Anal. Calcd. for $C_9H_8Cl_3NS$: C, 40.24; H, 3.00; Cl, 39.60; N, 5.22. Found: C, 40.33; H, 3.14; Cl, 39.59; N, 5.22.

N,N-Diethyl-α,α,α-trichlorothionacetamide (XIId).—A solution of N,N-diethyl-1,2,2-trichlorovinylamine[2] (4.8 g., 0.024 mole) in carbon tetrachloride (40 ml.) was stirred at 0° while chlorine was passed into the solution until it was no longer absorbed. The carbon tetrachloride was removed *in vacuo* and the residue was dissolved in methylene chloride (40 ml.). Hydrogen sulfide was passed through the solution for 1 hr. and the methylene chloride was removed *in vacuo*. The residue was dissolved in pentane and placed on a column of neutral alumina (Woelm) packed wet with pentane. Elution with pentane gave a yellow oil which was redissolved in pentane and placed on a fresh column of alumina. Elution with pentane gave N,N-diethyl-α,α,α-trichlorothionacetamide as a yellow oil (3.1 g., 0.0135 mole, 56%).

Anal. Calcd. for $C_6H_{10}Cl_3NS$: C, 30.72; H, 4.29; Cl, 45.34; N, 5.97. Found: C, 31.01; H, 4.66; Cl, 46.86; N, 5.77.

α,α-Dichlorothionacetanilide (Xb).—A mixture of α,α-dichloroacetanilide (5.1 g., 0.027 mole), phosphorus pentasulfide (2.8 g., 0.0125 mole), and benzene (25 ml.) was refluxed for 1 hr. and filtered. Chilling of the filtrate in an ice bath caused α,α-dichloroacetanilide (3.0 g., 59%) to separate. The filtrate was evaporated *in vacuo* and the residue was extracted with hot hexane. The hexane solution was filtered through charcoal and chilled. This produced α,α-dichlorothionacetanilide as a yellow solid (0.4 g., 0.0018 mole, 18% based on recovered starting material), m.p. 71–72°.

Anal. Calcd. for $C_8H_7Cl_2NS$: C, 43.65; H, 3.21; Cl, 32.21; N, 6.36; S, 14.57. Found: C, 44.36; H, 3.61; Cl, 31.69; N, 6.81; S, 14.11.

Reaction of N-Methyl-α,α,α-trichloroacetanilide and Phosphorus Pentasulfide.—A mixture of N-methyl-α,α,α-trichloroacetanilide (5.0 g., 0.02 mole), phosphorus pentasulfide, (4.4 g., 0.02 mole), and toluene (50 ml.) was refluxed for 16 hr. The toluene was removed *in vacuo* and the residue was extracted with hot benzene. The benzene solution was placed on a column of neutral alumina (Woelm) packed wet with pentane. Elution with benzene gave N-methyl-α,α-dichlorothionacetanilide (0.5 g., 0.002 mole, 10%), m.p. 103°. The infrared spectrum was identical with that of the sample prepared as described previously.

N-Methylthionacetanilide.[14]—N-Methylacetanilide (14.9 g., 0.1 mole) and phosphorus pentasulfide (22.2 g., 0.1 mole) were refluxed in xylene for 17 hr. The solution was decanted from a tarry residue and the xylene was distilled *in vacuo*. The residue was dissolved in benzene and placed on a column of alumina packed wet with hexane. Elution with benzene and recrystallization from benzene–hexane gave N-methylthionacetanilide (4.6 g., 0.028 mole, 28%), m.p. 56–58°.

Anal. Calcd. for $C_9H_{11}NS$: C, 65.40; H, 6.71; N, 8.48; S, 19.40. Found: C, 65.44; H, 7.01; N, 8.14; S, 19.14.

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[14] With Joan E. Fedder.

