An additional experiment with 4.27 g. (0.02 mole) of α-aminovalerophenone hydrochloride yielded 2.03 g. of crude acid mixture. A small sample (0.00861 g.) of the crude acid was dissolved in an ethyl acetate–Skelly-Solve B mixture and placed on a 1.5 × 35 cm. silicic acid chromatographic column using the procedure of Bhargava and Heidelberger[25] for the separation of carboxylic acids.

The eluent was collected in 3.5-ml. samples, diluted with 3.5 ml. of water and 0.4 ml. of n-butyl alcohol and titrated with 0.005 N sodium hydroxide (phenol red indicator). Two peaks resulted, the first peak (corresponding to that of pure α-phenylvaleric acid) using 59% of the total volume of alkali and the second peak (corresponding to that of pure benzoic acid) using 41% of the total volume of alkali. Thus the yields in the original acid sample were 1.36 g. (38%) of α-phenylvaleric acid and 0.67 g. (27.5%) of benzoic acid.

A mixture of 1.0 g. (0.0056 mole) of the supposed α-phenylvaleric acid and 5 ml. of thionyl chloride was refluxed for 30 min. and then poured into 15 ml. of ice-cold concentrated ammonia. The precipitated amide was collected by filtration. The yield of α-phenylvaleramide was 0.49 g. (49%), m.p. 82.5–84°. The product was recrystallized from a water–ethanol mixture, m.p. 83.5–85° (lit.[26] m.p. 83–85°).

The Reaction of Desylamine Hydrochloride with Nitrous Acid.—Desylamine hydrochloride (4.93 g. 0.02 mole) was treated with nitrous acid as in procedure A. On acidification of the sodium carbonate extract, 2.10 g. of solid was obtained. A small sample (0.00496 g.) of the crude acid was dissolved in an ethyl acetate–Skelly-Solve B mixture and placed on the silicic acid chromatographic column described above. Two peaks resulted, the first peak (corresponding to that of pure diphenylacetic acid) using 6.5% of the total volume of alkali and the second peak (corresponding to that of pure benzoic acid) using 93.5% of the total volume of alkali. Thus, the yields in the original acid sample were 0.22 g. (5%) of diphenylacetic acid and 1.88 g. (77%) of benzoic acid.

The Reaction of α-Aminocyclohexanone Hydrochloride with Nitrous Acid.— α-Aminocyclohexanone hydrochloride (14.95 g., 0.1 mole) was treated with nitrous acid as in procedure A. After neutralization the solution was extracted with ether and the ethereal extract was dried over anhydrous magnesium sulfate. The ether was removed by distillation and the residue was distilled at reduced pressure yielding 2.40 g. (21%) of cyclopentanecarboxylic acid, b.p. 76° (2.8 mm.) (lit.[27] b.p. 104° (11 mm.)). Its neutralization equivalent was 119.2 (calcd. 114.1).

(25) P. M. Bhargava and C. Heidelberger, THIS JOURNAL, 77, 166 (1955).

(26) Bayer & Co., German Patent 249,241; Chem. Zentr., 83, 396 (1912).

A second experiment with 2.99 g. (0.02 mole) of α-aminocyclohexanone hydrochloride yielded 0.74 g. of crude acid mixture. A small sample (0.00494 g.) of the crude acid was dissolved in an ethyl acetate–Skelly-Solve B mixture and placed on the silicic acid chromatographic column described above. Only one peak resulted (corresponding to that of pure cyclopentanecarboxylic acid). Only 56% of the acid was eluted leaving 44% of the crude acid which was not accounted for.

A mixture of 1.0 g. (0.0088 mole) of the supposed cyclopentanecarboxylic acid and 5 ml. of thionyl chloride was refluxed for 30 min. and then poured into 15 ml. of ice-cold concentrated ammonia. The precipitated amide was collected by filtration. The yield of cyclopentanecarboxamide was 0.51 g. (51%), m.p. 175–178°. The product was recrystallized from a water–ethanol mixture, m.p. 178–179° (lit.[27] m.p. 179°).

