Factors Controlling the Fate of Radical *ipso* Intermediates. Homolytic Alkylation of Furan Derivatives

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Summary Radical *ipso* σ-complex intermediates have been observed to lead also towards products other than those of *ipso* substitution; from the reaction of 1-adamantyl radicals with 5-nitro-2-methoxycarbonylfuran and 5-nitrofuran-2-carbaldehyde, products have been isolated which demonstrate that these intermediates lead to the elimination of a group from a substituent remote from the *ipso* position and to the coupling with other radicals.

We have recently reported several examples of the addition of a radical to an *ipso* position of an aromatic substrate to afford an *ipso* σ-complex; in all the cases investigated so far these intermediates evolve towards the products of *ipso* substitution by elimination of the group originally linked to the *ipso* carbon atom.[1] Thus, groups such as NO_2, COR, CHO, SO_2R, SOR, and, to a smaller extent, SR, OR, and halogen atoms were all displaced by nucleophilic alkyl radicals.[2–4] It was expected, however, that, depending on the attacking radical, the *ipso* substituent, and the aromatic substrate employed, processes other than *ipso* substitution should also be available to radical *ipso* σ-complexes.[2,4] We report now examples which demonstrate that these intermediates are trapped by other radicals and give rise to elimination of a group from a substituent remote from the *ipso* position.

On the basis of the known reactivity of furan towards free radicals[5] and knowledge about the factors controlling the competition between radical attack at an *ipso* or at an unsubstituted position of an aromatic compound,[4] we expected that the reaction of an alkyl radical with 2,5-disubstituted furans should give almost exclusively products derived from attack at the *ipso* positions. In fact, the reaction of 1-adamantyl (Ad•) with 5-nitro-2-methoxycarbonylfuran (**1a**) afforded a mixture of 5-(1-adamantyl)-2-methoxycarbonylfuran (**2a**) m.p. 102—103 °C (31·5%) and two compounds which, on the basis of analytical and spectral data,† were assigned the structures (**3a**), m.p. 124—125 °C (32%) and (**4a**) m.p. 121—122 °C (10%).‡ Similarly, (**2b**), m.p. 73—74 °C (35%), (**3b**), m.p. 128—130 °C (25%), and (**4b**), m.p. 108—110 °C (15%) were obtained from the reaction of Ad• with 5-nitrofuran-2-carbaldehyde (**1b**)† (Scheme).

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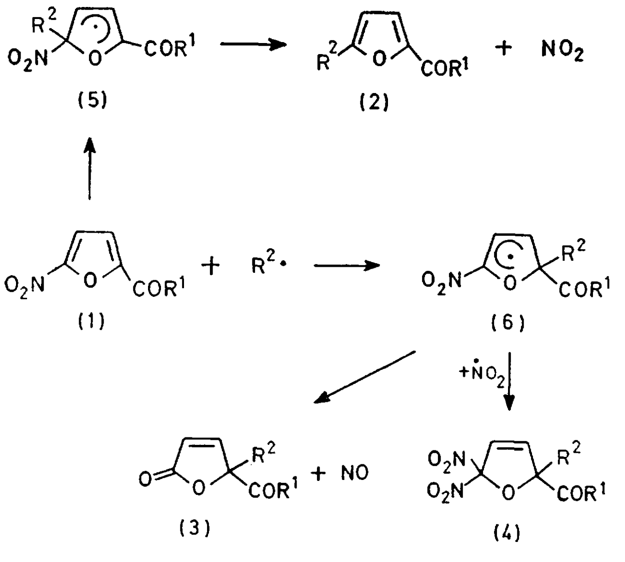
† Alkyl radicals were produced by the oxidative decarboxylation of the corresponding carboxylic acids and the reactions were carried out in $MeCN–H_2O$ as described in ref. 2. Satisfactory elemental analyses were obtained for all new compounds. Mass spectra were in agreement with the proposed structures. I.r. spectra (CH_2Cl_2) of compounds (**3a**) and (**3b**) showed strong absorptions at 1725 and 1770—1760 cm^{-1} (α,β-unsaturated γ-lactone, *cf.* ref. 6); the presence of NO_2 in compounds (**4a**—**c**) was confirmed by absorptions at 1580s and 1330w cm^{-1}. N.m.r. spectra of (**2**)—(**4**) were in accordance with the assigned structures. The alternative nitro–nitrite structure for compounds (**4a**—**c**) seemed unlikely because no absorption was observed in the 1610—1680 cm^{-1} region (N=O stretch in nitrites).

