its concentration. Its adaptation for use in DAS is rendered difficult by the insufficiently known association equilibria of the mostly ionic reagents, by their enhanced basicity, and by the possible reactivity of their ion pairs.

Ion Pairs as Possible Direct Substrates in E2C Reactions. Once it is accepted that ion pairs are more likely to undergo nucleophilic attack than the undissociated substrate, it may be expected that, at least in some cases, they are preferred to the latter in elimination reactions also. One might wonder if the prevalence of DAS as media for E2C reactions should not be ascribed to their proficiency at generating ion pairs. Some of the most notable characteristics of E2C,[36] such as the absolute trans elimination and a "loose" transition state, become self-explanatory, when ion pairs are considered as the direct substrates.[37,38] Research in progress in our laboratory indicates that the E2 reaction of tertiary alkyl bromides with bromide ion is competitively inhibited by added azide ion.

Registry No.—1, 4283-80-1.

References and Notes

(1) Part I: M. Anteunis and H. L. Peeters, *J. Org. Chem.*, **39**, 307 (1975).
(2) In part from the Ph.D. thesis of H. L. Peeters, Rijksuniversiteit Gent, 1973.
(3) A. J. Parker, *Quart. Rev., Chem. Soc.*, 163 (1962).
(4) Due to the ready solubility of AgBr in excess Br^-, with the attendant formation of $AgBr_2^-$ in DAS of high dielectric constant, a silver-silver bromide system is of no use in DMF.
(5) N. A. Rumbaut and H. L. Peeters, *Bull. Soc. Chim. Belg.* **79,** 45 (1970).
(6) Under typical reaction conditions $C_{Br^-} = 10^{-4}$ *M* corresponds to only 0.1% conversion and yet reduces C_{Ag^+} to 3×10^{-11} *M*.
(7) R. Alexander, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **89,** 3703 (1967).
(8) E. Price in "The Chemistry of Non-Aqueous Solvents," Vol. 1, J. J. Lagowski, Ed., Academic Press, New York, N. Y., 1966, p 67.
(9) If this precaution is omitted, consistently high values are obtained for the reaction rates.
(10) N. Kornblum and R. K. Blackwood, *J. Amer. Chem. Soc.*, **78,** 4037 (1956).
(11) S. D. Ross and M. Labes, *J. Amer. Chem. Soc.*, **79,** 4155 (1957).
(12) D. Cook and A. J. Parker, *J. Chem. Soc. B,* 142 (1968).
(13) A temperature correction was applied to the values derived from runs 14 and 18, based on E_a = 90.4 kJ mol^{-1}.
(14) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78,** 2770 (1956).
(15) H. M. R. Hofmann, *J. Chem. Soc.*, 6753 (1965).
(16) P. B. D. de la Mare, E. D. Hughes, C. K. Ingold, and Y. Pocker, *J. Chem. Soc.*, 2930 (1954); the value cited was derived from rate constants obtained by extrapolation from unimolecular reaction rates.
(17) A. Streitwieser, *J. Amer. Chem. Soc.* **78,** 4935 (1956).
(18) D. V. Banthorpe, "Elimination Reactions," Elsevier, Amsterdam, 1963, p 52.
(19) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940).
(20) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 450.
(21) This expression corresponds to the free azide ion concentration, as N_3H is a very weak acid in DMF.
(22) R. A. Sneen, *Accounts Chem. Res.*, **6,** 46 (1973), and references cited therein.
(23) Numbers were assigned to the different species and intermediates, in accordance with their place in the scheme (see Figure 5) presented in this paper, not with the chronology of appearance in the text. Product **7** is identical with structure **2** in the previous paper.[1]
(24) In fact, they preferred to picture **7** as quaternary ion, but at the time the greater nucleophilicity of oxygen in ambident reagents was insufficiently appreciated. See also comments in ref 1.
(25) S. G. Smith and S. Winstein, *Tetrahedron,* **3,** 317 (1958); R. Kuhn and H. Trischman, *Justus Liebigs Ann. Chem.*, **611,** 117 (1958); R. T. Major and H. J. Hess, *J. Org. Chem.*, **23,** 1563 (1958).
(26) H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.* **84,** 3599 (1962).
(27) H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.*, **85,** 2181 (1963).
(28) See, *e.g.*, D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 4054 (1960).
(29) S. Winstein and G. C. Robinson, *J. Amer. Chem. Soc.*, **80,** 169 (1958); S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *ibid.* **83,** 885 (1961); notations used were adapted from J. M. W. Scott, *Can. J. Chem.*, **48,** 3807 (1970).
(30) J. M. W. Scott and R. E. Robertson, *Can. J. Chem.*, **50,** 167 (1972).
(31) A. J. Parker, *Advan. Org. Chem.*, **5,** 1 (1965).
(32) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91,** 6031 (1969).
(33) R. A. Sneen and H. M. Robbins, *J. Amer. Chem. Soc.*, **91,** 3101 (1969).
(34) J. L. Kurz and J. C. Harris, *J. Amer. Chem. Soc.*, **92,** 4117 (1970); D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93,** 4821 (1971); D. J. Mc Lennan, *J. Chem. Soc., Perkin Trans. 2,* 1577 (1972); M. H. Abraham, *J. Chem. Soc., Chem. Commun.*, 51 (1973).
(35) J. M. W. Scott, *Can. J. Chem.*, **48,** 3807 (1970); F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, **94,** 2119 (1972); F. G. Bordwell, *Accounts Chem. Res.*, **5,** 374 (1972); V. J. Shiner, Jr., and R. D. Fisher, *J. Amer. Chem. Soc.*, **93,** 2553 (1971).
(36) P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *J. Amer. Chem. Soc.*, **94,** 2240 (1972), and preceding papers.
(37) The repeatedly cited objection that in the transition state C_α possesses but little positive charge[36] appears to have been deduced from relative rate measurements on only two substrates, where furthermore other influences might have been at work.[38]
(38) D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5029 (1970).

