Radical Adamantyldenitration in Polynitrobenzenes. Selectivity of Homolytic Aromatic *ipso* Substitution

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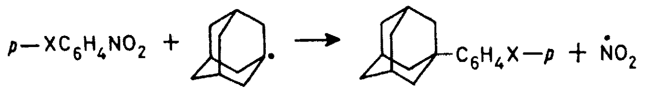
1-Adamantyl radicals react with 3,5-dinitro-1-X-benzenes (Ia—d), 2,4-dinitro-1-X-benzenes (IIa—e), and 2,4,6-trinitro-1-X-benzenes (IIIa—c) to effect selectively the displacement of the nitro group. This adamantyldenitration represents a further example of the ease of radical substitution at an *ipso* position. The same substrates react with phenyl and methyl radicals, but the reaction takes a completely different course; the only products obtained derive from attack at the unsubstituted nuclear positions. This drastic change of behaviour is attributed to the different polar character of adamantyl and phenyl or methyl radicals which determines a change in the nature of the transition state of the radical addition to the aromatic substrate.

SEVERAL examples have been recently reported by us and by others on the attack of carbon radicals at the *ipso* position of aromatic substrates;[1,2] among the possible reactions of the radical intermediate, that which has been demonstrated is the displacement of the group already linked to the aromatic ring, *i.e. ipso* substitution. Most of the examples studied were concerned with heteroaromatic substrates and nucleophilic radicals.

Very recently we found that displacement of the nitro group by alkyl radicals occurs easily for 2-nitrobenzothiazole and that this process can be efficiently effected even for nitrobenzenes provided they have an electron-withdrawing substituent in the *para* position.[3] Thus *p*-nitro-X-benzenes (X = CN, COMe, CO_2Me, CHO, SO_2R, or NO_2) underwent adamantyldenitration with 1-adamantyl radicals (Ad·) to afford the *p*-(1-adamantyl)-X-benzenes, in yields ranging from 45 to 60%.



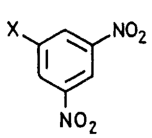
We have now examined the reaction of Ad· with several polynitrobenzenes with the aims of elucidating the factors governing the *ipso* substitution and of exploring its field of application; phenyl and methyl radicals were also employed in some cases for comparison.

RESULTS

1-Adamantyl, methyl, and phenyl radicals were produced from the corresponding carboxylic acids according to the general procedure introduced by Anderson and Kochi.[4]

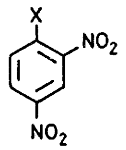
Three types of polynitrobenzenes were employed as aromatic substrates, the 3,5-dinitro-1-X-benzenes (Ia—d), the 2,4-dinitro-1-X-benzenes (IIa—e), and the 2,4,6-trinitro-1-X-benzenes (IIIa—c). With the exception of *m*-dinitrobenzene (Ia) which failed to give products from attack at the *ipso* position,[3] the other compounds gave rise selectively to the displacement of the nitro group by adamantyl radical.

From the reaction of (Ib—d) with Ad·, compounds (IVb—d) were obtained. Conversion was complete with 1,3,5-trinitrobenzene and product (IVb) was obtained in 50% yield; in the other two cases, under the standard conditions employed, the starting products were only partially converted (40%) and (IVc and d) were obtained in 60% yield based on converted products. Identification was carried out by i.r., n.m.r., and mass spectra.



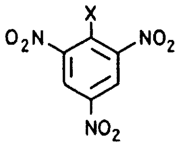
(I)

a; X = H
b; X = NO_2
c; X = CN
d; X = CO_2Me



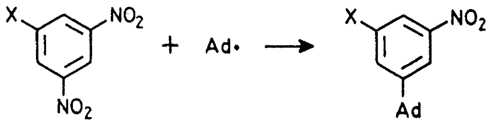
(II)

a; X = NO_2
b; X = CN
c; X = SO_2CHMe_2
d; X = $SO_2C_6H_4Me-m$
e; X = $SO_2C_6H_5$.

