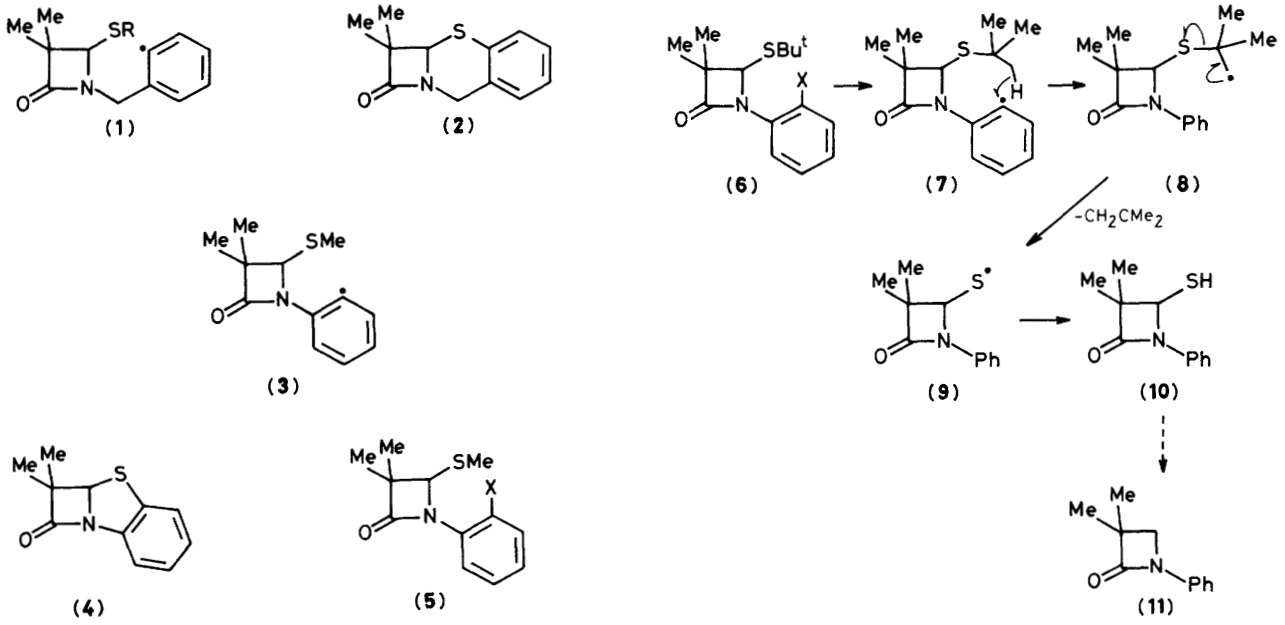
Formation of the azetidinonethiol (**10**) by treatment of the aryl halide (**6**) with tributylstannane involves an unusually rapid 1,7-hydrogen atom transfer followed by β-fission of the resultant radical (**8**).

We have recently shown[1] that the radicals (**1**; R = Bu^t or Me), generated from the corresponding aryl bromides by treatment with tributylstannane, undergo 1,6-cyclisation by an intramolecular S_H2 process to afford the tricyclic system (**2**). Since five membered rings are usually formed more readily than six in related homolytic ring closure processes[2] we expected that the radicals (**3**) and (**7**) would behave similarly to their higher homologues and smoothly afford (**4**) by displacement of R$^\cdot$ from sulphur.

Suitable precursors (**5**) and (**6**) were prepared as previously described[1] by consecutive treatment of the appropriate 3-alkylthio-2,2-dimethylpropanoyl chloride with *N*-chlorosuccinimide, *o*-halogenoaniline, and a strong base. When the methyl sulphide (**5**, X = Br) was heated with 1.1 molar equivalents of Bu_3SnH (0.01 M) in benzene only the direct reduction product (**5**, X = H) was formed in 70% yield. Some starting material (6%) was also isolated but the cyclised product (**4**) could not be detected. Since the experimental conditions were essentially the same as those which previously gave (**2**) in 42% yield,[1] it appears that 1,5-ring closure of



Scheme 1

radical (**3**) is very much slower than 1,6-ring closure of its higher homologue (**1**). We attribute this unexpected result[2] to the effect of the azetidinone ring on the strain energies of the corresponding transition structures.[3] It is noteworthy that ring closure by intramolecular addition in suitable azetidinonyl radicals shows anomolous regiochemistry.[1]

The reaction of tributylstannane with the t-butyl sulphide (**6**, X = I) followed a different course. None of the direct reduction product (**6**, X = H) could be detected but chromatography of the mixture gave 17% of 3,3-dimethyl-*N*-phenylazetidinone (**11**) and 42% of the thiol (**10**), m.p. 50—58 °C, ^{1}H n.m.r. ($CDCl_3$): δ 1.39 (3H, s, CH_3), 1.44 (3H, s, CH_3), 2.02 (1H, d, *J* 9 Hz, SH), 7.09—7.20, 7.31—7.42, and 7.47—7.56 (5H, 3m, ArH); ^{13}C n.m.r. ($CDCl_3$): δ 18.1, 21.8, 55.7, 62.6, 117.7. 124.3, 129.1, 136.4, 169.7. Unlike some azetidinonethiols,[4] compound (**10**) is moderately stable and can be safely recrystallized from warm non-polar solvents. However, in protic solvents it slowly decomposes. When treated with benzoyl chloride it formed a thiobenzoate, m.p. 101—107 °C.

Also obtained from this reaction was a trace (*ca.* 1%) of the cyclised product (**4**). It could not, however, be detected when the bromo compound (**6**, X = Br) was used as radical precursor. In this case the only product (60%) was the thiol (**10**); starting material (10%) was also isolated.

As the direct reduction product (**6**, X = H) was not obtained from either reaction it is unlikely to be an intermediate in the formation of the thiol (**10**). Nor is (**4**) likely to lie on the pathway to (**10**); attack of tributyltin radicals at sulphur would be expected to involve fission of the bond to the azetidinone ring, the weaker of the two C–S bonds. Also, the stoicheiometry of the reaction precludes the intermediacy of either (**4**) or (**6**, X = H) because two molar equivalents of stannane would be consumed.

We propose, therefore, that the formation of the thiol (**10**) involves 1,7-hydrogen atom migration followed by β-elimination as shown (Scheme 1). In support of this hypothesis, treatment of (**6**, X = I) with tributyltin deuteride gave thiol (**10**) containing no deuterium, and isobutylene, isolated as its dibromide from the effluent gas when the mixture was purged with nitrogen. A similar experiment with the methyl sulphide (**5**, X = Br) afforded a product (**5**, X = H) in which all of the deuterium resides in the *S*-methyl group.

The pathway to (**11**) from the radical (**7**) is less clear. Probably it arises from further reduction of the thiol in the form of the tributyltin thiolate.

As the competition between rearrangement of the radical (**7**) and its reaction with tributylstannane to give (**6**, X = H) appears to lie completely in favour of the former process, its rate constant cannot be accurately determined. However, on the basis of the reasonable assumptions (i) that the rate constant for reaction of (**7**) with stannane is close to that for phenyl radical (k = *ca.* 9×10^8 s^{-1} at 80 °C);[5] (ii) that a yield of (**6**, X = H) greater than 5% would have been detected; and (iii) that the mean value of [Bu_3SnH] during the reaction was about 0.01 M; it can be readily shown that the rate constant for the rearrangement of the radical (**7**) into (**8**) must be at least 1×10^8 s^{-1} at 80 °C. Similar considerations give much the same minimum value for the rate constant for rearrangement of (**3**).

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