One-electron Oxidation of Closed-shell Molecules. Part 4.[1a] Acid-induced Oxidative Cleavage of Substituted 1,2,2,2-Tetraphenylethanones (Benzpinacolones) with Diaroyl Peroxides

Toshikazu Kitagawa, Ken'ichi Takeuchi, Osamu Murai, Shin Matsui, Takeshi Inoue, Makoto Nishimura, and Kunio Okamoto *
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

---

The acid-induced oxidative cleavage of anispinacolone [1,2,2,2-tetrakis-(*p*-methoxyphenyl)ethanone] with diaroyl peroxides in 1,2-dichloroethane–trifluoroacetic acid (TFA) has been investigated. The principal two products after work-up are tris-(*p*-methoxyphenyl)methanol and *p*-methoxybenzoic acid; the latter was found as anhydrides in the reaction mixture. Free-radical formation in the course of the cleavage was verified by polymerization of added acrylonitrile in the oxidation by bis-(3,5-dinitrobenzoyl) peroxide. When the oxidation of [1,2-$^{13}C_2$]anispinacolone (90% ^{13}C) by dibenzoyl peroxide was carried out in a ^{13}C n.m.r. probe, an emission peak, assigned to *p*-methoxybenzoic trifluoroacetic anhydride, was observed. The logarithms of the rate constants for oxidation of *p*-substituted benzpinacolones by dibenzoyl peroxide were linearly correlated with the oxidation potentials of the benzpinacolones. These results are consistent with a single-electron transfer (s.e.t.) pathway from benzpinacolones to dibenzoyl peroxide. The oxidation is first-order in each reactant and is promoted by TFA. The effect of TFA is accounted for by two factors, (i) assisted O–O bond cleavage of the peroxide radical anion by TFA, and (ii) the formation of protonated peroxide, a more powerful oxidizing species. The former factor is dominant at lower TFA concentrations (<0.05M), the latter at higher concentrations.

Single-electron transfer (s.e.t.) mechanisms have been suggested for oxidation by diaroyl peroxide of various nucleophiles, *e.g.* dimethylaniline,[2] triphenylphosphine,[3] dibenzoylmethane,[4] and iodide ion.[5] However, very recently, examples of the intermolecular s.e.t. mechanism have been presented for the oxidation of non-nucleophilic electron-rich compounds.[6–8]

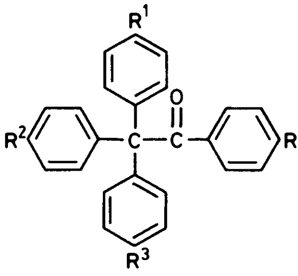
In Part 3[1] we reported on the oxidative cleavage of anispinacolone [1,2,2,2-tetrakis-(*p*-methoxyphenyl)ethanone] (**1a**) by dibenzoyl and bis-(3,5-dinitrobenzoyl) peroxide, as a novel example of one-electron oxidation by diaroyl peroxides [equation (1)].[1] We concluded that the cleavage of anispinacolone is initiated by an s.e.t. process, affording the corresponding radical cation. Furthermore, we found that the oxidation can proceed either *via* a bimolecular electron transfer pathway or *via* a unimolecularly produced benzoyloxyl radical. The mechanism changes from unimolecular to bimolecular with increase in polarity of the solvent or when electron-withdrawing substituents are present in the peroxide.

$$\underset{(\mathbf{1a})}{\mathrm{Mph_3C{-}COMph}} \longrightarrow [\mathrm{Mph_3C{-}COMph}]^{+\bullet} \longrightarrow \mathrm{Mph_3C^+} + {}^{\bullet}\mathrm{COMph} \quad (1)$$

$$\mathrm{Mph} = p\text{-}\mathrm{MeOC_6H_4}$$

A bimolecular one-electron oxidation by diaroyl peroxides is of interest in view of the mechanistic analogy with the one-electron oxidation of electron-rich aromatic molecules by molecular oxygen[9] and quinones.[10] A common observation for these reactions is that they are catalysed by added acids. Moreover, the oxidation does not occur, in most cases, unless a strong acid is added to the reaction system.

In the course of our studies on the oxidative cleavage of anispinacolone[1,11] we found similar acceleration by acids; oxidation by relatively unreactive diaroyl peroxides proceeds smoothly in the presence of trifluoroacetic acid (TFA), affording cleavage products in good yields. Accordingly, we have studied the oxidative cleavage of anispinacolone (**1a**) and other *p*-substituted benzpinacolones (**1b**—**i**) with diaroyl peroxides in 1,2-dichloroethane–TFA. The present paper describes the results of product analysis, CIDNP experiments, and a kinetic study.



	R1	R2	R3	R4
(1)a;	MeO	MeO	MeO	MeO
b;	MeO	MeO	H	H
c;	MeO	H	H	H
d;	Me	Me	Me	Me
e;	H	H	H	H
f;	Cl	Cl	Cl	Cl
g;	H	H	H	MeO
h;	H	H	H	Me
i;	H	H	H	Cl

Results and Discussion

Products of the Reaction of Anispinacolone (**1a**) *with Diaroyl Peroxides.*—Reactions were carried out in degassed ampoules, since anispinacolone (**1a**) is readily oxidized by molecular oxygen under acidic conditions.[12] Product analyses were carried out after work-up with water (Table 1).

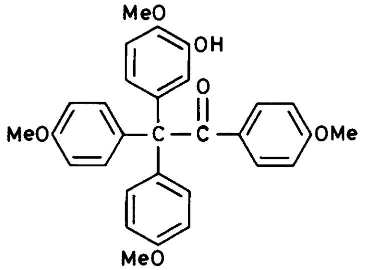
In the presence of TFA, oxidation of anispinacolone by dibenzoyl peroxide gave tris-(*p*-methoxyphenyl)methanol and *p*-methoxybenzoic acid in almost quantitative yields; virtually no reaction was observed without TFA. Benzoic acid (*ca.* 2 mol equiv.) was also formed, from the peroxide.

Electronegatively substituted diaroyl peroxides such as bis-(*p*-nitrobenzoyl), bis-(3,5-dinitrobenzoyl), and bis-[3,5-bis-(trifluoromethyl)benzoyl] peroxide similarly oxidized anispinacolone in the presence of TFA. Control experiments showed that self-decomposition of these peroxides is less than 5% under the same conditions. Therefore, the stoicheiometry of the oxidation is described by equation (2).

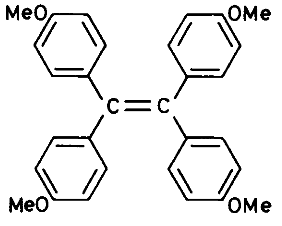
Table 1. Products of the reaction of anispinacolone (**1a**) with diaroyl peroxides in the presence or absence of acids in 1,2-dichloroethane: Mph = *p*-methoxyphenyl, $[(\mathbf{1a})]_0$ = $[\text{peroxide}]_0$ = 0.10M, $[\text{TFA}]_0$ = 2.0M, $[CF_3SO_3H]_0$ = 0.17M, $[BF_3{\cdot}OEt_2]_0$ = 0.30M

				Products (%)						Recovered (%)	
Peroxide, $(ArCO_2)_2$	Acid	T/°C	t/h	Mph_3COH	$MphCO_2H$	$ArCO_2H$[a]	(**2**)[b]	(**3**)[c]	Others	Peroxide	(**1a**)
$(PhCO_2)_2$	None	25	16	<0.3	*d*	*d*		0		99	*ca.* 100
	TFA	25	24	89	82	158		2		10	0
	$BF_3{\cdot}OEt_2$	50	24	64	29	68		5	*e*	8	<5
$(p\text{-}O_2NC_6H_4CO_2)_2$	None[f]	50	24	3	5	23		0		90	67
	TFA	25	24	78	77	142		15		0	0
	CF_3SO_3H	25	24	34	30	142		4	*g*	<5	<5
$[3,5\text{-}(O_2N)_2C_6H_3CO_2]_2$[h]	None	50	24	20	24	92		0		42	68
	TFA	25	7	83	76	100		0		*d*	6
$3,5\text{-}(CF_3)_2C_6H_3CO_2]_2$	None	50	24	7	4	25		0		84	81
	TFA	25	3	37	37	79		0		59	45
$(MphCO_2)_2$	TFA	25	0.2	4	64[i]			3	*j*	0	86
$p\text{-}O_2NC_6H_4CO\text{–}OO\text{–}COMph$	TFA	25	0.2	6	5	36[k]		2	*l*	0	96
Phthaloyl peroxide	TFA	25	24	30	44	96[m]	15	2		*d*	27
	CF_3SO_3H	25	24	30	32	74[m]	9	2	*n*	*d*	0