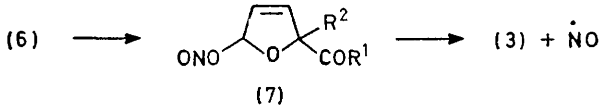
‡ *Added in proof*: The structure of compound (**4a**) has been confirmed by *X*-ray analysis.



Scheme **a**; R^1 = OMe, R^2 = Ad
b; R^1 = H, R^2 = Ad
c; R^1 = OMe, R^2 = Me

Attack at the *ipso* positions of (**1a**) was also observed with methyl radicals (formed from Me_2SO, H_2O_2, and FeS_4), to give 5-methyl-2-methoxycarbonylfuran (**2c**), 5-methyl-5-methoxycarbonylfuran-2(5*H*)-one (**3c**), and traces of 4-methyl-5-nitro-2-methoxycarbonylfuran. These results confirm a previous report by Rudqvist and Torssell.[6] In addition to these three compounds, however, we isolated traces of the oily product 5,5-dinitro-2-methyl-2-methoxycarbonyl-2,5-dihydrofuran (**4c**).‡

The formation of the products (**2a**—**c**), (**3a**—**c**), and (**4a**—**c**) clearly indicates that the addition of alkyl radicals occurs at both the *ipso* positions of (**1a**) and (**1b**) to give the *ipso* intermediates (**5a**—**c**) and (**6a**—**c**); the fates of the two σ-complexes are completely different, however. The radicals (**5**) give the alkyldenitration products (**2**) by elimination of •NO_2; this is therefore a further example of the well known radical displacement of the nitro group.[3,4] In contrast, *ipso* substitution is not observed in the case of (**6**). Both the R^2 and the COR^1 groups are strongly bonded to the *ipso* carbon atom; as a consequence neither of the two substituents can be easily eliminated and the radical (**6**) is forced to undergo other types of reactions from which compounds (**4**) and (**3**) are produced.



Although direct experimental evidence is not available at present, we suggest that the lactones (**3**) are formed from (**6**) through the rearrangement of the nitro group to form the nitrite radical (**7**) which then fragments into (**3**) and •NO. This reaction shows a close resemblance to the photochemical rearrangement of nitro compounds into aryloxyl radicals;[7] these rearrangements in fact are often postulated to proceed *via* the nitrite.[8] We assume that the *gem* dinitro-compounds (**4**) are derived from the coupling of (**6**) with the •NO_2 produced in the alkyldenitration of (**5**).

The dinitro-compound (**4a**) showed interesting behaviour; when heated above its m.p. (*ca.* 140 °C), either neat or in solution ($C_2H_2Cl_4$), it was quantitatively transformed into the lactone (**3a**) and nitrous vapours§ were liberated. This reaction probably proceeds through the homolytic fission of the carbon–nitrogen bond[9] to regenerate •NO_2 and the *ipso* intermediate (**6a**) which then rearranges and fragments as just suggested.¶

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§ The effluent gas was collected in an acidic solution of aniline; the formation of the diazonium salt was demonstrated by the characteristic reaction with β-naphthol.

¶ The formation of (**3a**) from (**4a**) could be explained in a different way. Nitroalkanes are known to rearrange thermally into alkyl nitrites (ref. 9) *via* a homolytic cleavage–recombination mechanism proceeding through a radical pair; in the present case (**4a**) should afford a *gem* nitro–nitrite derivative whose fragmentation would afford N_2O_3 and (**3a**). The thermal decomposition of (**4a**) was followed by i.r. spectroscopy but the characteristic absorption of the NO group of nitrites could not be observed; although this cannot be taken as a decisive proof, nevertheless the intermediate formation of the nitro–nitrite seems unlikely.

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