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Nucleofugality of Phenyl and Methyl Carbonates

Bernard Denegri and Olga Kronja*

Faculty of Pharmacy and Biochemistry, University of Zagreb, Ante Kovačića 1, 10000 Zagreb, Croatia

kronja@pharma.hr

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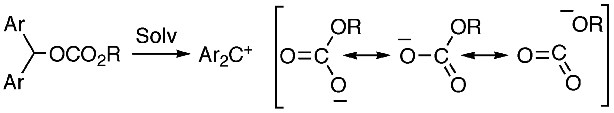

$k_{rel} = 1$ for R = CH_3
$k_{rel} \approx 20$ for R = C_6H_5

A series of X,Y-substituted benzhydryl phenyl carbonates **1** and X,Y-substituted benzhydryl methyl carbonates **2** were subjected to solvolysis in different methanol/water, ethanol/water, and acetone/water mixtures at 25 °C. The LFER equation, $\log k = s_f(E_f + N_f)$, was used to derive the nucleofuge-specific parameters (N_f and s_f) for phenyl carbonate (**1LG**) and methyl carbonate (**2LG**) leaving groups in a given solvent in S_N1 type reaction. Kinetic measurements showed that phenyl carbonates solvolyze one order of magnitude faster than methyl carbonates. Optimized geometries of **1LG** and **2LG** at B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p), and MP2(full)/6-311++G(d,p) levels revealed that negative charge delocalization in carbonate anions to all three oxygen atoms occurs due to negative hyperconjugation. Phenyl carbonate (**1LG**) is a better leaving group ($N_f = -0.84 \pm 0.07$ in 80% v/v aq EtOH) than methyl carbonate **2LG** ($N_f = -1.84 \pm 0.07$ in 80% v/v aq EtOH) because of more pronounced negative hyperconjugation, which is characterized with a more elongated RO−C bond and more increased RO−C−CO angle in **1LG** than in **2LG**. Calculated affinities of benzhydryl cation toward methyl and phenyl carbonate anions ($\Delta\Delta E_{aff} = 11.7$ kcal/mol at the B3LYP/6-311++G(d,p) level and $\Delta\Delta E_{aff} = 2.7$ kcal/mol at the PCM-B3LYP/6-311++G(d,p) level in methanol, respectively) showed that **1LG** is more stabilized than **2LG**, which is in accordance with greater solvolytic reactivity of **1** than **2**.

Introduction

Alkyl and aryl carbonates react with strong nucleophiles, yielding substitution products. The reaction is second-order and proceeds via a tetrahedral intermediate formed in an initial addition step to the carbonyl carbon atom, followed by displacement of the alcohol (phenol) in a stepwise or concerted manner.[1] This addition/elimination mechanism can be easily related to the nucleophilic substitution that carboxylic esters typically undergo. It has long been accepted that, if stabilized carbocation intermediates are produced by cleavage of the R−O bond in carboxylic esters, the hydrolysis mechanism changes, and in weakly basic to acidic medium, the esters hydrolyze in a S_N1 manner, producing the carbocation intermediate and the carboxylate ion (leaving group) in the rate-determining step.[2]

We assumed that in solvolytic conditions some aryl or alkyl carbonates can also undergo heterolytic R−O bond cleavage. A similar reaction was observed with allyl carbonates in which the carbonate acts as a leaving group in palladium-catalyzed substitution with a nucleophile.[3]

Therefore, we set out to examine solvolytic reactions that proceed via the S_N1 route in which a carbocation intermediate arises from departure of an alkyl or aryl carbonate anion. We have chosen to investigate the benzhydryl derivative of methyl and phenyl carbonates for several reasons. First, benzhydryl cations are such stable carbocations that their salts exist as stable compounds.[4] Even more important is that using the benzhydryl

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* To whom correspondence should be addressed. Phone: +385 1 481 8301. Fax: +385 1 485 6201.

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carbonates enabled us to determine the ability of alkyl and aryl carbonate anions as the leaving groups quantitatively and relate their solvolytic behavior to commonly used leaving groups.

Analogously to Mayr's procedure in construction of the nucleophilicity/electrophilicity scales,[5] the nucleofugality/electrofugality scales based on studying the solvolysis rates of a large variety of substituted benzhydryl substrates with different leaving groups in various solvents were developed recently. The absolute rate of the heterolysis reaction (S_N1) can be estimated with reasonable accuracy according to the following three-parameter LFER equation:[6]

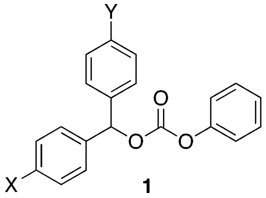
$$\log k = s_f (E_f + N_f) \tag{1}$$

in which k is the first-order rate constant (s^{-1}), s_f is the nucleofuge-specific slope parameter, N_f is the nucleofugality parameter, and E_f is electrofugality parameter.

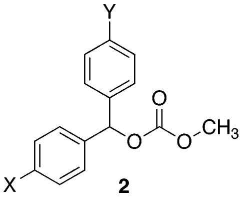
The nucleofugality (N_f) is obtained for the leaving group in a given solvent, while the electrofugality parameters (E_f) are independent variables that refer to the carbocation generated in the heterolysis reaction (S_N1). Such an approach separates the contributions of electrofuge and nucleofuge to overall solvolytic reactivity. Predefined parameters are $E_f = 0.00$ for dianysylcarbenium ion (X = Y = 4-OCH_3) and $s_f = 1.00$ for chloride nucleofuge in pure ethanol.[6a,c] In this special type of the linear free energy relationship, nucleofugality (N_f) of the given leaving group is defined as the negative intercept on the abscissa of log k (25 °C)/E_f plot.

Results and Discussion

Kinetic Studies. A series of benzhydryl phenyl carbonates (**1**) and benzhydryl methyl carbonates (**2**) were prepared from the corresponding benzhydrols and phenyl chloroformate and methyl chloroformate, respectively, according to the methods presented in the Experimental Section. The substrates were designed to enable all measurements at 25 °C, by adjusting the electrofugality of the benzhydrylium system (selecting appropriate X and Y on the benzhydryl rings). The solvolysis rates were measured in various solvents at 25 °C conductometrically or/and by potentiometric titration of the liberated acid. Details are given in Kinetic Methods (Experimental Section). The first-order rate constants are presented in Table 1.