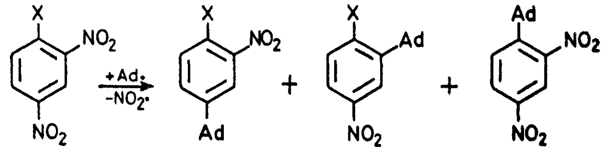


(III)

a; X = SO_2CHMe_2
b; X = CN
c; X = Cl



(I) (IV)



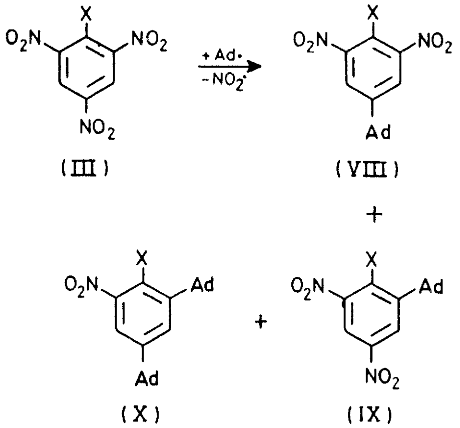
(II) (V) (VI) (VII)

In the case of the 2,4-dinitro-1-X-benzenes (II) Ad· can effect the displacement of either of the two nitro groups, and depending on the nature of the substituent X, products (V)—(VII) can be isolated. When a sulphonyl group is present in position 1 [compounds (IIc—e)] the reaction affords a single product deriving from the displacement of the nitro-group from position 4 [(Vc—e) in 65, 60, and 60% yields respectively]. I.r. and mass spectra indicate the presence of the sulphonyl, nitro, and 1-adamantyl groups and the position occupied by Ad can be demonstrated by n.m.r. spectroscopy. The β, γ, and δ protons of the bridgehead alkyl group gave rise to distinct absorptions which are characteristic of the absence of substituents *ortho* to the adamantyl group; in fact, it has already been observed for several aryladamantanes that, whenever an *ortho* substituent is present, the β-hydrogen atoms are deshielded and the adamantyl group gives rise to two broad singlets, of relative intensities 6 : 9 due to the δ and to the β plus γ protons respectively.[1,5]

Reaction of Ad• with 2,4-dinitrobenzonitrile (IIb) afforded a mixture of the two possible isomers deriving from the replacement of the nitro group in the 4- (Vb) or in the 2-position (VIb); the two products were obtained in almost equimolecular amounts (yield 40%). Structural attribution of (Vb) and (VIb) was easily accomplished on the basis of the considerations above and the appearance of the n.m.r. absorptions of the aliphatic protons of the adamantyl group.

Finally from the reaction of 1,2,4-trinitrobenzene (IIa) two products were isolated in the ratio 2 : 1 (yield 50%). To the major reaction product the structure 1-(1-adamantyl)-3,4-dinitrobenzene (Va) was easily assigned from its n.m.r. spectrum. The other isomer was demonstrated to be 1-(1-adamantyl)-2,4-dinitrobenzene (VIIa) by independent synthesis; the same compound is in fact obtained from the nitration of 1-(1-adamantyl)-4-nitrobenzene and this obviously excludes the other possible isomer (VIa).

The final type of substrate investigated was the 2,4,6-trinitro-1-X-benzenes (III); these reacted with adamantyl radicals leading to adamantyldenitration and again the nature of the products (VIII)—(X) was influenced by the nature of the substituent X. A distinction between the isomers (VIII) and (IX) is now made easier by inspection of the aromatic region of the n.m.r. spectra where (VIII) gives a singlet and (IX) an AB system. In this case also, when X = SO_2CHMe_2, *i.e.* compound (IIIa), a single substitution product was obtained in good yield (64%); the n.m.r. spectrum demonstrated that this compound was 4-(1-adamantyl)-1-isopropylsulphonyl-2,6-dinitrobenzene (VIIIa), resulting from the displacement of the nitro group in the 4-position.



Picryl chloride (IIIc) gave rise to two products in which the adamantyl radical effected *ipso* substitution at the 4- (VIIIc) and 2-positions (IXc); the two isomers were formed in 2 : 1 ratio (yield 35%).

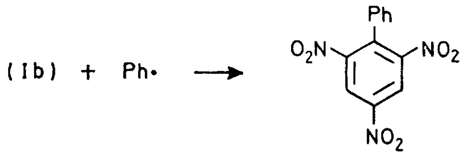
Finally, from the reaction of 2,4,6-trinitrobenzonitrile (IIIb) with Ad•, three compounds (yield 58%) were obtained, (VIIIb)—(Xb) (in 4 : 1 : 3 ratio). This is the first case in which substitution of two nitro groups is observed and it is of relevance to show whether (Xb) originates from (VIIIb) or (IXb) or from both. For this purpose (VIIIb) and (IXb) were made to react further with 1-adamantyl radicals; while (VIIIb) remained practically unchanged, (IXb) was almost completely transformed into (Xb).

Other products derived from Ad• were obtained in every case. As already reported these were acetyladamantane, formed by attack on acetonitrile used as solvent, and adamantan-1-ol;[5] other unidentified aliphatic compounds were also formed in smaller amounts.

