Structural Effects on the Reactivity of Carbon Radicals in Homolytic Aromatic Substitutions. Part III.[1] Reaction of the 1-Adamantyl Radical with Benzene Derivatives

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Homolytic substitution of monosubstituted benzenes by 1-adamantyl radical has been carried out and the reactivity and the polar character of the radical have been determined by examining the effects of substituents on isomer distributions and on relative reactivities. The results indicated that the 1-adamantyl radical has nucleophilic properties which are more pronounced than that of other more strained bridgehead radicals: it is suggested that this behaviour is attributable to the different role played by polar effects during the addition of bridgehead radicals to aromatic substrates. The syntheses of several monosubstituted 1-aryladamantanes are also described.

RECENT studies have provided evidence that an increase of the *s* character of an orbital occupied by an odd electron makes the resulting carbon radical less nucleophilic in its substitution reactions with homoaromatic substrates. Alkyl radicals [2] are generally of the π-type, with the unpaired electron in a p orbital and are therefore more nucleophilic than aryl [3] or vinyl [4] (σ-type) radicals or acetylenic radicals.[5] Radicals possessing a pure, or almost pure, sp^3 configuration can only be generated at the bridgehead position of a polycyclic hydrocarbon where the structural requirements of the molecule are satisfied by the pyramidal stereoconfigurational stability of the radical carbon atom. Results [1] on aromatic substitutions by the 1-norbornyl radical demonstrated the preference of this species to effect substitution at relatively electropositive positions of monosubstituted benzenes; in agreement with expectations therefore sp^3 hybridized radicals have a certain degree of nucleophilicity relative to sp^2 radicals. It must be noted, however, that, owing to the high ring strain of the norbornyl system, deformations of the radical centre are impossible and the orbital occupied by the odd electron is not pure sp^3, but very probably possesses slightly enhanced *s* character. On the other hand, less strained polycyclic systems such as bicyclo[2.2.2]octyl and adamantyl should have a perfectly pyramidal configuration, as indicated by recent theoretical studies.[6]

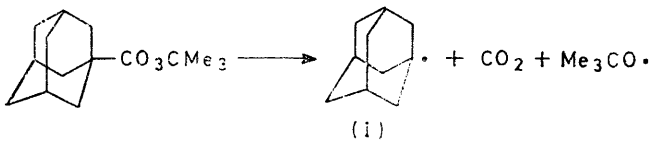
In a preliminary investigation [7] on the polar character of bridgehead radicals we found that the reactivity of these radicals towards *p*-difluorobenzene increased in the order 1-norbornyl, bicyclo[2.2.2]octan-1-yl, 1-adamantyl; this behaviour could be attributed to an enhanced con-

[1] Part II, L. Testaferri, M. Tiecco, P. Spagnolo, and P. Zanirato, *Gazzetta*, 1975, **105**, 761.
[2] J. R. Shelton and C. W. Uzelmeier, *J. Amer. Chem. Soc.*, 1966, **88**, 5222; F. Minisci, R. Mondelli, G. P. Gardini, and O. Porta, *Tetrahedron*, 1972, **28**, 2403.
[3] R. Ho, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, 1965, **21**, 955.
[4] P. Spagnolo and M. Tiecco, *Tetrahedron Letters*, 1968, 2313.
[5] G. Martelli, P. Spagnolo, and M. Tiecco, *J. Chem. Soc.* (*B*), 1970, 1413.
[6] P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 995.
[7] A. Mangini, P. Spagnolo, D. Tassi, and M. Tiecco, *Tetrahedron*, 1972, **28**, 3485.

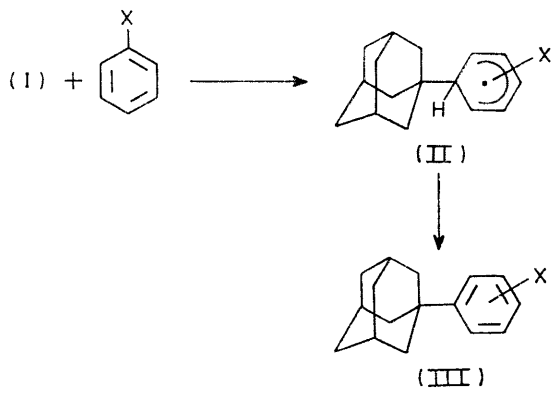
tribution of polar structures to the transition state of the addition step, on passing from the 1-norbornyl to the 1-adamantyl radical, made possible by the decreasing ring strains of the polycyclic systems. In order to clarify this point, reactions of the 1-adamantyl radical with several substituted benzenes have been carried out and the isomer distribution patterns and relative reactivities have been determined; thus, on the basis of these results, a comparison can be more confidently carried out with the already available data for the 1-norbornyl radical.

RESULTS AND DISCUSSION

1-Adamantyl radicals (I), produced from the thermal decomposition of the t-butyl ester of the adamantane-1-peroxycarboxylic acid, reacted with aromatic substrates *via* the intermediate cyclohexadienyl radicals (II), to form the 1-aryladamantanes (III) by further dehydrogenation; this process can be effected by several radical or non-radical species present in the reaction system. No detailed mechanistic investigations have been carried out in this respect, but in the light of the products obtained, it seems reasonable to assume that the general scheme for homolytic aromatic substitution reactions is valid in the present case.



(I)



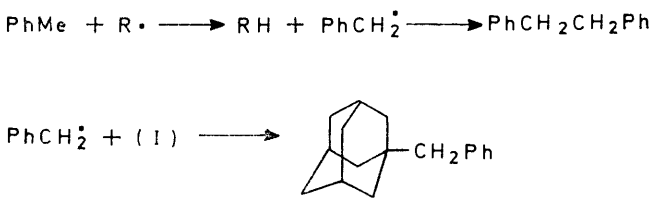
(II)

(III)

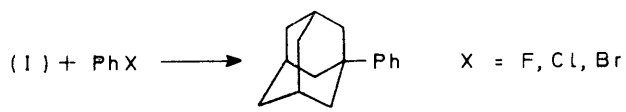
X=H, Me, Et, $CHMe_2$, CMe_3, OMe, F, Cl, Br, CO_2Me or CN

The substitution products (III) were obtained in yields ranging from 20 to 50% depending upon the nature of the substituent in the aromatic ring; yields were greater for electron-withdrawing substituents.