Pyrolysis Studies. VIII.[1] Polar Substituent Effects in the Vapor Phase Thermal Decomposition of Isopropyl Benzoates

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The absolute reaction rates of thermal decomposition of a series of *meta*- and *para*-substituted isopropyl benzoates have been measured in the vapor phase, using a new pyrolysis apparatus in which the pressure changes were monitored continuously and automatically. Electron-withdrawing substituents were found to increase the rate of decomposition and the relative rates were best correlated by Taft's σ^0-values ($\rho = 0.33$). The σ^0-values for the groups *p*-*t*-Bu, *p*-Ph, and β-naphthyl were found to be −0.18, +0.08, and +0.15, respectively. Differences between Taft's σ^0-values and Wepster's σ^n-values are discussed, and it is concluded that the Taft σ^0-values give the better measure of the polar effects of *meta* and *para* substituents. The physical properties of eleven new substituted isopropyl benzoates are reported.

For reactions and equilibria involving simple benzene derivatives, it has been fairly generally accepted that the Hammett σ-values derived from the ionization constants of substituted benzoic acids in water at 25° give quantitative measures of the relative polar effects of *meta*- and *para*-substituted phenyl groups.[3,4] However, this ionization is not entirely free from resonance effects as there is direct conjugation between the reaction site and the ring. For example, when the acids bear R^+ *para* substituents there is greater resonance stabilization in the free acid than in the anion, and this lowers the experimentally observed acidity and leads to anomalous σ-values.

Taft[4] and Wepster[5] recently have realized this and have published tables of revised σ-values, designated σ^0 and σ^n, respectively, which give a quantitative measure of the fundamental polar effects of the substituents. However, although both workers used essentially the same approach to the problem, the agreement between the σ^0- and the σ^n-values is not too precise, which is disturbing as it is necessary to have confident knowledge of these fundamental polar effects in order to understand and explain more complicated effects. It was, therefore, decided to evaluate and compare these two sets of polar substituent values by experiment, using data obtained from vapor phase kinetic studies. Measurements were confined to the vapor phase to preclude solvent effects since for some substituents Taft found it necessary to propose *two* σ^0-values, one to be used when dealing with studies in hydroxylic solvents and the other for nonhydroxylic solvents.[4]

Previous studies have shown that the relative rates of vapor phase pyrolysis of *meta*- and *para*-substituted ethyl benzoates to ethylene and the corresponding substituted benzoic acids correlate with Taft's σ^0-values better than with the normal Hammett σ-values.[1] Unfortunately, the σ-value in this reaction was rather small (0.20) and although the relative rates could be measured to within ±3%, this is not sufficiently precise to permit a meaningful comparison of σ^0 and σ^n correla-

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[1] Part VII: G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, **28**, 403 (1963).

[2] Postdoctoral Research Associate, 1961–1962.

[3] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

[4] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

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

TABLE I

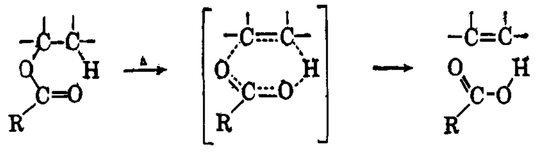
PHYSICAL CONSTANTS AND RATES OF PYROLYSIS OF SUBSTITUTED ISOPROPYL BENZOATES AT 337.4 ± 0.2°