[a] Calculated on the basis of the formation of 2 mol (200%) of acids from 1 mol of peroxides, except for $p\text{-}O_2NC_6H_4CO\text{–}OO\text{–}COMph$ and phthaloyl peroxide. [b] 2-(*m*-Hydroxy-*p*-methoxyphenyl)-1,2,2-tris-(*p*-methoxyphenyl)ethanone. [c] Tetrakis-(*p*-methoxyphenyl)ethylene. [d] Not determined. [e] MphCO–O–COPh (8%). [f] $[\text{peroxide}]_0$ = 0.031M, $[(\mathbf{1a})]_0$ = 0.061M. [g] $p\text{-}O_2NC_6H_4CO\text{–}OC_6H_4NO_2\text{-}p$ (*ca.* 10%). [h] $[\text{peroxide}]_0$ = $[(\mathbf{1a})]_0$ = 0.025M. [i] Containing *p*-methoxybenzoic acid produced from the peroxide. [j] MphCO–OMph (58%) and MphOH (23%). [k] *p*-Nitrobenzoic acid. [l] $p\text{-}O_2NC_6H_4CO\text{–}OMph$ (17%) and MphOH (59%). [m] Phthaloyl peroxide gives phthalic acid quantitatively during work-up with water. [n] 6-Methoxy-2,3-bis-(*p*-methoxyphenyl)benzofuran[12] (40%).



(**2**)



(**3**)

$$\underset{(\mathbf{1a})}{Mph_3C\text{–}COMph} + (ArCO_2)_2 \xrightarrow{H_2O} Mph_3COH + MphCO_2H + 2ArCO_2H \quad (2)$$

Mph = $p\text{-}MeOC_6H_4$

Ar = Ph, $p\text{-}O_2NC_6H_4$, $3,5\text{-}(O_2N)_2C_6H_3$, or $3,5\text{-}(CF_3)_2C_6H_3$

In the reaction with phthaloyl peroxide, oxidative cleavage products were obtained in *ca.* 30% yield, but there was also produced a ring-hydroxylated derivative of anispinacolone, in which the hydroxy group is attached to the *meta*-position of one of the *p*-methoxyphenyl groups, *i.e.* 2-(*m*-hydroxy-*p*-methoxyphenyl)-1,2,2-tris-(*p*-methoxyphenyl)ethanone (**2**).

In contrast to the aforementioned peroxides, bis-(*p*-methoxybenzoyl) peroxide and *p*-methoxybenzoyl *p*-nitrobenzoyl peroxide, which readily underwent carboxy inversion under acidic conditions, gave virtually no cleavage products; nearly all the anispinacolone remained unchanged.

In Table 1, the results of the oxidation in the presence of trifluoroborane–ether complex or trifluoromethanesulphonic acid are also listed. Trifluoroborane–ether was effective for the oxidation with dibenzoyl peroxide at 50 °C.* To some extent, the *p*-methoxybenzoyl moiety of anispinacolone (**1a**) was converted into benzoic *p*-methoxybenzoic anhydride (see later).

Oxidation by bis-(*p*-nitrobenzoyl) peroxide or phthaloyl peroxide proceeded at a lower CF_3SO_3H concentration, but the yields of cleavage products were not high because CF_3SO_3H induced ionic decomposition of the bis-(*p*-nitrobenzoyl) peroxide and protiodearylation of anispinacolone.[12]

In some of these experiments a small amount of tetrakis-(*p*-methoxyphenyl)ethylene (**3**) was detected as a by-product. This compound is also produced when anispinacolone is treated with trifluoroacetic anhydride. The olefin (**3**) presumably arises from anispinacolone by the action of anhydrides in the reaction mixture (see later), though the pathway of its formation has not been clarified.

Supposed Baeyer–Villiger Oxidation.—It was conceivable that the cleavage products of anispinacolone were derived by hydrolysis of an ester, tris-(*p*-methoxyphenyl)methyl *p*-methoxybenzoate, expected from the Baeyer–Villiger oxidation of anispinacolone. However, this possibility was ruled out by the result of direct oxidation of anispinacolone with trifluoroperacetic acid. Thus, no significant amount of tris-(*p*-methoxyphenyl)methanol nor of *p*-methoxybenzoic acid (4.7 and 6.2%, respectively) was observed; instead, the ring-hydroxylation product (**2**) (31%) was obtained. The sluggishness of anispinacolone towards Baeyer–Villiger oxidation may be ascribed to the steric hindrance of anispinacolone around its carbonyl group.

---

* The amount of thermal decomposition of dibenzoyl peroxide at 50 °C for 24 h in the absence of the acids is only 14%.[1b] This indicates that the reactions associated with the thermally formed benzoyloxyl or phenyl radicals are unimportant in the presence of the acids.

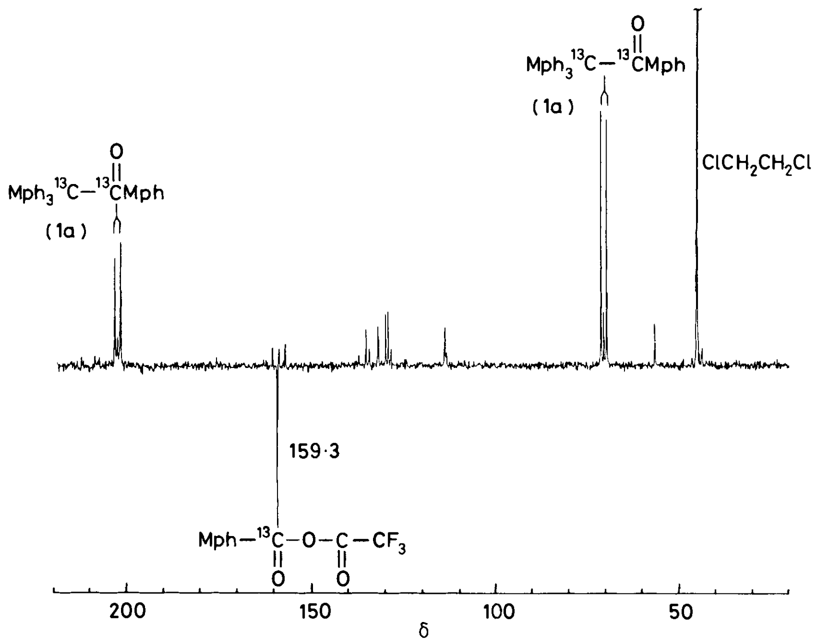


Figure 1. ^{13}C N.m.r. spectrum of the reaction mixture from Mph$_3$^{13}C–^{13}COMph (90% ^{13}C; 0.10M) and unlabelled dibenzoyl peroxide (0.10M) in 1,2-dichloroethane–TFA (2.0M) recorded at 25 °C *ca.* 1 min after preparation of the solution

Detection of Acid Anhydrides.—As shown in Table 1, benzoic *p*-methoxybenzoic anhydride was isolated when trifluoroborane–ether was used as catalyst. This fact led us to speculate that acid anhydrides are similarly formed when TFA is used. In fact, treatment with butylamine of the mixture obtained from the reaction of anispinacolone* and dibenzoyl peroxide in the presence of 2.0M-TFA, gave *N*-butylbenzamide (14%), *N*-butyl-*p*-methoxybenzamide (6.0%), and *N*-butyltrifluoroacetamide (75%). The sum of their yields (95%) was in agreement with the yield of tris-(*p*-methoxyphenyl)methanol (95%),† indicating that tris-(*p*-methoxyphenyl)methanol and acid anhydrides had been produced in 1:1 molar ratio.