Kinetics of the Oxidative Cleavage of α-Phenylbenzoins by Alkaline Hypobromite in Aqueous Dioxane[1]

Yoshiro Ogata* and Kenji Nagura

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

Received August 19, 1974

Oxidative cleavage of α-phenylbenzoins [$Ar^1Ar^2C(OH)COAr^3$] by hypobromous acid to give benzophenones and benzoic acids has been studied kinetically in alkaline 50 vol. % aqueous dioxane. The effect of ring substituents on the rate at 25° gives ρ values of +2.8 for the σ values on Ar^3 and +2.3 for the sum of σ values on Ar^1 and Ar^2. A mechanism is postulated, which involves the formation of hypobromite ester of substrate followed by a rate-determining attack of hydroxide ion on the carbonyl carbon to give the products.

Several papers were published on the oxidation of alcohols by halogen to carbonyl compounds.[2–4] The workers in the mechanistic studies of these reactions were interested mainly in speculation of the transition state, attacking agents, and their relative reactivities. There are a number of evidences[2] that the halogen oxidation of alcohol in acidic solutions occurs *via* a rate-determining abstraction of α-hydride ion by molecular halogen. On the other hand, for the oxidation by alkaline hypohalite, the intermediacy of hypohalite ester of substrate was postulated in some oxidations of alcohols, *i.e.*, the oxidation of alcohols[3] and the oxidative decarboxylation of α-hydroxycarboxylic acids.[4]

The oxidative decarboxylation of α-hydroxycarboxylic acids by alkaline hypohalite in an aqueous solution was re-

Table I
Pseudo-First-Order Rate Constant k_{obsd} for the Reaction of α-Phenylbenzoin with Bromine in Alkaline Aqueous Dioxane (50 vol. %) at 25°

$[Br_2]_a$,[a] M	$[NaOH]_a$,[a] M	$10^4 k_{obsd}$, sec^{-1}	$[Br_2]_a$,[a] M	$[NaOH]_a$,[a] M	$10^4 k_{obsd}$ sec^{-1}
0.100	0.100	6.04	0.100	0.350	13.0
0.100	0.110	7.11	0.100	0.500	13.2
0.100	0.125	10.1	0.200	0.200	12.4
0.100	0.150	13.6	0.500	0.500	31.2
0.100	0.200	12.8			

[a] Added concentration.

Table II
Relative Rate (k_{rel})[a] of the Reaction of Substituted α-Phenylbenzoins $[(p\text{-Y-}C_6H_4)(p\text{-Z-}C_6H_4)C(OH)\text{-}CO(C_6H_4\text{-W-}p)]$ with Bromine in Alkaline Aqueous Dioxane (50 vol. %) at 25°

	Substituents			
Registry no.	Y	Z	W	k_{rel}[a]
4237-46-1	H	H	H	1
53432-76-1	Cl	H	H	3.73
53432-77-2	Cl	Cl	Cl	37.9
53500-16-6	H	Cl	Cl	14.0
53432-78-3	Cl	Cl	MeO	1.78
53432-79-4	H	Cl	MeO	0.460
53432-80-7	H	MeO	Cl	0.987
4338-69-6	H	H	MeO	0.178
53432-81-8	H	Me	Me	0.121

[a] $k_{rel} = k_2(\text{substituted})/k_2(\text{unsubstituted})$. See eq 2.

