Investigations into Reaction Mechanisms of Peroxybenzoic Acid toward Diazodiphenylmethanes

RUGGERO CURCI,*[1] FULVIO DI FURIA, AND FRANCO MARCUZZI

Istituto di Chimica Organica dell'Universita', Centro C.N.R. di Meccanismi di Reazioni Organiche, 35100 Padova, Italy

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The reaction of diazodiphenylmethane Ph_2CN_2 with peroxybenzoic acid $PhCO_3H$ in benzene, Et_2O, or *i*-PrOH produces benzophenone in high yields along with benzoic acid and nitrogen, whereas no detectable amount of benzhydryl peroxybenzoate $PhC(=O)OOCHPh_2$ is formed. Reaction stoichiometry is 1 mol of peroxybenzoic acid (PBA) to 1 mol of diazodiphenylmethane (DDM) and a second-order-overall (order one in each of the reagents) kinetic law is obeyed. Kinetic data concerning reaction of DDM with PBA in nine solvents of varying characteristics show a parallelism with data for PBA oxidation of *p*-nitrodiphenyl sulfide and of cyclohexene. Substituents effects have been studied by measuring reaction rates for four substituted diazodiphenylmethanes $[XC_6H_4C(=N_2)C_6H_5$, with X = *p*-OCH_3, *p*-Cl,*m*-NO_2, *p*-$NO_2]$ with PBA and for DDM with *p*-nitroperoxybenzoic acid. The effect of isotopic substitution (PBA-d_1) on rates was also determined. Reaction mechanisms which account for the results are discussed.

Diazoalkanes represent a class of useful intermediates in organic chemistry and the kinetics and mechanisms of many reactions of these molecules have been investigated.[2] It is known that a large variety of carboxylic acids reacts with diazodiphenylmethane and substituted diazodiphenylmethanes to form the corresponding benzhydryl esters in good yields.[2] Reaction rate data have been employed to evaluate Hammett σ constants, to establish ρ–ρ relationships, to determine structure–reactivity–temperature correlations, and to separate polar from steric effects.[2-6]

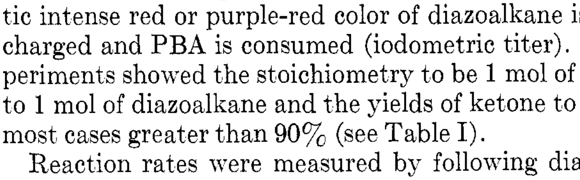
On the basis of much evidence, the accepted mechanism involves a rate-determining proton transfer to give an ion pair $[RCO_2^- \, {}^+N_2CHPh_2]$ followed by rapid expulsion of N_2 to yield a second ion pair $[RCO_2^- \, {}^+CHPh_2]$, which in turn collapses to form the ester or dissociates to give benzhydryl ethyl ether (in EtOH).[4,7]

Our interest in the field of peroxide reaction mechanisms[8] led us to investigate the reaction of peroxy acids with diaryldiazoalkanes, since it was believed these reactions might prove to be a convenient synthetic route to secondary and primary peroxy esters.[9] On the other hand, it had been reported that 9-diazofluorene yields 9-fluorenone upon reaction with peroxybenzoic acid.[10]

Using diphenyldiazomethane (DDM) and four other substituted diphenyldiazomethanes as substrates, we choose peroxybenzoic acid (PBA) as reaction partner because of the large body of kinetic data available for this representative peroxidic compound.[8,9] By determining reaction stoichiometry as well as by collecting kinetic data, we aimed to obtain information concerning the reaction course and the mechanisms.

Results and Discussion

We found that by reacting PBA (**1**) with DDM and four substituted diphenyldiazomethanes **2** in benzene Et_2O, or *i*-PrOH, the corresponding benzophenones **3** are obtained along with benzoic acid (BA) and nitrogen.



(1)

with X = H, *p*-OCH_3, *p*-Cl, *m*-NO_2, and *p*-NO_2

These reactions proceed smoothly at 25°. During the time that nitrogen is being evolved, the characteristic intense red or purple-red color of diazoalkane is discharged and PBA is consumed (iodometric titer). Experiments showed the stoichiometry to be 1 mol of PBA to 1 mol of diazoalkane and the yields of ketone to be in most cases greater than 90% (see Table I).