1



2

Electrofugality parameters (E_f) for all benzhydryl cations that are generated in solvolysis of the carbonates investigated here have previously been determined and also used as a basis set of E_f values for determining N_f and s_f parameters of numerous leaving groups (e.g., chloride, bromide, tosylate, *p*-nitrobenzoate, etc.).[6a] In order to calculate the nucleofugality parameters (N_f) and the slope parameters (s_f) for phenyl carbonate ($C_6H_5OCO_2^-$; **1LG**) and methyl carbonate ($CH_3OCO_2^-$; **2LG**), logarithms of the first-order rate constants were plotted against E_f. Excellent linear correlations were obtained (Table 2). The nucleofuge-specific parameters calculated from the equation given above are presented in Table 2. Selected plots of log k against E_f are given in Figure 1 (for all correlation lines, see Supporting Information).

In order to obtain nucleofuge-specific parameters (N_f and s_f) for **1LG** and **2LG** in commonly used solvents in which kinetic data could not be collected at conventional temperatures by conventional methods, log k values were plotted against Y_{OTs}. From log k/Y_{OTs} plots obtained in 60−90% aq ethanol (v/v) for both **1** and **2**, the reaction rates in pure ethanol and in 50% aq ethanol were obtained by extrapolation. Similarly, the extrapolated rates for **1** and **2** were extracted for 70% aq methanol (v/v) and for **1** in 80% aq acetone (v/v). By applying log k/E_f correlations, the nucleofuge-specific parameters were calculated in pure and 50% ethanol (v/v), in 70% methanol (v/v), and in 80% acetone (v/v) from extrapolated kinetic data (see Tables 1 and 2). Y_{OTs} has been chosen because of the similarity in structure of the tosylate as a leaving group and the carbonates, although correlations of log k with Y_{Cl} and log k with Y_{Br} gave the same results.

According to the kinetic measurements, it is evident that solvolysis of all substrates **1** and **2** follow S_N1 type displacement reaction. The most important parameters that indicate formation of the positive charge in transition state are the slopes of the reactions (Table 2), which are in the same range as s_f obtained in solvolysis of benzhydryl derivatives with other nucleofuges studied earlier.[6a] For example, the corresponding slopes obtained in solvolysis of benzhydryl tosylates are in the range between 0.75 and 0.89, while those of chlorides are between 1.02 and 0.98. Since E_f values correlate very well with Hammett σ^+ values ($r^2 = 0.992$), the slope parameter can be easily related to ρ^+, which was already suggested by Bentley, stating that $s_f E_f$ is compatible with $\rho^+\sigma^+$.[7] Therefore, s_f values obtained show that the extent of the positive charge on the reaction center generated in the transition state in solvolysis of benzhydryl carbonates is comparable to the extent of positive charge generated in solvolysis of benzhydryl derivatives with common leaving groups that follow the S_N1 route. This conclusion rules out the addition/elimination mechanism established for numerous carbonates.

Product Analysis. In order to get additional evidence for the solvolysis mechanism, we analyzed the reaction products. Series of benzhydryl phenyl carbonates **1** (X = 4-OCH_3, Y = 4-OPh; X = 4-OCH_3, Y = 4-CH_3; and X = 4-OCH_3, Y = H) and benzhydryl methyl carbonates **2** (X = 4-OCH_3, Y = 4-OCH_3; X = 4-OCH_3, Y = 4-OPh; X = 4-OCH_3, Y = 4-CH_3; and X = 4-OCH_3, Y = H) were solvolyzed for approximately 10 reaction half-lives in 100% methanol and 100% ethanol, and the products were isolated and analyzed by means of NMR. The key product that can rule out the second-order addition/elimination reaction and prove S_N1 displacement reaction is the benzhydryl methyl ether (for methanolysis) and benzhydryl ethyl ether (for ethanolysis) since these products can arise only if substitution on the secondary benzhydryl carbon occurs. In pure

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TABLE 1. Solvolysis Rate Constants of X,Y-Substituted Benzhydryl Phenyl Carbonates (1) and of X,Y-Substituted Benzhydryl Methyl Carbonates (2) in Various Solvents Measured at 25 °C