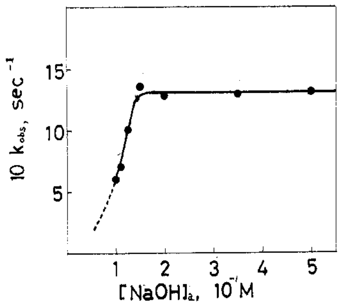


Figure 1. The effect of $[NaOH]_a$ on the rate of oxidative cleavage of α-phenylbenzoin by hypobromous acid in 50 vol. % aqueous dioxane at 25°; $[Br_2]_a$ = 0.100 M. Subscript a means added concentration.

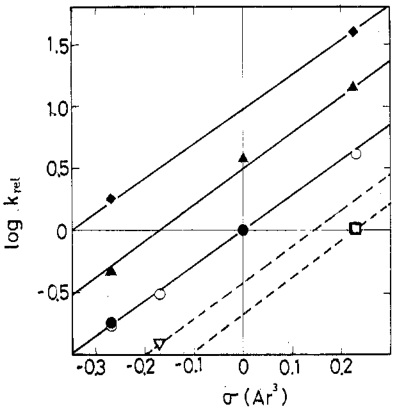
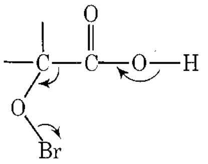
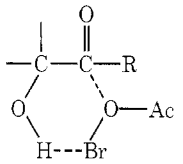


Figure 2. The plot of log k_{rel} against $\sigma(Ar^3)$ for the oxidative cleavage of α-phenylbenzoins $[Ar^1Ar^2C(OH)\text{–}COAr^3]$ by hypobromous acid in 50 vol. % aqueous dioxane at 25°: ◆, $Ar^1 = Ar^2 = p\text{-}Cl\text{–}C_6H_4$; ▲, Ar^1 = Ph, $Ar^2 = p\text{-}Cl\text{–}C_6H_4$; ●, $Ar^1 = Ar^2$ = Ph; ▽, Ar^1 = Ph, $Ar^2 = p\text{-}Me\text{–}C_6H_4$; □, Ar^1 = Ph, $Ar^2 = p\text{-}MeO\text{–}C_6H_4$. Open circle values were obtained from the intercepts in Figure 3.

ported[4] to have a mechanism[4b-d] which involves an intermediate such as A.



A



B

Donnelly and O'Donnell[5] reported that some α-ketols reacted with bromine in acetic acid to give the corresponding ketones and postulated a mechanism involving a six-membered cyclic transition state such as B because of the suppression of reaction by acetylation of hydroxy group and the necessity of the α-carbonyl group for the reaction.

The authors found that the bromine oxidation of α-ketols (α-phenylbenzoins) occurs also in alkaline solutions and is base catalyzed. The present paper describes our kinetic studies by means of glc and analysis of the reactant or product to speculate a mechanism for this reaction.

Results

Products. The reaction of α-phenylbenzoins $[Ar^1Ar^2C(OH)COAr^3$, **1**] with bromine in alkaline aqueous dioxane at 25° gives the corresponding benzophenones $(Ar^1Ar^2C{=}O)$ and benzoic acids (Ar^3COOH) in good yields. Similar results were obtained with the oxidation of α-phenylbenzoin by *tert*-butyl hypochlorite in *tert*-butyl alcohol containing sodium *tert*-butoxide at 25°, while the treatment of α-phenylbenzoin with molecular bromine in dry benzene gives no benzophenone.

Rate. The rates of the reaction of α-phenylbenzoins with a mixture of bromine and sodium hydroxide in 50 vol. % aqueous dioxane (1 vol. of dioxane mixed with 1 vol. of water) at 25° were measured by following α-phenylbenzoins or benzophenones by means of glc. Bromine (0.1–0.5 M) and sodium hydroxide (0.1–0.5 M) are much more in excess to the equivalent amount of substrate (0.005 M) so that the pseudo-first-order plots were linear up to 50–75% conversion.

$$v = k_{obsd}[\mathbf{1}] \qquad (1)$$

The kinetic data are listed in Table I. The value of k_{obsd} is proportional to the added concentration of bromine, $[Br_2]_a$, when added sodium hydroxide concentration, $[NaOH]_a$, was equal to $[Br_2]_a$.

$$v = k_2[\mathbf{1}][Br_2]_a \qquad (2)$$

As shown in Figure 1, the rate constant increases with increasing concentration of added sodium hydroxide at lower basicity, while it holds constancy at higher basicity.