Reaction rates were measured by following diazoalkane disappearance by standard spectrophotometric techniques.[3a] Pseudo-first-order integrated plots were linear up to 80–90% reaction and kinetic experiments indicated that the overall kinetic order is two (order one in each of the reagents). Considering the first three entries on Table II, a plot of log k_1 *vs.* log $[PBA]_0$ gives a straight line of slope 1.03. The third and fourth entries show that, at constant $[PBA]_0$, the k_1 value practically does not change upon nearly doubling $[DDM]_0$; finally, k_2 values, obtained as $k_1/[PBA]_0$, are reproducible and agree within the limits of experimental errors (*ca.* ±3%).

For the reaction between PBA and DDM in dioxane and $ClCH_2CH_2Cl$, the presence of 0.1 *M* nitrobenzene, an effective radical trap, caused practically no change in k_2 values (see Table II); this makes the intervention of radical pathways unlikely. By measuring the rates for the reaction between $PhCO_3D$ (PBA-d_1) and DDM in dioxane (at 31.5°), a primary isotope effect k^H/k^D of

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[1] To whom inquiries should be addressed: Department of Chemistry, Brown University, Providence, R. I. 02912.

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[4] (a) R. A. More O'Ferral and S. I. Miller, *ibid.*, **85**, 2440 (1963); (b) J. D. Sharp Ritter and S. I. Miller, *ibid.*, **86**, 1507 (1964); (c) R. A. More O'Ferral, W. K. Kwok, and S. I. Miller, *ibid.*, **86**, 5553 (1964).

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[9] A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, p 58 ff.

[10] A. Schonberg, W. I. Awad, and N. Latif, *J. Chem. Soc.*, 1368 (1951).

Table I

Yields of Corresponding Ketones in the Reaction of DDM and Substituted Diazodiphenylmethanes with PBA[a]

Diazoalkane	% purity[b]	Reaction solvent	% yield of ketone
$C_6H_5C(=N_2)C_6H_5$	93.0	Benzene	92.0
	93.0	Benzene	94.0[c]
	93.0	Et_2O	94.0
	93.0	*i*-PrOH	87.0[d]
	93.0	*i*-PrOH	99.0[e]
$C_6H_5C(=N_2)C_6H_4$-*p*-OCH_3	94.0	Benzene	96.0
$C_6H_5C(=N_2)C_6H_4$-*p*-Cl	90.0	Benzene	96.0
$C_6H_5C(=N_2)C_6H_4$-*m*-NO_2	96.0	Benzene	90.0
$C_6H_5C(=N_2)C_6H_4$-*p*-NO_2	99.0	Benzene	99.0

[a] Unless otherwise noted, yields of ketones were determined (±4%) by glpc after reacting PBA and the diazo compound in equimolar amounts. [b] ±4%, as determined by following a titrimetric method (Experimental Section). [c] In this experiment, yields were determined by separating and weighing the reaction products (see Experimental Section). [d] In this solvent, other reaction products observed were $PhCO_2CHPh_2$ (6.8%) and *i*-$PrOCHPh_2$ (3.7%). [e] Reaction was carried out using an excess of PBA, *i.e.*, ($[PBA]_0/[DDM]_0$) ≅ 20.

1.33 ± 0.04 was estimated (Table II). Data concerning the effect of changing reaction solvent on rates are also collected on Table II along with activation enthalpies in two typical[8a] reaction media.

A few experiments aimed to evaluate the difference in reaction rates among PBA and BA toward DDM were also carried out. It was found that PBA reacts in dioxane at 31.5° about 60 times as fast as BA with DDM (for BA + DDM reaction, it is $k_2 = 0.102 \times 10^{-2}\ M^{-1}\ sec^{-1}$); instead, in *i*-PrOH solvent at 25.0° the k_2 value found ($1.01 \times 10^{-1}\ M^{-1}\ sec^{-1}$) for the reaction of BA with diazodiphenylmethane indicates comparable rates for the acid and the peroxy acid (see also Table II).

