free energy associated with the concerted nucleophilic and electrophilic attacks at silicon and oxygen, respectively, would ensue.

Experimental Section[10]

Starting Materials.—Phenol, b.p. 182°, was distilled before use and 2,4,6-trichlorophenol, m.p. 68°, was recrystallized from glacial acetic acid.

Trimethylphenoxysilane.—This material was made from phenol (88.6 g., 0.94 mole) and chlorotrimethylsilane (153 g., 1.41 mole).[11] The silane (140 g., 84%) was purified by fractional distillation: b.p. 180°, lit.[11] b.p. 181.9-182.4°; $n^{25}D$ 1.4772, lit.[12] $n^{25}D$ 1.4753.

Reductive Cleavage of Trimethylphenoxysilane.—A suspension of lithium aluminum hydride (10 g., 0.26 mole) in 100 ml. of anhydrous ether was placed under a slight positive pressure of nitrogen and protected from moisture by using a sulfuric acid trap. To the stirred mixture was added trimethylphenoxysilane (84.2 g., 0.51 mole) in 80 ml. of ether at room temperature; no observable reaction took place. Anhydrous *p*-dioxane (180 ml.) was exchanged for the ether by the process of simultaneous addition and distillation. The mixture was then stirred at reflux temperature for 7 hr. After the unreacted lithium aluminum hydride was destroyed with an ethyl alcohol-ether mixture and cooled to 0°, the resulting mixture was poured onto an excess of dilute hydrochloric acid and ice. Product isolation was achieved by *quickly* extracting three times with 50-ml. portions of ether, washing the combined ethereal extract once with water, drying with sodium sulfate (overnight), and distilling the solvent. Fractional distillation of the crude product at reduced pressure gave phenol (40.5 g., 84%), b.p. 75° (10 mm.).

The identity and purity of the phenol was checked by comparison of infrared spectra and v.p.c. analysis with an authentic sample since its boiling point was very close to that of trimethylphenoxysilane.

A repeat of the above experiment was carried out using trimethylphenoxysilane (16.6 g., 0.1 mole), lithium aluminum hydride (2 g., 0.05 mole), and anhydrous ether (100 ml.), but this time the exit gases were passed through a trap cooled with isopropyl alcohol and Dry Ice. The mixture was stirred and heated at reflux temperature for 17 hr., after which time 7.5 g. of material had collected in the cold trap. Infrared analysis of the condensate (no solvent) indicated the presence of Me_3SiH,[13] since strong bands were present at 2145 and 1260 cm.$^{-1}$. The yield of phenol in this experiment was 9 g. (96%).

2,4,6-Trichlorophenoxysilane.—A solution of 2,4,6-trichlorophenol (50 g., 0.25 mole) and chlorotrimethylsilane (108.6 g., 1 mole) in 100 ml. of toluene was stirred at reflux temperature for 6 hr. using 1.6 g. of N,N-dimethylformamide as a catalyst.[14] The excess of chlorotrimethylsilane was distilled from the reaction mixture and the residue was fractionally distilled at reduced pressure to give 57 g. of impure product. Refractionation using a Nester-Faust Intermediate Laboratory spinning-band column gave 48.6 g. (70%) of the pure silane, b.p. 147° (20 mm.), $n^{25}D$ 1.5231.

Anal. Calcd. for $C_9H_{11}Cl_3OSi$: C, 40.30; H, 4.14. Found: C, 40.34; H, 4.13.

Reductive Cleavage of 2,4,6-Trichlorophenoxysilane.—A nitrogen atmosphere and a cold trap were incorporated in this experiment as previously described. 2,4,6-Trichlorophenoxysilane (40.5 g., 0.15 mole) was added dropwise to a stirred suspension of lithium aluminum hydride (2.85 g., 0.075 mole) in 100 ml. of anhydrous ether. An immediate exothermic reaction took place accompanied by a gas evolution. The rate of addition was adjusted so that the ambient temperature was approached. At the end of the addition (1 hr.), 4.3 g. of trimethylsilane had condensed in the trap. To ensure full reaction, the reaction was heated at reflux temperature for 5 hr., and a further quantity of trimethylsilane and ether was collected. The reaction complex was destroyed and ether extracted as previously described. The product, isolated by evaporating the water-free ethereal solution to dryness on a rotary evaporator under reduced pressure, consisted of 28.7 g. (97%) of reasonably pure 2,4,6-trichlorophenol, m.p. 66-67° (lit.[15] m.p. 68-69°).