Substituent Effects. The rates for some para-substituted α-phenylbenzoins $[Ar^1Ar^2C(OH)\text{–}COAr^3]$ were measured in 50 vol. % aqueous dioxane at 25°. The results are summarized in Table II. Relative rates $[k_2(\text{substituted})/k_2(\text{unsubstituted})]$ are plotted against Hammett's σ. The effect of substituents on the acyl side $[\sigma(Ar^3)]$ is shown in Figure 2; the plot which uses the sum of σ's for substituents on the carbinol side (Ar^1 and Ar^2) is shown in Figure 3. Assuming that the effect of substituent in Ar^1 and Ar^2 on $\rho(Ar^3)$ is negligible, the lines in Figure 2 were drawn to have the same slope. The lines in Figure 3 were drawn on the similar assumption. The intercept values at σ = 0 in

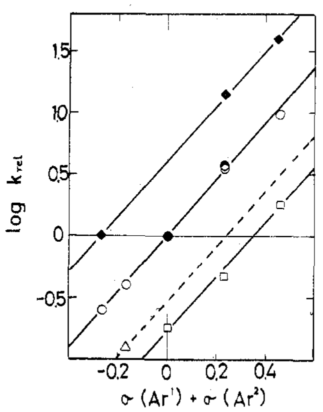


Figure 3. The plot of log k_{rel} against $\sigma(\text{Ar}^1) + \sigma(\text{Ar}^2)$ for the oxidative cleavage of α-phenylbenzoins [$\text{Ar}^1\text{Ar}^2\text{C(OH)–COAr}^3$] by hypobromous acid in 50 vol. % aqueous dioxane at 25°: ♦, $\text{Ar}^3 = p\text{-Cl–C}_6\text{H}_4$; ●, $\text{Ar}^3 = \text{Ph}$; △, $\text{Ar}^3 = p\text{-Me–C}_6\text{H}_4$; □, $\text{Ar}^3 = p\text{-MeO–C}_6\text{H}_4$. Open circle values were obtained from the intercepts in Figure 2.

Figure 2 were plotted as open circles in Figure 3; they were linear and justify the above assumption. The intercept values in Figure 3 were plotted in Figure 2 similarly and gave a straight line. These correlations give ρ values of +2.8 for σ values on Ar^3 and +2.3 for the sum of σ values on Ar^1 and Ar^2 [$\sigma(\text{Ar}^1) + \sigma(\text{Ar}^2)$].

Discussion

The oxidative cleavage of α-phenylbenzoin is favored by the presence of base. Added bromine can exist, *e.g.*, in the forms Br_2, HOBr, OBr^-, and Br_3^-, whose contents depend on the basicity of the solution.

$$\text{Br}_2 + \text{OH}^- \overset{K_3}{\rightleftharpoons} \text{HOBr} + \text{Br}^- \tag{3}$$

$$\text{HOBr} + \text{OH}^- \overset{K_4}{\rightleftharpoons} \text{OBr}^- + \text{H}_2\text{O} \tag{4}$$

$$\text{Br}_2 + \text{Br}^- \overset{K_5}{\rightleftharpoons} \text{Br}_3^- \tag{5}$$

The equilibrium constants K_3 ($[\text{HOBr}][\text{Br}^-]/[\text{Br}_2][\text{OH}^-] = 9.6 \times 10^5$)[4b,6] and K_4 ($[\text{OBr}^-]/[\text{HOBr}][\text{OH}^-] = 2.1 \times 10^5$)[4b,6] are large and the constant K_5 ($[\text{Br}_3^-]/[\text{Br}_2][\text{Br}^-] = 16$) is fairly small, so that added bromine should be most converted to hypobromous acid (HOBr), when $[\text{Br}_2]_a$ is nearly equal to $[\text{NaOH}]_a$, and HOBr should be converted to OBr^- when $[\text{Br}_2]_a < [\text{NaOH}]_a$.

Bell-shaped pH-rate profiles were reported in the oxidative decarboxylation of α-hydroxycarboxylic acids by hypobromous acid.[4] Barker[4d] and Pink[4b,c] interpretated these phenomena by assuming that HOBr is a sole effective oxidant; *i.e.*, the rate increases with increasing concentration of HOBr at lower pH and decreases with increasing conversion of HOBr to inert OBr^- at higher pH.

Our results on the oxidation of α-phenylbenzoin by hypobromous acid in alkaline aqueous dioxane (Figure 1) are different from the case of α-hydroxycarboxylic acids; *i.e.*, the rate constant increases with increasing concentration of added NaOH at lower basic solution, while it holds constancy at higher basic solution. This suggests that the rate should be proportional to $[\text{OBr}^-]$; *i.e.*, $[\text{OBr}^-]$ increases with increasing added NaOH at lower basicity and becomes constant at higher basicity.

However, hypobromous acid, but not OBr^-, should be a more effective oxidant for this reaction of α-phenylbenzoin because of the following reasons: (i) the oxidative cleavage of α-ketols proceeds by *tert*-butyl hypochlorite in *tert*-butyl alcohol containing sodium *tert*-butoxide or by acetyl hypobromite in acetic acid,[5] where hypohalite ion (OX^-) cannot be formed; (ii) ions of Br_3^- and OBr^- are inert in the oxidation of alcohols[2,3] and α-hydroxycarboxylic acids;[4] (iii) the treatment of α-phenylbenzoin with molecular bromine in dry benzene does not yield the cleavage products.