substrate	solvent[a]	X, Y	E_f [b]	k [c] (s^{-1})
1	100M	4-Me,4′-Me	-3.47	$(1.19 \pm 0.04) \times 10^{-4}$
		4-MeO,H	-2.06	$(1.53 \pm 0.05) \times 10^{-3}$
				$(1.48 \pm 0.01) \times 10^{-3}$ [d]
		4-MeO,4′-Me	-1.29	$(8.87 \pm 0.23) \times 10^{-3}$
		4-MeO,4′-PhO	-0.81	$(2.58 \pm 0.08) \times 10^{-2}$
	90M10W	4-Me,H	-4.68	$(3.30 \pm 0.05) \times 10^{-5}$
		4-Me,4′-Me	-3.47	$(4.06 \pm 0.04) \times 10^{-4}$
		4-MeO,H	-2.06	$(4.48 \pm 0.12) \times 10^{-3}$
				$(4.08 \pm 0.10) \times 10^{-3}$ [d]
		4-MeO,4′-Me	-1.29	$(2.40 \pm 0.06) \times 10^{-2}$
	80M20W	4-Me,H	-4.68	$(9.31 \pm 0.16) \times 10^{-5}$
		4-Me,4′-Me	-3.47	$(1.03 \pm 0.03) \times 10^{-3}$
				$(1.05 \pm 0.03) \times 10^{-3}$ [d]
		4-MeO,H	-2.06	$(9.36 \pm 0.08) \times 10^{-3}$
		4-MeO,4′-Me	-1.29	$(5.03 \pm 0.08) \times 10^{-2}$
	70M30W	4-Me,4′-Me	-3.47	2.30×10^{-3} [e]
		4-MeO,H	-2.06	1.86×10^{-2} [e]
		4-MeO,4′-Me	-1.29	9.55×10^{-2} [e]
	100E	4-Me,4′-Me	-3.47	1.17×10^{-5} [e]
		4-MeO,H	-2.06	3.09×10^{-4} [e]
		4-MeO,4′-Me	-1.29	1.58×10^{-3} [e]
	90E10W	4-Me,4′-Me	-3.47	$(7.22 \pm 0.17) \times 10^{-5}$
		4-MeO,H	-2.06	$(1.27 \pm 0.03) \times 10^{-3}$
				$(1.31 \pm 0.02) \times 10^{-3}$ [d]
		4-MeO,4′-Me	-1.29	$(7.17 \pm 0.13) \times 10^{-3}$
		4-MeO,4′-PhO	-0.81	$(2.18 \pm 0.06) \times 10^{-2}$
	80E20W	4-Me,4′-Me	-3.47	$(1.89 \pm 0.02) \times 10^{-4}$
				$(1.97 \pm 0.04) \times 10^{-4}$ [d]
		4-MeO,H	-2.06	$(2.71 \pm 0.06) \times 10^{-3}$
		4-MeO,4′-Me	-1.29	$(1.42 \pm 0.03) \times 10^{-2}$
		4-MeO,4′-PhO	-0.81	$(3.93 \pm 0.13) \times 10^{-2}$
	70E30W	4-Me,H	-4.68	$(3.47 \pm 0.05) \times 10^{-5}$
		4-Me,4′-Me	-3.47	$(4.17 \pm 0.10) \times 10^{-4}$
				$(4.48 \pm 0.16) \times 10^{-4}$ [d]
		4-MeO,H	-2.06	$(5.00 \pm 0.15) \times 10^{-3}$
		4-MeO,4′-Me	-1.29	$(2.47 \pm 0.05) \times 10^{-2}$
	60E40W	4-Me,H	-4.68	$(7.85 \pm 0.12) \times 10^{-5}$
		4-Me,4′-Me	-3.47	$(8.55 \pm 0.07) \times 10^{-4}$
				$(8.65 \pm 0.16) \times 10^{-4}$ [d]
		4-MeO,H	-2.06	$(8.76 \pm 0.17) \times 10^{-3}$
		4-MeO,4′-Me	-1.29	$(4.09 \pm 0.04) \times 10^{-2}$
	50E50W	4-Me,4′-Me	-3.47	1.41×10^{-3} [e]
		4-MeO,H	-2.06	1.29×10^{-2} [e]
		4-MeO,4′-Me	-1.29	6.61×10^{-2} [e]
	80A20W	4-Me,4′-Me	-3.47	3.55×10^{-6} [e]
		4-MeO,H	-2.06	8.13×10^{-5} [e]
		4-MeO,4′-Me	-1.29	4.47×10^{-4} [e]
	70A30W	4-Me,4′-Me	-3.47	$(2.94 \pm 0.09) \times 10^{-5}$
		4-MeO,H	-2.06	$(4.69 \pm 0.08) \times 10^{-4}$
				$(4.00 \pm 0.00) \times 10^{-4}$ [d]
		4-MeO,4′-Me	-1.29	$(2.32 \pm 0.04) \times 10^{-3}$
		4-MeO,4′-PhO	-0.81	$(5.09 \pm 0.02) \times 10^{-3}$
	60A40W	4-Me,4′-Me	-3.47	$(1.04 \pm 0.01) \times 10^{-4}$
		4-MeO,H	-2.06	$(1.33 \pm 0.02) \times 10^{-3}$
				$(1.39 \pm 0.06) \times 10^{-3}$ [d]
		4-MeO,4′-Me	-1.29	$(5.85 \pm 0.03) \times 10^{-3}$
1	50A50W	4-Me,4′-Me	-3.47	$(3.64 \pm 0.06) \times 10^{-4}$
				$(3.60 \pm 0.23) \times 10^{-4}$ [d]
		4-MeO,H	-2.06	$(3.61 \pm 0.07) \times 10^{-3}$
		4-MeO,4′-Me	-1.29	$(1.56 \pm 0.05) \times 10^{-2}$
2	100M	4-MeO,H	-2.06	$(7.28 \pm 0.15) \times 10^{-5}$
		4-MeO,4′-Me	-1.29	$(4.56 \pm 0.14) \times 10^{-4}$
		4-MeO,4′-PhO	-0.81	$(1.35 \pm 0.05) \times 10^{-3}$
		4-MeO,4′-MeO	0.00	$(9.31 \pm 0.15) \times 10^{-3}$
	90M10W	4-MeO,H	-2.06	$(2.16 \pm 0.04) \times 10^{-4}$
		4-MeO,4′-Me	-1.29	$(1.34 \pm 0.02) \times 10^{-3}$
		4-MeO,4′-PhO	-0.81	$(3.56 \pm 0.09) \times 10^{-3}$
		4-MeO,4′-MeO	0.00	$(2.36 \pm 0.06) \times 10^{-2}$
	80M20W	4-MeO,H	-2.06	$(4.49 \pm 0.05) \times 10^{-4}$
		4-MeO, 4′-Me	-1.29	$(2.82 \pm 0.04) \times 10^{-3}$
		4-MeO, 4′-PhO	-0.81	$(6.60 \pm 0.06) \times 10^{-3}$
		4-MeO, 4′-MeO	0.00	$(4.36 \pm 0.06) \times 10^{-2}$
	70M30W	4-MeO, H	-2.06	9.12×10^{-4} [e]
		4-MeO, 4′-Me	-1.29	5.62×10^{-3} [e]
		4-MeO, 4′-PhO	-0.81	1.23×10^{-2} [e]
		4-MeO, 4′-MeO	0.00	7.94×10^{-2} [e]
	100E	4-MeO, H	-2.06	1.23×10^{-5} [e]
		4-MeO, 4′-Me	-1.29	7.59×10^{-5} [e]
		4-MeO, 4′-PhO	-0.81	3.47×10^{-4} [e]
		4-MeO, 4′-MeO	0.00	2.75×10^{-3} [e]
	90E10W	4-MeO, H	-2.06	$(6.13 \pm 0.17) \times 10^{-5}$
		4-MeO, 4′-Me	-1.29	$(3.44 \pm 0.08) \times 10^{-4}$
		4-MeO, 4′-PhO	-0.81	$(1.14 \pm 0.01) \times 10^{-3}$
		4-MeO, 4′-MeO	0.00	$(8.46 \pm 0.06) \times 10^{-3}$
	80E20W	4-MeO, H	-2.06	$(1.39 \pm 0.04) \times 10^{-4}$
		4-MeO, 4′-Me	-1.29	$(8.20 \pm 0.08) \times 10^{-4}$
		4-MeO, 4′-PhO	-0.81	$(2.16 \pm 0.03) \times 10^{-3}$
		4-MeO, 4′-MeO	0.00	$(1.57 \pm 0.02) \times 10^{-2}$
	70E30W	4-MeO, H	-2.06	$(2.88 \pm 0.11) \times 10^{-4}$
		4-MeO, 4′-Me	-1.29	$(1.53 \pm 0.05) \times 10^{-3}$
		4-MeO, 4′-PhO	-0.81	$(3.58 \pm 0.07) \times 10^{-3}$
		4-MeO, 4′-MeO	0.00	$(2.55 \pm 0.05) \times 10^{-2}$
	60E40W	4-MeO, H	-2.06	$(5.22 \pm 0.16) \times 10^{-4}$
		4-MeO, 4′-Me	-1.29	$(2.76 \pm 0.08) \times 10^{-3}$
		4-MeO, 4′-PhO	-0.81	$(5.76 \pm 0.12) \times 10^{-3}$
		4-MeO, 4′-MeO	0.00	$(3.97 \pm 0.15) \times 10^{-2}$
	50E50W	4-MeO, H	-2.06	8.13×10^{-4} [e]
		4-MeO, 4′-Me	-1.29	4.37×10^{-3} [e]
		4-MeO, 4′-PhO	-0.81	7.94×10^{-3} [e]
		4-MeO, 4′-MeO	0.00	5.37×10^{-2} [e]
	70A30W	4-MeO, 4′-Me	-1.29	$(1.33 \pm 0.08) \times 10^{-4}$
		4-MeO, 4′-PhO	-0.81	$(3.04 \pm 0.03) \times 10^{-4}$
		4-MeO, 4′-MeO	0.00	$(2.29 \pm 0.06) \times 10^{-3}$
	60A40W	4-MeO, H	-2.06	$(7.78 \pm 0.06) \times 10^{-5}$
		4-MeO, 4′-Me	-1.29	$(3.87 \pm 0.13) \times 10^{-4}$
		4-MeO, 4′-MeO	0.00	$(6.02 \pm 0.13) \times 10^{-3}$
	50A50W	4-MeO, H	-2.06	$(2.39 \pm 0.01) \times 10^{-4}$
		4-MeO, 4′-Me	-1.29	$(1.12 \pm 0.02) \times 10^{-3}$
		4-MeO, 4′-MeO	0.00	$(1.50 \pm 0.01) \times 10^{-2}$