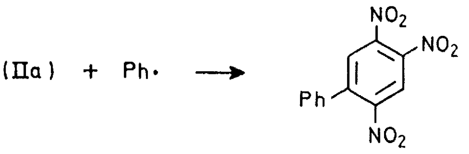
Attempts to detect the displaced NO_2 radical by e.s.r. spectroscopy were unsuccessful; for this purpose the reaction was carried out inside the cavity of an e.s.r. spectrometer using 1,3,5-trinitrobenzene (Ib) as substrate. The reaction was repeated by photolysing t-butyl adamantane-1-peroxycarboxylate in acetonitrile in the presence of the same aromatic compound, but conclusive evidence was not obtained. Thus, in order to elucidate the fate of the leaving group, the reaction of (Ib) with Ad• was carried out by the general procedure but using Ag_2SO_4 as catalyst and the aqueous layer was analysed for nitrites and nitrates;[6] this analysis demonstrated the absence of nitrites and the presence of nitrates.

Some representative substrates were then selected to investigate the behaviour of these molecules with other carbon radicals, such as the phenyl and the methyl radicals. In every case the only products obtained were those derived from attack at the unsubstituted nuclear positions; no evidence of *ipso* substitution could be obtained.

Thus, methyl radicals reacted with *p*-dinitrobenzene and 1,3,5-trinitrobenzene to give 2,5-dinitrotoluene and a mixture of 2,4,6-trinitrotoluene and 2,4,6-trinitro-*m*-xylene respectively; this latter result confirms a previous report in which methyl radicals were produced from the Fe^{3+} induced decomposition of hydrogen peroxide in dimethyl sulphoxide.[7] Similarly, phenyl radicals reacted with 1,3,5-trinitrobenzene (Ib) to give 2,4,6-trinitrobiphenyl (XI) and with 1,2,4-trinitrobenzene (IIa) to afford 2,4,5-trinitrobiphenyl (XII). Structure (XII) was assigned on the basis of the n.m.r. spectrum (in $CDCl_3$) which showed two singlets at δ 7.95 (6-H) and 8.45 (3-H); the two protons were not coupled thus indicating that they are *para* to each other.



(XI)



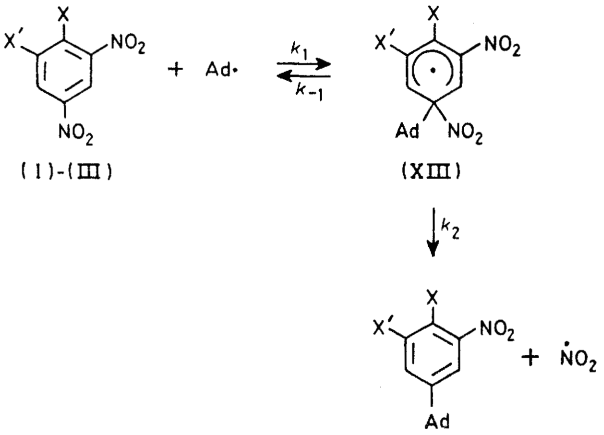
(XII)

DISCUSSION

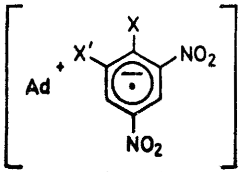
The results confirm that 1-adamantyl radicals easily react with nitrobenzenes to effect displacement of the nitro group, thus representing a remarkable example of homolytic aromatic *ipso* substitution.

An addition–elimination mechanism has been postulated for this kind of reaction[1,2] and we suggested that this operates in the present case as indicated in Scheme 1. Some of these displacement reactions showed features of reversibility.[1,2] In the adamantyldenitrations reported here, however, it can be assumed that the stability of the leaving NO_2 radical greatly assists the elimination step, making $k_2 \gg k_{-1}$, and thus leading to practically irreversible addition of the alkyl radical to the aromatic substrate. No direct evidence was obtained for the formation of NO_2, but nitrate ions were identified and it seems reasonable that this transformation can easily occur under the conditions employed.

The displacement of the nitro group does not occur with *o*- or *m*-dinitrobenzenes nor with *p*-nitrotoluene or *p*-nitroanisole, which can be recovered unchanged from reaction with Ad·.[3] In order to produce adamantyldenitration it is necessary that the aromatic substrate is strongly electron deficient, as is the case for compounds (I)—(III) and for nitrobenzenes with electron-withdrawing substituents in the *para* position.[3] This great substrate selectivity coupled with the well documented nucleophilic properties of the adamantyl radical,[1,5] suggests that polar structures, of the type (XIV), with charge separation from the radical to the substrate, considerably contribute to the stabilization of the transition state leading to the σ-complex.

