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One-electron Oxidation of Closed-shell Molecules. Part 3.[1] Oxidative Cleavage of 1,2,2,2-Tetrakis-(*p*-methoxyphenyl)ethanone with Dibenzoyl and Bis-(3,5-dinitrobenzoyl) Peroxides: Mechanistic Changeover of the Peroxide Function from Radical to Molecular Oxidation

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1,2,2,2-Tetrakis-(*p*-methoxyphenyl)ethanone (anispinacolone)(1) is cleaved by dibenzoyl peroxide (2) or bis-(3,5-dinitrobenzoyl) peroxide (3), affording tris-(*p*-methoxyphenyl)methyl benzoate (or 3,5-dinitrobenzoate) and benzoic (or 3,5-dinitrobenzoic) *p*-methoxybenzoic anhydride as the principal cleavage products. ^{13}C N.m.r. CIDNP studies by use of labelled anispinacolone (An$_3$*C·*CO·An; *C 90% ^{13}C) indicated that *p*-methoxybenzoyl radical is formed, presumably by way of the radical cation [anispinacolone]$^{+\cdot}$ which is produced by a single-electron transfer (s.e.t.) mechanism. The formation of the *p*-methoxybenzoyl radical was also indicated by spin-trapping experiments. The decomposition rates of (2) at 50.0 °C are unaltered on addition of (1) in nonpolar solvents such as dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, and benzene, whereas those of (3) are markedly accelerated. The cleavage of (1) by (2) is suppressed by added 3,4-dichlorostyrene by a factor of 6.7, whereas that of (1) by (3) is almost unaffected. These results suggest that in the case of dibenzoyl peroxide (2) the thermally produced benzoyloxyl radical works as a one-electron acceptor (or oxidant) upon (1), whereas when bis-(3,5-dinitrobenzoyl) peroxide (3) is used the peroxide molecule oxidizes (1), probably by way of an s.e.t. mechanism even in such nonpolar solvents. On the other hand, in polar solvents such as $(CF_3)_2CHOH$, tetramethylene sulphone, and acetonitrile the decomposition of (2) is accelerated by added anispinacolone, suggesting that the intermolecular s.e.t. reaction is partially involved in such polar solvents. Consequently, the oxidative cleavage of anispinacolone (1) by diaroyl peroxides provides the first example of dichotomy in the s.e.t. reaction of diaroyl peroxides, which can be considered a counterpart of the S_N1–S_N2 dichotomy in nucleophilic substitution, as far as the molecularity of the peroxide is concerned.

Although the oxidation by diaroyl peroxides of various nucleophiles, such as amines, phosphines, sulphides, electron-rich olefins, and carbanions, has been well documented in the literature,[2] there had been no previous reports on the oxidation of benzpinacolones, *e.g.* 1,2,2,2-tetrakis-(*p*-methoxyphenyl)-ethanone (anispinacolone) (1), by diaroyl peroxides, *e.g.*, dibenzoyl peroxide (2) or bis-(3,5-dinitrobenzoyl) peroxide (3), till we reported on this reaction in our previous communication.[1] We found incidentally in the course of a protiodearylation study of anispinacolone (1)[3] that this is cleaved by the diaroyl peroxide (2) or (3) in various organic solvents to afford primarily tris-(*p*-methoxyphenyl)methyl benzoate (or 3,5-dinitrobenzoate) and benzoic (or 3,5-dinitrobenzoic) *p*-methoxybenzoic anhydride, along with the further oxidized products of the benzoate ester. Meanwhile, it has been disclosed in these laboratories that cerium(IV) ammonium nitrate oxidation of (1) proceeds by an electron-transfer mechanism to give the cleavage products, *i.e.* tris-(*p*-methoxyphenyl)methanol and *p*-methoxybenzoic acid after work-up with water.[4]

With these results it was tempting to speculate that the diaroyl peroxide molecule could serve as a one-electron oxidant or else the aroyloxyl radical which is produced by thermal decomposition of diaroyl peroxide could induce one-electron oxidation.

In this context, the role of bibenzoyl peroxide as a one-electron oxidant has been clearly demonstrated by Pryor and his collaborators for the oxidation of *NN*-diphenylhydroxylamine[5] and dibenzenesulphenimide.[6] Similar single-electron transfer (s.e.t.) mechanisms for dibenzoyl peroxide have also been proposed by other investigators on the oxidation of potassium iodide,[7] dimethylaniline,[8] triphenylphosphine,[9] dibenzoylmethane,[10] Fe^{II},[11] and Cu^{I}.[12] Other examples of the s.e.t. reaction have been recently demonstrated to be diphenoyl[13] and phthaloyl peroxide[14] oxidations of aromatic amines, pyrene, anthracene, and some of their derivatives. Very recently Walling discussed the occurrence of the s.e.t. mechanism in slow organic reactions[15] and showed that the reaction of diaroyl peroxides, especially those containing electron-withdrawing groups, with dimethoxybenzene involves an s.e.t. process.[16]

However, little attention had been given to the role of the benzoyloxyl radical as a one-electron oxidant. In our previous communication,[1] we reported that the benzoyloxyl radical plays the role of a one-electron oxidant by abstracting a single electron from the pinacolone (1) and thus producing a radical cation [anispinacolone]$^{+\cdot}$ which readily cleaves into the tris-(*p*-methoxyphenyl)methyl cation and the *p*-methoxybenzoyl radical.[1] In contrast, bis-(3,5-dinitrobenzoyl) peroxide (3) has been found to oxidize (1) most probably by an intermolecular s.e.t. mechanism.[1]

In this paper we report on the details of this reaction, including the CIDNP experiments for the reaction mixture, the examination of the solvent effect on the rate, and the complete product analysis.

Results and Discussion

Products in the Reaction of Anispinacolone (1) *with Dibenzoyl Peroxide* (2) *in* 1,2-*Dichloroethane*.—All the reactions were carried out in the dark under nitrogen or argon. When a solution of anispinacolone (1) (0.100M) and dibenzoyl peroxide (2) (0.100M) in 1,2-dichloroethane was heated to 50 °C, it gradually turned orange. After 60 h, an iodometric titration on a portion showed that 20% of (2) had reacted, and a v.r. (visible region) spectrum for an acidified portion ex-

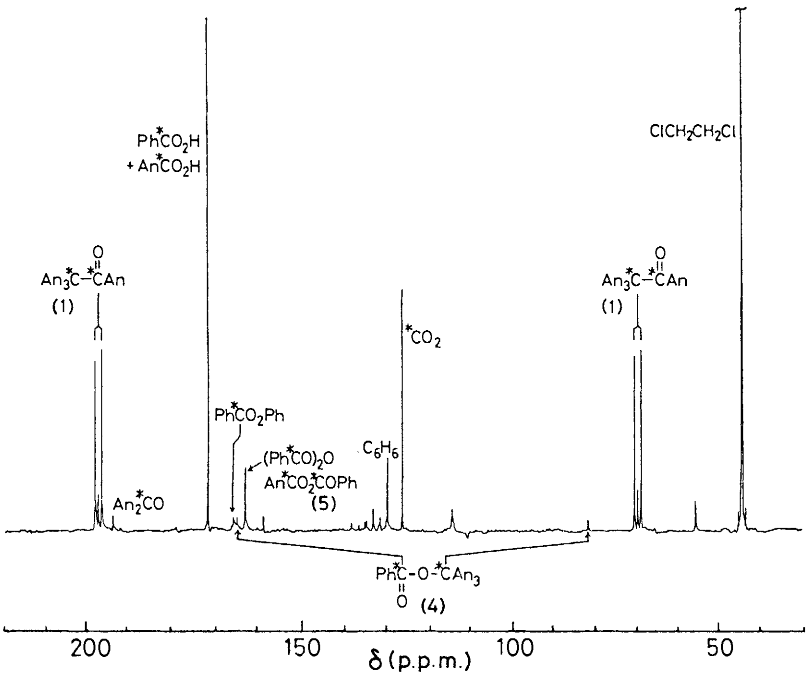

Figure 1. ^{13}C N.m.r. spectrum of the reaction mixture from $\mathrm{An_3{*}C{\cdot}{*}CO{\cdot}An}$ (0.10M) and $\mathrm{(Ph{*}CO_2)_2}$ (0.10M) in 1,2-dichloroethane for 51 h at 75 °C; *C, 90% ^{13}C. For the chemical shifts see Experimental section