The decomposition of the t-butyl ester of adamantane-1-peroxycarboxylic acid in benzene has already been investigated [7,8] and the nature of the product elucidated. With substituted benzenes the products have been identified, the major components being in every case 1-aryladamantanes (III) and adamantane. For the reaction in toluene two other products were formed in considerable amounts, namely bibenzyl and 1-benzyladamantane which can be explained by the intermediate formation of benzyl radicals by hydrogen abstraction from the solvent. Similarly from the reaction in ethyl-



benzene and cumene 2,3-diphenylbutane and the bicumyl, respectively, were formed; in the latter case the products of substitution of (I) in the ring were present in minute quantities and their identification and quantitative determination seemed not to be justified. As already shown for *p*-difluorobenzene,[7] when halogenobenzenes were employed as substrates substitution of the halogen atom took place, to a certain extent, to afford 1-phenyladamantane. This process was taken into consideration in the determination of the relative reactivities of halogenobenzenes.



The distribution of the positional isomers in each substrate was determined by g.l.c. and the results are collected in Table 1; all products were then isolated by column chromatography and/or preparative g.l.c. and identified by spectroscopic analysis and in most cases by comparison with authentic samples prepared independently. Syntheses of the positional isomers were carried out by classical reaction sequences (see Experimental section).

For the purpose of determining the relative reactivity of the various benzene derivatives, the adamantyl perester was allowed to decompose in a large excess of an equimolar mixture of benzene and monosubstituted benzene. In every case the effect of changing the composition of the mixture of the two substrates in competition was examined; the values obtained, corrected for the statistical factor employed, were unchanged over a large range in the ratio of the two benzene derivatives. In the case of benzonitrile alone it was observed that an increase in the proportion of PhCN, while leaving the isomer ratios unchanged, produced an increase in the relative reactivity; thus for benzonitrile–benzene in the ratios 2 : 1, 1 : 1, and 1 : 2 the relative reactivity values obtained were respectively 27.5, 21.1, and 18.5. We have no explanation at present for the behaviour of benzonitrile and the value in Table 1 refers to a 1 : 1 mixture. The generally accepted assumption that cyclohexadienyl radicals (II) are not selectively removed by side reactions was tested by carrying out the reactions in

[8] G. A. Razuvaev, L. S. Boguslavskaya, V. S. Etlis, and G. V. Brovkina, *Tetrahedron*, 1969, **25**, 4925.

the presence of nitrobenzene which is an effective oxidizing agent of cyclohexadienyl intermediates.[9] In all experiments performed no alteration in the proportion of adamantylbenzenes was observed while their yields were considerably increased. Isomer distributions and relative reactivities are collected in Table 1, together with the data for 1-norbornyl radical [1] for comparison.

TABLE 1

Distribution of the positional isomers and relative reactivities (K) in homolytic substitution by the 1-adamantyl [a] and 1-norbornyl radicals

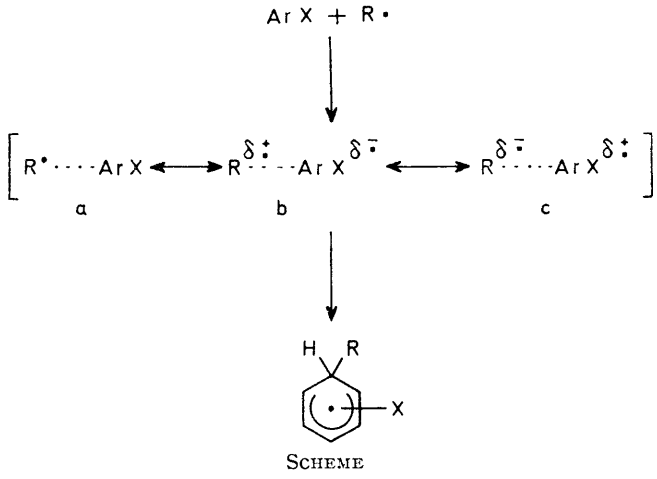
	1-Adamantyl radical [b]				1-Norbornyl radical [c]			
Substrate	*ortho*	*meta*	*para*	K	*ortho*	*meta*	*para*	K
C_6H_5OMe	38.0	31.0	31.0	0.65	51.1	32.2	17.2	0.9
C_6H_5Me		60.0	40.0	0.55				
C_6H_5Et		65.0	35.0	0.48	8.6	68.6	22.8	0.42
$C_6H_5CMe_3$		57.0	43.0	0.31		73.0	27.0	0.41
		60.0	*40.0*	*0.35*				
C_6H_5F	27.1	72.9		1.36	51.0	49.0		1.28
C_6H_5Cl		66.8	33.2	1.56				
		64.0	*36.0*	*1.65*				
C_6H_5Br		73.0	27.0	1.99				
$C_6H_5CO_2Me$		4.5	95.5	10.9	11.5	20.7	67.8	3.5
		6.0	*94.0*	*10.5*				
C_6H_5CN	7.4	4.7	87.9	21.1				
	7.6	*6.4*	*86.0*	*21.5*				

[a] Results are the average of three independent experiments; the experimental error is ±5%. [b] Values in italics refer to the reactions carried out in the presence of nitrobenzene. [c] From ref. 1.