					Analyses,[a] %						
					Calcd.			Found			
Substituent	Yield, %	M.p. or b.p. (mm.), °C.	$n^{20}D$	Empirical formula	C	H	N or X	C	H	N or X	$k \times 10^3$, sec.$^{-1}$
p-*t*-Bu	82	160–163 (27)	1.4943	$C_{14}H_{20}O_2$	76.32	9.15		76.27	9.25		1.08[b]
p-Me	15	110–111.5 (12)	1.4980	$C_{11}H_{14}O_2$	74.13	7.92		74.28	8.02		1.10
m-NH_2	14	130 (2.5)	1.5453	$C_{10}H_{13}NO_2$	67.02	7.31	7.82	67.10	7.45	7.92	1.10[b]
p-OMe	76	140–141 (14)[c]	1.5140[d]								1.11[b]
m-Me	62	108–110 (11)	1.4952	$C_{11}H_{14}O_2$	74.13	7.92		74.21	7.96		1.19
H	68	90 (9)[e]	1.4946[e]								1.24
m-OMe	16	100–102 (3.2)	1.5038	$C_{11}H_{14}O_3$	68.02	7.27		68.29	7.21		1.26[b]
p-F	42	96 (22)	1.4773	$C_{10}H_{11}FO_2$	65.92	6.08	10.42	65.86	6.38	10.21	1.38
3,4-C_4H_4[f]	47	118–120 (0.7)	1.5793	$C_{14}H_{14}O_2$	78.48	6.59		78.59	6.40		1.40
p-Cl	36	120–121 (14)	1.5088	$C_{10}H_{11}ClO_2$	60.46	5.58	17.85	60.64	5.68	17.91	1.56
m-F	19	100–101 (18)	1.4763	$C_{10}H_{11}FO_2$	65.92	6.08	10.42	65.87	6.22	10.68	1.60
m-Cl	68	118.5–120.5 (14)	1.5222	$C_{10}H_{11}ClO_2$	60.46	5.58	17.85	60.34	5.62	17.62	1.64
m-NO_2	42	118–120.5 (1.7)	1.5204	$C_{10}H_{11}NO_4$	57.42	5.30	6.69	57.17	5.45	6.84	2.09[b]
p-NO_2	66	111.5–112[g]									2.16[b]

[a] Analyses by A. Bernhardt, Mülheim (Ruhr), Germany. [b] Because of secondary decomposition, rates were obtained by plotting dE/dt against E (see Experimental section). [c] Lit. b.p. 146° (13 mm.) [A. Sosa, *Ann. chim.* (Paris), **14,** 5 (1940)]. [d] Lit. $n^{25}D$ 1.5107 [L. P. Kuhn, *J. Am. Chem. Soc.*, **71,** 1575 (1949)]. [e] Lit. b.p. 94° (10 mm.), $n^{20}D$ 1.4947 [M. Gordon, J. G. Miller, and A. R. Day, *ibid.*, **70,** 1946 (1949)]. [f] β-Naphthyl. [g] Lit. m.p. 111° [E. Buchner and J. Meisenheimer, *Ber.*, **38,** 627 (1905)].

tions. An attempt was made to improve the accuracy by measuring the absolute rates of decomposition in a static system but with limited success since the high temperatures caused considerable secondary decomposition of the eliminated benzoic acid.[1]

The mechanism of pyrolysis of esters of this type, *i.e.*, those containing at least one β-hydrogen atom, has been studied very thoroughly. It is generally accepted that the elimination is unimolecular, first order, and proceeds *via* a cyclic transition state in which the α-carbon atom develops some carbonium ion character.[6,7] Substituted isopropyl and *t*-butyl benzoates would be expected to decompose at lower temperatures as increased alkyl branching at the α-carbon will increase the stability of the incipient α-carbonium ion. Results from reaction series of this type will thus be more suitable for the evaluation of the Taft σ^0- and Wepster σ^n-substituent values as the ρ-values should be larger. Secondary decomposition of the eliminated benzoic acids should be much less at lower temperatures.



The present work reports on the vapor phase pyrolysis of *meta*- and *para*-substituted isopropyl benzoates,[8] also on a modified pyrolysis apparatus by which rate constants can be obtained accurately even in the presence of a small amount of secondary decomposition.