Structure Proof of Trimethylsilane.[16]—The condensate from the last experiment was allowed to warm to −40°. At this temperature a stream of chlorine gas was passed through the mixture while the temperature was allowed to rise gradually over a 30-min. period to 5°. After standing overnight in a stoppered flask, the chlorinated mixture was fractionally distilled to give 7.5 g. of chlorotrimethylsilane, b.p. 56° (lit.[17] b.p. 57.3°). The infrared spectrum of this material corresponded exactly with that of an authentic sample.

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[10] All melting points and boiling points are uncorrected, and fractional distillations were carried out through a precision-built Vigreux column having an approximate ten-theoretical-plate equivalent as described by J. D. Ray [*Rev. Sci. Instr.*, **28** (3), 200 (1957)], unless otherwise stated.

[11] S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

[12] J. L. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

[13] S. Kaye and S. Tannebaum, *J. Org. Chem.*, **18**, 1750 (1953).

[14] R. J. N. Thiesse, German Patent 1,163,824 (1964).

[15] N. A. Lange, "Handbook of Chemistry," 10th Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p. 704.

[16] A. G. Taylor and B. V. De G. Walden, *J. Am. Chem. Soc.*, **66**, 842 (1944).

[17] See ref. 1, p. 177.

Substituent Effects in Hydrolysis of Diaryl Carbonates

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In a previous paper[1] the rates of hydrolysis of diphenyl carbonate and phenyl benzoate were compared under acidic, basic, and "neutral" conditions, *i.e.*, without added acid or base. The present report describes the effect of substituents on the hydrolysis of symmetrical diaryl carbonates in neutral[2] and basic solution.

Basic Hydrolysis.—The second-order rate constants for reaction of substituted diaryl carbonates with hydroxide ion in 1:1 dioxane-water were measured at 20° by following the rate of appearance of the phenoxide ion spectrophotometrically, with the results shown in Table I. The reaction is quite sensitive to the electronic effects of the substituent, being accelerated by electron-withdrawing groups and retarded by electron-donating groups, as expected. The data for *meta* and *para* substituents were fitted to the Hammett equation,[3] using values of σ derived from the ionization constants of the substituted benzoic acids.[3]

TABLE I

RATES OF REACTION OF DIARYL CARBONATES WITH HYDROXIDE ION IN DIOXANE-WATER AT 20°

$$(XC_6H_4O)_2\,C{=}O + 4OH^- \rightarrow 2XC_6H_4O^- + CO_3^{2-} + H_2O$$

Substituent	*k*, l. mole^{-1} sec.$^{-1}$	Substituent	*k*, l. mole^{-1} sec.$^{-1}$
H	0.842	*m*-CH_3O	1.05
o-Cl	1.36	*p*-CH_3O	0.454
m-Cl	8.32	*m*-NO_2	155
p-Cl	7.48	*o*-CH_3	0.088
m-Br	7.60	*m*-CH_3	0.372
p-Br	7.95	*p*-CH_3	0.368

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[1] G. D. Cooper and B. Williams, *J. Org. Chem.*, **27**, 3717 (1962).

[2] The term "neutral" solution is used throughout this paper to denote reaction in the absence of added acid or base and does not imply reaction at controlled pH.

[3] L. P. Hammett, *Chem. Rev.*, **17**, 125 (1935).

$$\log \frac{k}{k_0} = \rho\sigma \qquad (1)$$

When *meta* substituents only were considered, an excellent fit to eq. 1 was obtained; standard least-squares treatment of the data[4] yielded $\rho = 3.234$, $\log k_0 = -0.2338$, with a correlation coefficient of 0.991. When both *meta* and *para* substituents were considered, the best fit was obtained for $\rho = 2.751$, $\log k_0 = 0.2648$. The correlation coefficient was only 0.958, not particularly high for a line with such a large slope. The values of log k for the *para*-substituted compounds all fell substantially above the line determined by the *meta* substituents. The substituents studied (Cl, Br, CH_3, and CH_3O) are all of the $+R$ type, thus capable of resonance interaction with a *p*-carbonyl group, so that σ constants derived from ionization of benzoic acids may be regarded as "exalted" rather than normal values.[5,6] A much better fit was obtained when Verkade's[6] "normal" σ values were used: $\log k = -0.04959 + 2.977\sigma$, $r = 0.980$.