As anticipated one of the features of the adamantyl radical is its great sensitivity to steric effects; *ortho*-substitution often does not occur at all and whenever it is encountered it is lower than in the case of 1-norbornyl radical. If it is considered that the *ortho*-position is the most reactive site for the majority of the radicals (*e.g.*, phenyl and methyl) the results obtained demonstrate the severe steric interactions occurring during substitution with these bridgehead radicals. But the most important conclusion from the results in Table 1 is that concerning the polar nature of the 1-adamantyl radical; both the isomer ratios and the relative reactivities indicate that the attacking species has nucleophilic character. The preference for the nuclear position with low electron density is demonstrated by the almost completely selective substitution in the *para*-position of the methyl benzoate and benzonitrile. More indicative still are the values for the relative reactivities; electron-releasing substituents produce a decrease and electron-withdrawing a considerable increase in the reactivity of the aromatic substrate with respect to benzene. A similar trend was also observed for the 1-norbornyl radical, but the selectivity shown by 1-adamantyl is considerably higher; in other words the 1-adamantyl radical is more nucleophilic than 1-norbornyl.

The results obtained for the 1-adamantyl radical confirm therefore that the radical produced on a carbon atom at the bridgehead position of a polycyclic system has nucleophilic character in agreement with expectation on the basis of the type of orbital occupied by the unpaired electron. Considerably different behaviour can however be deduced from the data collected in Table 1 for the two radicals 1-norbornyl and 1-adamantyl; we suggest that these differences are attributable to the different role played by polar effects during the addition step of the two radicals to the aromatic substrates.

It can be assumed that, in the transition state leading to the intermediate cyclohexadienyl radicals, some charge transfer from radical to substrate or *vice versa* might take place (Scheme).



SCHEME

The direction, as well as the degree, of charge separation will be determined by the requirements of both the radical R and the aromatic substrate; structure b will contribute for nucleophilic radicals, while structure c will assume some importance only for electrophilic radicals. The charge separation in the transition state for nucleophilic radicals implies the development of positive charge at the radical carbon atom and the degree to which this process occurs, for a given aromatic substrate, will depend upon the capability of this carbon atom to accommodate positive charge. Thus, in the case of the 1-norbornyl radical, because of the highly strained nature of the bicyclic system, the formation of an incipient carbocation at the bridgehead position is difficult; on the other hand, the absence of ring strain in the tricyclic system allows easier accommodation of the developing

[9] D. H. Hey, K. S. Y. Liang, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.* (*C*), 1967, 1153.

positive charge at the 1-position of adamantane.[10] In this latter case therefore polar structures assume greater importance and the radical has more pronounced nucleophilic character.

The importance of polar effects will obviously depend upon the nature of the aromatic substrate and it can be expected that, for the radicals under investigation, these effects are evident only for substrates with strongly electron-withdrawing substituents; in these cases the differences in total and partial relative reactivities become more important. For this reason we have recently undertaken an investigation utilizing as substrates the strongly deactivated protonated pyridines introduced by Minisci and his co-workers;[2] in these systems the differences in reactivities among bridgehead radicals, with different ring strain, can be more clearly defined.[11]

A much more complex picture arose when the 1-adamantyl radical (I) was allowed to react with naphthalene. First the ratio in which α- and β-(1-adamantyl)naphthalenes were formed was dependent on the temperature at which the peroxyester was decomposed. As shown in Table 2, at low temperature the

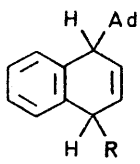
TABLE 2

Isomer distributions in the 1-adamantylation of naphthalene at different temperatures [a]

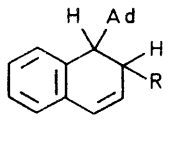
T/°C	α-Product	β-Product
20 [b]	66	34
60	54 (68)	46 (32)
100	52 (69)	48 (31)
140	45 (66)	55 (34)
180	29 (65)	71 (35)

[a] Results are the average of at least two independent experiments; the experimental error is ±5%. Values in parentheses refer to reactions carried out in the presence of copper(II) benzoate. [b] Decomposition of the peroxyester was effected by photolysis. [c] A reaction with nitrobenzene as additive afforded an α : β ratio of 65 : 35.

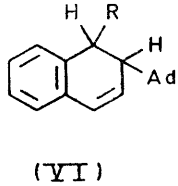
α-isomer predominates, while at high temperatures the β-isomer is preferentially formed; in every case the yields of substitution products were *ca.* 10%. All the reaction mixtures obtained after complete decomposition of the peroxyester, if heated for a few hours at 180°, gave rise to isomer ratios very similar to that obtained from decomposition at 180°. Clearly other products are formed which on warming revert to α- and β-(1-adamantyl)naphthalenes. Besides the two substitution products a considerable amount of a mixture of compounds could be obtained by column chromatography; this mixture had a very large melting range and the identification of the various components was not possible. The i.r. spectrum showed the absence of carbonyl functions and thermal decomposition afforded naphthalene, adamantane, and α- and β-(1-adamantyl)naphthalenes in the ratio of 40 : 60. Very probably this fraction consists of compounds originating from the intermediate cyclohexadienyl radicals by dimerization or coupling with other radicals; possible structures for these products are (IV)—(VI) resulting from the attack of (I) at the α- and β-positions of naphthalene.



(IV)



(V)



(VI)

The number of compounds with these structures is very large and this would explain the complex nature of the mixtures obtained. A possible explanation for the different isomer ratios at the various temperatures is found by assuming different ease of formation and fragmentation of dimeric products; moreover the formation of naphthalene and adamantane from their decomposition suggests that attack of the 1-adamantyl radical on naphthalene is significantly reversible at higher temperatures, especially for the α-position.

A more reliable value of the relative reactivity of the α- and β-positions seems to be that obtained at room temperature where the effects discussed above should play a minor role. Virtually the same values were obtained when the reactions were carried out in the presence of oxidizing agents, *e.g.* copper(II) benzoate or nitrobenzene, in which cases yields of substitution products were almost doubled.