Unfortunately, it was difficult to determine the structure of the originally formed anhydride because rapid exchange of acyl groups took place between anhydrides and acids. For example, equilibrium was reached within 10 min in the reaction of benzoic *p*-methoxybenzoic anhydride (0.10M) with TFA (0.5M) in 1,2-dichloroethane at 25 °C, producing, after treatment with butylamine, *N*-butylbenzamide, *N*-butyl-*p*-methoxybenzamide, and *N*-butyltrifluoroacetamide in the yields of 16, 5.5, and 78%, respectively.

Polymerization of Acrylonitrile.—In order to test for free-radical formation in the reaction pathway, TFA-catalysed oxidation with bis-(3,5-dinitrobenzoyl) peroxide was carried out in the presence of 3.0M-acrylonitrile. A precipitate (15 wt% based on acrylonitrile) was produced and identified as polyacrylonitrile from its i.r. absorption at 2 250 cm^{-1}. On the other hand, no polymer was formed without TFA. This result indicates that addition of TFA induced the formation of scavengeable radicals, presumably *p*-methoxybenzoyl and/or benzoyloxyl, to initiate the polymerization. It has been reported that the polymerization of acrylonitrile is initiated by *p*-methoxybenzoyl radicals in the oxidation of anispinacolone by Ce^{IV}.[11]

^{13}C *N.m.r. CIDNP Studies.*—In order to investigate the behaviour of the free radicals more thoroughly, ^{13}C CIDNP measurements were made by using carbon-13 labelled reactants.

Solutions of anispinacolone (0.10M) and dibenzoyl peroxide (0.10M) in 1,2-dichloroethane–TFA (2.0M) were prepared in n.m.r. tubes and their ^{13}C n.m.r. spectra were immediately recorded at 25 °C. In the oxidation of [1,2-^{13}C$_2$]anispinacolone (90% ^{13}C) with unlabelled dibenzoyl peroxide, the spectra obtained during the initial 30 min showed a strong emission peak at δ 159.2, which was replaced by a normal absorption signal as the reaction proceeded (Figure 1). This CIDNP signal was assigned to the labelled carbonyl carbon atom of *p*-methoxybenzoic trifluoroacetic anhydride, by comparison of its chemical shift with that of an authentic sample.‡ On the other hand, we were unable to observe CIDNP when unlabelled anispinacolone and di[*carbonyl*-^{13}C]benzoyl peroxide (90% ^{13}C) were employed.

These observations suggest that the *p*-methoxybenzoyl radical, generated *via* single-electron transfer from anispinacolone to dibenzoyl peroxide, produces *p*-methoxybenzoic trifluoroacetic anhydride. We have reported that the *p*-methoxybenzoyl radical is oxidized to the *p*-methoxybenzoyl cation by Ce^{IV}[11] and by bis-(3,5-dinitrobenzoyl) peroxide.[1a] In the present reaction this radical presumably undergoes one-electron oxidation by benzoyloxyl radical,§ followed by nucleophilic attack by TFA to give the mixed anhydride [equations (3)—(5)]. An application of Kaptein's rule[13]

---

* An excess of anispinacolone (1.5 molar equivalent) was used in order to attain total consumption of dibenzoyl peroxide, since the unchanged peroxide also produces *N*-butylbenzamide.

† Yields based on dibenzoyl peroxide.

‡ A solution of *p*-methoxybenzoic trifluoroacetic anhydride was prepared by mixing *p*-methoxybenzoic [^{13}C]acid (90% ^{13}C) and trifluoroacetic anhydride in 1,2-dichloroethane–TFA (2.0M). The ^{13}C n.m.r. spectrum of the solution showed two strong singlets (δ 159.3 and 173.0) corresponding to the labelled carbon atoms of *p*-methoxybenzoic trifluoroacetic anhydride and *p*-methoxybenzoic acid, respectively.

§ The alternative pathway to MphCO–O–COCF$_3$ in which MphCO$^•$ and PhCO$_2$$^•$ give MphCO–O–COPh, which then reacts more slowly with TFA, is less likely because we did not observe the CIDNP signal for the labelled carbonyl carbon atom of Mph^{13}CO–O–COPh (δ 161.6).[1a]

Table 2. Products of the oxidative cleavage of *p*-substituted benzpinacolones (0.1M) with dibenzoyl peroxide (0.10M) in 1,2-dichloroethane–TFA (2.0M) at 50 °C for 24 h

	Products (%)			Recovered (%)
Ar_3C–COAr	Ar_3COH	$ArCO_2H$	$PhCO_2H$	Ar_3C–COAr
(**1a**)[a]	71	79	180	0
(**1b**)	63	204[b]		27
(**1c**)	15	59[b]		78
(**1d**)	15	15	55	81
(**1e**)	10	56[b]		87
(**1f**)	3.2	3.5	15	89
(**1g**)	5.9	8.6	31	87
(**1h**)	11	11	38	89
(**1i**)	10	5.5	24	89

[a] Reaction time 2 h. [b] Containing benzoic acid produced from dibenzoyl peroxide.

Table 3. Second-order rate constants (k_2) for the oxidative cleavage of *p*-substituted benzpinacolones by dibenzoyl peroxide in 1,2-dichloroethane–TFA (2.0M) at 50 °C, and oxidation potentials (E_{ox}) of the benzpinacolones

Ar_3C–COAr	10^5k_2/l mol^{-1} s^{-1} [a]	E_{ox}/V *vs.* s.c.e.[b]
(**1a**)	340	1.14 ± 0.03
(**1d**)	2.0	1.52 ± 0.02
(**1e**)	1.3	1.78 ± 0.04
(**1f**)	0.38	1.81 ± 0.04
(**1h**)	1.4	1.71 ± 0.03

[a] Calculated from the yields of Ar_3COH in Table 2. [b] Measured by cyclic voltammetry in 1,2-dichloroethane with TFA (2.0M) and $Bu^n{}_4NClO_4$ (0.10M); [Ar_3C–COAr] = 3.0×10^{-3}M.

$$\mathrm{Mph_3C{-}COMph + (PhCO_2)_2 \xrightarrow{H^+} Mph_3C^+ + Mph\dot{C}O + PhCO_2H + PhCO_2^{\bullet}} \quad (3)$$

$$\mathrm{Mph\dot{C}O + PhCO_2^{\bullet} \longrightarrow Mph\overset{+}{C}O + PhCO_2^-} \quad (4)$$

$$\mathrm{Mph\overset{+}{C}O + CF_3CO_2H \longrightarrow MphCO{-}O{-}COCF_3 + H^+} \quad (5)$$

suggests that this electron transfer occurs out-of-cage, which accounts for the formation of a large amount of polyacrylonitrile in the polymerization experiment.

Oxidative Cleavage of Various p-*Substituted Benzpinacolones with Dibenzoyl Peroxide.*—In order to examine substituent effects, oxidation of benzpinacolones containing *p*-methoxy, *p*-methyl, and *p*-chloro groups (**1a**—**i**) was carried out in 1,2-dichloroethane–TFA (2.0M). Since the reactivity of compounds (**1b**—**i**) is lower than that of (**1a**), their reactions were conducted at 50 °C. Results of the product analysis after work-up with water are presented in Table 2.

The major products were triarylmethanol and substituted benzoic acid in each case. The yield of triarylmethanol decreased in the order *p*-methoxy (**1a**) > *p*-methyl (**1d**) > unsubstituted (**1e**) > *p*-chloro (**1f**) (all four aromatic rings had the same substituents). In addition, as observed for (**1a**—**c**) and (**1e**), the reactivity increased with the number of *p*-methoxy groups. Thus electron-donating substituents on the phenyl rings of the triarylmethyl group accelerate the oxidation. On the other hand, the results for (**1e**) and (**1g**—**i**) show that the substituent on the benzoyl moiety has little effect on reactivity.