Consequently, the rate should be expressed as

$$\begin{aligned} v &= k[\mathbf{1}][\text{OBr}^-] \\ &= kK_4[\mathbf{1}][\text{HOBr}][\text{OH}^-] \end{aligned} \tag{6}$$

This suggests that the mechanism involves the participation of one molecule each of **1** and HOBr and of OH^- in a rate-determining step. These facts can be explained by a mechanism such as Scheme I.

Scheme I

$$\underset{\mathbf{1}}{\text{Ar}^1\text{Ar}^2\text{C(OH)COAr}^3} + \text{HOBr} \underset{\text{fast}}{\overset{K_7}{\rightleftharpoons}} \underset{\mathbf{2}}{\text{Ar}^1\text{Ar}^2\text{C(OBr)COAr}^3} + \text{H}_2\text{O} \tag{7}$$

$$\mathbf{2} + \text{OH}^- \xrightarrow[\text{slow}]{k_8} \text{Ar}^1\text{Ar}^2\text{C=O} + \text{Ar}^3\text{CO}_2\text{H} + \text{Br}^- \tag{8}$$

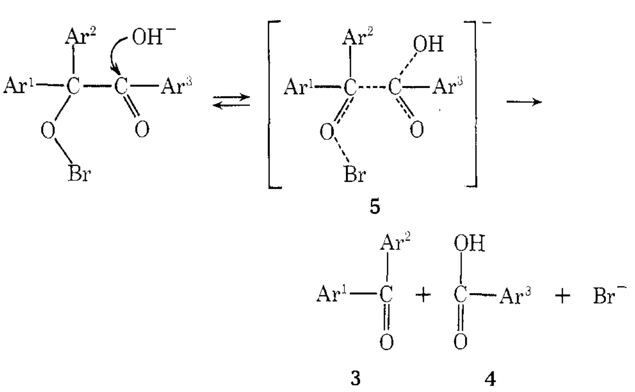
Hypobromite ester **2** formed by equilibrium 7 of substrate **1** with hypobromous acid[4] is attacked by hydroxide ion on the carbonyl carbon to give products. In this scheme, if eq 8 is a slow step, the rate should be expressed as

$$v = (k_8K_7/[\text{H}_2\text{O}])[\mathbf{1}][\text{HOBr}][\text{OH}^-] \tag{9}$$

which is consistent with our observation (eq 6).

The observed large ρ value of +2.8 for the substituents on Ar^3 is consistent with a nucleophilic attack of a base on the carbonyl carbon. Similar results (ρ = +2–3) were reported in the nucleophilic reactions of benzoyl compounds.[7] Electron-attracting groups on Ar^1 and Ar^2 should facilitate the formation of **2** (step 7) and an attack of hydroxide ion on the carbonyl group. The large ρ value of +2.3 for the substituents on Ar^1 and Ar^2 suggests that step 8 involves a transition state as **5** in Scheme II, where the α carbon is carbanion-like. Hydroxide ion attacks the carbonyl carbon to give complex **5**, which has a carbanion-like property at the α carbon, and then bromide ion and benzoic acid are eliminated to give benzophenone. The transition states may be more polarized forming species $\text{Ar}^1\text{Ar}^2\text{C–OBr}$ and Ar^3COOH. But it is difficult at present to decide which is the transition state.

Scheme II

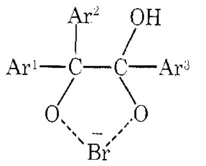


An alternative transition state is the one involving a cyclic intermediate **6**, which should give a $\rho(\text{Ar}^1, \text{Ar}^2)$ value lower than the observed ρ because of the decrease of the carbanion-like property of the α carbon.

Table III
Physical Properties of α-Phenylbenzoins [$(p\text{-Y-C}_6H_4)(p\text{-Z-C}_6H_4)C(OH)\text{-}CO(C_6H_4\text{-W-}p)$] and Elemental Analyses of New Compounds

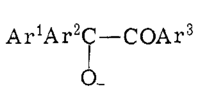
Substituents				% calcd					% found			
Y	Z	W	Mp, °C	C	H	O	Cl	Mol formula	C	H	O	Cl
H	H	H	84.0–85.2 (lit.[10a] 83–85)									
Cl	H	H	83.5–85.0 (lit.[10b] 84)									
Cl	Cl	Cl	139–140	61.33	3.35	8.17	27.15	$C_{20}H_{13}O_2Cl_3$	61.67	3.37	9.78	26.41
H	Cl	Cl	114–116	67.24	3.95	8.96	19.85	$C_{20}H_{14}O_2Cl_2$	67.33	3.97	8.72	19.24
Cl	Cl	MeO	130–133	65.13	4.16	12.39	18.31	$C_{21}H_{16}O_3Cl_2$	65.02	4.08	11.63	18.15
H	Me	Me	Liq	83.51	6.37	10.11		$C_{22}H_{20}O_2$	83.27	6.39	9.83	
H	H	MeO	105–107	79.22	5.70	15.08		$C_{21}H_{18}O_3$	79.30	5.81	14.93	
H	Cl	MeO	Liq	71.49	4.80	13.60	10.05	$C_{21}H_{17}O_3Cl$	71.48	4.98	13.54	9.78
H	MeO	Cl	93–94	71.49	4.80	13.60	10.05	$C_{21}H_{17}O_3Cl$	71.22	4.80	13.42	9.88