EXPERIMENTAL

I.r. (Perkin–Elmer 257) and n.m.r. (JEOL C60HL) spectra were recorded for CS_2 solutions. For all the 1-aryladamantanes investigated a deshielding of the β-hydrogen atoms of the adamantane was observed whenever an *ortho*-substituent was present; this behaviour, which was first observed [12] for the methoxy-group, seems to be a general feature which can be very useful in structure determination. The reaction mixtures were analysed by g.l.c. on a Varian Aerograph 1520 instrument equipped with a flame ionization detector. The following columns were used: A, 5% FFAP on 80—100 mesh Chromosorb W (2 m); B, 5% PFE (6 rings) on 80—100 mesh Silocel (1 m); and C, 5% LAC on 80—100 mesh Varaport 30 (2 m). Preparative g.l.c. was performed on a Varian Aerograph model 712 instrument incorporating a 10% PFE on 60—80 mesh Chromosorb W column (2 m). Light petroleum refers to the fraction, b.p. 40—60°.

t-Butyl adamantane-1-peroxycarboxylate,[8] 1-phenyladamantane,[13] 1-(*p*-tolyl)adamantane,[14] 1-(*m*-tolyl)adamantane,[14] 1-(*m*-bromophenyl)adamantane,[14] 1-(*p*-bromophenyl)adamantane,[14] 1-(*p*-cyanophenyl)adamantane,[15] and 1-benzyladamantane [15] were prepared by literature methods.

1-(m-*Ethyl- and* 1-(p-*Ethyl-phenyl*)*adamantane.*—To a suspension of iron(III) chloride (1 g) in ethylbenzene (20 ml) a solution of 1-bromoadamantane (6 g) in ethylbenzene (20 ml) was added dropwise over 1 h. After being stirred at 70° for 3 h longer, the mixture was poured into an excess of dilute hydrochloric acid and extracted with benzene. The

[10] R. C. Fort and P. v. R. Schleyer, *Adv. Alicyclic Chem.*, 1966, **1**, 283.
[11] M. Fiorentino, L. Testaferri, M. Tiecco, and L. Troisi, unpublished results.
[12] Soon Ng, *Spectroscopy Letters*, 1973, **6**, 353.
[13] H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, 1959, **92**, 1629.
[14] H. Stetter, J. Weber, and C. Wulff, *Chem. Ber.*, 1964, **97**, 3488.
[15] F. P. Stepanov, E. I. Dikolenko, and G. I. Danilenko, *Zhur. org. Khim.*, 1966, **2**, 640 (*Chem. Abs.*, 1966, **65**, 8783).

extracts were washed with water several times and dried. Removal of solvent left a residue (4 g) which was analysed by g.l.c. 1-Phenyladamantane and two major products in the ratio 60 : 40 were detected. By preparative g.l.c. three fractions were collected: (i) 1-phenyladamantane, m.p. and mixed m.p. 86—88°; (ii) 1-(m-*ethylphenyl*)*adamantane*, b.p. 173—175° at 15 mmHg (Found: C, 89.8; H, 10.2. $C_{18}H_{24}$ requires C, 89.95; H, 10.05%), $\nu_{max.}$ 785 and 700 cm^{-1} (*meta*-substitution), δ 1.21 (3 H, t, *J* 7.5 Hz), 1.85 (12 H, m), 2.08br (3 H, s) 2.58 (2 H, q, *J* 7.5 Hz), and 7.0 (4 H, m); (iii) 1-(p-*ethylphenyl*)*adamantane*, m.p. 56—58° (Found: C, 89.95; H, 10.4%), $\nu_{max.}$ 835 and 805 cm^{-1} (*para*-substitution) δ 1.18 (3 H, t, *J* 7.5 Hz), 1.75—1.85 (12 H, m), 2.0br (3 H, s), 2.5 (2 H, q, *J* 7.5 Hz), and 6.9 (4 H).

1-(m-*Aminophenyl*)*adamantane*.— *p*-(1-Adamantyl)-acetanilide [14] (16 g) was added in small portions to a stirred solution of fuming nitric acid (4 ml), acetic acid (16 ml), and acetic anhydride (16 ml) at 10°, stirring being continued for 1 h. The mixture was then poured into an excess of ice–water and the yellow solid which separated was filtered off, washed with a little water, and dried to give 4-(1-*adamantyl*)-2-*nitroacetanilide* (16 g), m.p. 211—213° (from ethanol) (Found: C, 68.7; H, 7.2; N, 8.85. $C_{18}H_{22}N_2O_3$ requires C, 68.75; H, 7.05; N, 8.9%). 4-(1-Adamantyl)-2-nitro-acetanilide (12 g) was refluxed for 5 h in a solution of potassium hydroxide (1 g) in 95% ethanol (60 ml). On cooling an orange precipitate formed. This was collected and dried to afford 4-(1-*adamantyl*)-2-*nitroaniline* (9 g), m.p. 222—224° (from ethanol) (Found: C, 70.25; H, 7.3; N, 10.2. $C_{16}H_{20}N_2O_2$ requires C, 70.55; H, 7.4; N, 10.3%). The aniline (13 g) in acetic acid (150 ml) was diazotised at 10° with sodium nitrite (5.2 g) in concentrated sulphuric acid (40 ml). After being stirred at 10° for 1 h, the resulting solution was added to 95% ethanol (300 ml), warmed on a steam-bath until nitrogen evolution ceased, and then poured into an excess of water. Extraction with ether and evaporation of solvent left an oily residue which was chromatographed on silica gel. Elution with ether–light petroleum (1 : 9) afforded 1-(m-*nitrophenyl*)*adamantane* (8.5 g), m.p. 84—86° (from ethanol) (Found: C, 74.5; H, 7.3; N, 5.5. $C_{16}H_{19}NO_2$ requires C, 74.65; H, 7.4; N, 5.4%), $\nu_{max.}$ 735 and 685 cm^{-1}, δ 1.80—1.90 (12 H, m), 2.09br (3 H, s), and 7.58 (4 H, m). This compound (1 g) was dissolved in 95% ethanol (30 ml) and hydrogenated over 10% palladium–charcoal at 3 atm. for 1 h. Removal of the catalyst by filtration and concentration, under vacuum, afforded 1-(m-*aminophenyl*)-*adamantane* (0.8 g), m.p. 135—137° (from ethanol) (Found: C, 84.55; H, 9.4; N, 6.3. $C_{16}H_{21}N$ requires C, 84.5; H, 9.3; N, 6.15%), $\nu_{max.}$ 3 390 and 3 330 (NH_2) and 770 and 695 cm^{-1} (*meta*-substitution).