The second-order rate constants for the oxidation of the five benzpinacolones (**1a**, **d**—**f**, and **h**) were estimated from the yields of Ar_3COH in Table 2 by using the equation $k_2t = 1/([Ar_3CCOAr]_0 - [Ar_3COH]_t) - 1/[Ar_3CCOAr]_0$ (Table 3). A fairly linear correlation (r −0.9583) was observed between the logarithms of the rate constants ($RT \ln k_2$) and the free energies of anodic oxidation (Faraday constant × E_{ox}; Table 3), indicating that the reaction is controlled by a single-electron transfer process. However, the absolute value of the observed slope (0.25) is much smaller than unity, in contrast to the Ce^{IV} oxidation of *p*-substituted benzpinacolones (slope 0.96).[11] This indicates that charge transfer is only partial at the transition state, as suggested by Walling[14] for the reaction between diacyl peroxides and electron donors.

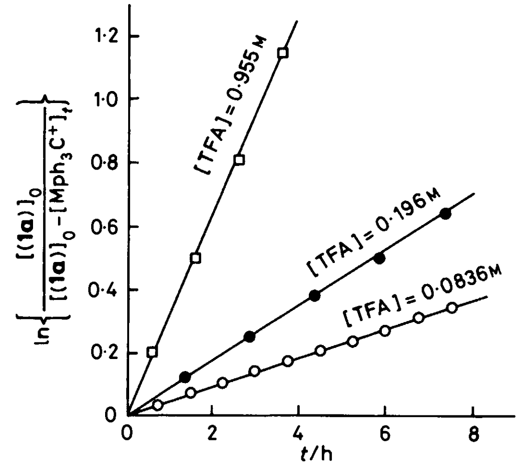


Figure 2. Pseudo-first-order plot for the oxidative cleavage of anispinacolone (**1a**) (5.0×10^{-3}M) by dibenzoyl peroxide (0.10M) in 1,2-dichloroethane–TFA at 50 °C

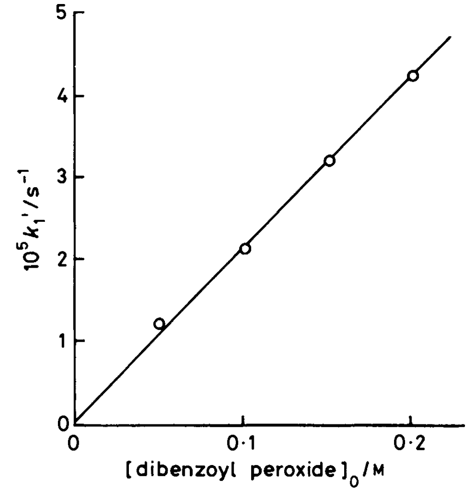


Figure 3. Plot of the pseudo-first-order rate constant (k_1') against the initial peroxide concentration for the oxidative cleavage of anispinacolone (**1a**) (5.0×10^{-3}M) by dibenzoyl peroxide in 1,2-dichloroethane–TFA (0.19M) at 50 °C

Kinetic Studies.—The rates of reaction of anispinacolone (**1a**) (5.0×10^{-3}M) with a 10- to 40-fold excess of dibenzoyl peroxide were determined by measuring the amount of tris-(*p*-methoxyphenyl)methyl cation by means of visible region spectrometry. A typical plot of ln $[(\mathbf{1a})]_0/\{[(\mathbf{1a})]_0 - [Mph_3C^+]_t\}$ against reaction time is shown in Figure 2. The linear plot passing through the origin indicates that the reaction is first-order in anispinacolone. In addition, a plot of pseudo-first-order rate

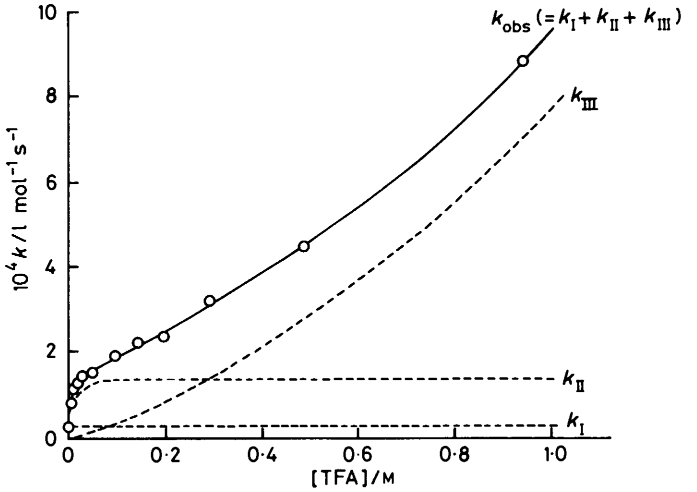


Figure 4. Plot of the observed second-order rate constant (k_{obs}) against the concentration of TFA for the oxidative cleavage of anispinacolone (**1a**) by dibenzoyl peroxide in 1,2-dichloroethane–TFA at 50 °C

constants ($k_1{}'$) against initial concentration of peroxide yielded a straight line (Figure 3), indicating that the rate is also first-order in dibenzoyl peroxide (BPO) [equation (6)].

$$d[Mph_3C^+]/dt = k_{obs}[Mph_3C\text{–}COMph][BPO] \quad (6)$$

The relationship between the concentration of TFA and the second-order rate constant (k_{obs}) is somewhat complicated (Figure 4). A small rate constant is observed even in the absence of TFA. The rate constant increases greatly with an increase in [TFA] at lower TFA concentrations (<0.05M), then rather gradually in more concentrated solutions. At a TFA concentration around 0.1M an inflection point was observed and the plot curved upwards at higher concentrations. This behaviour is accounted for by taking k_{obs} as the sum of the three contributions, shown by broken lines (k_I, k_{II}, and k_{III}) in Figure 4.

Previously, we reported that the uncatalysed reaction (k_I) starts with thermal decomposition of dibenzoyl peroxide to benzoyloxyl radical, which is followed by single-electron transfer from anispinacolone to the benzoyloxyl radical [equations (7) and (8)].[1] Since this process is not assisted by

$$(PhCO_2)_2 \longrightarrow 2PhCO_2{}^{\bullet} \quad (7)$$

$$Mph_3C\text{–}COMph + PhCO_2{}^{\bullet} \longrightarrow [MPh_3C\text{–}COMph]^{+\bullet} + PhCO_2 \quad (8)$$

acids, k_I is constant (0.24 × 10^{-4} l mol^{-1} s^{-1}) irrespective of the TFA concentration.

In the process represented by k_{II} the rate constant levels off at [TFA] >0.1M. The subsequent pathway, in which bimolecular single-electron transfer from anispinacolone to dibenzoyl peroxide molecule (BPO) occurs as an initial equilibrium, accounts for this kinetic behaviour [equations (9) and (10)].

$$Mph_3C\text{–}COMph + BPO \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} [Mph_3C\text{–}COMph]^{+\bullet} + [BPO]^{-\bullet} \quad (9)$$

$$[BPO]^{-\bullet} + TFA \longrightarrow PhCO_2{}^{\bullet} + PhCO_2H + CF_3CO_2{}^{-} \quad (10)$$

This process seems closely related to the one-electron oxidation of perylene by molecular oxygen[9] where an added acid stabilizes the superoxide anion by a hydrogen bond. When [TFA] is large enough the reversal of step (9) is suppressed; consequently k_{II} equals k_9, which corresponds to the maximum of the curve for k_{II} (1.4 × 10^{-4} l mol^{-1} s^{-1}). This value is far larger than that predicted from Marcus theory[15] (10^{-24} to 10^{-44} l mol^{-1} s^{-1}),* indicating that the process is not a mere single-electron transfer but that it involves some change in geometry of the molecules.[14]