[a] Binary solvents are v/v at 25 °C. A = acetone, E = ethanol, M = methanol, W = water. [b] Electrofugality parameters are taken from ref 6a. [c] Average *k* values (determined conductometrically unless otherwise noted) from three to six runs. Errors shown are standard deviations. [d] Determined titrimetrically by means of a pH-Stat. [e] Extrapolated from log k/Y_{OTs} plot.

alcohols, the substrates were quantitatively converted to *p*-methoxybenzhydryl methyl ether and *p*,*p*-dimethoxybenzhydryl ether, respectively, unambiguously excluding addition/elimination mechanism.

Quantum Chemical Calculations. Kinetic measurements revealed that phenyl carbonate (**1LG**) is a better nucleofuge than methyl carbonate (**2LG**). Carbonates **1** react about 20 times faster in all solvents used than the corresponding methyl carbonates **2** (Tables 1 and 2). Also, the slopes (s_f) obtained in solvolysis of **1** are lower by about 0.1 than that obtained in solvolysis of **2**, indicating that the substituents on the benzhydryl ring contribute slightly more to the solvolysis rates of methyl carbonates than that of phenyl carbonates.

In order to rationalize the greater reactivity of the phenyl carbonates than methyl carbonates, we carried out quantum chemical calculations to establish the affinity of the leaving groups toward benzhydrylium ion and also to get structural features of the phenyl carbonate anion (**1LG**) and methyl carbonate anion (**2LG**) that are responsible for greater reactivity of **1**. Calculations were performed using the Gaussian 03

TABLE 2. Nucleofugality Parameters N_f and s_f for Phenyl Carbonate (1LG) and Methyl Carbonate (2LG) in Various Solvents

leaving group	solvent[a]	N_f[b]	s_f[b]	r[c] (n)[d]
1LG	100M	−1.05 ± 0.13	0.88 ± 0.04	0.9982 (4)
	90M10W	−0.70 ± 0.12	0.83 ± 0.03	0.9990 (4)
	80M20W	−0.41 ± 0.14	0.79 ± 0.03	0.9984 (4)
	70M30W[e]	−0.18 ± 0.25	0.73 ± 0.07	0.9953 (3)
	100E[e]	−1.55 ± 0.09	0.98 ± 0.02	0.9998 (3)
	90E10W	−1.01 ± 0.07	0.93 ± 0.02	0.9995 (4)
	80E20W	−0.84 ± 0.07	0.87 ± 0.02	0.9994 (4)
	70E30W	−0.66 ± 0.09	0.83 ± 0.02	0.9995 (4)
	60E40W	−0.49 ± 0.10	0.79 ± 0.02	0.9993 (4)
	50E50W[e]	−0.34 ± 0.23	0.76 ± 0.06	0.9966 (3)
	80A20W[e]	−2.19 ± 0.00	0.96 ± 0.00	1 (3)
	70A30W	−1.85 ± 0.08	0.85 ± 0.02	0.9996 (4)
	60A40W	−1.51 ± 0.07	0.80 ± 0.02	0.9999 (3)
	50A50W	−1.17 ± 0.15	0.74 ± 0.03	0.9992 (3)
2LG	100M	−1.99 ± 0.02	1.02 ± 0.01	0.9999 (4)
	90M10W	−1.66 ± 0.05	0.98 ± 0.02	0.9997 (4)
	80M20W	−1.43 ± 0.08	0.95 ± 0.03	0.9989 (4)
	70M30W[e]	−1.19 ± 0.09	0.93 ± 0.04	0.9984 (4)
	100E[e]	−2.22 ± 0.11	1.15 ± 0.04	0.9988 (4)
	90E10W	−2.01 ± 0.06	1.04 ± 0.02	0.9996 (4)
	80E20W	−1.84 ± 0.07	0.99 ± 0.02	0.9995 (4)
	70E30W	−1.73 ± 0.11	0.94 ± 0.03	0.9986 (4)
	60E40W	−1.59 ± 0.13	0.90 ± 0.04	0.9977 (4)
	50E50W[e]	−1.51 ± 0.17	0.87 ± 0.06	0.9959 (4)
	70A30W	−2.74 ± 0.32	0.97 ± 0.09	0.9959 (3)
	60A40W	−2.42 ± 0.02	0.92 ± 0.01	0.9999 (3)
	50A50W	−2.09 ± 0.00	0.87 ± 0.00	1.0000 (3)

[a] Binary solvents are v/v at 25 °C. A = acetone, E = ethanol, M = methanol, W = water. [b] Errors shown are standard errors. [c] Correlation coefficient. [d] Number of data points. [e] Calculated from rates extracted from log k/Y_{OTs} by applying log k/E_f correlations.

program suite.[8] Geometries of carbonates **1** and **2** (X = Y = H) were fully optimized at B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) levels, and those of the anions **1LG** and **2LG** at B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p), and MP2/6-311++G(d,p). Stationary points were characterized as minima (no imaginary frequencies) by calculation of the harmonic vibration frequencies. The unscaled B3LYP and MP2 frequencies were used to calculate the zero-point energies. Total energies and unscaled zero-point vibrational energies along with Mulliken and NBO charges are given in the Supporting Information. In order to check the influence of the solvent on the structure of leaving groups **1LG** and **2LG** and their affinities toward benzhydrylium ion, we applied the polarizable continuum solvent model (PCM) with dielectric constant for methanol and optimized of the most stable conformers of methyl and phenyl carbonate ions at the B3LYP/6-311++G(d,p) level.