In Table III kinetic data aimed to elucidate the substituent effect on rates are collected; for the reaction between PBA and substituted diazodiphenylmethanes in dioxane, a plot of log (k_2/k_2^0) *vs.* Hammett σ values gives a straight line (correlation coefficient 0.990) of slope (Hammett ρ) −0.96. Therefore, whereas electron-withdrawing groups in the phenyl ring of DDM decrease the reaction rate with PBA, the reaction of DDM with *p*-nitroperoxybenzoic acid in dioxane at 31.5° proceeds about 4.2 times as fast as with PBA (Table III). This suggests that the diazoalkanes act as nucelophiles, whereas the peroxy acid is the electrophilic partner in these reactions.

On the basis of stoichiometry and kinetic data, two main reaction mechanisms can be envisaged. Mechanism I involves direct attack by the diazoalkane nucleophilic carbon atom on the O-O bond of the peroxy acid molecule. Reactions of nucleophilic displacement on peroxidic oxygen by carbon compounds have been reviewed by Edwards;[11] diazoalkanes, because of the "anion-like" behavior of the carbon atom, would be expected to be effective nucleophiles.

In the scheme shown, the structure of **4** bears much similarity to the transition states proposed for the oxidation of olefins and sulfides by peroxy acids. The intramolecular H-bonded structure of peroxy acids in such solvents as CCl_4 or benzene is well documented, as is the importance of cyclic transition states similar to **4** in order to by-pass significant charge separation by an intramolecular hydrogen transfer.[8,9] Actually, a linear relationship (slope 1.06, cor coeff 0.974) is observed among the logs of rates of DDM reaction with PBA and the logs of rates for *p*-nitrodiphenylsulfide (PNDS) oxidation by PBA, in a variety of solvents (Figure 1). A similar linear relationship (with lower slope) can also be obtained by plotting log k_2 for DDM reaction *vs.* log k_2 for cyclohexene epoxidation by PBA.[8a] The factors influencing the observed trend of rates in the given solvent series could be ascribed mainly to differences among ground-state and transition-state specific solvation of PBA molecules, as it has already been discussed in detail.[8]

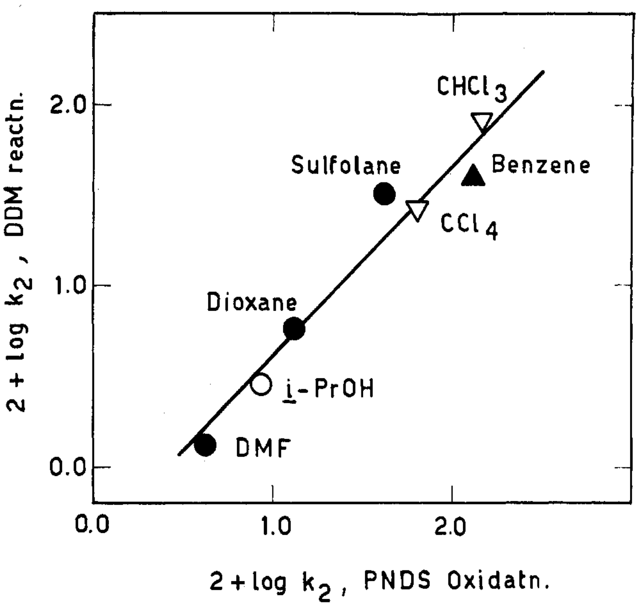
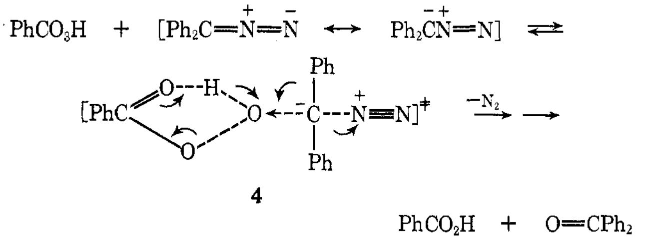


Figure 1.—Linear trend in the logarithmic plot of rate constants for the reaction of DDM with PBA *vs.* rate constants for the oxidation of *p*-nitrodiphenyl sulfide (PNDS) by PBA in various solvents.