hibited the formation of tris-(*p*-methoxyphenyl)methyl cation in 13% yield. Work-up of the reaction mixture afforded tris-(*p*-methoxyphenyl)methanol * and *p*-methoxybenzoic acid (10%) as the cleavage products from anispinacolone, and benzoic acid (44%) † coming from dibenzoyl peroxide. In addition to these compounds, *p,p'*-dimethoxybenzophenone,‡ which is formed by further oxidation of tris-(*p*-methoxyphenyl)methyl benzoate (4), was obtained in 8%, and unchanged anispinacolone recovered in 76% yield.

In another experiment conducted at 50 °C for 840 h, benzoic anhydride (8%) and benzoic *p*-methoxybenzoic anhydride (7%) were isolated by distillation *in vacuo*, after free acids had been removed by brief work-up with cold aqueous sodium hydrogencarbonate.

These results suggested that the reaction in its early stages could be formulated as in equation (1).

$$\underset{(1)}{\mathrm{An_3C{\cdot}CO{\cdot}An}} + \underset{(2)}{\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}O{\cdot}COPh}} \longrightarrow \underset{(4)}{\mathrm{An_3C{\cdot}OCO{\cdot}Ph}} + \underset{(5)}{\mathrm{AnCO{\cdot}O{\cdot}COPh}} \quad (1)$$

$$\mathrm{An} = p\text{-}\mathrm{CH_3OC_6H_4}$$

The formation of the benzoate ester (4) and the mixed anhydride (5) was shown directly by ^{13}C n.m.r. for the reaction mixture which was obtained by starting with labelled (1) and (2), $\mathrm{An_3{*}C{\cdot}{*}CO{\cdot}An}$, and $\mathrm{(Ph{\cdot}{*}CO{\cdot}O)_2}$, where *C designates 90% ^{13}C enrichment (Figure 1). The assignments were performed with the aid of the spectra for the reaction mixture from unlabelled (1) and labelled (2) and that from labelled (1) and unlabelled (2).

In a control experiment of the thermal decomposition of dibenzoyl peroxide alone, no benzoic anhydride was formed in agreement with the reported results.[17] Therefore, the formation of benzoic anhydride (Figure 1) indicates that benzoic *p*-methoxybenzoic anhydride once formed was converted into the former anhydride by reacting with benzoic acid which was produced by thermal decomposition of dibenzoyl peroxide (2). As described later, the mixed anhydride (5) is considered to come from *p*-methoxybenzoyl chloride and benzoic acid.

Products in the Reaction of Anispinacolone (1) *with Bis-*(3,5-*dinitrobenzoyl*) *Peroxide* (3) *in* 1,2-*Dichloroethane*.—The reaction of (1) and (3) also exhibited orange colouration as the reaction progressed, indicating the formation of tris-(*p*-methoxyphenyl)methyl cation. Work-up of the reaction mixture with water afforded tris-(*p*-methoxyphenyl)methanol and *p*-methoxybenzoic acid as the main cleavage products from (1), and 3,5-dinitrobenzoic acid from (3) (Table 1). As neutral products, *p,p'*-dimethoxybenzophenone § (10—12%) and an aroyloxylated derivative (6) of anispinacolone (17%), which carries a 3,5-dinitrobenzoyloxy-group in the *meta*-position of one of the *p*-methoxyphenyl groups {1,2,2-tris-(*p*-methoxyphenyl)-2-[*p*-methoxy-*m*-(3,5-dinitrobenzoyloxy)-phenyl]ethanone} (Table 2) were also obtained.

A ^{13}C n.m.r. spectrum of the reaction mixture showed the formation of *p*-methoxybenzoic 3,5-dinitrobenzoic anhydride, which was also identified by transformation to a mixture of

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* Although a qualitative analysis by t.l.c. showed the formation of tris-(*p*-methoxyphenyl)methanol, its isolation from the reaction mixture containing unchanged (2) encountered difficulties owing to the transformation of the alcohol to unidentified substances during work-up.

† Based on the formation of two moles (200%) of benzoic acid from one mole of (2).

‡ The mechanism of the formation of *p,p'*-dimethoxybenzophenone from (4) has not been clarified.

§ *p,p'*-Dimethoxybenzophenone is considered to arise from further oxidation of tris-(*p*-methoxyphenyl)methyl 3,5-dinitrobenzoate (7), since prolonged reaction time in the presence of excess of (3) increased the yield of the former and decreased that of the latter.

Table 1. Yields of tris-(*p*-methoxyphenyl)methanol, *p*-methoxybenzoic acid, and 3,5-dinitrobenzoic acid in the reaction of (1) with (3) in 1,2-dichloroethane after water work-up: Ar = 3,5-dinitrophenyl; An = *p*-methoxyphenyl

	Concentration (M)				Products (%)		
Run	An_3CCOAn (1)	$(ArCO_2)_2$ (3)	Temp. (°C)	Time (h)	An_3COH	$AnCO_2H$	$ArCO_2H$ [a]
1	0.025	0.025	50	24	20	24	92
2	0.025	0.025	50	36	25	26	123
3	0.050	0.050	86	3	35	41	160

[a] Calculated on the basis of 200% for formation of two moles of acid from one mole of (3).

Table 2. Detailed analysis of the neutral products in the reaction of (1) with (3) in 1,2-dichloroethane: An = *p*-methoxyphenyl

	Concentration (M)				Products (%)			Recovered (%)	
Run	(1)	(3)	Temp. (°C)	Time (h)	An_3COH	An_2CO	(6) [a]	(1)	(3)
4 [b]	0.10	0.10	75	2	18	12	17 [d]	18	23 [f]
5 [c]	0.040	0.040	50	20	20	10	[e]	45	43 [f]
6 [c]	0.040	0.040	50	90	26	12	[e]	29	9 [f]

[a] 1,2,2-tris-(*p*-methoxyphenyl)-2-[*p*-methoxy-*m*-(3,5-dinitrobenzoyloxy)phenyl]ethanone. [b] Separated by silica t.l.c. after water work-up. [c] The reaction mixture was directly subjected to separation with an alumina column. [d] On separation with an alumina column, (6) was hydrolysed to give the corresponding phenol. [e] Not analysed. [f] Determined by iodimetry.