None of the groups for which data are available are of the $-R$ type, which might be expected to require the use of σ^- rather than σ. Attempts to measure the rate of reaction of *p*-nitrophenyl carbonate were unsuccessful; reaction was essentially finished before mixing of the reagents could be completed.[7]

Steric Effect of *ortho* Substituents.—*ortho* substituents on the ring exert a very large steric effect. The reaction of hydroxide ion with *o*-chlorophenyl carbonate is slightly faster than with the unsubstituted compound, owing to the accelerating electronic effect of the chlorine atom, but it is only about one-fifth as fast as the reaction with the *meta* and *para* isomers. Similarly, the rate of reaction of *o*-tolyl carbonate is approximately one-fourth that of the *meta* and *para* compounds. Although a single *o*-methyl group in each ring causes only a moderate decrease in rate, the introduction of a second *o*-methyl group causes the reaction to be almost too slow for detection at 20°. The hydrolysis of 2,6-xylyl carbonate is slower by 5 orders of magnitude than the hydrolysis of diphenyl carbonate. A small part of this retardation is due to the electronic effect of the two methyl groups, which would reduce the rate by a factor of approximately 10,[8] but most of it must be ascribed to the steric effect. The magnitude of this steric effect is comparable with that observed in the hydrolysis of esters of 2,6-dimethylbenzoic acid.[9] The blocking groups in the 2,6-xylyl carbonate are one atom further removed from the carbonyl carbon, which is presumed to be the reaction site, but there are four of them, compared with two in the 2,6-dimethylbenzoates, compensating for their greater distance.

Hydrolysis in Neutral Solution.—The rates of hydrolysis of several carbonates in 1:1 dioxane–water at 100° are listed in Table II. The bromometric method used for following the rate of phenol formation was unsatisfactory when applied to most *ortho*- and *para*-substituted phenols so that the measurements were limited to *meta*-substituted carbonates. The data gave an excellent fit to the Hammett equation with $\rho = 3.394$, $\log k_0 = -4.944$, and a correlation coefficient of 0.998. This value of ρ is almost identical with the value for reaction with hydroxide ion at 20°, suggesting the possibility that hydrolysis under these conditions might be due to reaction with hydroxide ion from autoionization of water. There was no indication in any case of autoinhibition by the acidic reaction products, however, so that hydrolysis in all cases is presumably of the $B_{Ac}2$ type, in which a water molecule attacks the carbonyl group of the neutral ester.[1]

TABLE II

HYDROLYSIS OF ARYL CARBONATES IN DIOXANE–WATER AT 100°

$$(XC_6H_4O)_2C{=}O + H_2O \longrightarrow CO_2 + 2XArOH$$

Subtituent	k, sec.$^{-1}$ × 10^5
H	1.31
m-OCH_3	2.22
m-CH_3	0.63
m-Cl	19.5
m-NO_2	315.0

Experimental Section

Preparation of Carbonates.—The diaryl carbonates were in most cases prepared by passing phosgene into a cold solution of the phenol in 10% sodium hydroxide. *p*-Nitrophenyl carbonate was prepared by nitration of diphenyl carbonate,[10] and 2,6-xylyl carbonate was prepared by ester exchange between 2,6-xylenol and diphenyl carbonate.[11] The properties of those carbonates which have not previously been reported are listed in Table III.

TABLE III

Compd.	M.p., °C.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
$(m\text{-}BrC_6H_4O)_2C{=}O$	92.5–93	42.0	2.2	41.7	2.4
$(m\text{-}CH_3CO_6H_4O)_2C{=}O$	62.5–63	65.7	5.1	65.3	5.2
$(p\text{-}CH_3OC_6H_4O)_2C{=}O$	93–93.5	65.7	5.1	65.3	5.3

Rate of Reaction with Hydroxide Ion.—Solutions of the carbonate in 1:1 dioxane–water and sodium hydroxide in the same solvent were brought to the reaction temperature (20°) in a constant-temperature bath. Equal volumes of the two solutions were quickly mixed and transferred to a 1-cm. cell in a Beckman DU spectrophotometer equipped with a jacket through which water was circulated from the constant-temperature bath. The wave length scanner was set at the proper position for the substituted phenoxide ion, and the absorbance was measured at appropriate intervals. For the very fast reactions absorbance was recorded automatically. A large excess of hydroxide ion was used so that the reactions could be treated as pseudo first order. In most cases the initial concentration after mixing was 0.75×10^{-4} M in carbonate and 10^{-2} M in hydroxide ion. Plots of $\log A_\infty - A$ were linear over at least 90% of the reaction in all cases except for 2,6-xylyl carbonate, which was followed only for 5% of reaction. The second-order rate constants

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[4] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[5] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 577.