Mechanism I



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The *ca.* 3.5 kcal mol^{-1} difference found in $\Delta H^{\neq}$ values for the reaction in dioxane and 1,2-dichloroetane (Table I) is in the expected direction, as is also the difference in $\Delta S^{\neq}$ values. The observed isotope effect (k^H/k^D = 1.33) is also consistent with a transition state structure such as **4**, being near to the values of 1.15 and 1.10 found respectively in the reaction of peroxyacetic acid with *p*-nitroaniline and of *m*-chloroperoxybenzoic acid with Schiff bases.[12,13]

Another mechanism resembling that accepted for the reaction of carboxylic acids with DDM could be drawn; this would imply the preliminary formation of peroxy

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[12] K. M. Ibne-Rasa and J. O. Edwards, *J. Amer. Chem. Soc.*, **84**, 763 (1962).

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TABLE II

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION OF DDM WITH PBA IN VARIOUS SOLVENTS

Solvent	$\epsilon^{25°}$	T, °C	$10^2 k_1$,[a] sec^{-1}	$10^2 k_2$,[a] M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
Dioxane	2.21	31.5	0.152[b]	5.60	9.6[g]	−33.0[g]
			0.335[c]	6.00		
			0.640[d]	5.80		
			0.660[e]	6.00		
		20.0		2.87		
		25.0		3.23		
		25.0		3.16[f]		
		30.0		4.58		
		40.0		8.24		
Dioxane (PBA-d_1)		31.5		4.40		
1,2-Dichloroethane	10.4	31.5		56.8	5.8[g]	−40.0[g]
		10.0		24.8		
		20.0		40.5		
		20.0		38.0[f]		
		30.0		52.2		
$CHCl_3$	4.81	31.5		79.7		
CCl_4	2.24	31.5		25.8		
Benzene	2.28	31.5		39.0		
Sulfolane	41.4[h]	31.5		34.0		
THF	7.6	31.5		1.90		
i-PrOH	18.3	31.5		2.90		
		25.0		1.50		
DMF	36.7	31.5		1.44		

[a] k_1 values were obtained from pseudo-first-order integrated plots; in these runs usually $[DDM]_0$ ranged from 0.4×10^{-2} to 0.6×10^{-2} M, whereas $[PBA]_0$ was from 0.05 to 0.08 M (unless otherwise noted). Second-order rate constants were obtained as $k_2 = k_1/[PBA]_0$. [b] $10^2[DDM]_0 = 0.565$ M; $10^2[PBA]_0 = 2.72$ M. [c] $10^2[DDM]_0 = 0.565$ M; $10^2[PBA]_0 = 5.58$ M. [d] $10^2[DDM]_0 = 0.565$ M; $10^2[PBA]_0 = 11.0$ M. [e] 10^2 $[DDM]_0 = 1.09$ M; $10^2[PBA]_0 = 11.0$ M. [f] In the presence of 0.1 M $PhNO_2$. [g] At 25.0°. [h] At 30.0°.

TABLE III

SUBSTITUENT EFFECTS ON THE REACTION OF SOME SUBSTITUTED DIARYLDIAZOMETHANES $(XC_6H_4)C_6H_5CN_2$ WITH PEROXYBENZOIC ACIDS $YC_6H_4CO_3H$ IN DIOXANE AT 31.5°

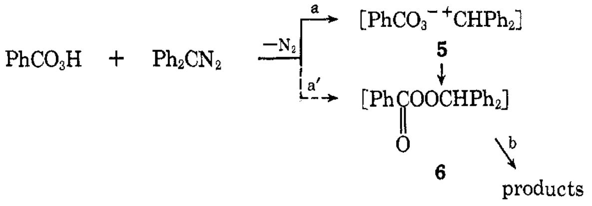
Substituent	$10^2 k_2$[a]	(k_2/k_2^0)	σ[b]
For Y = H, X = *p*-OCH_3	11.6	1.98	−0.268
H	5.85	1.00	0.000
p-Cl	4.04	0.691	+0.226
m-NO_2	1.61	0.275	+0.710
p-NO_2	0.95	0.162	+0.778
For X = H, Y = H	5.85	1.00	0.000
p-NO_2	24.7	4.22	+0.778

[a] From pseudo-first-order runs (see also footnote *a* of Table I). [b] σ values are from J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962.

ester **6**, which would in turn easily decompose to yield benzophenone and benzoic acid.