Experimental

Ester Preparation.—Most esters were prepared from the substituted benzoyl chlorides by refluxing with isopropyl alcohol and pyridine. The acyl chlorides, if not commercially available, were prepared from the acids using thionyl chloride. The *m*-amino ester was prepared from the *m*-amino acid and isopropy alcohol using dry hydrogen chloride as a catalyst. Liquid esters were purified by careful fractionation and solid esters were purified by crystallization to constant melting point. Compounds were stored in the dark under refrigeration to prevent decomposition and formation of free radicals which interfere in the pyrolysis and lead to anomalous rate data. The physical constants, yields, and elemental analysis are given in Table I.

Method of Pyrolysis. A. Apparatus.—The pyrolysis apparatus has been described previously[6,9] except for a new automatic pressure monitoring system which is shown schematically in Fig. 1.

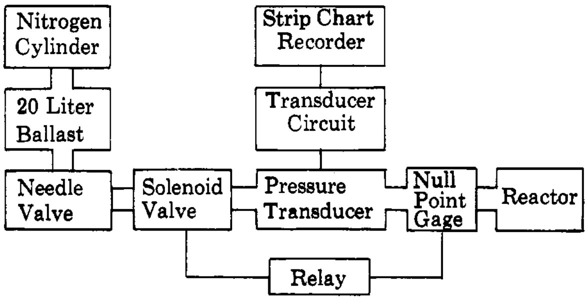


Fig. 1.—Automatic pressure monitoring system.

In the original system,[9] the relay was connected to an electric bell and the pressure on the measuring side of the null point gage was adjusted and measured manually as the reaction proceeded. In the new system, the relay was connected to a small solenoid valve so that the pressure on the measuring side of the gage increased smoothly and automatically as the pressure inside the reactor increased. The pressure was recorded continuously on a Brown 2-mv. strip-chart recorder using a Dynisco 0–30-p.s.i.a. (0–1600 mm.) pressure transducer which gave an output of 0–30 mv. with 6-v. excitation. In order to cover the full pressure range, the transducer circuit included a means by which a back e.m.f. of 0–28 mv. could be superimposed on the transducer output in progressively increasing steps of 2 mv.[10] This made it possible to record pressures continuously from 0 to 1600 mm. to within ±0.05 mm.

B. Injection of Samples.—Each ester was injected as a 1:1 solution in cyclohexene or chlorobenzene in volumes of 200–500 μl. Using a conventional hypodermic syringe, however, air was sometimes sucked into the evacuated reactor between the barrel

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(6) G. G. Smith, F. D. Bagley, and R. Taylor, *J. Am. Chem. Soc.*, **83,** 3647 (1961).

(7) R. Taylor, G. G. Smith, and W. H. Wetzel, *ibid.*, **84,** 4817 (1962).

(8) Data for the *t*-butyl benzoates will be reported later.

(9) G. G. Smith and F. D. Bagley, *Rev. Sci. Instr.*, **32,** 703 (1961).

(10) Details of the circuitry are available on request.

and the plunger of the syringe, and the oxygen tended to activate the surface.[7,9] This activation was avoided by mounting a toy balloon filled with pure nitrogen over the end of the syringe with an elastic band. (If a little nitrogen is sucked into the reactor it does not matter as it exerts a constant pressure throughout the reaction.) In all cases the reaction temperature was 337.4 ± 0.2°.

Calculation of Rate Constants.—Since the recorded pressure-transducer output E was found to vary linearly with the absolute pressure P, first-order rate constants were calculated directly from the slopes of plots of log $(E_\infty - E_t)$ against time. Values of E and the elapsed time t were obtained directly from the recorder chart, usually at one minute intervals, although with a continuous record there is no limit to the number of available (E, t) values, and rates of relatively fast decompositions can be accurately determined.

For reactions in which the acidic products underwent secondary decomposition, rate constants were obtained from the initial slopes of plots of dE/dt against E (Fig. 2). (For a first-order vapor phase decomposition $dP/dt = -kP + C$, and E is linearly related to P so that $dE/dt = -kE + C'$.) Using this method it is not necessary to extrapolate back to E_0 (or P_0) in order to calculate E_∞ (or P_∞). Another advantage is that compounds can be injected in solution without having to correct for the partial pressure of the solvent. Results thus far obtained indicate that while this method is less precise than that outlined previously, the reproducibility is at least within ±3%, and is often much better, as shown in Fig. 2.