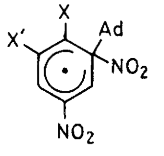


SCHEME 1

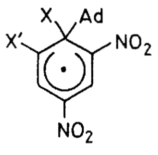


(XIV)

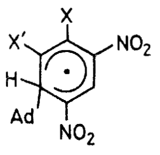
The experimental observations fit well with such a transition state, with the character of a charge transfer complex, as has been suggested for other systems having similar properties.[1,8,9] In this light it is understandable that the major factor controlling the positional selectivity is the local charge density at the nuclear positions which suffer attack and this can explain the preference for the positions bearing the nitro groups. In the nitrobenzene derivatives (I)—(III) in fact, several centres [see (XIII) and (XV)—(XVII)] are available for attack by the adamantyl radical. In all the cases studied however (except for 1,2,4-trinitrobenzene) the products observed derive from (XIII) and (XV); no evidence of the formation of compounds from (XVI) and (XVII) was obtained. Thus, despite the greater stabilization which can be reached in (XVI) and (XVII) the reaction occurs selectively at the carbon atoms holding the nitro groups clearly indicating that the process is not governed by the stability of the intermediates.



(XV)



(XVI)



(XVII)

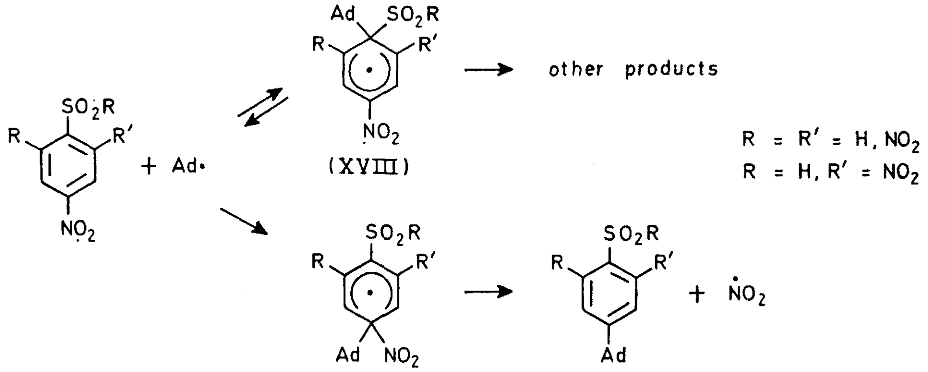
In the case of 1,2,4-trinitrobenzene (IIa) only, substitution at the 1-position, *i.e.* through the intermediate (XVI), was observed; once again however the displaced group was nitro and therefore in this case both the stability of the σ-complex and the local charge density act in the same direction. It is relevant anyhow that in this substrate the major reaction product was that from attack at the 4-position.

Like NO_2, the sulphonyl group is easily displaced by adamantyl radical when linked to the 2-position of benzothiazole;[1] one should therefore expect that, as is observed for 1,2,4-trinitrobenzene (IIa), substitution of the SO_2R group should also occur to a certain extent. This however was not observed in the substrates studied here, (IIc—e) and (IIIa), nor with the *p*-nitrophenyl phenyl sulphone.[3] Attack at the 1-position probably does occur in these compounds, but the elimination of the sulphonyl group is presumably not so easy as that of the nitro group, so that the intermediate (XVIII) either reverts to the starting products or it is diverted to other unidentified compounds by dimerization or coupling with other radicals (Scheme 2).

In these sulphonyl derivatives, the adamantyl radical attacks the 4-position only. The simplest reason which comes to mind to explain the lack of substitution products from the 2-position is steric hindrance; the bulky SO_2R prevents coplanarity of the nitro group with the benzene ring, thus making attack by the carbon radical unfavourable.

Once one of the nitro groups has been substituted by the adamantyl radical in substrates (I)—(III), the products formed are no longer sufficiently electron deficient to suffer a further attack and the reaction does not proceed. This is very likely the reason why 1,3-di-(1-adamantyl)-4-cyano-5-nitrobenzene (Xb) is formed from 1-(1-adamantyl)-2-cyano-3,5-dinitrobenzene (IXb) and not from 1-(1-adamantyl)-4-cyano-3,5-dinitrobenzene (VIIIb); compound (IXb), in fact, like substrates of the type (II), is still a strongly electron deficient compound.

Another very interesting point is the drastic change in behaviour on passing from 1-adamantyl to phenyl and methyl radicals. For 1,3,5-trinitrobenzene (Ib), for instance, the first radical gives rise exclusively to the displacement of the nitro group, *i.e.* to substitution at an *ipso* position; the phenyl radical, on the contrary, selectively attacks the unsubstituted nuclear positions.