According to mechanism II, the separation of opposite charges which obtains upon formation of the intermediate ion pair **5** leads one to expect a significant increase in rate on increasing medium polarity.

Mechanism II



Indeed, Roberts, *et al.*, have shown that the logs of rates for reaction of BA with DDM increase linearly with the Kirkwood function $[(\epsilon - 1)/(2\epsilon + 1)]$ for various EtOH–water mixtures and that addition of nitrobenzene (ϵ 34.8) to EtOH (ϵ 24.3) also increases the rate.[3a] Inspection of kinetic data given on Table II, however, shows no clear dependence of rates on solvent dielectric constant. For example, the reaction rate in benzene (ϵ 2.28) is *ca.* 27 times as fast as in DMF (ϵ 36.7); within a series of similar solvents, the rate constant for solvent 1,2-dichloroethane (ϵ 10.4) is about 22 times higher than for CCl_4 (ϵ 2.24) but it is *lower* than that for $CHCl_3$ (ϵ 4.81).

Furthermore, in alcoholic solvents, as far as the out-of-cage reaction of benzhydryl cation with the nucleophilic solvent (to give Ph_2CHOR) can be competitive with recombination of $PhCH^+$ with $PhCO_3^-$ (to form **6**), a meaningful decrease in ketone yield might be expected. Instead, only a small decrease in the yield of $Ph_2C{=}O$ was observed when the reaction between PBA and DDM (in equimolar amounts) was performed in *i*-PrOH (see Table I); nevertheless, in this case, upon comparison with authentic samples, both benzhydryl isopropyl ether and benzhydryl benzoate were detected as reaction side products. This is not surprising since, as mentioned earlier, PBA and BA show similar rates in reacting with DDM in *i*-PrOH; therefore, as the reaction between PBA and DDM proceeds, the benzoic acid produced can itself react with the diazo compound in a consecutive reaction yielding the ether and the ester.[3-7] Indeed, when DDM was reacted with PBA excess in *i*-PrOH, benzophenone was produced in almost quantitative yield (Table I) and sizable amounts of *i*-$PrOCHPh_2$ and $PhCO_2CHPh$ could no longer be detected by glpc, tlc, or pmr.

All evidences so far collected, therefore, seem to point out that, should mechanism II hold for these reactions, it is unlikely that the reaction proceeds *via* the intermediate formation of an ion pair such as **5**. However, the possibility remains that the intermediate peroxy ester **6** is formed directly from the reactants (path a′), perhaps *via* a cyclic transition state not too dissimilar to **4**.

It is apparent that more data need to be collected concerning the stability of secondary peroxy esters such as **6**; to our knowledge no benzhydryl peroxy ester **6** has yet been reported nor has any *sec*-diaryl peroxybenzoate. The difficulties arising in the syntheses of secondary peroxy esters are well recognized; these stem primarily from the easy decomposition of such compounds in the presence of bases as well as from the facile homolytic or heterolytic O–O bond cleavage, often accompanied by rearrangements.[14] Actually, our preliminary attempts to obtain **6** through the imidazolide route[14] have been so far unsuccessful; *sec*-butyl peroxyacetate has been reported by Mosher, *et al.*, to decompose (at 64.5°) much faster than the isomeric *tert*-butyl perester, yielding methyl ethyl ketone and acetic acid as major products *via* a cyclic transition state.[15]

It was reported that α-phenylethyl peroxyacetate $CH_3C(=O)OOCH(CH_3)Ph$ is sufficiently stable to be isolated upon reacting α-phenylethyl hydroperoxide with ketene.[9] Our preliminary experiments, however, indicate that on reacting PBA with $Ph(CH_3)C=N_2$ in CCl_4 solution again only acetophenone and benzoic acid are formed; furthermore, pmr spectra of the above said reaction solution at *ca.* −8° showed no evidence for intermediate formation of α-phenylethyl peroxybenzoate.