In a third experiment α-aminocyclohexanone hydrochloride (7.5 g., 0.05 mole) was treated with nitrous acid as in procedure B-1 except that the combined ether layers were washed only with water and dried over magnesium sulfate. The ether was removed by distillation and the residue was heated under reflux for 4 hr. with 50 ml. of anhydrous methanol and 10 g. of ion exchange resin Amberlite IR-120, which had been washed thoroughly with methanol and dried in vacuo. The methanol was evaporated, the residue was picked up in methylene chloride and the solution was washed with 5% sodium carbonate and with water and dried over magnesium sulfate. Examination of the solution by gas chromatography using the column and procedure described above showed the probable presence of methyl cyclopentanecarboxylate, methyl 5-hexenoate and methyl 6-hydroxyhexanoate, as well as other neutral material.[28] The presence of the latter two esters was inferred from the agreement of retention times with those observed for a crude mixture of esters and neutral materials obtained under the same conditions from the reaction of 6-aminohexanoic acid with nitrous acid. This tentative identification was supported by comparison of the infrared spectra of the two methylene chloride solutions, both of which showed the bands expected for compounds containing the hydroxyl (3490 (w)), ester carbonyl (1835(s)) and terminal vinyl group (1640(w), 915(s) cm.⁻¹).[29]

(27) N. Zelinsky, Ber., 41, 2627 (1908).

(28) Based on incomplete experiments with other α-amino ketones; other materials probably present include α-hydroxycyclohexanone and 1,2-cyclohexanedione, the latter resulting from the oxidation of the former.

(29) In view of the announced intentions of Edwards and Lesage[7] to study this particular reaction in detail, at the moment we plan no experiments with α-aminocyclohexanone beyond those described here.

The Effect of the Nature of the Leaving Group upon Relative Solvolytic Reactivity[1]

BY MARC S. SILVER

A series of substituted benzhydryl p-nitrobenzoates have been prepared and the rates of the acid-catalyzed and neutral solvolyses of these compounds in aqueous acetone have been determined. It has been established that alkyl-oxygen fission occurs, primarily by correlating the solvolysis rates with σ⁺. The ρ-values for the neutral solvolysis (−4.12 to −3.69) are appreciably different from those for the acid-catalyzed reaction (−2.65 to −2.33). The significance of this difference is discussed briefly.

Perusal of several articles on the general nature of the solvolysis reaction[2–4] reveals that relatively little attention has been focused on the effect of the

(2) A. Streitwieser, Jr., Chem. Revs., 56, 571 (1956).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, chapter VII.

(4) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, chapters 5, 6.

leaving group X upon the solvolytic behavior of RX. In 1957, however, Fainberg and Winstein[5] systematically studied variations in the ratios of solvolysis rates for bromides to chlorides[k(RBr)/k(RCl), R = t-butyl, neophyl, α-phenylethyl and benzhydryl] as a function of solvent composition.

(5) (a) A. H. Fainberg and S. Winstein, THIS JOURNAL, 79, 1597, 1602, 1608 (1957); (b) S. Winstein, A. H. Fainberg and E. Grunwald, ibid., 79, 4146 (1957).

TABLE I

RELATIVE REACTIVITY OF *t*-BUTYL, α-PHENYLETHYL AND BENZHYDRYL HALIDES[a]

| | | | $k(R_1X)/k(R_2X)$ | |
R₁X	R₂X	EtOH	80% dioxane- 20% H₂O	HOAc[b]
[C₆H₅]₂CHCl	*t*-BuCl	327[b]	15.8[b]	18.6
[C₆H₅]₂CHBr	*t*-BuBr	282[c]	7.1[c]	4.0
C₆H₅CHClCH₃	*t*-BuCl	1.8[b]	0.29[b]	0.38
C₆H₅CHBrCH₃	*t*-BuBr	1.4[c]	0.13[c]	0.13
[C₆H₅]₂CHCl	C₆H₅CHClCH₃	182[b]	54[b]	49
[C₆H₅]₂CHBr	C₆H₅CHBrCH₃	197[c]	56[c]	30

[a] Based on data from ref. 5 and 6.　[b] Temperature 50°.　[c] Temperature 25°.

They found[5] that this ratio increased appreciably on going from carboxylic acid-containing solvents to those which did not contain these acids, and interpreted the data in terms of hydrogen-bonding phenomena.[5b]

the results just quoted do not suggest much difference between solvolyses *avec* and *sans* ion-pair formation, it was believed that further examination of possible differences between the two modes of reaction was warranted. A series of substituted benzhydryl *p*-nitrobenzoates is a likely place to begin. The esters can be solvolyzed under both neutral and acid-catalyzed conditions. If alkyl-oxygen fission can be demonstrated, this will provide the desired change in the nature of the ionization process,[7] and correlation with the Hammett equation[8] affords a sensitive probe into the transition states for the reactions.