1-(m-*Methoxyphenyl*)*adamantane*.— 1-(*m*-Aminophenyl)-adamantane (1 g) was diazotised as described before for 4-(1-adamantyl)-2-nitroaniline. The diazonium salt solution was slowly added to methanol (30 ml) and warmed until decomposition of the diazonium salt was complete. The mixture was cooled, poured into water, and extracted with ether. Evaporation of solvent left a residue which was chromatographed on silica gel. Elution with ether–light petroleum (5 : 95) gave 1-(m-*methoxyphenyl*)*adamantane* (0.3 g), m.p. 63—65° (from methanol) (Found: C, 84.2; H, 9.3. $C_{17}H_{22}O$ requires C, 84.25; H, 9.15%), $\nu_{max.}$ 770 and 695 cm^{-1}, δ 1.75—1.9 (12 H, m), 2.05br (3 H, s), 3.65 (3 H, s, OCH_3), and 6.7 (4 H, m).

1-(p-*Methoxyphenyl*)*adamantane*.— 1-Bromoadamantane (2 g) was allowed to react with anisole in the presence of iron(III) chloride as described above for the reaction with ethylbenzene. Concentration under vacuum left a residue which, after column chromatography on silica gel [ether–light petroleum (1 : 9) as eluant] afforded 1-(p-*methoxyphenyl*)*adamantane* (1.2 g), m.p. 82—83° (from methanol) (Found: C, 84.2; H, 9.15%), δ 1.70—1.81 (12 H, m), 1.92br (3 H, s), 3.58 (3 H, s, OCH_3), 6.48 (2 H), and 6.93 (2 H).

1-(o-*Fluorophenyl*)*adamantane*.—A mixture of 1-bromo-adamantane (5 g) and *m*-fluoroacetanilide (10 g) was stirred at 150° overnight. After addition of hydrochloric acid (50 ml; 1 : 1v/v) the mixture was refluxed for 4 h. On cooling a precipitate formed which was collected, washed with a little ethanol, and dried. The solid (3 g) was dissolved in 2N-hydrochloric acid (75 ml) and treated at 0° with sodium nitrite (1 g); the resulting solution was poured into 40% hypophosphorous acid (50 ml) and kept overnight at room temperature. Extraction with ether and evaporation gave an oil which was chromatographed on an alumina column. Elution with light petroleum afforded 1-(o-*fluorophenyl*)-*adamantane* (0.5 g), m.p. 74—76° (Found: C, 83.35; H, 8.4; F, 8.2. $C_{16}H_{19}F$ requires C, 83.45; H, 8.3; F, 8.25%), $\nu_{max.}$ 750 cm^{-1} (*ortho*-substitution), δ 1.78br (6 H, s), 2.00br (9 H, s), and 6.95 (4 H, m).

1-(m-*Fluorophenyl*)*adamantane*.—This compound was obtained from 1-(*m*-aminophenyl)adamantane by a standard procedure,[16] m.p. 57—59° (from ethanol) (Found: C, 83.45; H, 8.35; F, 8.2%), $\nu_{max.}$ 775 and 695 cm^{-1}, δ 1.73—1.84 (12 H, m), 2.06br (3 H, s), and 6.90 (4 H, m).

1-(p-*Fluorophenyl*)*adamantane*.—This compound was prepared from 1-(*p*-aminophenyl)adamantane [14] as described above for the *meta*-isomer, m.p. 74—75° (from methanol) (Found: C, 83.8; H, 8.35; F, 8.25%), $\nu_{max.}$ 835 and 805 cm^{-1}, δ 1.75—1.88 (12 H, m), 2.05br (3 H, s), and 6.95 (4 H, m).

1-(o-*Bromophenyl*)*adamantane*.—This compound (0.8 g) was prepared from 1-bromoadamantane (3 g) and *m*-bromo-acetanilide (15 g) following the procedure employed for the synthesis of 1-(*o*-fluorophenyl)adamantane, m.p. 96—98° (from methanol) (Found: C, 66.5; H, 6.6; Br, 27.1. $C_{16}H_{19}Br$ requires C, 66.0; H, 6.55; Br, 27.4%), $\nu_{max.}$ 750 cm^{-1} (*ortho*-substitution), δ 1.75br (6 H, s), 2.18br (9 H, s), and 7.13 (4 H, m).

1-(o-*Chlorophenyl*)*adamantane*.—This compound (0.6 g) was obtained from 1-bromoadamantane (2 g) and *m*-chloro-acetanilide (12 g) following the same procedure described for 1-(*o*-fluorophenyl)adamantane, m.p. 95—97° (Found: C, 77.9; H, 7.85; Cl, 14.15. $C_{16}H_{19}Cl$ requires C, 77.9; H, 7.75; Cl, 14.35%), $\nu_{max.}$ 750 cm^{-1}, δ 1.78br (6 H, s), 2.12br (9 H, s), and 7.05 (4 H, m).