In conclusion, the results so far collected seem to point out that mechanism I should be preferred over mechanism II for the reactions studied; further work, presently in progress in these laboratories, is aimed to elucidate other aspects of the reactivity of diazoalkanes toward peroxy acids as well as toward other organic peroxides.

Experimental Section

Materials and Apparatus.—Melting points and boiling points are not corrected. Pmr spectra were recorded using a Varian A-60 or Perkin-Elmer R 12 spectrometer (both at 60 MHz) and a 90-MHz Bruker HFX-90 instrument. Ir spectra were obtained employing Perkin-Elmer 337 or 621 spectrophotometers; uv–visible spectra were recorded on a Cary 15 or Coleman-Hitachi 124 instrument.

The **diazoalkanes** listed below were prepared by oxidation of the corresponding hydrazones with Ag_2O or HgO in Et_2O.[16,17]

Diazodiphenylmethane: mp 29–31°; ir (liquid film) 2035 cm^{-1} ($>C=\overset{+}{N}=\overset{-}{N}$); vis max (dioxane) 525 nm (ϵ 94) [lit.[3a,17,18] mp 29–32°; ir (CH_2Cl_2) 2025 cm^{-1}; vis max (EtOH) 525 nm (ϵ 94)].

Diazo(*p*-chlorophenyl)phenylmethane: mp 27–28°; ir (liquid film) 2040 cm^{-1} (CNN); vis max (dioxane) 520 nm (ϵ 74) [lit.[19] mp 26–27°; vis max (MeCN) 526 nm (ϵ 85)].

Diazo(*m*-nitrophenyl)phenylmethane: thick oil; ir (liquid film) 2045 cm^{-1} (CNN); vis max (dioxane] 390 nm (ϵ 570) [lit.[19] oil; vis max (MeCN) 395 nm (ϵ 576)].

Diazo(*p*-nitrophenyl)phenylmethane: mp 80–83°; ir (Nujol) 2045 cm^{-1} (CNN); vis max (dioxane) 425 nm (ϵ 305) (lit.[20] mp 70–78°).

Diazo(*p*-methoxyphenyl)phenylmethane: mp 53–54°; ir (Fluorolube) 203 cm^{-1} (CNN); vis max (dioxane) 530 nm (ϵ 78).

1-Diazo-1-phenylethane: unstable oil; ir (liquid film) 2040 cm^{-1} (CNN); pmr (CCl_4) τ 7.53 (s, 3, $N_2=CCH_3$) and 3.0–2.0 ppm (m, 5, $C_6H_5CN_2$) (lit.[21] mp *ca.* −10°).

Purity of diazoalkanes samples was determined through the following procedure: A weighed amount of diazoalkane was dissolved in a suitable amount of dry dioxane in a volumetric flask; aliquots (2–3 ml) of this stock solution were allowed to react with a known excess of benzoic acid in MeCN (20–30 ml) and the unreacted excess acid was determined by titration with 0.1 *M* $Bu_4N^+OH^-$ in benzene–MeOH (thymol blue). Satisfactorily pure diazo compound samples were stored in a desiccator placed into a freezer (at *ca.* −20°) and used within a few days.

The hydrazones, starting materials for the synthesis of the listed diazoalkanes, have been prepared by the method of Szmant and McGinnis;[22] they were carefully purified by column (silica gel) chromatography (eluents: benzene, $CHCl_3$) and their purity was checked by comparison of their melting points with those reported in the literature,[19,22–24] as well as by recording their ir and pmr spectra.

Peroxybenzoic acid was prepared according to the method given by Swern, *et al.*,[25] using 98% H_2O_2 (FMC Corp.): mp 41–42°;[2] ir (CCl_4) 3260 (OH) and 1732 cm^{-1} (C=O); pmr (benzene-d_6) τ 3.3–2.1 (m, 5, $C_6H_5CO_3H$) and −1.35 ppm (broad s, 1, $-CO_3H$).