Results

The *p*-nitrobenzoates of several monosubstituted benzhydrols were prepared by conventional methods. The substituent groups were *p*-methoxy, *m*-methoxy, *p*-methyl, *m*-methyl, *p*-chloro and *m*-chloro. The rates of solvolysis of the esters were

TABLE II

RATES OF SOLVOLYSIS OF SOME BENZHYDRYL *p*-NITROBENZOATES $p\text{-}NO_2C_6H_4CO_2CHC_6H_5C_6H_4X$ IN AQUEOUS ACETONE[a,b]

| | 10^5k, 90%, no H⁺ | | | 10^5k, 75%, no H⁺ | | | 10^5k, 90%, H⁺ | | | 10^5k, 75%, H⁺ | | |
X	95.8°	104.9°	114.6°	95.8°	104.9°	114.6°	95.8°	104.9°	114.6°	95.8°	104.9°	114.6°
H	...	.....	0.127	....	0.98	2.06	..	1.81[d]	6.02	..	0.91	2.90
m-CH₃	...	.....	0.220	....	1.65	4.01	..	2.72[d]	8.38	..	1.32	4.42
p-CH₃	...	0.63[c]	1.44	4.72	10.8	25.4	..	9.4	29.4	1.64	4.5	16.9
m-CH₃O	...	.....	.....	....	0.66	1.62	..	1.40[d]	4.43[e]	..	0.62	1.90
p-CH₃O	47.7[c]	103[c]	200	455	1030	1950	43.1	131	360	..	..	...
m-Cl	...	.....	.....	....	.....	.....	..	.....	0.56[e]	..	..	...
p-Cl	...	.....	.....	....	.....	1.08	..	0.76[d]	2.40[e]	..	..	1.24

[a] All rate constants in sec.⁻¹.　[b] [H⁺] = 0.0078 M for 90% acetone and 0.0083 M for 75% acetone in acid-catalyzed runs; [NaClO₄] = 0.0076 M for 90% acetone and 0.0079 M for 75% acetone in uncatalyzed runs; concentrations refer to 25°.　[c] Corrected for a different solvent batch so as to compare to other runs in this solvent; maximum applied correction was 4%.　[d] Calculated by assuming that for benzhydryl *p*-nitrobenzoate, 104.9°, 90%, no H⁺, $k = 0.06 \times 10^{-5}$ sec.⁻¹ and that $\rho^+ = -4.0$; the maximum correction applied for the uncatalyzed reaction was 4%.　[e] A Hammett plot of the measured points for the uncatalyzed reaction under these conditions was made; the rate of the uncatalyzed reaction of this compound was estimated from the plot and subtracted from the observed acid-catalyzed rate, to give the tabulated value; maximum applied correction was 2%.

Another consideration of the effect of X upon the behavior of RX is the variation in the ratio of solvolysis rate for one alkyl group to that for another group as X is changed, that is, the ratio $k(R_1X)/k(R_2X)$ as a function of X. Table I shows that this ratio, under any given set of reaction conditions, is often relatively independent of the nature of X, at least over the limited range of RX considered. The approximate invariance of the ratio can also be seen for the quotient $k(t\text{-amyl } X)/k(t\text{-butyl } X)$. Assuming a value of 1.00 for X = Cl, this ratio has the value[2] 1.07, 1.14 and 3.8 for X = Br, I and $\overset{+}{S}Me_2$, respectively, at 25° in 80% ethanol. The constancy of these rate ratios is not surprising in terms of the SN1 hypothesis,[3,6] since the transition state for all the reactions mentioned can be described usefully as one in which the alkyl fragment approximates an alkyl carbonium ion.