In the region [TFA] >0.1M, k_{III} can be calculated by the equation $k_{III} = k_{obs} - (k_I + k_{II}) = k_{obs} - (0.24 + 1.4) \times 10^{-4}$ l mol^{-1} s^{-1}. Figure 4 shows that k_{III} is not proportional to [TFA], but the plot of log k_{III} against the acidity function (H_0)[16] of the solvent (see Experimental section) gave a straight line with a slope of 1.18 (Figure 5). Generally such linearity implies that a protonated species is involved in the rate-determining step.[17] On the basis of the electrophilic nature of protonated carbonyl compounds, such a protonated anispinacolone is excluded as the electron donor. Accordingly, the pathway shown in equations (11) and (12), where protonated

$$BPO + H^+ \rightleftharpoons BPOH^+ \quad (11)$$

$$Mph_3C\text{–}COMph + BPOH^+ \longrightarrow [Mph_3C\text{–}COMph]^{+\bullet} + PhCO_2{}^{\bullet} + PhCO_2H \quad (12)$$

dibenzoyl peroxide (BPOH$^+$) acts as a one-electron oxidant, is suggested. Protonation of dibenzoyl peroxide was monitored by measuring the ^{13}C chemical shift of the carbonyl carbon atom of labelled di[*carbonyl*-^{13}C]benzoyl peroxide (90% ^{13}C) in various 1,2-dichloroethane–TFA mixtures (Figure 6). It is generally recognized[18] that the n.m.r. chemical shift exhibits a sigmoid dependence on the acidity function of the solvent. Although in the present study the chemical shift of the protonated dibenzoyl peroxide could not be evaluated owing to incomplete protonation even in neat TFA, it is clear from the shape of the H_0–δ(^{13}C) curve that protonation of dibenzoyl peroxide begins for practical purposes at around H_0 1. This H_0 value corresponds to [TFA] ≃ 0.1M, at which the k_{III} process begins to develop. Consequently, dibenzoyl peroxide must be activated by protonation, producing a much more powerful oxidant than dibenzoyl peroxide itself.† A similar type of acid catalysis has been reported for TFA-induced oxidation of aromatic molecules by substituted quinones.[10]

In conclusion, the acid catalysis in the present reaction can be explained in terms of the action of acid on dibenzoyl peroxide (k_{III}) and on its radical anion (k_{II}). The former reaction exhibits specific acid catalysis similarly to the quinone oxidation.[10] As to the latter process, we consider that since [BPO]$^{-\bullet}$ is expected to be a stronger base than trifluoroacetate anion, proton transfer from TFA to [BPO]$^{-\bullet}$ occurs at a rate comparable to that of diffusion, and the O–O bond is cleaved instantaneously. This means that in the k_{II} process not only protons but also TFA

---

* According to Marcus theory the rate constant for outersphere electron transfer $A + B \longrightarrow A^{+\bullet} + B^{-\bullet}$ is predicted by equation (i),

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \quad (i)$$

where k_{11} is the self-exchange rate constant for A and $A^{+\bullet}$, k_{22} is that for B and $B^{-\bullet}$, and K_{12} is the equilibrium constant for the cross reaction. The value f is given by the equation $\ln f = (\ln K_{12})^2/4 \ln (k_{11}k_{22}/Z^2)$, Z being the collision frequency of the neutral molecules (10^{11} l mol^{-1} s^{-1}). In the present case K_{12} is estimated to be 10^{-34} from the difference between the oxidation peak potential of anispinacolone (1.14 V *vs.* s.c.e.; *cf.* Table 3) and the reduction peak potential of dibenzoyl peroxide (−1.05 V *vs.* s.c.e.). The calculated values of k_{12}, with k_{11} and k_{22} 10^4—10^9 l mol^{-1} s^{-1}, are 10^{-24}—10^{-44} l mol^{-1} s^{-1}.

† Attempts to measure the reduction peak potential of protonated dibenzoyl peroxide were not successful owing to interference from an intense H$^+$ reduction peak.

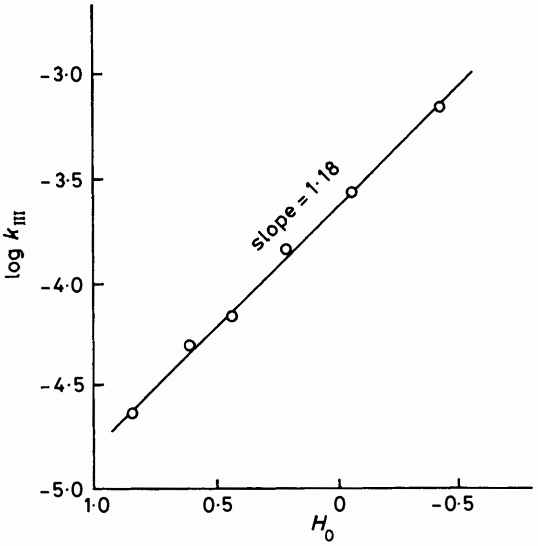


Figure 5. Relation between log k_{III} and H_0 of the solvent

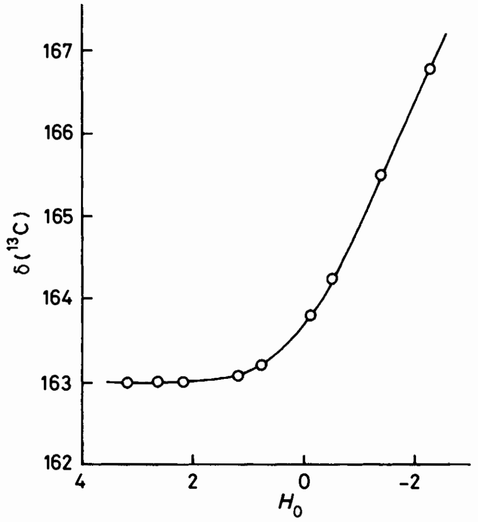


Figure 6. Correlation of ^{13}C chemical shift with H_0 for the carbonyl carbon of labelled dibenzoyl peroxide [$(Ph^{13}CO_2)_2$; 90% ^{13}C; 0.10M] in 1,2-dichloroethane–TFA mixtures at 50 °C. Chemical shifts are based on benzene (δ 128.5)

molecules act as catalysts. Hence, in this process general acid catalysis might be operative, in contrast to the k_{III} process where specific acid catalysis is operative.

It has been proposed that TFA-catalysed benzoyloxylation of substituted benzenes by dibenzoyl peroxide proceeds *via* an ionic pathway, where the peroxide co-ordinated to a proton is cleaved heterolytically.[19] In contrast, the present investigation has demonstrated that anispinacolone is oxidized not *via* such an ionic pathway but *via* single-electron transfer from anispinacolone to a dibenzoyl peroxide molecule or to its protonated form.

Experimental

I.r. spectra were taken with a Hitachi 215 spectrophotometer and visible region electronic spectra with a Hitachi 200–10 or a Shimadzu 50M spectrophotometer. ^1H N.m.r. spectra were taken with a Hitachi R-24 (60 MHz) or a Nicolet NP-300 NB (300 MHz) spectrometer. ^{13}C N.m.r. spectra were recorded with a JEOL JNM FX100 (25 MHz) spectrometer operating in the Fourier transform mode.