Optimized B3LYP/6-311++G(d,p) structures of the most stable conformers of **1** and **2** and those of the leaving groups

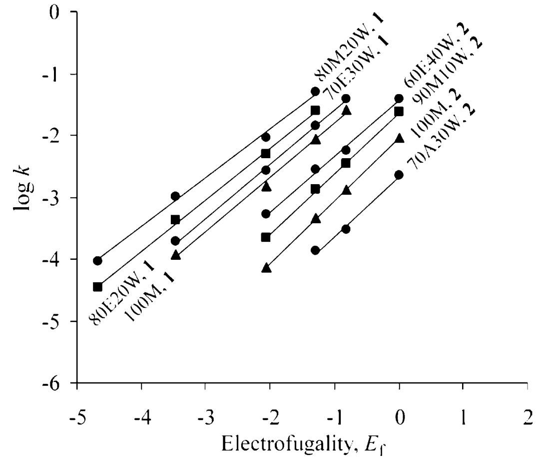

FIGURE 1. Selected plots of log k (25 °C) versus E_f for the solvolysis of X,Y-substituted benzhydryl phenyl carbonates (**1**) and benzhydryl methyl carbonates (**2**) in binary aqueous solvents of methanol, ethanol, and acetone (v/v).

1LG and **2LG** are presented in Figure 2, along with some important parameters (bong lengths, NBO charges, and angles). The second value for each datum in Figure 2 represents the same parameter obtained by employing the solvent model (PCM-B3LYP/6-311++G(d,p) level).

Both phenyl and methyl carbonates converged to energy minimum structures (seven for phenyl carbonate and six for methyl carbonate; see Supporting Information) which can be, in analogy to rotamers of esters, thioesters, and chloroformates, characterized as *cis*,*cis*-planar, *cis*,*trans*-planar, and *trans*,*cis*-planar.[9] The *cis* and *trans* refer to the position of the alkyl or aryl substituents toward the carbonate carbonyl group. Because of the large benzhydryl group, *trans*,*trans*-planar rotamers for both **1** and **2** were not located as energy minimum structures. For both carbonates **1** and **2**, the most stable rotamer is the *cis*,*cis*-planar (Figure 2).

The affinity of the benzhydryl cation toward a given carbonate, presented with the process indicated below (R is CH_3 and C_6H_5, respectively)

$$\mathrm{Ph_2CH^+ + ROCOO^- \rightarrow Ph_2CHOCO_2R}$$

is calculated according to the following equation, taking the calculated energies for the most stable conformer:[10]

$$\Delta E_{af} = E_{calc}(cis,cis\text{-planar } \mathrm{Ph_2CHOCOOR}) - [E_{calc}(\mathrm{Ph_2CH^+}) + E_{calc}(\mathrm{ROCOO^-})] \quad (2)$$

Affinities along with some relevant data are presented in Table 3. The results show that the affinity of the benzhydryl cation toward **2LG** ($CH_3OCO_2^-$) is larger than that toward **1LG** ($C_6H_5OCO_2^-$) by more than 10 kcal/mol ($\Delta\Delta E_{aff}$ = 15.4 kcal/mol at the B3LYP/6-311G(d,p) level and $\Delta\Delta E_{aff}$ = 11.7 kcal/mol at the B3LYP/6-311++G(d,p) level, respectively); that is, the phenyl carbonate anion is more stabilized than the methyl carbonate anion, which is in accordance with experimental

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[8] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.02; Gaussian, Inc.: Wallingford, CT, 2004.

[9] (a) Matzner, M.; Kurkjy, R. P.; Cotter, R. J. *Chem. Rev.* **1964**, *64*, 645−687 and references cited therein. (b) Nagy, P. I.; Tejada, F. R.; Sarver, J. G.; Messer, W. S. *J. Phys. Chem. A* **2004**, *108*, 10173−10185 and references cited therein.

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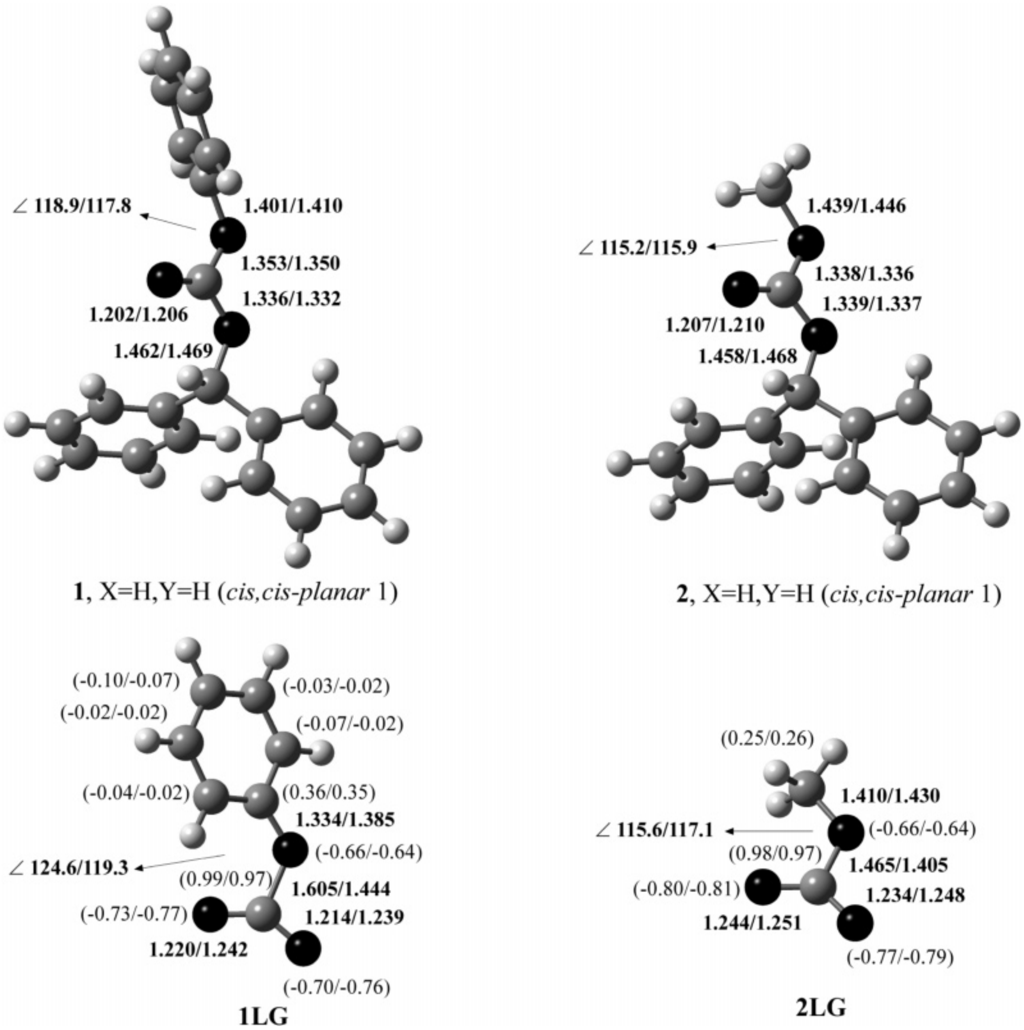