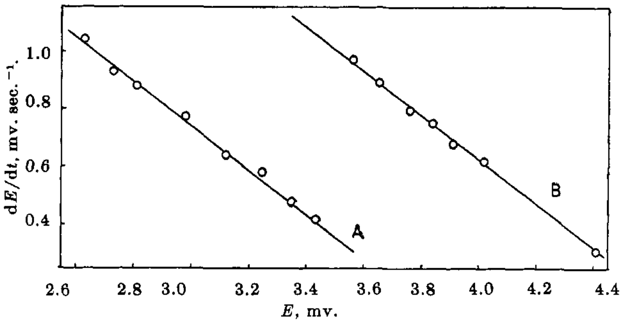

Fig. 2.—Plots of dE/dt against E for pyrolysis of isopropyl *m*-methoxybenzoate at 341.2 ± 0.2° for two different initial pressures. Least squares treatment of data gives for A, $k = 1.27 \times 10^{-3}$ sec.$^{-1}$; for B, $k = 1.26 \times 10^{-3}$ sec.$^{-1}$.

Product Analyses.—The pyrolysis products were collected in a liquid nitrogen trap attached directly behind a valve leading to the vacuum system. In order to ensure that trace amounts could be detected, products were accumulated in the trap from five 0.5-cc. runs. While the products were still at the liquid nitrogen temperature (−196°) a sample was taken with a long needle and a 3-cc. syringe. This sample produced only one peak (N_2) from a 2-m. silica gel gas chromatographic column. After the products were allowed to warm to Dry Ice–isopropyl alcohol temperature (−72°) a v.p.c. analysis showed only two peaks which proved to be nitrogen and propene.

The acids were reclaimed from the trap as solids. These product analyses added to the excellent kinetic data and $\rho\sigma^0$ plot conclusively demonstrates the fact that at this temperature (337°) the pyrolysis of isopropyl benzoates in a carefully deactivated reactor follow first-order kinetics to greater than 90% to give propylene and acids and the rate can be accurately followed by continuously measuring the change in pressure.

At 530° (the temperature necessary to pyrolyze primary alkyl benzoates with a contact time of less than a second) besides olefins and acids, other products are produced as well. This confirms a well established fact[1,11] that secondary esters pyrolyze at lower temperatures without complication, whereas primary esters pyrolyze at high temperatures to products in addition to olefins and acids.

Results and Discussion

Decompositions were found to follow the expected first-order kinetics, and rate constants were calculated as explained in the Experimental section. Each ester was pyrolyzed at least three times and the mean values of the rate constants are given in Table I. Average deviations from the mean were within ±1% except for isopropyl *m*-amino- and isopropyl *p*-*t*-butylbenzoates (both ±2%), and isopropyl *p*-methoxy- and *m*-nitrobenzoates (both ±2.7%). These four compounds showed secondary decomposition and their rate constants were obtained from the initial slopes of plots of dE/dt against E.

The results are largely as expected from the previous work on the pyrolysis of *meta*- and *para*-substituted ethyl benzoates.[1] The rate of elimination is accelerated by electron-withdrawing substituents and retarded by electron-releasing substituents, and the relative rates are correlated very well by Taft's σ^0-values[12] as shown in the lower plot in Fig. 3. For substituents which have two σ^0-values, the values for *nonhydroxylic* solvents are preferred. This points to specific solvent–solute interactions being responsible for the "solvent effects" observed in solution studies, rather than the change in phase.[13] The ρ-value of 0.33 is slightly higher than that observed in the ethyl benzoate series,[1] (0.20) as expected. Deviations of individual points from the line lie within the estimated errors in log k/k_0 due to experimental uncertainties in the rate constants, and within the standard errors in the σ^0-values quoted by Taft.[4]

