

Radical Alkyldenitration. A Synthetically Useful Example of Homolytic Aromatic *Ips*o-Substitution Reactions

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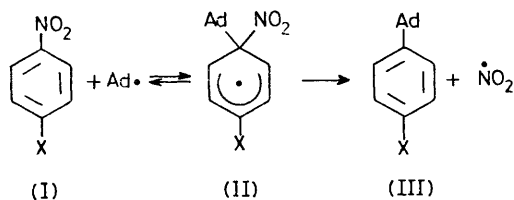
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Summary Nucleophilic alkyl radicals react with nitroaromatic compounds to give alkyldenitration products in good yields; in benzene derivatives displacement of the nitro-group occurs easily when an electron-withdrawing substituent is present in the *para* position.

THE displacement of several groups from electron-deficient heteroaromatic substrates by nucleophilic carbon radicals has been reported very recently.¹⁻⁶ Alkyldenitration occurs in the acyl derivatives of pyridine,^{1,3} quinoline,² and benzothiazole,^{1,4} and acyldeacylation was effected in the 2-acylbenzothiazoles;^{2,6} many other groups were also displaced from the 2-position of benzothiazole by the 1-adamantyl⁵ (Ad·) and acetyl⁶ radicals.

The results now presented deal with a new displacement process,⁷ alkyldenitration which, besides representing a remarkable example of homolytic aromatic *ipso* substitution reactions, can also have considerable synthetic importance. Adamantyl radicals, produced from adamantane-1-carboxylic acid (15 mmol), (NH₄)₂S₂O₈ (20 mmol), and AgNO₃ (0.3 mmol), react with the *para*-substituted nitrobenzenes (I) (3 mmol) in acetonitrile-water (50 ml; 4:1, v/v), to give the *para*-substituted 1-adamantylbenzenes (III) in good yields. The starting compounds (I) were completely converted and the adamantyldenitration products (III) were isolated by column chromatography. Yields and physical properties of compounds (III) are in the Scheme.

The same reaction occurs readily with 2-nitrobenzothiazole, the 2-(1-adamantyl)benzothiazole being isolated in quantitative yields; MeĊHEt and Me₂CHCH₂· radicals also react with the same substrate, but conversions were *ca.* 50% and the yields of the displacement product were lower (40 and 25% respectively).



SCHEME

X	% Yields of (III)	M.p. ^a /°C
NO ₂	60	129—130 (Lit. ⁸ 129—130)
SO ₂ Ph	60	182—184
CN	50	127—128 (Lit. ⁸ 126—127)
CO ₂ Me	60	144—145 (Lit. ⁹ 146—148)
COMe	60	108—109 (Lit. ¹⁰ 105—107)
CHO ^b	45	99—100

^a Compounds (III) were identified by i.r., n.m.r., and mass spectra and whenever possible by mixed m.p. Acetyladamantane and adamantan-1-ol were also isolated.³ ^b Identification was confirmed by oxidation to the known⁸ carboxylic acid with silver oxide.

Displacement of the nitro group by Ad \cdot did not occur with *p*-nitrotoluene, *p*-nitroanisole, and nitrobenzene; in the latter case the only substitution product obtained was *p*-nitroadamantylbenzene in agreement with previous results with electron-poor monosubstituted benzenes.⁹ Moreover, the same reaction carried out on *o*- and *m*-dinitrobenzenes and *o*- and *m*-nitrotoluenes did not give products derived from attack at the *ipso*-position. For the reaction to occur, it is therefore necessary that an electron withdrawing group is present in the *para* position of nitrobenzene. The substrates thus become strongly electron deficient and this would facilitate the charge separation from the radical to the substrate and consequently increase the importance of polar structures which contribute to the stabilization of the transition state of the addition step leading to (II). The observed reactivity can also be explained in terms of the frontier MO approximation. The nucleophilic Ad \cdot will be characterized by a high energy singly occupied MO and the important interaction will be with the LUMO of the arom-

atic substrates; high reactivity will be observed with substrates having a low energy LUMO, *i.e.* with nitrobenzenes bearing electron-withdrawing substituents in the *para*-position. Preliminary INDO calculations support this interpretation.

Once the nitro-group in (I) has been replaced, the products (III) which are formed are no longer sufficiently electron-deficient to suffer attack by the adamantyl radical and the reaction does not proceed further.

Most of the groups X, when linked to an electron-poor substrate like benzothiazole, can be easily displaced by nucleophilic carbon radicals.^{5,6} In the present case the reaction gives rise exclusively to the denitration products (III) and studies are presently under way to elucidate the factors responsible for the observed selectivity of this alkyl denitration process, as well as the fate of the displaced nitro-group.

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⁷ Previous examples of the radical denitration process are represented by the reaction of methyl 5-nitrofuran-2-carboxylate with methyl radicals from which methyl 5-methylfuran-2-carboxylate was obtained in 15% yields (K. Torssell, *Angew. Chem. Internat. Edn.*, 1972, 11, 241) and by the decomposition of perfluorobenzoyl peroxide in pentafluoronitrobenzene from which minute amounts of perfluorobiphenyl and perfluorophenyl benzoate were isolated [P. H. Oldham and G. H. Williams, *J. Chem. Soc. (C)*, 1970, 1260]. Displacement of the nitro-group by hydroxyl radicals, produced in several ways, has also been reported (Fr. Fichter and G. Bonhôte, *Helv. Chim. Acta*, 1920, 3, 395; H. Loebel, G. Stein, and J. Weiss, *J. Chem. Soc.*, 1950, 2704; K. Eiben, D. Schulte-Frohlinde, C. Suarez, and H. Zorn, *Internat. J. Radiation Phys. Chem.*, 1971, 3, 409).

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