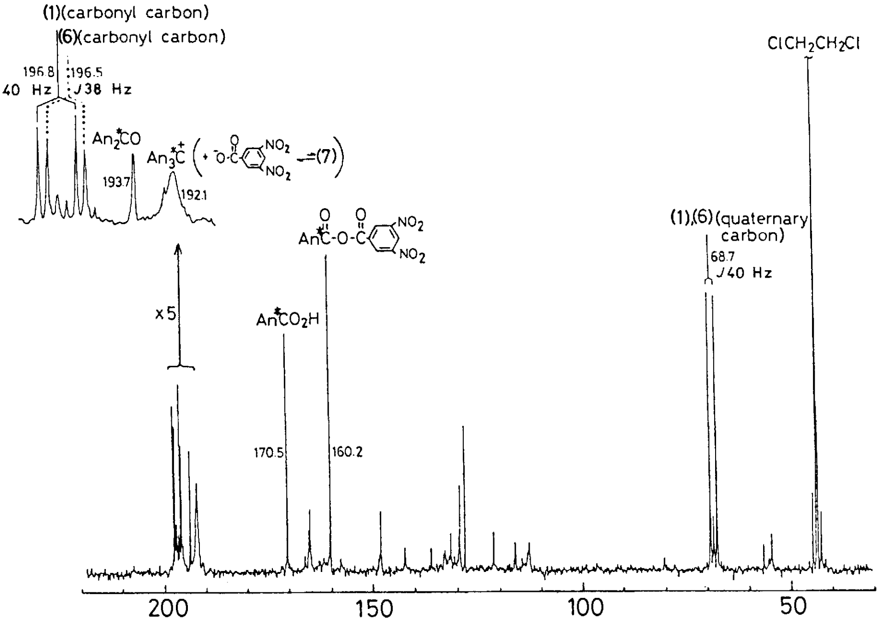

Figure 2. ^{13}C N.m.r. spectrum of the reaction mixture from $An_3{}^*C{\cdot}{}^*CO{\cdot}An$ (0.10M) and unlabelled bis-(3,5-dinitrobenzoyl) peroxide (3) (0.10M) in 1,2-dichloroethane for 70 min at 65 °C; *C, 90% ^{13}C

N-butyl-*p*-methoxybenzamide, *N*-butyl-3,5-dinitrobenzamide, and the corresponding acids by adding butanamine.*

The other products were directly detected by ^{13}C n.m.r. for the reaction mixture which was obtained by using labelled anispinacolone ($An_3{}^*C{\cdot}{}^*CO{\cdot}An$; *C 90% ^{13}C) and unlabelled bis-(3,5-dinitrobenzoyl) peroxide (Figure 2).

Thus the present reaction can be formulated by the two processes (2) and (3), at least in the early stages of the reaction. The presence of *p*-methoxybenzoic acid in the reaction mixture (Figure 2) can be rationalized by the acid exchange between the mixed anhydride and 3,5-dinitrobenzoic acid.

Effect of Added Anispinacolone (1) *on the Decomposition Rate of Dibenzoyl Peroxide* (2) *and Bis-*(3,5-*dinitrobenzoyl*) *Peroxide* (3).—As regards the molecularity of the reactions of dibenzoyl peroxides with various compounds two possibilities are generally postulated, the peroxide either reacts bimolecularly with the compound in question or it thermally decomposes to afford the benzoyloxyl radical, which then reacts with the substrate. A powerful means of distinguishing the two possibilities is to examine the effect of added substrate on the decomposition rate of the peroxide. If they react bimolecularly, the decomposition rate of the peroxide must be enhanced; otherwise the rate would not be enhanced by the added substrate.

In order to distinguish between the two mechanistic possi-

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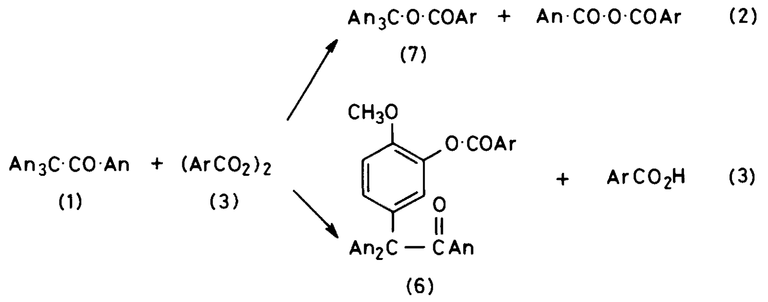
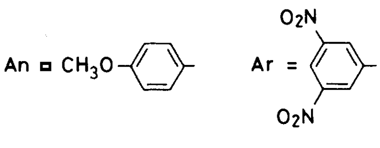
* The analysis was conducted on a reaction mixture which did not contain any unchanged (3), since the peroxide produces the amide.





bilities the initial decomposition rates of the peroxides (2) (0.050M) and (3) (0.040M) were determined by iodimetry in the absence and presence of anispinacolone (1) (0.050 or 0.040M) at 50 °C in 1,2-dichloroethane. The decomposition rate of (2) was essentially unaffected by added (1), with the initial rates being $(8.6 \pm 0.5) \times 10^{-8}$ mol l^{-1} s^{-1} in the absence of (1) and $(7.5 \pm 0.5) \times 10^{-8}$ mol l^{-1} s^{-1} in the presence of (1) (0.050M). On the other hand, the rate of (3) was markedly accelerated by a factor of 38, with the rates $(46 \pm 4) \times 10^{-8}$ *versus* $(1.2 \pm 0.1) \times 10^{-8}$ mol l^{-1} s^{-1}. These results suggest that when (2) is used the decomposition of the peroxide is rate controlling, and the species which reacts with anispinacolone is principally the benzoyloxyl radical, whereas in the case of (3) the reacting species is the peroxide molecule itself. However, dibenzoyl peroxide reacts intermolecularly, at least in part, when a polar solvent such as 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP), tetramethylene sulphone, or acetonitrile is used.

Rate Retardation by Added 3,4-*Dichlorostyrene*.—It is well known that added olefins, especially 3,4-dichlorostyrene, efficiently trap the benzoyloxyl radical and retard the decomposition of dibenzoyl peroxide by depressing the induced decomposition.[18] Therefore, if anispinacolone (1) reacts with the benzoyloxyl radical, the addition of 3,4-dichlorostyrene would markedly retard the rate of reaction of (1). On the other hand, if (1) reacts with the dibenzoyl peroxide molecule, the rate would be unaffected.

When the reaction of anispinacolone (1) (0.050M) with dibenzoyl peroxide (2) (0.050M) was conducted in 1,2-dichloroethane at 50.0 °C in the presence of added 3,4-dichlorostyrene (0.20M), the initial rate of reaction of (2) was depressed by a factor of *ca.* 2. The retarding effect of 3,4-dichlorostyrene (0.20M) on the rate of formation of tris-(*p*-methoxyphenyl)methyl benzoate was more striking. The rate decreased from $(3.7 \pm 0.4) \times 10^{-8}$ to $(0.55 \pm 0.05) \times 10^{-8}$ mol l^{-1} s^{-1}. During the reaction polymers precipitated. On the other hand, the rate of reaction of (1) with bis-(3,5-dinitrobenzoyl) peroxide (3) was almost unaffected by added 3,4-dichlorostyrene (0.20M), thereby no polymers being formed. The results again indicate that the principal reacting species in the case of dibenzoyl peroxide is the benzoyloxyl radical, and that it is the peroxide molecule when bis-(3,5-dinitrobenzoyl) peroxide is used.

^{13}C *N.m.r. CIDNP Studies*.—In order to elucidate the mechanism of the cleavage of anispinacolone (1) in the reaction with the peroxides (2) and (3), CIDNP studies were conducted by using ^{13}C Fourier transform n.m.r. on the reaction of labelled $An_3{}^*C{\cdot}{}^*CO{\cdot}An$ (*C 90% ^{13}C) with the unlabelled peroxides at 65 °C in 1,2-dichloroethane.