Peroxybenzoic acid-*d*$_1$ was obtained by shaking a benzene solution of the peracid-*h* in a separatory funnel with successive small portions of D_2O (Merck, ≥99.5%) deuterium label) until in the pmr spectrum the broad signal at τ −1.35 ppm (see above) had completely disappeared. Upon removal of the solvent *in vacuo*, a white solid residue was obtained which was handled in a drybox, mp 40–42°. The deuterium content of the sample was determined from its ir spectrum in CCl_4; the OH peak at 3260 cm^{-1} was used for analysis, after its extinction coefficient had been evaluated from spectra of the undeuterated acid. The proportion of peroxybenzoic acid-*h* in the deuterio peracid was found to be of *ca.* 4%.

***p*-Nitroperoxybenzoic acid** was also obtained and purified by the Swern's method, mp 136–137° dec (lit.[25] mp 138° dec. Iodometric analysis[25] indicated a purity of 97–99% for all peroxy acids listed above.

Benzhydryl isopropyl ether was synthetized by reacting benzhydryl chloride with *i*-PrONa in *i*-PrOH at reflux: bp 114–115° (0.5 mm); pmr (neat liquid) τ 8.92 [d, 6, J = 6.2 Hz, $CH(CH_3)_2$], 6.43 [heptuplet, 1, J = 6.2 Hz; $CH(CH_3)_2$], 4.62 [s, 1, $(C_6H_5)_2CH$], and 3.2–2.5 ppm [m, 10, $(C_6H_5)_2CH$]. *Anal.* Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.50; H, 8.02.

Benzhydryl benzoate was prepared by reacting benzhydryl alcohol with benzoyl chloride in pyridine; it was recrystallized from aqueous ethanol, mp 87–88° (lit.[3a] mp 87–88°).

Benzene, chloroform, 1,2-dichloroethane, carbon tetrachloride, 2-propanol, dioxane, tetrahydrofuran (THF), and acetonitrile solvents (C. Erba, high purity) were purified according to standard procedures[26] and fractionally distilled through an efficient column. ***N,N*-Dimethylformamide (DMF) and tetrahydrothiophene 1,1-dioxide (sulfolane)** were purified as already reported.[8a]

Reaction Stoichiometry.—The reaction studied was shown to have a stoichiometry of 1 mol of diazoalkane to 1 mol of peracid by the nearly quantitative isolaton of the products. In a typical experiment, DDM (1.0 g, 5.15 mmol) in dry benzene (30 ml) was added dropwise to a stirred solution of PBA (0.72 g, 5.2 mmol) of the same solvent (50 ml) at room temperature. The reaction solution was extracted with five 20-ml portions of 5%

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aqueous $NaHCO_3$, the benzene layer dried ($MgSO_4$), and the solvent removed *in vacuo*, thus yielding 0.88 g (4.83 mmol, 94% yield) of benzophenone, mp 46–48°. The alkaline aqueous extracts were brought up to pH 1 (6 *N* HCl) and in turn extracted with benzene, and the benzene extract was dried ($MgSO_4$) and, after solvent removal, gave 0.61 g (5.0 mmol, 96% yield) of benzoic acid, mp 120–122°. To determine the ketone yields by glpc (Table I), stoichiometric amounts (usually *ca.* 2 mmol) of diazoalkane and peracid were allowed to react in the given solvent containing a known amount of a suitable internal standard, thereafter following the known analytical procedure;[27] glpc data were obtained on a Varian-Aerograph 1520 gas chromatograph using a 7 ft × 0.25 in. 5% SE-30 on Chromosorb W (60–80 mesh) column and a 6 ft × 1/8 in. 10% Carbowax 20M-TPA on Chromosorb W (60–80 mesh) column, tc detector, He carrier gas at *ca.* 30 ml/min.