1-(m-*Chlorophenyl*)*adamantane*.— 1-(*m*-Aminophenyl)-adamantane (1 g) in acetic acid (20 ml) and 25% sulphuric acid (20 ml) was treated at room temperature with sodium nitrite (0.6 g) in water (25 ml). After being stirred for 1 h at 0°, the mixture was added dropwise to a stirred solution of copper(I) chloride (3 g) in concentrated hydrochloric acid (20 ml), stirring being continued for 4 h at 80°. Extraction with ether and concentration under vacuum afforded an oil which was chromatographed on silica gel (light petroleum as eluant) to give 1-(m-*chlorophenyl*)*adamantane* (0.5 g), m.p. 94—95° (from ethanol) (Found: C, 77.9; H, 7.85; Cl, 14.25%), $\nu_{max.}$ 775 and 690 cm^{-1} (*meta*-substitution), δ 1.75—1.90 (12 H, m), 2.05br (3 H, s), and 7.05 (4 H, m).

1-(p-*Chlorophenyl*)*adamantane*.—This compound was pre-

[16] A. J. Vogel, 'Practical Organic Chemistry,' Longman, London, 1967, 3rd edn., p. 609.

pared from 1-(*p*-aminophenyl)adamantane [14] as described for the *meta*-isomer, m.p. 90—91° (from methanol) (Found: C, 77.7; H, 7.85; Cl, 14.4%), $\nu_{max.}$ 830 and 805 cm^{-1}, δ 1.75—1.85 (12 H, m), 2.08br (3 H, s), and 7.10 (4 H).

1-(o-*Cyanophenyl*)*adamantane*.—A mixture of 1-(*o*-bromophenyl)adamantane (0.5 g) and copper(I) cyanide (0.5 g) in dimethylformamide (30 ml) was refluxed for 15 h, cooled, treated with a solution of iron(III) chloride (4 g) in 2N-hydrochloric acid (15 ml), and kept at 80° for 1 h. Extraction with benzene and concentration of the solvent left a residue which was chromatographed on silica gel [ether–light petroleum (1 : 9) as eluant] to give 1-(o-*cyanophenyl*)-*adamantane* (0.3 g), m.p. 121—123° (Found: C, 86.0; H, 8.15; N, 5.8. $C_{17}H_{19}N$ requires C, 86.05; H, 8.05; N, 5.9%), $\nu_{max.}$ 755 cm^{-1}, δ 1.81br (6 H, s), 2.12br (9 H, s), and 7.33 (4 H, m).

1-(m-*Cyanophenyl*)*adamantane*.— 1-(*m*-Bromophenyl)-adamantane (0.4 g) treated as described above for the *ortho*-isomer, afforded the desired product (0.2 g), m.p. 146—148° (Found: C, 86.05; H, 8.15; N, 6.0%), $\nu_{max.}$ 785 and 690 cm^{-1}, δ 1.78—1.91 (12 H, m), 2.09br (3 H, s), 7.28 (2 H), and 7.41 (2 H).

1-(o-*Methoxycarbonylphenyl*)*adamantane*.— 1-(*o*-Bromophenyl)adamantane (1.5 g) in anhydrous ether (10 ml) was added dropwise at 0° to an ethereal solution of n-butyllithium, prepared from lithium (0.15 g) and n-butyl bromide (1.3 ml) in ether (50 ml). The resulting solution was stirred at 0° for 1 h, poured into a slurry of dry ice in ether, and left overnight. Water was added and the organic layer was separated and extracted with 10% sodium hydroxide. The combined extracts were acidified with dilute hydrochloric acid and extracted with ether. The residue (0.5 g) was directly treated with diazomethane to give an oil which was chromatographed on silica gel. Elution with a mixture of ether and light petroleum (1 : 9) afforded 1-(o-*methoxycarbonylphenyl*)*adamantane*, m.p. 46—48° (Found: C, 79.8; H, 8.15. $C_{18}H_{22}O_2$ requires C, 79.95; H, 8.2%), $\nu_{max.}$ 1 725 (C=O) and 745 cm^{-1} (*ortho*-substitution), δ 1.75br (6 H, s), 2.0br (9 H, s), 3.73 (3 H, s), and 7.18 (4 H, m).

1-(m-*Methoxycarbonylphenyl*)*adamantane*.— 1-(*m*-Cyanophenyl)adamantane (0.1 g) was refluxed in 20% potassium hydroxide (5 ml) for 15 h. After being cooled, the mixture was acidified with dilute hydrochloric acid and extracted with ether. The solvent was evaporated and the residue was directly treated with diazomethane to give an oil which was chromatographed on silica gel. Elution with a mixture of ether and light petroleum (1 : 9) gave 1-(m-*methoxycarbonylphenyl*)*adamantane*, m.p. 70—72° (Found: C, 79.8; H, 8.35%), $\nu_{max.}$ 1 740 (C=O) and 750 and 690 cm^{-1} (*meta*-substitution).

1-(p-*Methoxycarbonylphenyl*)*adamantane*.—This compound was prepared from 1-(*p*-cyanophenyl)adamantane [15] as described above for the *meta*-isomer, m.p. 146—148° (from ethanol) (lit.,[17] 143°), $\nu_{max.}$ 1 725 (C=O), 765, and 705 cm^{-1}, δ 1.78—1.93 (12 H, m), 2.08br (3 H, s), 3.73 (3 H, s), 7.21 (2 H), and 7.75 (2 H).

α-(1-*Adamantyl*)*naphthalene*.—This compound was prepared from 1-bromoadamantane (2 g) and α-acetamidonaphthalene (9 g) following the procedure described above for 1-(*o*-fluorophenyl)adamantane. Column chromatography on silica gel, using light petroleum as eluant, afforded naphthalene and α-(1-*adamantyl*)*naphthalene* (0.5 g), m.p. 196—198° (from ethanol) (Found: C, 91.55; H, 8.4 $C_{20}H_{22}$ requires C, 91.6; H, 8.4%), $\nu_{max.}$ 790 and 770 cm^{-1}, δ 1.7—2.5 (15 H, m), 7.1—7.9 (6 H, m), and 8.4—8.7 (1 H, m).