Scheme II is similar to E2 elimination. The substituent effect on the rate of E2 elimination of HBr from β-arylethyl bromides ($\rho = +2.14$)[8] is fairly close to the observed values (+2.3). Further, a similar mechanism was suggested in the alkali cleavage of α-hydroperoxy ketone.[9a]



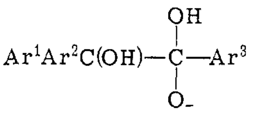
6

Other mechanisms, which involve the formation of intermediates such as **7a** and **7b** formed by the equilibrium of **1**



$Ar^1Ar^2\underset{O^-}{C}—COAr^3$

7a

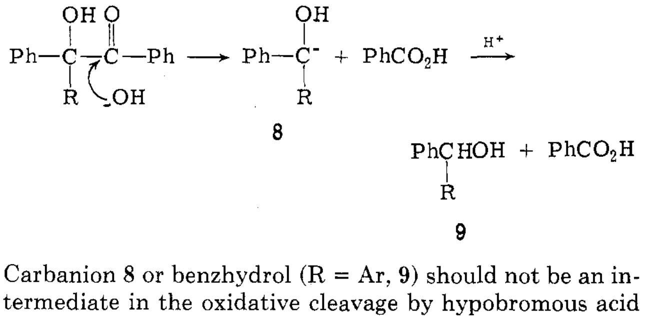


$Ar^1Ar^2C(OH)—\underset{O^-}{\overset{OH}{C}}—Ar^3$

7b

with hydroxide ion followed by an attack of hypobromous acid, cannot explain the observed substituent effects described below, although they may lead to the observed rate eq 6. The observed ρ values are much larger than those predicted from the correlation of pK_a of substrate with σ, where K_a is an equilibrium constant for $1 \rightleftharpoons 7a + H^+$. An electrophilic attack of hypobromous acid would decrease further the ρ values. Moreover, the mechanism involving an intermediate **7a** would require that $\rho(Ar^1 + Ar^2) > \rho(Ar^3)$. The mechanism involving an intermediate **7b** which is formed by the OH^- attack on the carbonyl carbon would require also a smaller $\rho(Ar^1 + Ar^2)$ value than observed because of the insulation of Ar^1 and Ar^2 from the carbonyl group by the α carbon and an electrophilic attack of hypobromous acid.

Sharp and Miller[9b] reported on the alkali cleavage of α-substituted benzoins in aqueous methanol at *ca.* 60°, suggesting the mechanism



8

9

Carbanion **8** or benzhydrol (R = Ar, **9**) should not be an intermediate in the oxidative cleavage by hypobromous acid because of the following reasons. (i) The cleavage with alkali alone, which proceeds at *ca.* 60°, cannot occur in our conditions (at 25°). (ii) The reaction of **8** with HOBr would be fast, while the observed rate depends on the concentration of HOBr. If the reaction of HOBr with **8**, which is in a mobile equilibrium with **7b**, were a slow step, the rate would be suppressed by produced Ar^3COOH in the equilibrium. (iii) No abnormal product (RCOOH) was detected, which was obtained in a considerable yield in the case of the cleavage with alkali alone.[9b]

Donnelly's mechanism should be excluded at least in an alkaline solution, since it cannot explain the rate law and substituent effect.

Experimental Section

Materials. Para-substituted α-phenylbenzoins were prepared by treatment[10] of phenyl- and *p*-chlorophenylmagnesium bromide with corresponding substituted benzils ($p\text{-Z-C}_6H_4\text{-CO-CO-C}_6H_4\text{-W-}p$). They were purified by recrystallizations from *n*-hexane when they were solid and by column chromatography (silica gel–benzene) when they were liquid. The substituents, melting points, and elemental analyses for new compounds of α-phenylbenzoins [$(p\text{-Y-C}_6H_4)(p\text{-Z-C}_6H_4)C(OH)\text{-}CO(C_6H_4\text{-W-}p)$] are listed in Table III. They were identified by ir spectra.