In the reaction with dibenzoyl peroxide (2), two emission signals corresponding to the carbonyl carbon of *p*-methoxybenzaldehyde and that of *p*-methoxybenzoyl chloride were observed at δ 189.2 and 166.6 p.p.m., respectively, over 15 min from the beginning of the reaction. On cooling the reaction mixture to 25 °C the formation of *p*-methoxybenzoyl chloride was confirmed, but the absorption signal of *p*-methoxybenzaldehyde was unseen.

These results suggest that the *p*-methoxybenzoyl radical, which emerges *via* the single-electron transfer from (1) to the benzoyloxyl radical [equation (4)], abstracts a hydrogen or a chlorine atom from 1,2-dichloroethane [equations (5) and (6)], although the fate of the solvent radicals ($ClCH_2\dot{C}HCl$ and $ClCH_2\dot{C}H_2$) has not been clarified. Presumably, *p*-methoxybenzaldehyde once formed reacts with benzoyloxyl radical and regenerates the *p*-methoxybenzoyl radical [equation (7)]. The ease of hydrogen abstraction from aldehydes by various radicals has been established in the literature.[19] The efficient abstraction of a chlorine atom of carbon tetrachloride by the benzoyl radical has also been demonstrated.[17a]

$$PhCO_2{}^{\cdot} + An_3CCOAn \longrightarrow PhCO_2{}^{-} + An_3C^{+} + An\dot{C}O \quad (4)$$

$$An\dot{C}O + ClCH_2CH_2Cl \longrightarrow AnCHO + ClCH_2\dot{C}HCl \quad (5)$$

$$An\dot{C}O + ClCH_2CH_2Cl \longrightarrow AnCOCl + ClCH_2\dot{C}H_2 \quad (6)$$

$$AnCHO + PhCO_2{}^{\cdot} \longrightarrow An\dot{C}O + PhCO_2H \quad (7)$$

Previously we suggested the intermediacy of a radical cation (8) in the reaction of (1) with cerium(IV) ammonium nitrate.[4] In the present reaction it also seems reasonable to postulate the radical cation (8), although we were unable to obtain supporting evidence in an e.s.r. study.

$$[An_3C{\cdot}CO{\cdot}An]^{+\cdot}$$
(8)

In the reaction with bis-(3,5-dinitrobenzoyl) peroxide (3) a strong emission signal was observed at δ 163.6 p.p.m., which lasted over 20 min from the beginning of the reaction. (A similar spectrum was recorded for the reaction in acetonitrile.) As the reaction proceeded the signal weakened, and a new normal absorption signal, which was assigned to the enriched

Table 3. Initial rates of decomposition of (2) and formation of (4) in the reaction of (1) with (2) in various solvents at 50.0 °C: $[(2)]_0$ 0.050M

Solvent	$[An_3C{\cdot}CO{\cdot}An]_0$/M	$10^8\{-d[(2)]/dt\}_0$ [a]/mol l^{-1} s^{-1}	$10^8\{d[(4)]/dt\}_0$ [a]/mol l^{-1} s^{-1}
CH_2Cl_2	0.050	4.5	0.59
	None	4.5	
$ClCH_2CH_2Cl$	0.050	7.5 (4.3) [b]	3.7 (0.55) [b]
	None	8.6 (4.3) [b]	
$CHCl_3$	0.050	3.3	<0.14
	None	3.8	
C_6H_6	0.050	3.8	<0.01
	None	3.6	
CCl_4	0.050	3.3	<0.03
	None	2.6	
$(CF_3)_2CHOH$ (HFIP)	0.050	9.4	1.2
	None	3.8	
Tetramethylene sulphone	0.050	21	4.1
	None	13	
CH_3CN	0.050	13	6.8
	None	5.1	
$CH_3OCH_2CH_2OH$	0.050	23	7.2
	None	~130 (2.5) [b]	
$CH_3CONHCH_3$	0.050	14	3.3
	None	49	

[a] The rates are accurate to within ±10%. [b] In the presence of added 3,4-dichlorostyrene (0.20M).

carbonyl carbon of *p*-methoxybenzoic 3,5-dinitrobenzoic anhydride, appeared at δ 160.4 p.p.m. It is noted that no normal absorption signal was observed at δ 163.6 p.p.m. after the emission signal had disappeared. At present the assignment of the emission signal is difficult, but one possibility is attributed to the polarized *p*-methoxybenzoyl cation, which has been reported to appear at δ 161.5 p.p.m. This cation may be produced by the one-electron oxidation of the *p*-methoxybenzoyl radical by the peroxide molecule [equation (8)].*

The consumption of the *p*-methoxybenzoyl cation *via* the cation–anion combination pathway (9) can explain the fact that a normal absorption signal was not observed at δ 163.6 p.p.m., where the emission had appeared, and also the fact that the absorption signal at δ 160.4 p.p.m. was not preceded by a CIDNP signal.

$$An\dot{C}O + (ArCO_2)_2 \longrightarrow An\overset{+}{C}O + ArCO_2^- \overset{\cdot\cdot}{+} ArCO_2^{\bullet} \quad (8)$$

$$An\overset{+}{C}O + ArCO_2^- \longrightarrow An{\cdot}CO{\cdot}O{\cdot}COAr \quad (9)$$

The occurrence of the emission in the one-electron oxidation of the *p*-methoxybenzoyl radical [equation (8)] is in accord with Kaptein's expression, $\Gamma = \mu\varepsilon\Delta gA$.[21] In general, the *g*-value of a carbon radical is smaller than that of an oxygen radical, giving a negative Δg.[22] The hyperfine coupling constant of the benzoyl radical is positive,[23] resulting in a positive A. Since the *p*-methoxybenzoyl radical is produced from the singlet state and reacts with the peroxide (3) out-of-cage, both μ and ε are negative. Thus the net effect becomes negative, suggesting the occurrence of an emission signal for the polarized *p*-methoxybenzoyl cation. On the other hand, if s.e.t. occurred from the *p*-methoxybenzoyl radical to the 3,5-dinitrobenzoyloxyl radical in the cage ($\mu < 0$, $\varepsilon > 0$), then the net effect would be positive to exhibit enhanced absorption.

In the reaction of anispinacolone with dibenzoyl peroxide (2) the *p*-methoxybenzoyl radical is not oxidized by the peroxide, but it abstracts hydrogen or chlorine from the solvent 1,2-dichloroethane. Such a contrast in the behaviour of the *p*-methoxybenzoyl radical towards the two different peroxides can be ascribed to the increased electron affinity of bis-(3,5-dinitrobenzoyl) peroxide (3). In fact, the reduction peak potentials of (2) and (3) determined by cyclic voltammetry in dichloromethane were −1.05 ± 0.03 and −0.73 ± 0.05 V *versus* a saturated calomel electrode (s.c.e.) respectively.

Spin-trapping of the p-*Methoxybenzoyl Radical.*—Previously, we demonstrated the formation of the *p*-methoxybenzoyl radical in the oxidative cleavage of anispinacolone (1) with cerium(IV) ammonium nitrate by spin-trapping with 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene.[4] An application of this technique to the reaction of (1) with (2) showed faint signals due to the spin adduct, but they disappeared on heating to 50 °C.† In contrast, the reaction of (1) with (3) exhibited distinct signals at 50 °C. The nitrogen splittings (a_N) of 7.59 G and the *g*-value of 2.006 92 agreed, within experimental errors, with the values of the authentic radical (a_N 7.54 G, g 2.006 92 in acetic acid).[4,‡] The success in trapping of the *p*-methoxybenzoyl radical in the latter case suggests that the radical escapes from the solvent cage, and supports the conclusion of the CIDNP study that the *p*-methoxybenzoyl radical is oxidized by the bis-(3,5-dinitrobenzoyl) peroxide molecule out-of-cage.