[6] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).

[7] This does not necessarily mean that the rate was so fast that the "exalted" σ^- value would be required for correlation. A small increase in rate over that observed for the *m*-nitro compound would be enough to make it impossible to measure the rate by the method used.

[8] From the measured ρ value for the reaction, assuming a σ value of -0.34 for two *o*-methyl groups (ref. 6, p. 619).

[9] The rates of reaction of benzoic and 2,6-dimethylbenzoic esters have not been measured under identical conditions, but extrapolation to 25° of the rate of reaction of hydroxide ion with methyl 2,6-dimethylbenzoate in 60 vol. % aqueous dioxane [H. L. Goering, R. Rubin, and M. S. Newman, *J. Am. Chem. Soc.*, **76**, 787 (1954)] and comparison with the rate of saponification of methyl benzoate in 60 vol. % aqueous acetone [E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938)] indicates that the two *o*-methyl groups retard the rate by a factor of 10^5.

[10] J. M. A. Hoeflake, *Rec. trav. chim.*, **36**, 24 (1916).

[11] We are indebted to Drs. D. F. Loncrini and R. J. Prochaska for this material.

reported in Table I were obtained by dividing the pseudo-first-order rate constant by hydroxide ion concentration. It has previously been shown that rate constants obtained in this way for hydrolysis of diphenyl carbonate are independent of hydroxide ion concentration.[1]

Rates in Neutral Solution.—Rates in 1:1 dioxane–water at 100° were determined by bromometric titration of phenol, following the procedure previously described.[1] Reactions were followed to at least 85% of completion and the first-order rate constants were determined graphically in the usual manner.

Catalyst Selectivity in Semihydrogenation of Some Conjugated Acetylenes[1]

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Semihydrogenation of an acetylene provides a classic route to the *cis* double bond. Both palladium[2] and Raney nickel[3] have been used with success. For isolated triple bonds the selectivity may approach 100%,[4] although it runs about 95% in general synthetic use.[5] It has been reported that selective reduction of a triple bond in a conjugated system proceeds with less success,[6] but no quantitative data have been provided. Faced with the need of some conjugated systems containing *cis* double bonds, we had occasion to examine quantitatively some examples of catalytic semihydrogenation of some enynes and dienynes.

The results of the semihydrogenation of three enynes and one dienyne over the Lindlar catalyst are shown in Table I. In no case does the rate of hydrogen uptake show a break after absorption of 1 mole of hydrogen, and the products shown in the table are obtained by arbitrary interruption of the reaction after addition of 1 mole of hydrogen. Analysis of the reaction mixtures was performed by gas chromatography. A second dienyne, 1,2-dicyclohexenylacetylene, was also submitted to the same reaction, but the products could not be analyzed successfully by gas chromatography. We were able to show by a combination of spectral and chemical methods that the reduction mixture contained unreduced starting material, overreduction products in which the triple bond had been completely reduced and some in which one of the cyclohexene double bonds was reduced, and not more than 50% of *cis*-1,2-dicyclohexenylethylene. Schlatmann and Havinga[7] have reported similar results for the semihydrogenation of 1-(2-methylcyclohexenyl)-2-cyclohexenylacetylene.

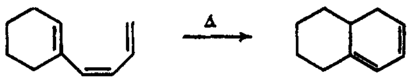
TABLE I

PRODUCTS OF SEMIHYDROGENATION OF ENYNES AND DIENYNES[a]

Substrate	Product composition (%)
$C_6H_9C\equiv CH$	$C_6H_9CH{=}CH_2$ (86)
	$C_6H_9CH_2{-}CH_3$ (8)
	$C_6H_9C\equiv CH$ (6)
$C_6H_9C\equiv C{-}CH_3$	$C_6H_9CH{=}CH{-}CH_3$, *cis* (76), *trans* (2)
	$C_6H_9CH_2{-}CH_2{-}CH_3$ (8)
	$C_6H_9C\equiv C{-}CH_3$ (14)
$C_6H_9C\equiv C{-}Et$	$C_6H_9CH{=}CH{-}Et$, *cis* (85), *trans* (5)
	$C_6H_9CH_2{-}CH_2{-}Et$ (5)
	$C_6H_9C\equiv C{-}Et$ (5)
$C_6H_9C\equiv C{-}CH{=}CH_2$	$C_6H_9CH{=}CH{-}CH{=}CH_2$, *cis* (47), *trans* (7)
	$C_6H_9CH{=}CH{-}Et$, *cis* (13), *trans* (8)
	$C_6H_9C\equiv C{-}Et$ (8)
	$C_6H_9CH_2CH_2Et$ (4)
	$C_6H_9C\equiv C{-}CH{=}CH_2$ (8)
	Unidentified (5)