SCHEME 2

Clearly the factors which influence the course of the substitution process with adamantyl radicals are different from those operating in the case of phenylation and methylation. It is well documented that both phenyl and methyl radicals are very weakly polar;[5,10,11] in their reactions with aromatic compounds it is therefore difficult to imagine that polar structures of the type (XIV) play a significant role. The transition state of the addition step cannot be suggested to be similar to a charge transfer complex, as in the case of the very nucleophilic adamantyl radical, but rather has the character of a σ-complex [10,11] intermediate. As a consequence phenyl and methyl radicals will react with the nitro derivatives (I)—(III) at the nuclear positions giving rise to the more stable cyclohexadienyl intermediate. It is a peculiarity of the substrates employed in the present investigation that they confirm so clearly such substantially different chemical reactivity; previous examples of *ipso* substitution reactions by various carbon radicals were in fact obtained with heteroaromatic compounds such as pyridine, quinoline, and benzothiazole [1-3] with leaving groups in the more reactive nuclear positions of the molecule either from the point of view of charge density or of the stability of the intermediate σ-complex. Under these circumstances therefore, although the substrates were strongly electron deficient, no clear indication can be obtained of the factors controlling the addition process in the cases where weakly polar radicals were employed.

EXPERIMENTAL

Product characterization was accomplished by n.m.r. ($CDCl_3$) (JEOL C60HL) and i.r. (CH_2Cl_2) spectroscopy (Perkin-Elmer 257) and mass spectrometry (Varian MAT 311 A at 70 eV using an all glass inlet system). M.p.s are uncorrected. G.l.c. analyses were carried out with a Carlo Erba Fractovap G1 instrument and e.s.r. experiments with a Varian E 109 E spectrometer. Satisfactory analytical data were obtained for new compounds.

Materials.—Adamantane-1-carboxylic acid and some of the aromatic compounds used as starting materials were commercial products. 2,4-Dinitrophenyl phenyl sulphone,[12] 2,4-dinitrophenyl 3-methylphenyl sulphone,[13] 1-isopropylsulphonyl-2,4-dinitrobenzene,[14] 2,4-dinitrobenzonitrile,[15] 1,2,4-trinitrobenzene,[16] and 2,4,6-trinitrobenzonitrile [17] were prepared as described in the literature.

1-*Isopropylsulphonyl*-2,4,6-*trinitrobenzene* (IIIa).—Propane-2-thiol (2.5 g) was dissolved in a solution of sodium hydroxide (1.3 g) in ethanol (100 ml) and water (10 ml) and the mixture dropped into a solution of picryl chloride (8.1 g) in ethanol (35 ml). The mixture was refluxed for 10 min and then left to cool to room temperature. Isopropyl 2,4,6-trinitrophenyl sulphide separated as needles (3.5 g), m.p. 30—32°. The sulphide (1.9 g) was dissolved in acetic acid (50 ml) containing 120 volume hydrogen peroxide (10 ml) and the solution warmed on a water-bath for 45 min. The mixture was poured onto ice and the precipitated sulphone filtered and crystallized from ethanol (1.2 g), m.p. 224—225°, $\delta(C_3D_6O)$ 9.1 (2 H, s), 4.15 (1 H, septet), and 1.5 (6 H, d), $\nu_{max.}$ 1 580, 1 560, 1 370 (NO_2), 1 350, and 1 160 (SO_2) cm^{-1}, *m/e* 277 (9%, $M - C_3H_6$), 197 (17), 120 (5), 75 (12), 74 (15), 62 (7), 43 (100), and 41 (70).

1-(1-*Adamantyl*)-2,4-*dinitrobenzene* (VIIa).—A solution of 1-(1-adamantyl)-4-nitrobenzene [18] (0.2 g) in acetic acid (50 ml) and HNO_3 (5 ml) was warmed at 70 °C for 2 h and then poured onto ice. The solid was filtered, dried, and chromatographed through a silica gel column using light petroleum–ethyl ether (7 : 3) as eluant. The physical and analytical data of (VIIa) are reported below.

Reaction of Adamantyl Radicals with Compounds (I)—(III).—All the reactions were carried out by the following general procedure. To a stirred solution of a nitro compound (I)—(III) (3 mmol), adamantane-1-carboxylic acid (15 mmol), and $AgNO_3$ (0.3 mmol) in 4 : 1 v/v acetonitrile–water (50 ml), a saturated solution of $(NH_4)_2S_2O_8$ (20 mmol) in water was added dropwise, under reflux, over *ca.* 20 min. Stirring and heating was continued for 30 min and the cooled solution was then poured onto ice and NH_3; the mixture was extracted with chloroform and the organic layer was washed with 5% NaOH and with water. The solution was dried and the solvent evaporated. The residue was chromatographed through a silica gel column using light petroleum–ethyl ether (7 : 3) as eluant. The separation of the various components was monitored by t.l.c. Reaction yields are reported in the Results section. Physical and spectral data of the reaction products are given below.