1, X=H,Y=H (*cis,cis-planar* 1)

2, X=H,Y=H (*cis,cis-planar* 1)

1LG

2LG

FIGURE 2. Optimized B3LYP/6-311++G(d,p) structures of benzhydryl phenyl carbonate **1** (the most stable conformer), benzhydryl methyl carbonate **2** (the most stable conformer), phenyl carbonate ion **1LG**, and methyl carbonate ion **2LG** in the gas phase. Selected bond lengths (angstroms), angles (degrees), and B3LYP/6-311++G(d,p) NBO charges (in parentheses) are given for the gas phase (first values) and in methanol (second value; PCM-B3LYP/6-311++G(d,p) level).

TABLE 3. Affinities of Benzhydryl Cation toward R-carbonate Anions (1LG and 2LG), Group NBO Charges, and C-OR Bond Lengths in 1LG and 2LG

			group NBO charges		
leaving group	level of theory	$\Delta E_{\mathrm{aff}}{}^{a}$ (kcal mol^{-1})	R-oxy moiety	carboxylate moiety	C−OR bond length (Å)
1LG (R = Ph)	B3LYP/6-311G(d,p)	−120.18	−0.624	−0.376	1.680
	B3LYP/6-311++G(d,p)	−113.53	−0.562	−0.438	1.605
	PCM− B3LYP/6-311++G(d,p)^{b}	−22.51	−0.440	−0.560	1.444
	MP2(full)/6-311++G(d,p)		−0.571	−0.429	1.598
2LG (R = CH_3)	B3LYP/6-311G(d,p)	−135.60	−0.437	−0.563	1.479
	B3LYP/6-311++G(d,p)	−125.23	−0.411	−0.589	1.465
	PCM− B3LYP/6-311++G(d,p)^{b}	−25.21	−0.374	−0.626	1.405
	MP2(full)/6-311++G(d,p)		−0.431	−0.569	1.461

[a] $\Delta E_{\mathrm{aff}} = E_{\mathrm{calc}}$(*cis,cis*-planar $Ph_2CHOCOOR$) − [$E_{\mathrm{calc}}(Ph_2CH^+) + E_{\mathrm{calc}}(ROCOO^-)$]; E_{calc} values were corrected for (unscaled) ZPE. [b] Polarizable continuum solvent model with dielectric constant for methanol.

findings that **1** solvolyzes faster than **2**. Calculations employing the solvent model (PCM) show the same but less pronounced effect ($\Delta\Delta E_{\mathrm{aff}} = 2.70$ kcal/mol).

Structural Features and Reactivity of Carbonates. The outstanding feature of both carbonates is that the negative charge is delocalized to three oxygen atoms almost equally rather than only two oxygens that are involved in resonance (see NBO charges in Figure 2). This observation suggests that, besides resonance, negative hyperconjugation[11] occurs in both ions **1LG** and **2LG**, presented in Scheme 1.

Because of the negative hyperconjugation, the C−OR bonds are longer in both anions **1LG** and **2LG** than in corresponding

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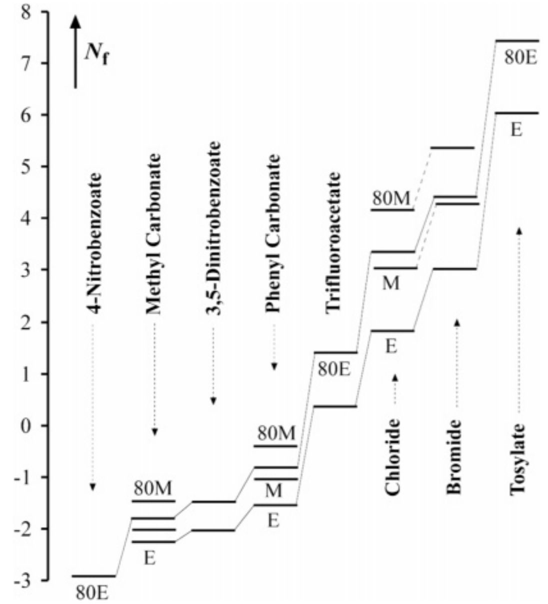
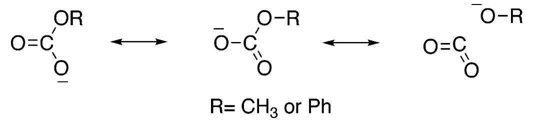


FIGURE 3. Relative nucleofugalities N_f for typical leaving groups in various solvents. Mixtures of solvents are given as v/v: solvents: E = pure ethanol, 80E = 80 aq ethanol, M = methanol, 80M = 80% aq methanol.