[a] C_6H_9 = 1-cyclohexenyl.

In the course of this work two new *cis*-dienes and a *cis*-triene were obtained. The two dienes were isolated by preparative chromatography and identified by their ultraviolet and n.m.r. spectra as compared with the spectra of the products obtained from them by treatment with iodine in diffuse sunlight. Both *cis*-dienes undergo a thermal 1,5 hydrogen shift, a reaction which Wolinsky, Chollar, and Baird have shown to be diagnostic of *cis*-dienes.[8] The *cis*-triene was identified by comparison with a synthetic sample.[9] The *cis* configuration of the double bond was confirmed by the valence isomerization[10] occurring on the gas chromatographic column. The cyclized product was obtained *via* preparative chromatography and identified by its spectral properties and dehydrogenation to naphthalene.



The data of Table I provide several interesting conclusions. For the three enynes studied, addition occurs exclusively at the triple bond, and the stereoselectivity is not greatly different from that generally observed with isolated triple bonds. Unlike the situation with isolated triple bonds,[11] further hydrogenation of the product proceeds to an appreciable extent while the enyne is still present. For the examples studied here, this overreduction problem is not serious and the reaction is synthetically useful. Since it has been shown[12] that the order of bond selectivity is

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[1] The authors are pleased to acknowledge partial financial support from the National Science Foundation under Grant G-23072.

[2] (a) O. Isler, W. Huber, A. Ronco, and M. Kofler, *Helv. Chim. Acta*, **30**, 1911 (1947); (b) H. Lindlar, *ibid.*, **35**, 446 (1952); (c) D. J. Cram and M. Cordin, *J. Am. Chem. Soc.*, **77**, 4090 (1955).

[3] (a) N. A. Khan, *ibid.*, **74**, 3018 (1952); (b) W. Oroshnik, G. Karmas, and A. D. Mebane, *ibid.*, **74**, 295 (1952), and subsequent papers.

[4] E. F. Meyer and R. L. Burwell, *ibid.*, **85**, 2877 (1963).

[5] R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press Inc., New York, N. Y., 1955, pp. 22–27.

[6] (a) I. Heilbron, E. R. H. Jones, and F. Sondheimer, *J. Chem. Soc.*, 1586 (1947); (b) L. Crombie, S. H. Harper, and D. Thompson, *ibid.*, 2906 (1951); (c) L. Crombie, *ibid.*, 1007 (1955); (d) L. Crombie, S. H. Harper, and F. C. Newman, *ibid.*, 3963 (1956); (e) A. Butenandt, E. Hecker, and H. G. Zachau, *Chem. Ber.*, **88**, 1185 (1955); (f) W. Oroshnik and A. D. Mebane, *J. Am. Chem. Soc.*, **76**, 5719 (1954); (g) W. Oroshnik, *ibid.*, **78**, 2651 (1956).

[7] J. L. M. A. Schlatmann and E. Havinga, *Rec. trav. chim.*, **80**, 1101 (1961).

[8] J. Wolinsky, B. Chollar, and M. D. Baird, *J. Am. Chem. Soc.*, **84**, 1775 (1962).

[9] J. Tashiro, Ph.D. Thesis, Oregon State University, 1964.

[10] See, for example, E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Letters*, 385 (1965); E. Vogel, W. Grimme, and E. Dinne, *ibid.*, 391 (1965); D. W. Glass, J. W. H. Watthey, and S. Winstein, *ibid.*, 377 (1965).

[11] For an excellent review of this subject, see G. C. Bond and P. B. Wells, *Advan. Catalysis*, **15**, 91 (1964).

[12] N. A. Dobson, G. Eglinton, M. Krishnamurti, R. A. Raphael, and R. G. Willis, *Tetrahedron*, **16**, 16 (1961).