1-(1-*Adamantyl*)-3,5-*dinitrobenzene* (IVb). This had m.p. 164—166 °C, δ 8.85 (1 H, t, 4-H), 8.5 (2 H, d, *J* 1.8 Hz, 2-6-H), 2.15br (3 H, s, γ-H), 1.95br (6 H, s, β-H), and 1.75br (6 H, s, δ-H), $\nu_{max.}$ 2 900, 2 840 (Ad), 1 540, and 1 350 cm^{-1} (NO_2), *m/e* 302 (100%, *M*), 259 (11, $M - C_3H_7$), 246 (32), 245 (29, $M - C_4H_9$), 135 (26), 107 (12), 94 (75), 93 (38), 91 (12), 81 (19), 79 (30), and 67 (16).

1-(1-*Adamantyl*)-3-*cyano*-5-*nitrobenzene* (IVc). This had m.p. 180—182°, δ 8.4 (1 H, m, 6-H), 8.25 (1 H, m, 2-H), 7.9 (1 H, m, 4-H), 2.15br (3 H, s, γ-H), 1.95br (6 H, s, β-H), and 1.8br (6 H, s, δ-H), $\nu_{max.}$ 2 900, 2 840 (Ad), 2 240 (CN), 1 530, 1 350 (NO_2), and 800 cm^{-1}, *m/e* 282 (100%, *M*), 239 (10), 226 (32), 225 (32), 212 (9), 179 (11), 135 (24), 95 (12), 94 (63), 93 (28), 79 (16), and 67 (9).

1-(1-*Adamantyl*)-3-*methoxycarbonyl*-5-*nitrobenzene* (IVd). This had m.p. 192—194°, δ 8.75 (1 H, m), 8.45 (2 H, m), 2.15br (3 H, s, γ-H), 2.0br (6 H, s, β-H), and 1.8br (6 H, s, δ-H), $\nu_{max.}(CHCl_3)$ 2 900, 2 850 (Ad), 1 720 (CO), 1 530, and 1 350 cm^{-1} (NO_2), *m/e* 315 (100%, *M*), 284 (8, *M* — OMe), 272 (9, $M - C_3H_7$), 259 (29), 258 (39, $M - C_4H_9$), 245 (6), 153 (6), 135 (14), 95 (7), 94 (35), 93 (12), 91 (5), 79 (14), and 67 (6).

1-(1-*Adamantyl*)-3,4-*dinitrobenzene* (Va). This had m.p. 160—162°, δ 7.85—7.75 (3 H, m), 2.15br (3 H, s, γ-H), 1.95br (6 H, s, β-H), and 1.8br (6 H, s, δ-H), $\nu_{max.}$ 2 900, 2 840 (Ad), 1 540, 1 365 (NO_2), 850, and 840 cm^{-1}, *m/e* 302 (100%, *M*), 259 (8, $M - C_3H_7$), 246 (22), 245 (24, $M - C_4H_9$), 135 (16), 94 (61), 93 (25), 91 (7), 79 (18), and 67 (10).

1-(1-*Adamantyl*)-2,4-*dinitrobenzene* (VIIa). This had m.p. 72—74°, δ 8.45—7.6 (3 H, m), 2.05br (9 H, s, β- and γ-H), and 1.75br (6 H, s, δ-H), $\nu_{max.}$ 2 900, 2 850 (Ad), 1 530, 1 360 (NO_2), and 840 cm^{-1}, *m/e* 302 (19%, *M*), 285 (100), 284 (67), 267 (23), 215 (19), 204 (24), 191 (26), 180 (27), 175 (30), 165 (67), 95 (20), 93 (38), 91 (26), 81 (31), 79 (61), and 67 (32).

1-(1-*Adamantyl*)-4-*cyano*-3-*nitrobenzene* (Vb). This had m.p. 178—179°, δ 8.3 (1 H, m), 7.8 (2 H, m), 2.2br (3 H, s, γ-H), 2.0br (6 H, s, β-H), and 1.85br (6 H, s, δ-H), $\nu_{max.}$ 2 900, 2 850 (Ad), 2 230 (CN), 1 540, 1 350 (NO_2), and 840 cm^{-1}, *m/e* 282 (100%, *M*), 239 (12, $M - C_3H_7$), 226 (30), 225 (30, $M - C_4H_9$), 212 (11), 179 (13), 135 (25), 94 (75), 93 (28), 91 (10), 79 (26), and 67 (14).