SCHEME 1



carbonates **1** and **2**. Also, RO−C−CO angles are increased. This trend is much more pronounced in phenyl carbonate anion **1LG** than in anion **2LG** (see details in Figure 2). By detailed comparison of the anion structures obtained computationally, it could be seen that the amount of negative charge generated is distributed differently in **1LG** and **2LG** since in **1LG** the phenyl group efficiently accommodates the negative charge to its *o*- and *p*-positions by resonance. It is illustrative to compare the distribution of the negative charge between the carboxylate moiety and the RO group of the anion (Table 3). Even though, in both cases, the oxygen in the RO group has a considerable amount of negative charge, it is evident that in **1LG** the phenoxy group carries more partial negative charge than the methoxy group in **2LG**. In accord with this observation is an unusually long C−O bond (1.6 Å) in **1LG**. Therefore, because of more efficient delocalization of the negative charge due to negative hyperconjugation in **1LG**, the solvolytic reactivity of **1** is larger than that of **2**. It should be noted that the same but less pronounced structural features for anions were obtained by applying the solvent model calculation.

It is useful to compare the leaving group ability (nucleofugality) of carbonates and commonly used leaving groups. The relative nucleofugalities are presented in Figure 3. The nucleofugality of carbonates is comparable to those of some carboxylates in which the carboxylate anion is stabilized by negative inductive effect of the substituent on the carboxylate group. Thus, according to N_f values, the ability of leaving groups decrease as follows:

$$\mathrm{OTs^-} > \mathrm{Br^-} > \mathrm{Cl^-} > \mathrm{CF_3CO_2^-} > \mathrm{C_6H_5OCO_2^-}\ (\mathbf{1LG}) > \mathrm{DNB} > \mathrm{CH_3OCO_2^-}\ (\mathbf{2LG}) > \mathrm{PNB}$$

Interestingly, the effect of stabilization of two nitro groups in 3,5-dinitrobenzoate (DNB) is smaller than the effect of the phenoxy group in **1LG** but larger than the effect of the methoxy group in **2LG**. However, the stabilization effect of both the phenoxy and the methoxy group is larger than that of only one nitro group, so the corresponding *p*-nitrobenzoates solvolyze by 1 and 2 orders of magnitude slower, respectively. Figure 3 also shows that the solvent effect is the largest on chlorides, somewhat less on bromide and tosylate, but much less pronounced on weaker leaving groups in which charge delocalization occurs.

Finally, according to eq 1, from earlier published E_f parameters for numerous electrofuges and from N_f parameters presented here (Table 2), one can determine how to handle carbonates during preparation. For example, the half-life of allyl methyl carbonates ($E_f \approx -6$ for any allyl cation)[6a] in 50% (v/v) aqueous acetone at room temperature is about 2 years ($k \approx 10^{-8}$), while the half-life of cumyl phenyl carbonate ($E_f = -5.0$ for cumyl cation) in 100 MeOH at 25 °C is about 1 day ($k \approx 10^{-6}$).

Experimental Section

Substrate Preparation.

NMR spectra are presented in the Supporting Information.

4-Methoxy-4′-phenoxybenzhydrol. The title compound was prepared by a standard Grignard reaction of 4-phenoxyphenylmagnesium bromide (5.0 g, 20.1 mmol of 4-bromodiphenyl ether, and 0.8 g, 32.9 mmol of magnesium) with 4-methoxybenzaldehyde (2.5 g, 18.4 mmol) in ether. Recrystallization from light petroleum/ether (4:1) afforded white crystals of 4-methoxy-4′-phenoxybenzhydrol (3.12 g, yield = 55%).

4-Methoxy-4′-methylbenzhydrol. The title compound was prepared by a standard Grignard reaction of 4-methylphenylmagnesium bromide (8.0 g, 46.8 mmol of 4-bromotoluene, and 1.2 g, 49.4 mmol of magnesium) with 4-methoxybenzaldehyde (4.5 g, 33.1 mmol). Recrystallization from light petroleum/ether (4:1) afforded white crystals of 4-methoxy-4′-methylbenzhydrol (4.9 g, yield = 65%).

4,4′-Dimethoxybenzhydrol, 4-Methoxybenzhydrol, 4,4′-Dimethylbenzhydrol, and 4-Methylbenzhydrol were prepared by the reduction of the commercially available substituted benzophenones with sodium borohydride in methanol.

4-Methoxy-4′-methylbenzhydryl phenyl carbonate (1, X = 4-OCH$_3$, Y = 4′-CH$_3$). A solution of phenyl chloroformate (4.4 g, 28.0 mmol) in benzene (20 mL) was added dropwise to the previously prepared vigorously stirring solution of 4-methoxy-4′-methylbenzhydrol (4.3 g, 18.9 mmol) and pyridine (4.5 g, 57.0 mmol) in benzene (50 mL). The reaction mixture was stirred for 12 h under the atmosphere of argon at ambient temperature. The solid pyridinium chloride was then removed by filtration, while the excess of pyridine was removed by dilute hydrochloric acid (vigorous stirring). The benzene layer was separated and washed with aqueous sodium bicarbonate (1×) and water (2×) in the separatory funnel. After drying over anhydrous sodium sulfate, benzene was evaporated in vacuo to give pale yellow oil (4.6 g; yield ≈ 70%).

Additional purification (column chromatography, preparative chromatography, TLC, vacuum distillation, methods for crystallization) resulted with decomposition of the carbonate. According to the NMR spectra (see Supporting Information), the crude product did not contain the starting materials and other noticeable impurities.

4-Methoxy-4′-phenoxybenzhydryl phenyl carbonate (1, X = 4-OCH$_3$, Y = 4′-OPh) was prepared from the 4-methoxy-4′-phenoxybenzhydrol (1.5 g) according to the procedure described for 4-methoxy-4′-methylbenzhydryl phenyl carbonate (**1**, 4-X = 4-OCH$_3$, 4′-Y = CH$_3$), yielding the title compound as a pale yellow oil; yield ≈ 75%. **1**, X = 4-OCH_3, Y = 4′-OPh, was very unstable, and its decomposition started with complete removal of benzene.

4-Methoxybenzhydryl phenyl carbonate (1, X = 4-OCH_3, Y = H). 4-Methoxybenzhydrol (2.0 g) was treated according to the procedure for preparation of **1**, X = 4-OCH_3, Y = 4′-CH_3. After drying over anhydrous sodium sulfate and evaporation of benzene in vacuo, a residue was recrystallized from light petroleum affording white crystals (yield ≈ 77%).

4,4′-Dimethylbenzhydryl phenyl carbonate (1, X = Y = 4-CH_3). The procedure is the same as described above for **1**, X = 4-OCH_3, Y = H. Starting with 4,4′-dimethylbenzhydrol (2.0 g), the title compound was obtained as white crystals (yield ≈ 70%).

4-Methylbenzhydryl phenyl carbonate (1, X = 4-CH_3, Y = H). The procedure is the same as described above for **1**, X = 4-OCH_3, Y = H. From 4-methylbenzhydrol (1.5 g), the title compound was obtained as white crystals (yield ≈ 68%).