Materials.—Reagents were of reagent-grade quality except when otherwise noted. 1,2-Dichloroethane was refluxed over P_2O_5 and distilled. TFA, trifluoromethanesulphonic acid, and acrylonitrile were distilled (b.p.s 70.8—71.3 and 75 °C at 30 mmHg, and 76.8—77.5 °C, respectively). Dibenzoyl peroxide was purified by reprecipitation from a solution in chloroform by adding chilled methanol. The following compounds were prepared as described in the literature: bis-(*p*-nitrobenzoyl) peroxide,[20] m.p. 156 °C (decomp.) [lit.,[20] 156 °C (decomp.)]; bis-[3,5-bis(trifluoromethyl)benzoyl] peroxide,[21] m.p. 96.2—97.1 °C (lit.,[21] 98—99.5 °C); bis-(*p*-methoxybenzoyl) peroxide,[22] m.p. 128 °C (decomp.) [lit.,[22] 127—128 °C (decomp.)]; *p*-methoxybenzoyl *p*-nitrobenzoyl peroxide,[23] m.p. 106 °C (decomp.) [lit.,[23] 107—108 °C (decomp.)]; phthaloyl peroxide,[24] m.p. 122—124 °C (lit.,[24] 126 °C); anispinacolone (**1a**),[25] m.p. 141.8—142.7 °C (lit.,[26] 136—137 °C); 2,2-bis-(*p*-methoxyphenyl)-1,2-diphenylethanone (**1b**),[25] m.p. 123.0—124.5 °C; 1,2,2,2-tetrakis-(*p*-methylphenyl)ethanone (**1d**),[27] m.p. 154—155 °C (lit.,[27] 137—138; lit.,[28] 145—146 °C); 1,2,2,2-tetraphenylethanone (**1e**),[29] m.p. 183.1—184.1 °C (lit.,[29] 179—180 °C); 1,2,2,2-tetrakis-(*p*-chlorophenyl)ethanone (**1f**),[30] m.p. 188—190 °C (lit.,[30] 194.4—195.5 °C); 1-(*p*-methoxyphenyl)-2,2,2-triphenylethanone (**1g**),[31] m.p. 183.5—185.0 °C (lit.,[31] 184—185 °C). Bis-(3,5-dinitrobenzoyl) peroxide, m.p. 159—160 °C (decomp.) [lit.,[32] 161—162 °C (decomp.)], was synthesized by the method described for bis-(*p*-nitrobenzoyl) peroxide.[21] 1-(*p*-Chlorophenyl)-2,2,2-triphenylethanone (**1i**), m.p. 165—166 °C (lit.,[33] 168 °C), was synthesized by the method used for (**1g**).[31] *N*-Butylbenzamide, b.p. 140 °C at 0.7 mmHg (lit.,[34] m.p. 41—42 °C), *N*-butyl-*p*-methoxybenzamide, m.p. 55—56 °C (lit.,[35] 54 °C), and *N*-butyltrifluoroacetamide, b.p. 66—67 °C at 4 mmHg (lit.,[36] 105 °C at 11 mmHg), were prepared by treating benzoic anhydride, *p*-methoxybenzoic anhydride, and trifluoroacetic anhydride, respectively, with butylamine in 1,2-dichloroethane. The syntheses of labelled dibenzoyl peroxide, anispinacolone, and *p*-methoxybenzoic acid are described in our previous report.[1a]

2-(p-*Methoxyphenyl*)-1,2,2-*triphenylethanone* (**1c**).—A solution (200 ml) of phenylbenzoin[37] (20.0 g, 69 mmol), m.p. 82.5—84.5 °C, anisole (15 ml, 0.14 mol), and TFA (30 ml) in 1,2-dichloroethane was heated in a sealed tube at 100 °C for 20 min. Work-up gave a brown oil, which afforded *compound* (**1c**) (15.3 g, 58%) after recrystallization from benzene–ethanol (1:15); m.p. 137.0—137.5 °C (Found: C, 85.85; H, 5.65. $C_{27}H_{22}O_2$ requires C, 85.7; H, 5.85%); $\nu_{max.}$(KBr) 1 680m, 1 515s, 1 444m, 1 263m, 1 185m, and 1 037m cm^{-1}; δ(CCl_4) 3.68 (3 H, s), 6.68 (2 H, d, *J* 9.2 Hz), 7.0—7.3 (15 H, m), and 7.62 (2 H, dd, *J* 7.4 and 2.2 Hz).

1-(p-*Methylphenyl*)-2,2,2-*triphenylethanone* (**1h**).—To triphenylmethylsodium {prepared from triphenylmethyl chloride (4.0 g, 14 mmol) and sodium amalgam [sodium (1.0 g) and mercury (120 g)] in ether (60 ml) by the method of Renfrow and Hauser[38]} was added *p*-methylbenzoyl chloride (2.2 g, 14 mmol) in ether (20 ml) over 5 min and the mixture was stirred for 30 min. Work-up afforded a brown oil, which was recrystallized from benzene–ethanol (1:2) and separated by t.l.c. (SiO_2; benzene–hexane 6:4) to give *compound* (**1h**) (0.82 g, 16%), m.p. 162.5—164.0 °C (Found: C, 89.45; H, 6.4. $C_{27}H_{22}O$ requires C, 89.45; H, 6.1%); $\nu_{max.}$(CCl_4) 1 680s, 1 608s, 1 498s, 1 449m, 1 228m, 1 185s, 1 040m, 850m, and 700vs cm^{-1}; δ(CCl_4) 2.21 (3 H, s), 6.7—7.2 (17 H, m), and 7.50 (2 H, d, *J* 8.6 Hz).

2-(m-*Hydroxy*-p-*methoxyphenyl*)-1,2,2-*tris*-(p-*methoxyphenyl*)*ethanone* (**2**).—A solution (18 ml) of anispinacolone (**1a**)

(851 mg, 1.82 mmol) and bis-(3,5-dinitrobenzoyl) peroxide (759 mg, 1.80 mmol) in 1,2-dichloroethane was kept at 75 °C for 2 h under argon. The solution was chromatographed over basic alumina (ether–methanol 1:1) and then separated by t.l.c. (SiO_2; benzene–ether 1:1) to afford pale yellow crystals (65 mg). Recrystallization from hexane–benzene (1:1) gave *compound* (**2**) (46 mg) containing 1 mol equiv. of benzene, which was removed by heating at 130 °C for 15 min *in vacuo* ($< 10^{-3}$ mmHg); m.p. 157.5—158.5 °C (Found: C, 74.05; H, 5.8. $C_{30}H_{28}O_6$ requires C, 74.35; H, 5.8%); $\nu_{max.}$(KBr) 3 440w, 2 845w, 1 675m, 1 600s, 1 512s, 1 504s, 1 461m, 1 440m, 1 305m, 1 280s, 1 260s, 1 188s, 1 172s, 1 035s, and 815m cm^{-1}; δ($CDCl_3$; 300 MHz) 3.68 (3 H, s), 3.69 (6 H, s), 3.75 (3 H, s), 5.60 (1 H, s), 6.59 (2 H, d, *J* 9.0 Hz), 6.61 (1 H, dd, *J* 2.0 and 8.3 Hz), 6.66 (1 H, d, *J* 8.3 Hz), 6.71 (4 H, d, *J* 9.2 Hz), 6.78 (1 H, d, *J* 2.0 Hz), 7.06 (4 H, d, *J* 9.2 Hz), and 7.65 (2 H, d, *J* 9.0 Hz).

Product Studies.—In a representative run, a solution (10.0 ml) of dibenzoyl peroxide (0.247 g, 1.02 mmol) and TFA (1.5 ml, 20 mmol) in 1,2-dichloroethane was placed in a 20 ml ampoule with a branch, and anispinacolone (**1a**) (0.469 g, 1.00 mmol) was placed in the branch. After the solution had been degassed ($< 10^{-3}$ mmHg) and the ampoule sealed, the anispinacolone was transferred to the solution. The ampoule was covered with aluminium foil and kept at 25.0 ± 0.1 °C. After 24 h a portion (4.3%) of the reaction mixture was diluted by a factor of 15 000 with 1,2-dichloroethane containing 2% (v/v) TFA, and the amount of tris-(*p*-methoxyphenyl)methyl cation (94%) was determined from the absorbance at 487 nm. The rest of the mixture was diluted with ether and extracted with aqueous 5% $NaHCO_3$, from which a mixture of *p*-methoxybenzoic acid (0.118 g, 0.78 mmol) and benzoic acid (0.185 g, 1.51 mmol) was obtained. The organic layer was washed with aqueous 10% NaCl, dried ($MgSO_4$), and separated by t.l.c. (SiO_2; benzene–ether 98:2) to give tris-(*p*-methoxyphenyl)methanol (0.300 g, 0.856 mmol), tetrakis-(*p*-methoxyphenyl)ethylene (**3**) (9.6 mg, 0.021 mmol), and a small amount of unchanged dibenzoyl peroxide (0.10 mmol by iodometric titration).