The rate-determining step of all the solvolyses thus far discussed, with the exception of those of the sulfonium salts, involves ion-pair formation. The solvolysis of the charged sulfonium salts cannot occur with ion-pair formation. Although

measured in 75% and 90% aqueous acetone under both neutral and acid-catalyzed conditions at approximately constant ionic strength (Table II). After some initial difficulties, good first-order plots were obtained (see Experimental). The pseudo first-order rate constants for the acid-catalyzed solvolyses (Table II) were obtained by subtracting the appropriate rate constant for the uncatalyzed reaction from the rate constant observed under acidic conditions (which thus represents the sum of the rate constants for the acid-catalyzed and uncatalyzed reactions).

For those compounds that were studied in the same solvent at three temperatures, E_a and log A were calculated for the Arrhenius equation (Table III). Where four or more esters were studied under the same experimental conditions, correlation was made with the Hammett equation, utilizing the σ^+, and, in two runs, also the σ- values of Brown and Okamoto.[9] All Hammett equation calculations were by the method of least squares[10] and the results are given in Table IV.

The rate constants for the *p*-methoxy ester in

(6) For our purposes, discussion in terms of the simple SN1 scheme[6] is generally satisfactory. For more detailed analyses of solvolysis reactions, see, for instance, S. Winstein and A. H. Fainberg, THIS JOURNAL, 79, 5937 (1957), and earlier papers by Winstein.

(7) See the work of H. L. Goering and E. F. Silversmith, *ibid.*, 77, 6249 (1955).

(8) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, chapter VII.

(9) H. C. Brown and Y. Okamoto, THIS JOURNAL, 80, 4979 (1958).

(10) H. H. Jaffé, *Chem. Revs.*, 53, 191 (1953).

TABLE III

ARRHENIUS RATE EQUATION PARAMETERS FOR THE SOLVOLYSIS OF p-NO$_2$C$_6$H$_4$CO$_2$CHC$_6$H$_5$C$_6$H$_4$X IN AQUEOUS ACETONE[a]

X	Acetone, %	[HClO$_4$][b,c]	[NaClO$_4$][b]	Ea, kcal./ mole	log A[d]
p-CH$_3$	75	0	0.0079	25.4	10.7
p-CH$_3$O	75	0	.0079	22.0	10.7
p-CH$_3$O	90	0	.0076	21.6	9.5
p-CH$_3$	75	0.0083	0	35.8	18.5
p-CH$_3$O	90	0.0078	0	32.4	18.0

[a] Calculated from rates at 114.6°, 104.9° and 95.8° by least squares. [b] At 25°. [c] The parameters for the acid-catalyzed reactions were calculated from second-order rate constants, allowance being made for solvent expansion; see Experimental. [d] The units of A are sec.$^{-1}$ for the uncatalyzed reaction and mole^{-1} 1. sec.$^{-1}$ for the catalyzed reactions.

TABLE IV

CORRELATION OF THE RATES OF SOLVOLYSIS OF BENZHYDRYL p-NITROBENZOATES WITH THE HAMMETT EQUATION

Acetone, %	T, °C.	[HClO$_4$]	[NaClO$_4$]	ρ	s[a]	r[b]	n[c]
90[d]	114.6	0	0.0076	-4.12	0.132	0.997	4
75[d]	114.6	0	.0079	-3.69	.080	.998	6
75[d]	104.9	0	.0079	-3.86	.084	.998	5
90[d]	114.6	0.0078	0	-2.38	.049	.999	7
90[d]	104.9	.0078	0	-2.43	.047	.999	6
75[d]	114.6	.0083	0	-2.65	.042	.996	5
75[d]	104.9	.0083	0	-2.33	.036	.997	4
75[e]	104.9	0	0.0079	-7.95	.670	.898	5
90[e]	114.6	0.0078	0	-3.71	.336	.939	7

[a] The standard deviation of experimental measurements from the regression line. [b] The correlation coefficient. [c] The number of compounds involved in the calculation of ρ. [d] Calculated using σ^+. [e] Calculated using σ.

75% acetone should only be regarded as good estimates, since the ester reacted very rapidly under the experimental conditions. Because of this high reactivity in the neutral reaction in 75% acetone, no determination of the acid-catalyzed rate of the p-methoxy ester in this solvent was possible. Thus the Hammett correlations for the acid-catalyzed reactions in 75% acetone do not include points for the p-methoxy group. For the compounds in the present study, it is for p-methoxy that σ and σ^+ differ most significantly, although there is also an appreciable difference between these parameters for p-methyl and p-chloro. Both of the last-named substituents were studied in the acid-catalyzed reaction in 75% acetone at 114.6°, while only the p-methyl group was included at 104.9°.