Products. α-Phenylbenzoin (0.6 g) was treated with a mixture of bromine (0.1 *M*) and sodium hydroxide (0.1 *M*) in 50 vol. % aqueous dioxane (1 vol. of dioxane mixed with 1 vol. of water) (100 ml) at 25° for 3 hr. The reaction mixture was extracted with benzene and washed with aqueous $Na_2S_2O_3$ and water. Benzophenone (0.3 g, 80%; mp 160–161°) was obtained from the organic layer and was identified by melting point, glc, and ir spectra which were consistent with those of the authentic sample. A Hitachi K-53 gas chromatograph with a flame ionization detector was used with a column packed with DEGS (13%) on Chromosorb W at the temperature increasing by 10°/min from 140 to 225° or SE-30 (3%) on Chromosorb W at the temperature increasing by 10°/min from 200 to 280° with N_2 as a carrier gas in a flow rate of 45–50 cm^3/min. Benzoic acid (0.07 g, 30%) was obtained from the aqueous layer by extraction with benzene after acidifying with aqueous HCl; mp 122°. Other para-substituted α-phenylbenzoins ($Ar^1Ar^2C(OH)COAr^3$) yielded corresponding benzophenones ($Ar^1Ar^2C{=}O$) by the similar treatments. The products were identified by glc analysis in comparison with the authentic samples which were of commercial source or were prepared from the corresponding benzhydrols.

Similar results have been obtained with the oxidative cleavage of α-phenylbenzoin with *t*-BuOCl in *t*-BuOH containing *t*-BuONa at 25°. Products were benzophenone and *tert*-butyl benzoate. On the other hand, the treatment of α-phenylbenzoin (0.1 g) with molecular bromine (0.3 g) in dry benzene (5 ml) gave no benzophene but two other products (*ca.* 5%, unknown).

Kinetics. The rate of oxidation of α-phenylbenzoins (3.0–4.0 × 10^{-3} *M*) by a mixture of excess bromine (0.1–0.5 *M*) and NaOH (0.1–0.5 *M*) at $[NaOH]_a > [Br_2]_a \gg [substrate]_0$ was measured by means of glc analysis of the remaining α-phenylbenzoins or produced benzophenones, where subscripts a and 0 mean added and initial concentrations, respectively.

A kinetic procedure was as follows. A mixture of appropriate amounts of NaOH and Br_2 was thermostated at 25°. The reaction was started by addition of α-phenylbenzoin. At appropriate time intervals, aliquots were taken out and extracted with benzene. The contents of α-phenylbenzoin and benzophenone were measured by glc with a column packed with SE-30 as stated above. The plot of log ([substrate]$_0$/[substrate]) against time gives a straight line up to 50–75% conversion. The data were reproducible to within 5%.

Acknowledgments. The authors are grateful to Shionogi Pharmaceutical Co. for their elemental analyses and Mitsubishi Kasei and Mitsubishi-Monsanto Chemical Co. for their gifts of solvents.

Registry No.—Bromine, 7726-95-6; dioxane, 123-91-1; hypobromous acid, 13517-11-8.

References and Notes

(1) Contribution No. 210.
(2) P. Aukett and I. R. L. Barker, *J. Chem. Soc., Perkin Trans. 2,* 568 (1972), and references therein.
(3) (a) N. C. Deno and N. H. Potter, *J. Amer. Chem. Soc.,* **89,** 3555 (1967); (b) M. C. Agrawal and S. P. Mushran, *J. Chem. Soc., Perkin Trans. 2,* 762 (1973); (c) Y. Ogata and K. Nagura, *J. Org. Chem.,* in press.
(4) (a) R. M. Purkayastha and R. C. Ghosh, *Z. Phys. Chem.,* **7,** 285 (1930); (b) J. M. Pink and R. Stewart, *Can. J. Chem.,* **49,** 649 (1971); (c) J. M. Pink and R. Stewart, *ibid.,* **49,** 654 (1971); (d) P. Aukett and I. R. L. Barker, *J. Chem. Soc., Perkin Trans. 2,* 965 (1972); (e) B. Perlmutter-Hayman and Y. Weissmann, *J. Amer. Chem. Soc.,* **91,** 668 (1969); (f) M. Caplow, *ibid.,* **93,** 230 (1971).
(5) J. A. Donnelly and R. O'Donnell, *J. Chem. Soc., Perkin Trans. 1,* 1875 (1972).
(6) J. M. Pink, *Can. J. Chem.,* **48,** 1169 (1970).
(7) (a) A. J. Speziale and D. E. Bissing, *J. Amer. Chem. Soc.,* **85,** 3878 (1963); (b) N. Wang and C. H. Wang, *J. Org. Chem.,* **36,** 3178 (1971).
(8) (a) C. H. Depuy and D. H. Froemsdoef, *J. Amer. Chem. Soc.,* **79,** 3710 (1957); (b) C. H. Depuy and C. A. Bishop, *ibid.,* **82,** 2532 (1960); (c) W. H. Saunders, Jr., and D. H. Edison, *ibid.,* **82,** 138 (1960).
(9) (a) F. G. Bordwell and A. C. Knipe, *J. Amer. Chem. Soc.,* **93,** 3416 (1971); (b) D. B. Sharp and E. L. Miller, *ibid.,* **74,** 5643 (1952).
(10) (a) M. S. Kharash, W. Nudenberg, and S. Archer, *J. Amer. Chem. Soc.,* **65,** 495 (1943); (b) J. F. Eastham, J. E. Huffaber, V. F. Raaen, and C. J. Collins, *ibid.,* **78,** 4323 (1956); (c) M. A. Mihailescu and S. P. Caragea, *Bull. Acad. Roum., Sect. Sci.,* **12,** 7 (1929); *Chem. Abstr.,* **24,** 2116 (1930).