Rates of Reaction in Different Solvents.—The rates of s.e.t. reactions are usually solvent dependent, increasing with solvent polarity.[16] In order to gain further supporting evidence for the mechanistic dichotomy in the reaction of anispinacolone (1) with diaroyl peroxides, the rates of reaction in various solvents were measured and the results summarized in Tables 3 and 4.

In the reactions of dibenzoyl peroxide (2) the observed

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* Previously, we had attributed the emission and the absorption signals to polarized and unpolarized *p*-methoxybenzoic 3,5-dinitrobenzoic anhydride, respectively. Later, we noticed that the carbonyl carbon of the *p*-methoxybenzoyl cation appears at δ 161.5 p.p.m.[20]

† This would be ascribed to the low efficiency of the benzoyloxyl radical in the s.e.t. reaction and the instability of the spin adduct.

‡ Homolytic dissociation of (1) into $An_3C^{\cdot}$ and $An\dot{C}O$ was not observed under the reaction conditions.

Table 4. Initial rates of decomposition of (3) and formation of (7) in the reaction of (1) with (3) in various solvents at 50.0 °C [a]

Solvent	Concentration (M) (1)	(3)	$10^8\{-d[(3)]/dt\}_0$/mol l^{-1} s^{-1}	$10^8\{d[(7)]/dt\}_0$/mol l^{-1} s^{-1}	10^5k_2 [b]/l mol^{-1} s^{-1}
CH_3CN	0.040	0.040	63	54	34
	0.040	None	3.0		
$ClCH_2CH_2Cl$	0.040	0.040	46	20	12
	0.040	None	1.2		
C_6H_6	0.020	0.020	4.6	1.0	2.5
	0.020	None	0.5		

[a] The rates are accurate to within ±10%. [b] The rate constant for the formation of (7).

effects can be divided into three categories with regard to the rate of consumption of dibenzoyl peroxide, (a) the rate is unaffected by added (1) as seen for relatively nonpolar solvents CH_2Cl_2, $ClCH_2CH_2Cl$, $CHCl_3$, C_6H_6, and CCl_4, (b) the rate is greatly accelerated by added (1) in the highly polar solvents HFIP, tetramethylene sulphone, and acetonitrile, and (c) the rate is greatly decelerated by added (1) in 2-methoxyethanol and *N*-methylacetamide.*

In HFIP, tetramethylene sulphone, and acetonitrile the decomposition rates of (2) is accelerated by added (1) (0.050M) by the factors of 2.5, 1.6, and 2.5 at 50.0 °C, respectively. The rate enhancement would be explained in terms of incursion of the intermolecular single-electron transfer from anispinacolone (1) to dibenzoyl peroxide (2) in such polar solvents. A ^{13}C CIDNP study at 65 °C of the reaction in acetonitrile showed a strong emission signal at δ 189.9 p.p.m., indicating the formation of *p*-methoxybenzaldehyde. Clearly the *p*-methoxybenzoyl radical abstracts a hydrogen atom from acetonitrile, although the fate of the solvent radical ($^{\cdot}CH_2CN$) has not been investigated.

The decomposition rates of (2) in 2-methoxyethanol and *N*-methylacetamide in the absence of (1) are significantly higher than those in the other solvents, suggesting that the benzoyloxyl radical principally abstracts a hydrogen from the solvent, and the produced solvent radical causes induced decomposition of the peroxide. Actually in 2-methoxyethanol the addition of 3,4-dichlorostyrene (0.20M) greatly suppressed the rate by a factor of 50. In this solvent the addition of (1) (0.050M) also depressed the decomposition rate of (2) by a factor of 6. Thus the rate depression by added (1) is most probably ascribed to the inhibition of the induced decomposition of (2) through the trapping of the benzoyloxyl radical by (1).

On the other hand, the decomposition of bis-(3,5-dinitrobenzoyl) peroxide (3) in any solvent is accelerated by added (1), (1) thereby affording tris-(*p*-methoxyphenyl)methyl 3,5-dinitrobenzoate (7) as the cleavage product. The plots of the yield of the ester against reaction time were similar in shape to each other, reaching 20—30% when all the peroxide was consumed. The initial rate of the consumption of (3) and that of the formation of (7) increases in the order benzene < 1,2-dichloroethane < acetonitrile. Especially, the second-order rate constants for the formation of (7) calculated by assuming the second-order kinetics are linearly correlated with Kosower's Z values [24] and Dimroth and Reichardt's $E_T(30)$ values [25] of the solvents (Figure 3), suggesting that the s.e.t. process is the rate-controlling step.

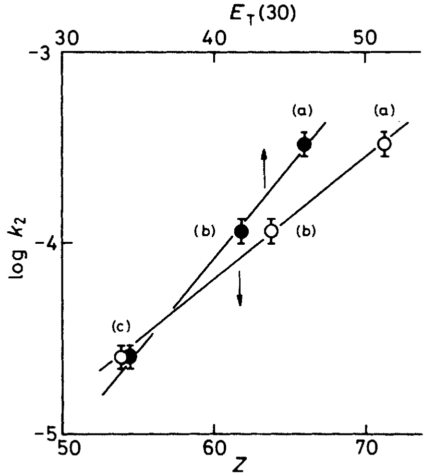

Figure 3. A plot of log k_2 for the formation of tris-(*p*-methoxyphenyl)methyl 3,5-dinitrobenzoate (7) in the reaction of (1) with (3) at 50.0 °C against Z and $E_T(30)$ values of the solvents; (a) acetonitrile, (b) 1,2-dichloroethane, (c) benzene

The Course of Formation of Benzoic p-*Methoxybenzoic Anhydride in the Reaction of Anispinacolone* (1) *with Dibenzoyl Peroxide* (2).—In the previous sections it has been shown that the *p*-methoxybenzoyl radical is undoubtedly formed by the one-electron oxidation of anispinacolone by the benzoyloxyl radical in 1,2-dichloroethane and that the *p*-methoxybenzoyl radical reacts with the solvent to produce *p*-methoxybenzaldehyde and *p*-methoxybenzoyl chloride. In contrast to such observations, the products isolated were *p*-methoxybenzoic acid and benzoic *p*-methoxybenzoic anhydride. The *p*-methoxybenzoyl radical might react with unchanged dibenzoyl peroxide to form the mixed anhydride *via* induced decomposition. However, we did not observe any ^{13}C CIDNP signals supporting the direct formation of the anhydride. Therefore, this process is unimportant under the present reaction conditions. The most probable course to the mixed anhydride is the simple reaction of *p*-methoxybenzoyl chloride with benzoic acid.

Examination of the Charge-transfer Complex Formation.—Walling and Zhao observed that the solutions of bis-(*p*-nitrobenzoyl) peroxide and *p*-dimethoxybenzene develop an immediate yellow-brown colour on mixing in the cold.[16] On this basis, they suggested that the reaction between the two compounds starts with the formation of charge-transfer complexes.