Formation of Tetrakis-(p-*methoxyphenyl*)*ethylene* (**3**) *in the Reaction of Anispinacolone* (**1a**) *with Trifluoroacetic Anhydride.*—Anispinacolone (0.234 g, 0.499 mmol), trifluoroacetic anhydride (0.20 ml, 1.4 mmol), and TFA (0.75 ml, 10 mmol) were kept in 1,2-dichloroethane (5 ml) in a degassed ampoule at 25.0 °C for 24 h in the dark. A part (4.5 ml) of the reaction mixture was diluted with ether and extracted with aqueous 5% $NaHCO_3$, from which *p*-methoxybenzoic acid (5.7 mg, 0.037 mmol) was obtained. The organic layer was washed with 10% NaCl, dried ($MgSO_4$), and separated by t.l.c. (SiO_2; benzene–ether 9:1) to give tetrakis-(*p*-methoxyphenyl)ethylene (**3**) (71.8 mg, 0.159 mmol), tris-(*p*-methoxyphenyl)methanol (9.6 mg, 0.027 mmol), and unchanged anispinacolone (55.3 mg, 0.118 mmol).

Baeyer–Villiger Oxidation of Anispinacolone (**1a**).—A solution of trifluoroperacetic acid (0.10M) and TFA (2.0M) in 1,2-dichloroethane was prepared from trifluoroacetic anhydride and hydrogen peroxide by the procedure of Hawthorne.[39] This solution (10.0 ml) was placed in a 30 ml ampoule with a branch, and anispinacolone (0.469 g, 1.00 mmol) was placed in the branch. The ampoule was degassed ($< 10^{-3}$ mmHg) and sealed, and then the anispinacolone was transferred to the solution. After the ampoule had been kept at 25.0 °C for 1 h in the dark, a portion (0.500 ml) was subjected to iodometric titration, showing that no peroxy acid remained unchanged. Another part (9.00 ml) of the mixture was diluted with ether and extracted with aqueous 5% $NaHCO_3$, from which *p*-methoxybenzoic acid (8.5 mg, 0.056 mmol) was obtained. The organic layer was washed with aqueous 10% NaCl, dried ($MgSO_4$), and separated by t.l.c. (SiO_2; benzene–ether 9:1) to give tris-(*p*-methoxyphenyl)methanol (14.9 mg, 0.043 mmol), the hydroxylated product (**2**) (0.135 g, 0.279 mmol), and unchanged anispinacolone (0.208 g, 0.444 mmol).

Table 4. Values of pK_{BH^+} for substituted aniline indicators

	pK_{BH^+}	
Indicator	In $ClCH_2CH_2Cl$–TFA	In H_2O at 25 °C[a]
2-Methylaniline	2.36	4.44
3-Chloroaniline	1.46	3.52
4-Nitroaniline	0.03	1.00
2-Nitroaniline	−0.56	−0.30
4-Chloro-2-nitroaniline	−1.06	−1.06

[a] From ref. 18.

Trapping of Anhydrides with Butylamine.—Anispinacolone (0.703 g, 1.50 mmol), dibenzoyl peroxide (0.244 g, 1.01 mmol), and TFA (1.5 ml, 20 mmol) were kept in 1,2-dichloroethane (10.0 ml) at 25.0 °C for 24 h (procedure already described). To a portion (5.00 ml) of the mixture was added butylamine (2.0 ml, 20 mmol) at 0 °C, and the solution was stirred at 0 °C for 15 min. The solution was washed with aqueous 5% $NaHCO_3$ and aqueous 10% NaCl, dried ($MgSO_4$), and concentrated to *ca.* 5 ml, then subjected to g.l.c. analysis (SE-30; 3 mm × 1 m). The amount of *N*-butyltrifluoroacetamide was determined at a column temperature of 83 °C by using *p*-t-butyltoluene as standard, and the amounts of *N*-butylbenzamide and *N*-butyl-*p*-methoxybenzamide were determined at 175 °C by using diphenyl ether as standard.

Polymerization of Acrylonitrile initiated by the Reaction of Anispinacolone (**1a**) *with Bis-*(3,5-*dinitrobenzoyl*) *Peroxide.*—A solution (40.0 ml) of anispinacolone (0.025M), bis-(3,5-dinitrobenzoyl) peroxide (0.025M), acrylonitrile (3.0M), and TFA (2.0M) in 1,2-dichloroethane was kept at 25.0 °C under nitrogen. After 25 h in the dark, methanol (40 ml) was added; the precipitate was separated by filtration and washed with methanol to give yellowish crystals (0.92 g; 15 wt% based on acrylonitrile), $\nu_{max.}$(KBr) 2 250 cm^{-1}. No polymer was detected in a control experiment without TFA.

^{13}C *N.m.r. CIDNP Studies.*—A solution of anispinacolone (0.10M), dibenzoyl peroxide (0.10M), and TFA (2.0M) in 1,2-dichloroethane was prepared in an n.m.r. tube. A D_2O capillary tube was placed coaxially inside the tube as an external lock. The free space was flushed with argon and the tube sealed with a polyethylene cap. The tube was placed in the n.m.r. probe which had been maintained at 25 ± 1 °C, and the measurement was started immediately. The temperature indicator was calibrated by using CCl_4–$(CD_3)_2CO$ as an n.m.r. thermometer.[40] Generally, 40—160 free induction decays were accumulated using a 45° pulse and a pulse interval of 1.5 s.

Rate Measurements.—Samples of a solution of anispinacolone in 1,2-dichloroethane and of dibenzoyl peroxide plus TFA were placed in the two ends of H-shaped ampoules. Each solution was degassed ($< 10^{-3}$ mmHg), and the solutions were mixed at 50.0 °C. The ampoules were covered with aluminium foil and kept at 50.0 ± 0.1 °C in a thermostat. At appropriate intervals one of the mixtures was diluted with 1,2-dichloroethane containing 2% (v/v) TFA and the amount of tris-(*p*-methoxy-

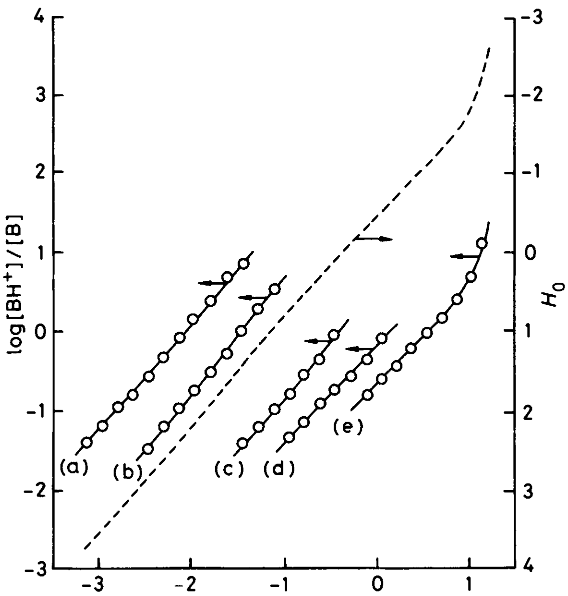


Figure 7. Values of log[BH$^+$]/[B] of substituted aniline indicators in various 1,2-dichloroethane–TFA mixtures at 50 °C: (a) 2-methylaniline; (b) 3-chloroaniline; (c) 4-nitroaniline; (d) 2-nitroaniline; (e) 4-chloro-2-nitroaniline. The broken line indicates the dependence of the H_0 value on the TFA concentration

phenyl)methyl cation was determined from the absorbance at $\lambda_{max.}$ 487 nm (ε 102 000).