β-(1-*Adamantyl*)*naphthalene*.—(i) To a stirred solution of succinic anhydride (12.8 g) and 1-phenyladamantane (16.5 g) in nitrobenzene (70 ml), aluminium chloride (26 g) was added portionwise over 1 h and the mixture kept at 0—5°. Stirring was continued for 24 h at room temperature and the mixture was decomposed with dilute HCl and extracted with ether; the organic layer was separated, washed with water, dried, and distilled. Column chromatography on silica gel [using pentane–ether (1 : 1) as eluant] afforded 2-(p-1-*adamantylbenzoyl*)*propionic acid* (9 g), m.p. 152—154° (Found: C, 77.05; H, 7.9. $C_{20}H_{24}O_3$ requires C, 76.9; H, 7.75%). A mixture of zinc turnings [16 g; amalgamated by shaking with $HgCl_2$ (1.6 g), concentrated HCl (1 ml), and water], concentrated HCl (28 ml), and the acid (8 g) was refluxed 24 h. Additional HCl was added during this period. The reaction mixture was cooled and extracted with ether; the organic layer was washed, dried, and evaporated to afford a residue which was purified by column chromatography on silica gel using light petroleum–ether (1 : 1) as eluant. Pure 3-(p-1-*adamantylphenyl*)*butyric acid* (5.3 g), m.p. 127—129° was obtained (Found: C, 81.25; H, 8.75. $C_{20}H_{26}O_2$ requires C, 80.5; H, 8.8%), $\nu_{max.}$ 1 700 and 800 cm^{-1}. Cyclization of this compound (5 g) with polyphosphoric acid (16 g) at 80° for 40 min and then at 120° for 90 min afforded, after extraction with ether and evaporation, 7-(1-*adamantyl*)-3,4-*dihydronaphthalen*-1(2H)-*one* (1.1 g), m.p. 155—157° (from methanol) (Found: C, 85.6; H, 8.7. $C_{20}H_{24}O$ requires C, 85.65; H, 8.65%), $\nu_{max.}$ 1 690 cm^{-1}. Reduction of this ketone (0.9 g), following the procedure described above for the keto-acid, gave 7-(1-*adamantyl*)-1,2,3,4-*tetrahydronaphthalene* (0.5 g), m.p. 76—78° (from methanol) (Found: C, 89.95; H, 9.9. $C_{20}H_{26}$ requires C, 90.15; H, 9.85%). This compound (0.4 g) and sulphur (0.2 g) were heated at 230° for 12 h; after cooling, the mixture was extracted with ether and the residue, after evaporation of the solvent, was passed through a silica gel column using light petroleum as eluant. The first fractions contained the desired β-(1-*adamantyl*)*naphthalene* (0.1 g), m.p. 133—135° (from methanol) (Found: C, 91.5; H, 8.5. $C_{20}H_{22}$ requires C, 91.6; H, 8.4%), $\nu_{max.}$ 810 and 740 cm^{-1}, δ 1.7—2.25 (15 H, m) and 7.15—7.9 (7 H, m).

(ii) A solution of 1-bromoadamantane (2.2 g) in CS_2 (10 ml) was added at 0—5° to a suspension of iron(III) chloride (0.6 g) and naphthalene (25.5 g) in CS_2 (40 ml). Stirring was continued at room temperature for 3 h and the mixture then poured into dilute HCl. Extraction with ether and evaporation of the solvent afforded a residue which was purified by column chromatography as described in (i). The first fractions contained unchanged naphthalene and later fractions afforded β-(1-adamantyl)naphthalene (1 g), identical with the compound obtained in (i).

Decomposition of t-Butyl Adamantane-1-peroxycarboxylate in Aromatic Solvents.—Solutions of t-butyl adamantane-1-peroxycarboxylate (1 g) in aromatic solvents (50 ml) were kept at 90° for 4 days. Solvents were distilled off and the reaction products separated by column chromatography (silica gel) or preparative g.l.c. In some cases a complete separation could not be achieved but fractions containing mixtures of isomeric substitution products were collected. 1-Aryladamantanes were characterized by comparison with authentic samples by i.r. and n.m.r. spectroscopy and, when possible, by mixed m.p. 1-(o-*Methoxy*-, 1-(m-*t-butyl*-, and

[17] T. J. Broxton, G. Capper, L. W. Deady, A. Lenko, and R. D. Topson, *J.C.S. Perkin II*, 1972, 1237.

1-(p-*t-butyl-phenyl*)*adamantane* were identified by i.r. and n.m.r. spectroscopy and elemental analysis.

Reaction in toluene. Preparative g.l.c. afforded (i) bibenzyl, (ii) 1-benzyladamantane (i.r. and n.m.r. spectra identical with those of an authentic [15] sample), and (iii) a mixture of 1-(*m*-tolyl)- and 1-(*p*-tolyl)-adamantane. I.r. analysis of the reaction mixture before chromatography showed that no *ortho*-isomer was present.

Reaction in ethylbenzene. Preparative g.l.c. gave three fractions: (i) 2,3-diphenylbutane, (ii) 1-(*m*-ethylphenyl)-adamantane, and (iii) 1-(*p*-ethylphenyl)adamantane. No *ortho*-isomer was shown to be present by i.r. analysis of the mixture before separation.

Reaction in isopropylbenzene. The main reaction product was bicumyl; other products were formed in very small amounts and were therefore not identified.