We carefully examined if colouration occurs on mixing (1) and (3) in benzene, 1,2-dichloroethane, and acetonitrile at

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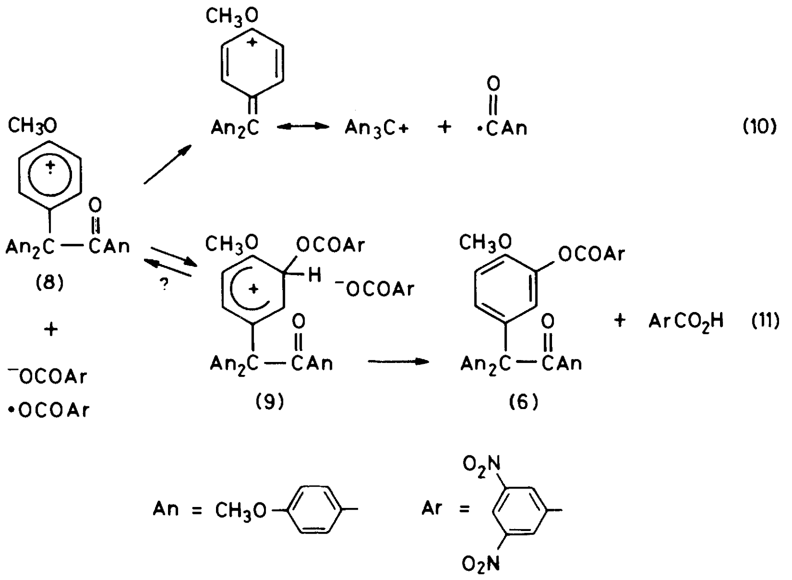
* As a parameter of solvent polarity which controls the s.e.t. ability, Kosower's Z value [24] or Dimroth and Reichardt's $E_T(30)$ value [25] appears adequate. According to these values, the solvents in the category (a) may be classified to nonpolar solvents and those in (b) and (c) to polar ones.



room temperature, but no immediate colour development was observed. Detailed spectral study on the solution in 1,2-dichloroethane for various concentrations in the range 1×10^{-2}—1×10^{-5}M in each of (1) and (3) afforded the spectra which resulted from mere summation of the absorbances exhibited by each component over a range 230—900 nm. When the solution {[(1)] = [(2)] = 0.01M} was heated to 50 °C under argon, a yellow colour developed ($\lambda_{max.}$ 485 nm), but the v.r. spectrum was completely superimposable with that of tris-(*p*-methoxyphenyl)methyl cation. Although these observations do not necessarily exclude the possibility of the formation of only slight amounts of charge-transfer complexes, it appears more plausible that the two components react directly without prior formation of charge-transfer complexes because of severe steric congestion in (1).

A possible mechanism involves the formation of a radical cation (8) by the single-electron transfer from one of the *p*-methoxyphenyl groups of the tris-(*p*-methoxyphenyl)-methyl moiety in (1) to the peroxide (3), which then cleaves to the tris-(*p*-methoxyphenyl)methyl cation and the *p*-methoxybenzoyl radical [equation (10)]. If this is the case, the aroyloxylation is considered to occur *via* the addition of the aroyloxyl radical to (8), followed by deprotonation [equation (11)], in the manner proposed by Walling and Zhao for the reaction of *p*-dimethoxybenzene with bis-(*p*-nitrobenzoyl) peroxide.[16] Although this mechanism can account for the present results, the comparison of the redox potentials suggests that the s.e.t. between (1) and (3) is highly unfavourable, since the oxidation peak potential of (1) is 1.68 ± 0.05 V and the reduction peak potential of (3) is −0.73 ± 0.05 V, both in dichloromethane *versus* s.c.e.*

Conclusions.—Anispinacolone (1) is oxidatively cleaved by dibenzoyl peroxide (2) to the tris-(*p*-methoxyphenyl)methyl cation and the *p*-methoxybenzoyl radical by way of s.e.t. mechanisms. In non-polar solvents such as chloroalkanes and benzene the actual one-electron acceptor is the thermally produced benzoyloxyl radical. On the other hand, in polar solvents such as HFIP, tetramethylene sulphone, and acetonitrile the peroxide molecule also plays a role as a one-electron acceptor.

In marked contrast to the behaviour of (2), bis-(3,5-dinitrobenzoyl) peroxide (3) oxidatively cleaves (1), probably by way of an intermolecular s.e.t. process, even in nonpolar solvents such as 1,2-dichloroethane and benzene. Consequently, as far as the molecularity of the peroxide is concerned, the dichotomy in these s.e.t. reactions can be considered as a counterpart of the S_N1–S_N2 dichotomy in nucleophilic substitution.

Experimental

M.p.s and b.p.s are uncorrected. I.r. and u.v. spectra were measured with Hitachi 215 and 200-10 spectrophotometers, respectively. E.s.r. spectra were recorded on a JEOL PE-2X spectrometer. ^{1}H N.m.r. spectra were measured with Hitachi R-24 (60 MHz) or Varian HR-220 (220 MHz) spectrometers. ^{13}C N.m.r. spectra were recorded on a JEOL JNM FX100 (25 MHz) spectrometer operating in the Fourier transform mode.

Materials.—All reagents were of reagent-grade quality except when otherwise noted. Dibenzoyl peroxide (2) was purified by reprecipitation from a chloroform solution by adding chilled methanol. Bis-(3,5-dinitrobenzoyl) peroxide (3) was prepared following the method described for bis-(*p*-nitrobenzoyl) peroxide,[27] m.p. 162 °C (decomp.) [lit.,[28] 161—162 °C (decomp.)]. Anispinacolone (1),[29] m.p. 141.8—142.7 °C (lit.,[30] 136—137 °C), and 3,4-dichlorostyrene,[31] b.p. 86—89 °C at 5 mmHg (lit.,[31] 95 °C at 5 mmHg), were prepared as described in the literature. *N*-Butyl-3,5-dinitrobenzamide was prepared following the literature method,[32] m.p. 104.4—105.0 °C (lit.,[32] 105 °C). Dichloromethane and carbon tetrachloride were dried over $CaCl_2$ and distilled. Chloroform was washed with H_2SO_4, aqueous $NaHCO_3$, and then aqueous NaCl, dried over $CaCl_2$, and distilled. Tetramethylene sulphone was distilled from NaOH, b.p. 104.5—106.5 °C at 0.3 mmHg. *N*-Methylacetamide was distilled from H_2SO_4, b.p. 77—84 °C at 10 mmHg, stored over CaO for 16 h, and then distilled, b.p. 76.9—78.9 °C at 8 mmHg. 2-Methoxyethanol was dried over molecular sieves 4A and distilled. Acetonitrile and 1,2-dichloroethane were refluxed over P_2O_5 and distilled. Benzene was distilled from sodium. HFIP was distilled from molecular sieves 4A.

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* There might exist an alternative mechanism which involves the direct formation of (9) *via* an ionic mechanism, followed by heterolytic cleavage of the carbon–oxygen bond to form (8). If this is the case, the s.e.t. mechanism is only apparent. Further study is in progress.

Labelled 1,2,2,2-*Tetrakis*-(p-*methoxyphenyl*)*ethanone* (*Anispinacolone*).—To an ether solution of *p*-methoxyphenylmagnesium bromide which was prepared from *p*-bromoanisole (23.8 g, 0.127 mol) and Mg (3.24 g, 0.133 mol) was introduced $^{13}CO_2$ (^{13}C 90%) by using argon as a carrier at 0 °C over 70 min: the labelled carbon dioxide was generated by dropwise addition of 10% HCl (50 ml) to a suspension of $Ba^{13}CO_3$ (^{13}C 90%; Merck Sharp and Dohme Canada) (10.1 g, 0.0508 mol) in water and dried with Drierite. The reaction mixture was worked up in the usual manner to afford *p*-methoxybenzoic acid (5.03 g). Labelled *p*-methoxybenzoic acid was converted into *p,p′*-dimethoxybenzophenone,[33] and then transformed to labelled anispinacolone in the manner described in the literature [29] in 60% overall yield from *p*-methoxybenzoic acid, m.p. 138.5—139.5 °C (lit.,[30] 136—137 °C for the unlabelled compound).