1-(1-*Adamantyl*)-2-*cyano*-5-*nitrobenzene* (VIb). This had m.p. 194—196°, δ 8.2—7.7 (3 H, m), 2.2br (9 H, s, β- and γ-H), 1.8br (6 H, s, δ-H), $\nu_{max.}$ 2 900, 2 850 (Ad), 2 225 (CN), 1 560, 1 350 (NO_2), and 840 cm^{-1}, *m/e* 282 (100%, *M*), 239 (9, $M - C_3H_7$), 225 (24, $M - C_4H_9$), 202 (21), 179 (30), 135 (33), 107 (16), 94 (38), 93 (62), 91 (24), 79 (33), and 67 (21).

1-(1-*Adamantyl*)-4-*isopropylsulphonyl*-3-*nitrobenzene* (Vc). This had m.p. 128—130°, δ 8.0—7.5 (3 H, m), 3.9 (1 H, septet, C*H*Me_2), 2.15br (3 H, s, γ-H), 1.95br (6 H, s, β-H), 1.8br (6 H, s, δ-H), and 1.4 (6 H, d, CH*Me*$_2$, *J* 7 Hz), $\nu_{max.}$ 2 900, 2 840 (Ad), 1 540, 1 360 (NO_2), 1 305, 1 140 (SO_2), and 900 cm^{-1}, *m/e* 363 (8%, *M*), 333 (9), 321 (100, $M - C_3H_6$), 257 (25), 241 (41), 201 (26), 200 (43), 135 (22), 94 (38), 93 (23), 91 (11), 79 (25), and 67 (13).

1-(1-*Adamantyl*)-4-m-*tolylsulphonyl*-3-*nitrobenzene* (Vd). This had m.p. 143—145°, δ(CS_2) 8.15—7.25 (7 H, m), 2.4 (3 H, s, Me), 2.15br (3 H, s, γ-H), and 1.95—1.7br (12 H, m, β- and δ-H), $\nu_{max.}$ 2 900, 2 825 (Ad), 1 505, 1 350 (NO_2), 1 330, and 1 150 cm^{-1} (SO_2), *m/e* 411 (3%, *M*), 338 (11), 306 (9), 165 (13), 152 (18), 139 (29), 135 (30), 115 (20), 107 (25), 93 (56), 91 (100), 81 (19), 79 (75), and 67 (38).

1-(1-*Adamantyl*)-4-*phenylsulphonyl*-3-*nitrobenzene* (Ve). This had m.p. 141—143°, δ 8.4—7.5 (8 H, m), 2.15br (3 H, s, γ-H), 1.95br (6 H, s, β-H), and 1.8br (6 H, s, δ-H), $\nu_{max.}(CS_2)$ 2 900, 2 840 (Ad), 1 355 (NO_2), 1 330, 1 160 (SO_2), 740, and 675 cm^{-1}, *m/e* 397 (18%, *M*), 380 (32), 379 (80), 304 (100), 302 (51), 257 (28), 149 (51), 135 (55), 95 (17), 94 (22), 93 (24), and 77 (26).

1-(1-*Adamantyl*)-4-*isopropylsulphonyl*-3,5-*dinitrobenzene* (VIIIa). This had m.p. 208—210°, δ 7.7 (2 H, s, 2-, 6-H), 4.05 (1 H, septet, C*H*Me_2), 2.15br (3 H, s, γ-H), 1.95br (6 H, s, β-H), 1.8br (6 H, s, δ-H), and 1.5 (6 H, d, CH*Me*$_2$, *J* 7 Hz), $\nu_{max.}$ 2 900, 2 850 (Ad), 1 560, 1 360 (NO_2), 1 340, and 1 140 cm^{-1} (SO_2), *m/e* 408 (3%, *M*), 378 (7), 366 (100, $M - C_3H_6$), 349 (7, $M - C_3H_7O$), 286 (34), 135 (36), 107 (8), 94 (29), 93 (22), 91 (9), 81 (10), 79 (23), and 67 (13).

1-(1-*Adamantyl*)-4-*cyano*-3,5-*dinitrobenzene* (VIIIb). This had m.p. 183—185°, δ 8.3 (2 H, s, 2-, 6-H), 2.15br (3 H, s, γ-H), 1.95br (6H, s, β-H), and 1.8br (6 H, s, δ-H), $\nu_{max.}$ 2 900, 2 840 (Ad), 2 240 (CN), 1 550, and 1 340 cm^{-1} (NO_2), *m/e* 327 (90%, *M*), 284 (7, $M - C_3H_7$), 270 (15, $M - C_4H_9$), 135 (25), 107 (17), 105 (17), 94 (100), 93 (51), 91 (8), 79 (32), and 67 (17).