Reaction in t-butylbenzene. By preparative g.l.c. two fractions were collected: (i) 1-(m-*t-butylphenyl*)*adamantane*, b.p. 138—140° at 0.5 mmHg (Found: C, 89.6; H, 10.55. $C_{20}H_{28}$ requires C, 89.5; H, 10.5%), $\nu_{max.}$ 785 and 700 cm^{-1} (*meta*-substitution), δ 1.25 (9 H, s), 1.73—1.85 (12 H, m), 2.00br (3 H, s), and 6.9 (4 H, m), (ii) 1-(p-*t-butylphenyl*)-*adamantane*, m.p. 136—138° (Found: C, 89.35; H, 10.7%), $\nu_{max.}$ 835 and 805 cm^{-1} (*para*-substitution), δ 1.23 (9 H, s), 1.73—1.84 (12 H, m), 1.96br (3 H, s), and 6.99 (4 H). The absence of *ortho*-isomer was confirmed by i.r. analysis of the crude reaction mixture.

Reaction in anisole. Preparative g.l.c. gave 1-(o-*methoxyphenyl*)*adamantane*, m.p. 105—107° (Found: C, 84.05; H, 9.0%), $\nu_{max.}$ 750 cm^{-1} (*ortho*-substitution), δ 1.71 br(6 H, s), 1.98br (9 H, s), 3.68 (3 H, s), and 6.75 (4 H, m) and a mixture of the *meta*- and *para*-isomers.

Reaction in fluorobenzene. Preparative g.l.c. gave (i) 1-phenyladamantane, (ii) 1-(*o*-fluorophenyl)adamantane, and (iii) a mixture of the *meta*- and *para*-isomers.

Reaction in bromobenzene. By preparative g.l.c. three fractions were obtained. The first contained 1-phenyladamantane, the second 1-(*m*-bromophenyl)adamantane, and the third 1-(*p*-bromophenyl)adamantane. Analysis of the reaction mixture by g.l.c. showed no trace of the *ortho*-isomer.

Reaction in chlorobenzene. By preparative g.l.c. two fractions were obtained: (i) 1-phenyladamantane and (ii) a mixture of 1-(*m*- and 1-(*p*-chlorophenyl)adamantane. Absence of the *ortho*-isomer was confirmed by g.l.c. analysis of the crude mixture before separation.

Reaction in benzonitrile. Column chromatography on silica gel using ether–light petroleum (1 : 9) as eluant afforded a first fraction containing a mixture of 1-(*o*- and 1-(*m*-cyanophenyl)adamantane; a second fraction contained the pure *para*-isomer.

Reaction in methyl benzoate. Column chromatography on silica gel using ether–light petroleum (1 : 9) as eluant afforded two fractions: (i) a mixture of 1-(*m*- and 1-(*p*-methoxycarbonylphenyl)adamantane and (ii) the pure *para*-isomer. G.l.c. analysis of the crude reaction mixture before column chromatography showed that the *ortho*-isomer was not present.

Reaction in naphthalene. A mixture of t-butyl adamantane-1-peroxycarboxylate (3.5 g) and naphthalene (50 g) was kept at 100° for 4 days. The excess of naphthalene was removed by sublimation in vacuum and the residue was analysed by g.l.c.; naphthalene, adamantane, and α- and β-(1-adamantyl)naphthalene (in the ratio 52 : 48) were identified. The products were then separated by column chromatography on silica gel using light petroleum as eluant: the first fractions contained naphthalene and adamantane, followed by α-(1-adamantyl)naphthalene, m.p. and mixed m.p. 196—198°, and β-(1-adamantyl)-naphthalene, m.p. and mixed m.p. 133—135° (total yield of isomers 0.3 g). Elution was continued with light petroleum–ether (9 : 1) and several fractions were collected containing viscous products, which solidified on treatment with methanol; this solid (3.7 g) melted over a very large range (170—220°) and any attempt to isolate a pure compound by crystallization or by further chromatography failed. The i.r. spectrum showed the presence of absorptions characteristic of the adamantane system and of aromatic hydrogens and the absence of carbonyl functions; the n.m.r. spectrum was extremely complex and did not give any useful information. When heated at 180° for several hours, partial decomposition of this mixture occurred and naphthalene, adamantane, and α- and β-(1-adamantyl)naphthalene (in the ratio 40 : 60) were identified and isolated. Refluxing this solid in toluene with *o*-chloranil gave essentially the same results.

Determination of Isomer Distributions and Relative Reactivities.—Solutions (*ca.* 0.1M) of t-butyl adamantane-1-peroxycarboxylate in equimolar mixtures of benzene and monosubstituted benzene were put in sealed 2 ml glass tubes and heated at 80° for 4 days. The mixtures were directly analysed by g.l.c. without manipulation. Pure substitution products were used to determine the relative detector response. The adamantan-1-ylfluorobenzenes could not be resolved completely but only a separation of the *ortho*- from the *meta*- plus *para*-isomers could be achieved. Three independent experiments were performed with each substrate. The averaged values of the isomer ratios and of the relative reactivities are reported in Table 1. The substitution products were obtained in 20—50% yields, based on the amount of the t-butyl adamantane-1-peroxycarboxylate employed. Experiments were also carried out using different molar ratios of the two aromatic solvents in competition; with the exception of benzonitrile, the values of the relative reactivities, when corrected for the statistical factor employed, were identical with those obtained using equimolar mixtures. Addition of small amounts of nitrobenzene did not produce appreciable variations of the isomer ratios and relative reactivities (see Table 1).

The decomposition of the t-butyladamantane-1-peroxycarboxylate in naphthalene was carried out at different temperatures and the isomer ratios obtained are collected in Table 2. In the reactions carried out at 20 and 60°, benzene was added in order to have an homogeneous solution, and phenyladamantane was observed in the reaction products; decomposition of the peroxyester at 20° was effected by photolysis. Portions of the reaction mixtures at various temperatures, after complete decomposition of the peroxyester, were kept at 180° for several hours; in every case the α : β ratio changed from the values reported in Table 2 to 30 ± 5 : 70 ± 5. Also reported in Table 2 are the values obtained at various temperatures in the presence of copper(II) benzoate; yields of substitution products increased to *ca.* 25%, while in the absence of additive yields were 10—15%, depending upon the temperature at which the reactions were carried out.

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