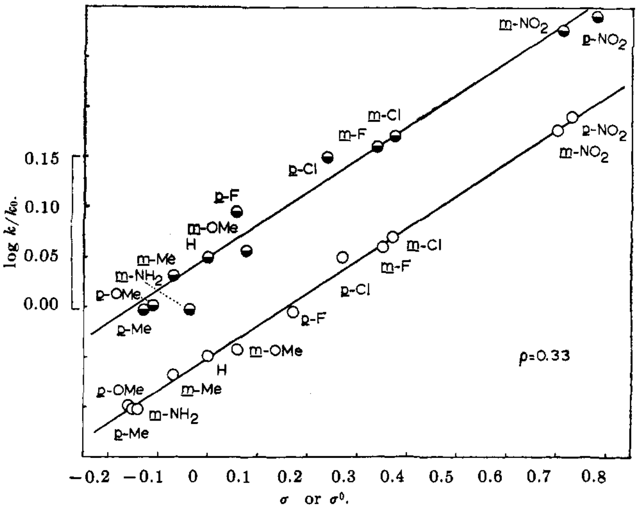

Fig. 3.—Wepster σ^n plot (upper), and Taft σ^0 plot (lower) for pyrolysis of substituted isopropyl benzoates at 337.4 ± 0.2°.

The upper plot in Fig. 3 shows that the correlation between the same relative rate data and Wepster's σ^n-values is less precise, and this indicates that Taft's σ^0-values give a more correct measure of the relative polar effects of the substituents.

Both Wepster and Taft approached the problem of determining polar substituent constants in the same way. They chose rate and equilibrium constant data for "resonance free" reactions and equilibria involving *meta*- and *para*-substituted phenyl compounds, and

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(11) (a) G. F. Smith and F. D. Bagley, Survey Paper, American Documentation Institute, Library of Congress, Washington 25, D. C., Serial No. 7281; (b) C. D. Hurd, "The Pyrolysis of Organic Compounds," The Chemical Catalog Co., Inc., New York, N. Y., 1929.

(12) A similar plot using the normal Hammett σ-values shows a good deal of scatter and is much less satisfactory.

(13) *Cf.* R. Taylor and G. G. Smith, *Tetrahedron*, in press (1963).

calculated ρ^0(or ρ^n)-values by assuming that for certain substituents σ^0 (or ρ^n) was equivalent to the normal Hammett σ. Then knowing ρ^0 or ρ^n for a particular reaction they were able to calculate σ^0- or σ^n-values for other substituents. Finally, best values were obtained by statistical averaging. Taft was very careful in his choice of reactions, to avoid resonance complications, and used only data pertaining to compounds which had at least one insulating methylene group between the reaction center and the ring. Also, in setting up his master ρ^0-values he very wisely used data from *meta*-substituted compounds only. Wepster, however, was not so cautious. In many of his "resonance free" reaction series, the reaction center was in direct conjugation with the ring, and he also used some data from *para*-substituted compounds (especially for the groups *p*-NO_2 and *p*-COMe) in setting up his master ρ-values. Taft found these two substituents to require two σ^0-values, one for hydroxylic and one for nonhydroxylic solvents. Wepster did, in fact, find that second-order resonance effects ("saturation" effects) were operating in some of his reaction series, particularly those involving anilinium ion formation, and he does say that the best σ^n-values would probably be obtained from systems with an insulating bridge between benzene ring and reaction center. In his reference 17 he actually gives modified σ^n-values for the groups *p*-F, *p*-Cl, and *p*-Br which are almost identical with Taft's σ^0-values.

As the Taft approach appears to be sounder theoretically and his σ^0-values for nonhydroxylic solvents correlate well with experimental results obtained in the vapor phase, we conclude that these values give a good quantitative measure of the relative polar effects of *meta*- and *para*-substituted phenyl groups.