Labelled Dibenzoyl Peroxide.—Labelled benzoic acid was prepared in the manner described for labelled *p*-methoxybenzoic acid, converted into benzoyl chloride with $SOCl_2$, and then transformed to labelled dibenzoyl peroxide with Na_2O_2. The reprecipitated material from chloroform and methanol showed 100% active oxygen on iodimetry.

Labelled Benzoic p-*Methoxybenzoic Anhydride*.—The mixed anhydride labelled with 90% ^{13}C on the carbonyl carbon of the *p*-methoxybenzoyl moiety was prepared from labelled *p*-methoxybenzoic acid and unlabelled benzoyl chloride following the literature method.[34] The enriched carbon showed a signal at δ 161.6 p.p.m. in 1,2-dichloroethane.

Tris-(p-*methoxyphenyl*)*methyl Benzoate*.—To lithium tris-(*p*-methoxyphenyl)methoxide which was prepared by adding 1.58M-n-butyl-lithium in hexane (3.8 ml, 6.00 mmol) to tris-(*p*-methoxyphenyl)methanol (2.10 g, 5.99 mmol) in THF at 0 °C under nitrogen was added benzoyl chloride (0.848 g, 6.03 mmol) in anhydrous THF (10 ml) at 0 °C. The resulting solution was allowed to stand at room temperature overnight, and then refluxed for 2 h. After filtration of the precipitated LiCl, THF was evaporated to afford a reddish oil. The carbinyl and carbonyl carbons exhibited signals at δ 80.5 and 163.9 p.p.m., respectively, in 1,2-dichloroethane.

Products in the Reaction of (1) *with* (2).—A typical example follows. Dibenzoyl peroxide (242 mg, 1.00 mmol) and anispinacolone (468 mg, 1.00 mmol) were allowed to react in 1,2-dichloroethane (10 ml) at 50 °C for 60 h by the method similar to that used for the rate measurements. After the reaction mixture had been diluted to 20 ml with 1,2-dichloroethane, two 1.000 ml portions were subjected to iodimetric titration to show that 80% dibenzoyl peroxide remained unchanged. A further 1.000 ml portion was diluted by a factor of 10 with 1,2-dichloroethane containing 2(v/v)% trifluoroacetic acid, and the amount of tris-(*p*-methoxyphenyl)methyl cation was determined to be 13% from its absorbance at 487 nm. The rest of the mixture (17.0 ml) was diluted with ether (30 ml) and quickly extracted with cold 5% $NaHCO_3$ (50 ml × 2). The combined aqueous layers were washed with ether (50 ml) and acidified with concentrated HCl to give a mixture of *p*-methoxybenzoic acid (1.9 mg, 0.012 mmol) and benzoic acid (43 mg, 0.35 mmol). The combined ether layers were vigorously stirred with 5% $NaHCO_3$ (100 ml) for 7.5 h at room temperature in order to hydrolyse the acid anhydrides, and then extracted with 5% $NaHCO_3$ (100 ml × 2). The combined $NaHCO_3$ extracts were washed with ether (100 ml) and acidified with concentrated HCl to give another mixture of *p*-methoxybenzoic acid (12 mg, 0.076 mmol) and benzoic acid (2.6 mg, 0.021 mmol). The combined ether layers were concentrated to *ca*. 20 ml, and then unchanged dibenzoyl peroxide was converted into benzoic acid by adding 5 g of 50% aqueous KI and acetic acid (30 ml). After the mixture had stood for 15 min, 10% aqueous $Na_2S_2O_3$ (30 g) and ether (200 ml) were added, and then the mixture was washed with 5% $NaHCO_3$ (200 ml × 3). The combined aqueous layers were extracted with ether (150 ml × 2) and the combined ether layers were washed with 10% NaCl, dried ($MgSO_4$), and then the ether was evaporated. Separation of the residue with t.l.c. (SiO_2, benzene–ether 95 : 5) yielded anispinacolone (301 mg, 0.643 mmol), *p,p′*-dimethoxybenzophenone (17 mg, 0.070 mmol), and unidentified substances. Each of the above products showed a ^1H n.m.r. spectrum identical with that of the authentic sample. Another expected product from anispinacolone, *i.e.*, tris-(*p*-methoxyphenyl)methanol, could not be isolated from any of the neutral fractions. A control experiment showed that the alcohol changes to unknown substances during the treatment with KI in the presence of (2).

Isolation of Benzoic p-*Methoxybenzoic Anhydride*.—A solution of anispinacolone (940 mg, 2.00 mmol) and dibenzoyl peroxide (485 mg, 2.00 mmol) in 1,2-dichloroethane (20 ml) was heated in an ampoule under nitrogen at 50 °C for 840 h. To 19 ml of the reaction mixture was added ether (50 ml) and the solution briefly extracted with cold 5% aqueous $NaHCO_3$. The aqueous layer was acidified with concentrated HCl to give a mixture of *p*-methoxybenzoic acid (33 mg, 0.22 mmol) and benzoic acid (167 mg, 1.37 mmol). The ether layer was washed with 10% NaCl, dried ($MgSO_4$), and the ether evaporated to give a brown oil (1.41 g). A part of the oil (1.16 g) was distilled by bulb-to-bulb distillation at 0.1 mmHg in an oil-bath heated to 180 °C to give crystals as a distillate. The residue was separated by means of t.l.c. (SiO_2, benzene–ether 95 : 5) to give unchanged anispinacolone (438 mg). Redistillation of the distillate at 140 °C at 0.1 mmHg gave a mixture of benzoic anhydride (14 mg), benzoic *p*-methoxybenzoic anhydride (6.4 mg), and benzoic acid (17 mg), and a residue composed of benzoic anhydride (14 mg) and benzoic *p*-methoxybenzoic anhydride (21 mg).

Products in the Reaction of (1) *with* (3).—The procedure is essentially the same as that described for the reaction of (1) with (2). The substitution product (6) was isolated by means of t.l.c. (SiO_2, 1,2-dichloroethane) and h.p.l.c. (8 mm × 30 cm μ-Porasil, Waters; hexane–chloroform). The use of alumina column gave the hydrolysed product of (6).

Characterization of (6).—The purification of (6) was considerably difficult because of its ease of hydrolysis even in an h.p.l.c. column. Therefore, the sample containing a small amount of hydrolysed product was subject to characterization, m.p. 115 °C (decomp.); δ_H (220 MHz; $CDCl_3$) 3.74 (6 H, s), 3.76 (3 H, s), 3.78 (3 H, s), 6.73 (2 H, d, *J* 8.2 Hz), 6.81 (4 H, d, *J* 9.9 Hz), 7.14 (4 H, d, *J* 9.9 Hz), 7.69 (2 H, d, *J* 8.2 Hz), 9.17 (2 H, s), and 9.21 (1 H, s), with the protons of the aroyloxylated *p*-methoxyphenyl group being difficult to observe, δ_C ($ClCH_2CH_2Cl$) 54.9, 55.1, 55.7, 68.6, 111.1, 112.6, 113.0, 122.5, 124.8, 129.3, 129.6, 131.5, 132.8, 133.2, 134.9, 137.5, 138.0, 148.4, 148.9, 157.9, 160.3, 161.9, and 196.3 p.p.m.; $\delta_{max.}$ ($CHCl_3$) 2 850w, 1 760m, 1 674m, 1 552s, and 1 348s cm^{-1} (Found: C, 61.75; H 4.7; N, 3.55. Calc. for $C_{37}H_{30}N_2O_{11}$: C, 65.5; H, 4.45; N, 4.15%).