4,4′-Dimethoxybenzhydryl methyl carbonate (2, X = Y = 4-OCH_3). 4,4′-Dimethoxybenzhydrol (1.0 g, 4.1 mmol) and pyridine (2.0 g, 25.3 mmol) were dissolved in dry benzene (20 mL). A solution of methyl chloroformate (1.5 g, 10.5 mmol; commercially available) in benzene (30 mL) was then added dropwise to the previously prepared vigorously stirring solution. Stirring was continued for the next 12 h in the argon atmosphere at ambient temperature. The solid pyridinium chloride was removed by filtration, while the excess of pyridine was removed by dilute hydrochloric acid (vigorous stirring). The benzene solution was washed with water in a separatory funnel (2×) and dried over anhydrous sodium sulfate. Solvent and other possible volatile materials were then evaporated in vacuo, yielding pale yellow oil (1.0 g, yield ≈ 80%). Additional purification (column chromatography, preparative chromatography, TLC, vacuum distillation, methods for crystallization) resulted with decomposition of the carbonate. According to the NMR spectra (see Supporting Information), the crude product did not contain the starting materials and other noticeable impurities.

4-Methoxy-4′-phenoxybenzhydryl methyl carbonate (2, X = 4-OCH_3, Y = 4′-OC_6H_5). The procedure is the same as described above for **2**, X = Y = 4-OCH_3. From 4-methoxy-4′-phenoxybenzhydrol (1.0 g), the title compound was obtained as pale yellow oil; yield ≈ 80%.

4-Methoxy-4′-methylbenzhydryl methyl carbonate (2, X = 4-OCH_3, Y = 4′-CH_3). The procedure is the same as described above for **2**, X = Y = 4-OCH_3. From 4-methoxy-4′-methylbenzhydrol (1.5 g), the title compound was obtained as a pale yellow oil; yield ≈ 80%.

4-Methoxybenzhydryl methyl carbonate (2, X = 4-OCH_3, Y = H). 4-Methoxybenzhydrol (1.5 g) was treated according to the procedure described for **2**, X = Y = 4-OCH_3. After removal of benzene and other volatile materials in vacuo, the residue was recrystallized from the light petroleum, yielding white crystals (yield ≈ 80%).

Kinetic Methods.

Solvents were purified and dried according to the standard procedures.

Conductivity Method. Freshly prepared solvents (30 mL) were thermostated at 25(±0.01) °C for several minutes prior to addition of the substrate. Typically, 10−40 mg of substrate was dissolved in 0.10−0.15 mL of dichloromethane and injected into the solvent. Concentration of the carbonates in the reaction mixtures was 10^{-3} to 5×10^{-3} M.

Increase of conductance during solvolysis was recorded automatically by means of WTW LF 530 conductimeter using a Pt electrode LTA 1/NS. Rate constants were obtained by least-squares fitting of the conductivity to the first-order kinetic equation for 3−4 half-lives.

In order to achieve a complete ionization of a liberated weak acid, in solvolysis of substituted benzhydryl methyl carbonates and substituted benzhydryl phenyl carbonates, a proton sponge base [1,8-bis(dimethylamino)naphthalene] was added in a range of concentrations for each given aqueous binary mixture presented in Table 4. The optimal concentration range of the proton sponge base in each aqueous binary mixture was determined to fulfill the following criteria: (A) Correlation coefficients of the fitted conductivities were $r > 0.995$; (B) deviations among rate constants calculated at $2\tau_{1/2}$, $3\tau_{1/2}$, and $4\tau_{1/2}$ for an individual run were within 5%; (C) deviations of the rate constants for a given carbonate in the given concentration range of the base were within experimental error (Table 1); (D) rate constant for the solvolysis of the substituted benzhydryl chlorides determined under the same conditions agreed within an experimental error or were slightly decreased with respect to the rate constants determined without a presence of the proton sponge base (see Table S1 in the Supporting Information); and (E) the values of the rate constants obtained conductometrically and titrimetrically were the same in the limits of the experimental error (Table 4).

TABLE 4. Experimental Concentrations (c_0) of Proton Sponge Base and the Substrates 1 and 2 in Kinetic Measurements of the Solvolysis Rates of the Substituted Benzhydryl Carbonates

	conductivity method		titrimetric method (pH-Stat)	
solvent[a]	c_0(PSB)[b] (mM)	c_0(PSB)/c_0(S)[b]	end-point (pH)	c_0(S) (mM)
100M	8.0−16.0	4.0−6.0	10.0	7.0
90M10W	4.5−16.0	1.5−2.5	10.0	5.0
80M20W	3.0−8.0	1.5−2.5	10.0	7.0
90E10W	45.0−110.0	25.0−55.0	10.5	4.0−7.0
80E20W	45.0−60.0	15.0−30.0	10.5	5.0
70E30W	15.0−30.0	4.0−15.0	10.0	4.0−6.0
60E40W	4.5−8.0	1.5−3.0	10.0	4.0−5.0
70A30W	15.5	5.0−15.0	10.5	2.0−5.0
60A40W	8.0	2.5−4.5	10.0	5.0
50A50W	3.0−4.5	1.5−3.0	10.0	4.0−5.0

[a] Binary solvents are v/v at 25 °C. A = acetone, E = ethanol, M = methanol, W = water. [b] PSB = Proton sponge base: [1,8-bis(dimethylamino)naphthalene]; S = substrate (**1** and **2**).

Titrimetric Method. Titrimetric rate constants for solvolysis of the substituted benzhydryl phenyl carbonates were obtained by means of pH-Stat with end-point set at pH = 10.0−10.5, which was the lowest pH that provided a complete ionization of the liberated phenyl carbonic acid (Table 4). Titrimetric experiments were carried out by Radiometer Analytical workstation TIM856. Typically, 30 mL of (4.0−7.0) × 10^{-3} M solution of carbonate was thermostated at 25 °C, and the liberated phenyl carbonic acid was continuously titrated by using a 0.06−0.10 M solution of NaOH in the same solvent mixture. First-order rate constants were obtained by least-squares fitting of data to the first-order kinetic equation for 3−4 half-lives.

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Supporting Information Available: Calculated energies, group charges, and Cartesian coordinates for optimized geometries of carbonates, ^1H NMR and ^{13}C NMR spectra of **1** and **2**, and corresponding alcohols, correlations of log k versus E_f for solvolyses of the substituted benzhydryl carbonates. This material is available free of charge via the Internet at http://pubs.acs.org.

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