Some compounds were studied in the present work and in the pyrolysis of ethyl aryl carbonates (paper IX), for which σ^0-values were not previously available. It was possible to assign the following σ^0-values by substitution in the equation $\log k/k_0 = \rho\sigma^0$[14]: *p*-Ph, +0.08; *p*-*t*-Bu, −0.18; 3,4-C_4H_4(β-naphthyl), +0.15.

It should be added that Norman and co-workers[15] recently made an almost duplicate approach to the problem using much of the same reaction rate and equilibrium data as did Taft. Their handling of this data was slightly different though, and, like Wepster, they did not notice any solvent effects. The Norman values, designated σ_G do not correlate the present data as well as do Taft's, the deviation being very marked in the case of *m*-NO_2. Interestingly, Norman and coworkers also drew attention to the danger of using the substituents *p*-NO_2 and *p*-COMe in setting up master ρ-values. They say this is likely to lead to anomalies because of second-order resonance effects.

In view of what has been said previously, it is a little surprising that the pyrolysis of alkyl benzoates proves to be a reaction which shows a resonance-free σ^0 correlation, as there is no insulating methylene bridge between reaction center and the ring, especially as the transition state involves a degree of charge separation formally similar to that in the benzoate anion. A similar anomaly is observed in the case of ion-pair formation between substituted benzoic acids and 1,3-biphenylguanidine in benzene solution.[4,16] Evidently the difference in resonance stabilization between the ground state and the transition state (or between reactant and product in the cases of equilibria) only becomes important when the carboxylate anion is fully developed; with incipient species the "resonance effect" is apparently negligible.

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We are grateful to Mr. D. V. White and Mr. V. R. Rice for assistance with synthetic work.

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[14] σ^0 for *p*-Ph was obtained from phenyl ethyl carbonate data only; σ^0 for *p*-*t*-Bu and β-naphthyl were obtained by averaging the values from the two studies: G. G. Smith, D. A. K. Jones, and R. Taylor, Paper IX, *J. Org Chem.*, **28**, 3547 (1963).

[15] R. O. C. Norman, G. K. Radda, D. A. Brimacombe, P. D. Ralph; and E. M. Smith, *J. Chem. Soc.*, 3247 (1961).

[16] M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Std.*, **60**, 569 (1958).

Another Example of the Novel Conversion of a Phosphonate to a Phosphate

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Treatment of diethyl α-(*N*-alkylamino)benzylphosphonates with thionyl chloride, *p*-nitrophenol, and triethylamine causes conversion to the triethylamine salt of di-*p*-nitrophenyl hydrogen phosphate. The products of conversion were compared with compounds of known structure obtained by another preparation and found to be identical. New *N*-alkylaminophosphonourethans and α-*N*-alkylaminophosphonates are also reported.

As part of a continuous program looking toward the synthesis of a more specific organophosphorus enzyme inhibitors,[1b] a number of new phosphonate esters have been prepared (Table I). However, the desired phosphonate was I, and its synthesis was attempted *via* the well known route shown on p. 3500, col. 1.

The product of the reaction was not I, but rather II, and, the isolation of this triethylamine salt of di-*p*-nitrophenyl hydrogen phosphate in fair yield is another of the few known examples of the conversion of phosphonate to a phosphate.

Other such rearrangements known to us are Perkow's[2] rearrangement reaction between trialkyl phos-

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[1] (a) This manuscript does not indorse nor recommend any instruments or products as may be named herein; (b) E. L. Becker, T. R. Fukuto, B. Boone, D. C. Canham, and E. Boger, *Biochem. J.*, **2**, 72 (1963).

[2] W. Perkow, *Ber.*, **87**, 755 (1954); W. Perkow, K. Utterich, and F. Meyer, *Naturwiss.*, **39**, 353 (1952).