1-(1-*Adamantyl*)-2-*cyano*-3,5-*dinitrobenzene* (IXb). This had m.p. 222—224°, δ 8.65 (1 H, d, 4-H), 8.55 (1 H, d, 6-H, *J* 2 Hz), 2.25br (9 H, s, β- and γ-H), and 1.8br (6 H, s, δ-H), $\nu_{max.}$ 2 900, 2 840 (Ad), 2 230 (CN), 1 560, and 1 345 cm^{-1} (NO_2), *m/e* 327 (100%, *M*), 270 (9, $M - C_4H_9$), 247 (16), 246 (14), 135 (21), 107 (11), 105 (14), 94 (12), 93 (38), 91 (18), 79 (31), and 67 (22).

1,3-*Di*-(1-*adamantyl*)-4-*cyano*-5-*nitrobenzene* (Xb). This had m.p. 233—235°, δ 7.8 (1 H, d, 6-H), 7.65 (1 H, d, 2-H, *J* 1.8 Hz), 2.25br (9 H, s, β- and γ-H), 2.15br (3 H, γ-H), and 1.95—1.75br (18 H, m), $\nu_{max.}$ 2 860, 2 810 (Ad), 2 200 (CN), 1 520, and 1 330 cm^{-1} (NO_2), *m/e* 416 (100%, *M*), 385 (12), 359 (5, $M - C_4H_9$), 265 (17), 135 (38), 93 (14), 79 (17), and 67 (9).

1-(1-*Adamantyl*)-4-*chloro*-3,5-*dinitrobenzene* (VIIIc). This had m.p. 180—181°, δ 7.9 (2 H, s, 2-, 6-H), 2.15br (3 H, s, γ-H), 1.95br (6 H, s, β-H), and 1.8br (6 H, s, δ-H), $\nu_{max.}$ 2 900, 2 850 (Ad), 1 550, and 1 340 cm^{-1} (NO_2), *m/e* 338 (37%, $M + 2$), 336 (100, *M*), 293 (9, $M - C_3H_7$), 281 (12), 280 (24), 279 (24, $M - C_4H_9$), 135 (18), 94 (95), 93 (47), 91 (13), 79 (39), and 67 (20).

1-(1-*Adamantyl*)-2-*chloro*-3,5-*dinitrobenzene* (IXc). This had m.p. 126—128°, δ 8.4 (1 H, d, 4-H), 8.25 (1 H, d, 6-H, *J* 2 Hz), 2.25br (9 H, s, β- and γ-H), and 1.8br (6 H, s, δ-H), $\nu_{max.}$ 2 900, 2 850 (Ad), 1 550, 1 530, and 1 345 cm^{-1} (NO_2), *m/e* 338 (36%, $M + 2$), 336 (100, *M*), 295 (6), 293 (7, $M - C_3H_7$), 282 (11), 281 (11), 280 (34), 279 (31, $M - C_4H_9$), 167 (56), 135 (62), 94 (80), 93 (97), 91 (17), 81 (31), 79 (48), 71 (60), and 67 (31).

Reactions with Methyl and Phenyl Radicals.—These reactions were carried out according to the general procedure reported above using acetic and benzoic acids as radical precursors.

The reaction of *p*-dinitrobenzene with methyl radicals was examined by g.l.c. which demonstrates the absence of *p*-nitrotoluene and the presence of 2,5-dinitrotoluene.

The same radical reacted with 1,3,5-trinitrobenzene (Ib) to afford a mixture of 2,4,6-trinitrotoluene and 2,4,6-trinitro-*m*-xylene which could not be separated by column chromatography; their identities were however easily established from the n.m.r. spectrum of the mixture.[7]

Reaction of phenyl radicals with (Ib) afforded 2,4,6-trinitrobiphenyl (XI) identical to an independently prepared sample; 3,5-dinitrobiphenyl was not detected.

Reaction of phenyl radicals with 1,2,4-trinitrobenzene (IIa) afforded a single product identified as the 2,4,5-*trinitrobiphenyl* (XII) (40%), m.p. 135—136°, δ 8.45 (1 H, s, 3-H), 7.95 (1 H, s, 6-H), 7.65—7.25 (5 H, m), $\nu_{max.}$ 2 950, 1 550, 1 350 (NO_2), 860, and 835 cm^{-1}, *m/e* 289 (55%, *M*), 261 (100), 167 (39), 150 (54), 149 (99), 139 (73), and 77 (30).

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