Determination of H$_0$.—The H_0 values for various 1,2-dichloroethane–TFA mixtures were determined by Hammett's step method,[16] using five substituted anilines as indicator bases (B). For each base the ratio [BH$^+$]/[B] was measured spectrophotometrically at 50 ± 1 °C (Figure 7). The vertical difference (Δlog[BH$^+$]/[B]) for any two adjacent curves was constant within ±0.01. As is usual practice in dealing with nonaqueous systems, the pK_{BH^+} value of 4-chloro-2-nitroaniline (−1.06)[18] in aqueous solution at 25 °C was chosen as standard, on the basis of which pK_{BH^+} values of other indicators were calculated by the equation pK_{BH^+} = −1.06 + Δlog[BH$^+$]/[B] (Table 4).* From these results the H_0 value (≡pK_{BH^+} − log[BH$^+$]/[B]) was evaluated over a range of TFA concentrations from 7.5 × 10^{-4} to 13.1M. The dependence of H_0 on log [TFA] is illustrated in Figure 7.

^{13}C *Chemical Shift of the Carbonyl Carbon Atom of Dibenzoyl Peroxide*.—The ^{13}C n.m.r. spectra of labelled dibenzoyl peroxide were measured at 50 ± 1 °C for 0.10M-solutions in 1,2-dichloroethane–TFA mixtures by using the signal of 1,2-dichloroethane as a reference. Since the position of the signal of 1,2-dichloroethane changed appreciably with TFA concentration, chemical shifts were calibrated on the basis of the signal position of benzene (δ 128.5) measured in the same solvent at 50 °C. The chemical shift of benzene is known to be almost constant in various solvents including TFA.[41]

Cyclic Voltammetry.—The oxidation peak potentials of benzpinacolones (3.0 × 10^{-3}M) and the reduction peak potential of dibenzoyl peroxide (5.0 × 10^{-3}M) were measured by cyclic voltammetry in 1,2-dichloroethane–TFA (2.0M) and dichloromethane, respectively, with Bu$^n_4$NClO$_4$ (0.10M) as supporting electrolyte. A three-electrode cell was used with platinum wire working and auxiliary electrodes and a saturated calomel reference electrode. The measurements were carried out with a Hokuto-Denko HA-104 potentiostat and a Hokuto-Denko HB-107A function generator at a scan rate of 0.1 V s^{-1}.

References

1 (*a*) Part 3, K. Takeuchi, O. Murai, S. Matsui, T. Inoue, T. Kitagawa, and K. Okamoto, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1301; (*b*) K. Okamoto, K. Takeuchi, O. Murai, S. Matsui, T. Inoue, and T. Kitagawa, *Tetrahedron Lett.*, 1981, **22**, 2785.
2 (*a*) M. Imoto and S. Choe, *J. Polym. Sci.*, 1955, **15**, 485; (*b*) C. Walling and N. Indictor, *J. Am. Chem. Soc.*, 1958, **80**, 5814; (*c*) L. Horner and K. Sherf, *Justus Liebigs Ann. Chem.*, 1951, **537**, 35.
3 K. Tokumaru and O. Simamura, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 333.
4 T. Suehiro, *J. Chem. Soc. Jpn.*, 1958, **79**, 624.
5 (*a*) G. Tsuchihashi, S. Miyajima, T. Otsu, and O. Simamura, *Tetrahedron*, 1965, **21**, 1039; (*b*) G. Tsuchihashi, M. Matsushima, S. Miyajima, and O. Simamura, *ibid.*, p. 1049.
6 D. F. Church and W. A. Pryor, *J. Org. Chem.*, 1980, **45**, 2866.
7 (*a*) K. A. Horn and G. B. Schuster, *J. Am. Chem. Soc.*, 1979, **101**, 7097; (*b*) J. J. Zupancic, K. A. Horn, and G. B. Schuster, *ibid.*, 1980, **102**, 5279; (*c*) K. A. Horn and G. B. Schuster, *Tetrahedron*, 1982, **38**, 1095.
8 C. Walling and C. Zhao, *Tetrahedron*, 1982, **38**, 1105.
9 W. I. Aalbersberg, J. Gaaf, and E. J. Mackor, *J. Chem. Soc.*, 1961, 905.
10 W. J. Sep, J. W. Verhoeven, and Th. J. de Boer, *Tetrahedron*, 1979, **35**, 2161.
11 K. Okamoto, K. Takeuchi, O. Murai, and Y. Fujii, *J. Chem. Soc., Perkin Trans. 2*, 1979, 490.
12 K. Okamoto, I. Nitta, and H. Shingu, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1464.
13 R. Kaptein, *Chem. Commun.*, 1971, 732.
14 C. Walling, *J. Am. Chem. Soc.*, 1980, **102**, 6854.
15 R. A. Marcus, *J. Phys. Chem.*, 1963, **67**, 853.
16 L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, 1932, **54**, 2721.
17 L. P. Hammett, 'Physical Organic Chemistry,' 2nd edn., McGraw-Hill, New York, 1970, ch. 9.
18 E. M. Arnett and G. Scorrano, *Adv. Phys. Org. Chem.*, 1976, **13**, 83.
19 N. Kamigata, H. Minato, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 894.
20 C. C. Price and E. Krebs, *Org. Synth.*, 1955, Coll. Vol 3, p. 649.
21 J. Lichtenberger and F. Weiss, *Bull. Soc. Chim. Fr.*, 1962, 915.
22 C. C. Price, R. W. Kell, and E. Krebs, *J. Am. Chem. Soc.*, 1942, **64**, 1103.
23 F. D. Greene and J. Kazan, *J. Org. Chem.*, 1963, **28**, 2168.
24 K. E. Russell, *J. Am. Chem. Soc.*, 1955, **77**, 4814.
25 R. K. Miller and H. A. Neidig, *Proc. Penna. Acad. Sci.*, 1950, **24**, 122 (*Chem. Abstr.*, 1952, **46**, 5558e).
26 R. E. Buckles, R. E. Erickson, J. D. Snyder, and W. B. Person, *J. Am. Chem. Soc.*, 1960, **82**, 2444.
27 M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, 1927, **49**, 236.
28 H. Wieland, H. vom Hove, and K. Börner, *Justus Liebigs Ann. Chem.*, 1926, **446**, 31.
29 L. F. Fieser and K. L. Williamson, 'Organic Experiments,' 5th edn., D. C. Heath and Co., Lexington, 1983, p. 304.
30 H. L. Bradlow and C. A. VanderWerf, *J. Am. Chem. Soc.*, 1947, **69**, 1254.
31 R. C. Fuson and P. E. Wiegert, *J. Am. Chem. Soc.*, 1955, **77**, 1138.
32 A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, 1951, **73**, 3883.
33 W. Schlenk and R. Ochs, *Chem. Ber.*, 1916, **49**, 608.
34 H. W. Grimmel, A. Guenther, and J. F. Morgan, *J. Am. Chem. Soc.*, 1946, **68**, 539.
35 H. Schönenberger, J. Holzheu-Eckardt, and E. Bamann, *Arzneim. Forsch.*, 1964, **14**, 324.
36 M. Pailer and W. J. Hübsch, *Monatsh. Chem.*, 1966, **97**, 1541.
37 S. F. Acree, *Chem. Ber.*, 1904, **37**, 2753.

---

* Since the pK_{BH^+} values calculated for other bases do not coincide with those in the aqueous system at 25 °C (Table 4), this choice of the standard pK_{BH^+} value should be taken as tentative. However, the matter is unimportant for the present discussion because the choice does not affect the H_0 difference.

38 W. B. Renfrow, Jr., and C. R. Hauser, *Org. Synth.*, 1943, Coll. Vol. 2, p. 607.

39 M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Am. Chem. Soc.*, 1958, **80**, 6393.

40 J. J. Led and S. B. Petersen, *J. Magn. Reson.*, 1978, **32**, 1.

41 G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, 1972, **94**, 3089.

Received 13*th December* 1985; *Paper* 5/2189