Kinetics.—Kinetic data were obtained according to standard spectrophotometric techniques.[8a] The change of absorbance with time at the wavelength of maximum absorption in the visible for each diazoalkane (where PBA and reaction products are essentially transparent) was monitored by using a Gilford 2400 recording spectrophotometer equipped with a thermostatic cell holder. Temperature control was better than ±0.5°. Rate constants were obtained from pseudo-first-order integrated plots on the basis of the following equation.

$$-\log (A_t - A_\infty) = (k_1/2.3)t - \log (A_0 - A_\infty)$$

Rate constants reported in Tables II and III are average values from at least two independent experiments whose results of which agree within the limits of experimental errors (±4%). The rate constants obeyed the Arrhenius equation and the activation parameters were evaluated by standard methods;[8a] precision in the estimation of $\Delta H^{\neq}$ is better than ±0.8 kcal mol^{-1} and better than ±3 cal deg^{-1} mol^{-1} for $\Delta S^{\neq}$.

Registry No.—$C_6H_5C(=N_2)C_6H_5$, 883-40-9; $C_6H_5C(=N_2)C_6H_4$-*p*-OCH_3, 20359-74-4; $C_6H_5C(=N_2)C_6H_4$-*p*-Cl, 1140-33-6; $C_6H_5C(=N_2)C_6H_4$-*m*-NO_2, 1218-71-9; $C_6H_5C(=N_2)C_6H_4$-*p*-NO_2, 13271-32-4; 1-diazo-1-phenylethane, 22293-10-3; *p*-nitroperoxybenzoic acid, 943-39-5; benzhydryl isopropyl ether, 5670-79-1; PBA, 93-59-4; PBA-d_1, 31657-65-5.

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Stereochemistry of the Addition of *N*-Arylmaleimides to the Acridizinium Ion[1]

CHARLES K. BRADSHER* AND DONALD J. HARVAN

P. M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

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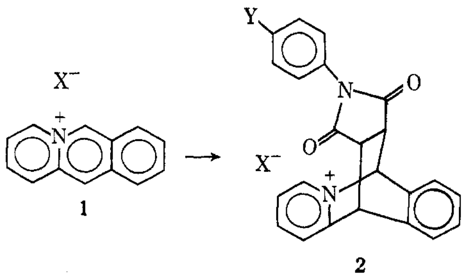
The cycloaddition of *N*-arylmaleimides to the acridizinium nucleus occurs stereospecifically anti with regard to the benzenoid nucleus. In strong acid *cis*-12,13-dicarboxy-6,11-dihydro-6,11-ethanoacridizinium salts undergo rearrangement affording a trans structure. Pyrolysis of the acridizinium arylmaleimide addition products affords derivatives of *N*-aryl-1-(2-pyridyl)naphthalene-2,3-dicarboximide.

The acridizinium ion (1) was the first positively charged alkenophile found to undergo a 4 + 2 cycloaddition reaction.[2] Although recently there has been a large increase in the number of examples of such cycloadditions,[3-6] for only five of the adducts is the *stereochemistry* known. It is already clear that despite the stereoselectivity shown in the cationic addition reaction the presence of the positive charge makes it impossible to apply without modification the rules[7] which have proved so useful in understanding the classical Diels–Alder reaction, and indeed, there exists some evidence that the cationic cycloaddition may not be concerted.[5,8]



The purpose of the present study was to determine whether the stereochemistry of the cycloaddition of *N*-arylmaleimides to the acridizinium ion was altered by changes in polarity of the *N*-aryl group and to learn something about the chemistry of the products. Two general procedures were used for the preparation of the adducts. Either the salt **1** was suspended in acetic acid and heated with the maleimide at 100°, or a melt was formed by heating the reactants at 160–170° without solvents. The high-temperature reaction had the advantage of being quite rapid and giving clean reaction products although the yields were slightly lower. Both reaction conditions led to the isolation of the same product, which seemed to consist of a single stereoisomer. As may be seen from Table I all adducts possessed carbonyl absorptions at 1704–1715 and 1783–1790 cm^{-1}. As would be expected from known imide spectra,[9] the lower frequency absorptions (asymmetric carbonyl stretch) were significantly the weaker of the two.

The nmr showed the expected doublets at approximately δ 5.7 for the bridgehead proton at C-11 and δ

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