Analysis of the Mixed Anhydride in the Reaction of (1) *with* (3) *by* N-*Butylamide Formation*.—A solution of anispinacolone (0.469 g, 1.00 mmol) and bis-(3,5-dinitrobenzoyl) peroxide (0.844 g, 2.00 mmol) in 1,2-dichloroethane (20 ml) was heated under argon at 75.0 °C for 20 h. An iodimetric titration of a portion showed that all the peroxide had reacted. The rest of the reaction mixture (18.5 ml) was diluted with 1,2-dichloroethane (200 ml) and washed with cold 5% $NaHCO_3$ (200 ml × 2) and cold 10% NaCl, and dried ($MgSO_4$). Evaporation of the solvent afforded a reddish oil (900 mg), which was then treated with butanamine (1.0 ml, 10 mmol) in 1,2-dichloroethane (10 ml) at 0 °C for 5 min and then at 25 °C for 30 min. The reaction mixture was diluted, washed with 10% HCl, and then with 5% $NaHCO_3$ in order to extract organic acids. Acidification of the alkaline extract, followed by extraction afforded an orange solid (111 mg), which was determined by ^1H n.m.r. to be a mixture of 3,5-dinitrobenzoic acid and *p*-methoxybenzoic acid (1 : 1.38 mols). The organic layer afforded a brown oil (620 mg), which was found by h.p.l.c. analysis (3 mm × 30 cm, μ Porasil, Waters; hexane–chloroform) to contain *N*-butyl-3,5-dinitrobenzamide and *N*-butyl-*p*-methoxybenzamide in yields of 59 and 4% based on (1), respectively. A control experiment using 4-methoxybenzoic 3,5-dinitrobenzoic anhydride (87 mg, 0.25 mmol) and butanamine (0.25 ml, 2.5 mmol) under similar conditions afforded *N*-butyl-3,5-dinitrobenzamide and *N*-butyl-*p*-methoxybenzamide in 92 and 9% yield, respectively, and 3,5-dinitrobenzoic acid and *p*-methoxybenzoic acid in 8 and 87%, respectively.

Product Studies by ^{13}C *N.m.r.*—A typical example follows. 1,2-Dichloroethane (0.4 ml) was directly distilled from P_2O_5 under argon through a double-ended syringe needle and rubber septa into a dried test tube containing labelled anispinacolone (15 mg, 0.032 mmol) and labelled dibenzoyl peroxide (7.8 mg, 0.032 mmol). The solution was transferred into a micro-n.m.r. cell under argon and the cell sealed. It was covered with aluminium foil, kept at 75.0 °C for 51 h in a constant-temperature bath, and subjected to ^{13}C n.m.r. measurement. Generally the spectra were obtained employing a 6 024 Hz width in 8 192 data points and a 45° pulse with a pulse repetition of 1.5 s, and by using D_2O as an internal lock. The assignments of the signals exhibited by the carbonyl carbons of the products were based on the chemical shifts of authentic samples determined in 1,2-dichloroethane: δ (p.p.m.) in parentheses: (p-$CH_3O{\cdot}C_6H_4)_3C{\cdot}O{\cdot}CO{\cdot}Ph$ (163.9), p-$CH_3O{\cdot}C_6H_4CO{\cdot}O{\cdot}CO{\cdot}Ph$ (161.6), $(PhCO)_2O$ (161.7), $Ph{\cdot}CO{\cdot}O{\cdot}Ph$ (164.6), $PhCO_2H$ (172.4), and p-$CH_3O{\cdot}C_6H_4CO_2H$ (171.3). For comparison, (p-$CH_3O{\cdot}C_6H_4{\cdot}CO)_2O$ and $(PhCO_2)_2$ exhibit their carbonyl signals at δ 164.4 and 162.9 p.p.m., respectively.

^{13}C *N.m.r. CIDNP Studies.*—A typical procedure follows. In a dried 10 mm n.m.r. cell were placed dibenzoyl peroxide (0.100 mmol), labelled anispinacolone (0.101 mmol), 1,2-dichloroethane, D_2O capillary, and a Teflon plug. The free space was flushed with argon and the cell sealed with a polyethylene cap. The cell was placed in the n.m.r. probe which had been maintained at 65 ± 1 °C, and the measurement started immediately. The temperature indicator was calibrated by using CCl_4–$(CD_3)_2CO$ as an n.m.r. thermometer.[35] Generally, 40 free induction decays were accumulated using a 45° pulse and pulse interval of 1.5 s. The spectra were recorded employing a 6 024 Hz width in 8 192 data points.

Rate Measurements.—A typical example follows. Dibenzoyl peroxide (0.242 g, 1.00 mmol) and anispinacolone (0.469 g, 1.00 mmol) were placed in a long-necked ampoule. A three-way stopcock was attached and the air replaced with nitrogen by repeated evacuation and filling with nitrogen. After adding 1,2-dichloroethane (20.0 ml) the ampoule was covered with aluminium foil and kept at 50.0 °C in a thermostat. At appropriate intervals *ca.* 1.2 ml portions were withdrawn by means of a syringe and their 1.000 ml portions were diluted to appropriate concentrations with 1,2-dichloroethane containing 2(v/v)% trifluoroacetic acid and subjected to v.r. analysis. The quantity of tris-(*p*-methoxyphenyl)methyl cation was determined at $\lambda_{max.}$ 487 nm by using ε 102 000. The quantity of unchanged dibenzoyl peroxide was determined by iodimetric titration for 1.000 ml portions to the starch end point in the usual manner. The initial rates were determined from the tangents extrapolated to time zero.

Spin Trapping of p-*Methoxybenzoyl Radical.*—In a quartz sample cell of inside diameter 2 mm was placed the spin trap, 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene[36] (2—3 mg). A solution of anispinacolone (1) (0.05M) and a solution of bis-(3,5-dinitrobenzoyl) peroxide (3) (0.02M), both in 1,2-dichloroethane, were introduced in a ratio of 2 : 5. After outgassing with high purity nitrogen for 5 min the cell was sealed with Parafilm, and the first e.s.r. scan was taken at 50 °C. The nitrogen hyperfine splitting for the *p*-methoxybenzoyl spin adduct was accurate to ±0.04—0.05 G. The *g* value was determined with an accuracy of ±0.000 05 by utilizing that of the perylene radical cation in concentrated sulphuric acid as a standard (*g* 2.002 583).[37] An attempt to trap the *p*-methoxybenzoyl radical in the reaction of (1) with (2) resulted in observation of a very weak signal of the spin adduct at room temperature, which completely disappeared at 50 °C. Control experiments showed that the spin trap is inactive towards (1)—(3).

Cyclic Voltammetry.—The reduction peak potentials were measured for 0.005M-peroxide in 0.1M-$Bu^n{}_4NClO_4$ in CH_2Cl_2 using a three-electrode cell with platinum wire and auxiliary electrodes and a saturated calomel reference electrode. Scanning was conducted at a rate of 0.1 V s^{-1} under irreversible conditions.

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