Homoconjugation Effects in the Diels–Alder Reaction of 1-(Substituted phenyl)-3,4-dimethylenepyrrolidines

Peter V. Alston and Raphael M. Ottenbrite*

Department of Chemistry and Pharmaceutical Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284

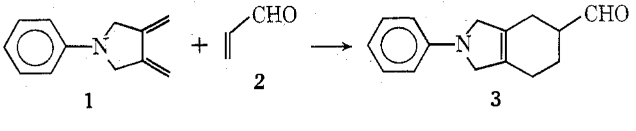
Received July 19, 1974

A kinetic study of the substituent effect on the diene reactivity of 1-(substituted phenyl)-3,4-dimethylenepyrrolidines in the Diels–Alder reaction was carried out. It was found that electron-withdrawing groups increased the rate of reaction and electron-donating groups decreased the rate. Hammett correlations of this substituent effect were obtained with $\sigma\ n$ values in three solvents: methylene chloride, dimethyl sulfoxide, and tetrahydrofuran. A determination of the relative frontier orbital energies of these exocyclic dienes indicated that the effect of the substituent on the rate of the Diels–Alder reaction was primarily through a homoconjugative interaction. This interaction altered the LUMO energies of the diene causing a novel substituent effect on the reaction rate.

The effect of spiroconjugation and homoconjugation on the chemical reactivity and the electronic spectrum of spirarenes is currently of considerable interest.[1-4] It has been found that two seemingly independent π systems with a specific stereochemical relationship interact through a spatial mode such that the energies of the respective HOMO's and LUMO's are influenced. It is well known[5-10] that the HOMO and LUMO energies of the reactants in the Diels–Alder reaction can be used to predict both the reactivity and regioselectivity of this reaction. Recently Semmelhack, *et al.,*[11] have attempted to explain diene reactivity in the Diels–Alder reaction through spiroconjugative effects. In this paper, we have investigated the effect of homoconjugation on the diene reactivity of 1-(substituted phenyl)-3,4-dimethylenepyrrolidines in the Diels–Alder reaction.

Kinetic Study

The 1-(substituted phenyl)-3,4-dimethylenepyrrolidines (**1**) were allowed to react with acrolein (**2**) to give the corresponding Diels–Alder adducts (**3**) in quantitative yield (determined by nmr). The concentrations of the reactants at any given time during the reaction of the exocyclic dienes with acrolein were determined by means of nmr spectroscopy. The reaction which is shown below is uncomplicated by side reactions. The rate of reaction was usually followed by observing the change in chemical shift of the aldehyde proton in going from acrolein to the Diels–Alder product.[12] This change in chemical shift was 4–8 Hz depending on the solvent used and afforded distinct integrations of the area of each peak. In the cases where the change in chemical shift was not large enough to give a complete separation of the reactant and product aldehyde proton peaks, the reaction was followed by the disappearance of the vinyl peaks (δ 5.55) of the diene and the aldehyde proton peaks were used as the internal standard.



It was found that a plot of log ([acrolein]$_t$/[diene]$_t$) *vs.* time for all dienes used yielded a straight line. This linear relationship indicates that the reaction is second order overall, first order with respect to acrolein and the diene. The rate constant of the reaction was determined from the slope of the straight line as follows.

$$\text{rate constant } (k) = \frac{2.303 \times \text{slope} \times 60 \text{ sec/min}}{[\text{acrolein}]_{t=0} - [\text{diene}]_{t=0}}$$

Hydroquinone was used as an inhibitor of the polymerization of the reactants in the reaction. The concentration of hydroquinone used was usually 0.01–0.02 *M.* It was found that the concentration of hydroquinone had no effect on the observed rate constant of this reaction.

The possibility that charge-transfer interaction between the aryl group of the diene and acrolein could have an effect on the observed rate constant was investigated. The reaction of 1-(*p*-methoxyphenyl)-3,4-dimethylenepyrrolidine with acrolein was carried out with varying concentra-