Discussion

Before considering possible differences between the transition states for the acid-catalyzed and neutral solvolyses, we must rigorously demonstrate that alkyl–oxygen fission has occurred in these ester reactions. Davies and Kenyon[11] have discussed stereochemical and isotope studies as methods for establishing alkyl–oxygen ester cleavage. More indirect procedures have been employed in the present instance. Referring first to the acid-catalyzed ester solvolyses, many examples have revealed[12] that reactions of this type that proceed

via alkyl–oxygen cleavage are characterized by unusually large log A and E_a terms, derived from the Arrhenius rate equation.[13] For instance, the acid-catalyzed solvolysis of diphenylmethyl benzoate in 60% acetone has[12] $E_a = 31$ kcal. and log $A = 15.1$ and the acid-catalyzed solvolysis of p-methoxybenzhydryl benzoate in 80% acetone has[14] $E_a = 29.7$ kcal. and log $A = 16.3$. Both of these benzoates are presumed to be reacting with alkyl–oxygen fission. In contrast, the acid-catalyzed solvolysis of diphenylmethyl formate in 60% acetone, proceeding by the more common acyl–oxygen fission, has[12] $E_a = 18.6$ kcal. and log $A = 9.8$. The values for the Arrhenius parameters entered in Table III thus strongly suggest that alkyl–oxygen cleavage has occurred in the present acid-catalyzed solvolyses.

Correlation of rates of reaction[9] with σ^+ has introduced a potentially powerful tool for conclusively demonstrating alkyl–oxygen cleavage in the solvolysis of these benzhydryl p-nitrobenzoates. The σ^+-values correlate many reactions which are characterized by strong resonance interactions between electron-releasing substituents and electron-deficient centers,[15] and alkyl–oxygen ester fission is acompanied by this kind of interaction. If the σ^+-criterion is applied first to the acid-catalyzed ester solvolysis, for which we have already adduced some evidence in favor of alkyl–oxygen fission, it must be noted that the reaction is in reality a two-step process. The first is the equilibrium protonation, which should correlate with σ in the present case. The second is the rate-determining heterolysis, which should correlate with σ^+. The fact that the acid-catalyzed reactions correlate so well with σ^+ (Table IV) suggests that ρ for the equilibrium step is small and definitely establishes that alkyl–oxygen cleavage has occurred in the acid-catalyzed solvolysis.

The utility of σ^+ correlations in proving alkyl–oxygen ester fission is most readily evidenced in the neutral ester solvolysis, where no difficulty from pre-equilibria enters. The data of Table IV show that here, also, alkyl–oxygen cleavage is observed. The uncatalyzed benzhydryl p-nitrobenzoate solvolysis thus resembles the solvolysis of benzhydryl chlorides, a reaction whose rate correlates[16] with σ^+ and which primarily involves[6] rate-determining formation of benzhydryl carbonium ions; the ρ for the solvolysis of the benzhydryl chlorides at 25° in ethanol is -4.05, quite similar to the ρ for the solvolysis of the neutral benzhydryl p-nitrobenzoates. The effect of change[14] in solvent composition upon the rate constants (Table II) is also in accord with the assumption, with which we now proceed, that in the reactions reported herein alkyl–oxygen fission has occurred.

Turning now to possible differences between the transition states for the acid-catalyzed and neutral

(11) A. G. Davies and J. Kenyon, Quart. Revs., 9, 203 (1955).

(12) See, for references, G. J. Harvey and V. R. Stimson, J. Chem. Soc., 3629 (1956).

(13) Throughout this discussion, the E_a and log A terms for the acid-catalyzed reactions refer to second-order rate constants.

(14) S. R. Johns and V. R. Stimson, J. Chem. Soc., 467 (1960).

(15) However, see G. S. Hammond, J. Peloquin, F. T. Fang and J. K. Kochi, THIS JOURNAL, 82, 443 (1960), on the benzyl carbonium ion.

(16) Y. Okamoto and H. C. Brown, J. Org. Chem., 22, 485 (1957).

TABLE V

MELTING POINTS AND ANALYSES OF ALCOHOLS AND ESTERS

	Melting points, °C.			Analyses of p-nitrobenzoates			
	X = OH		X = p-NO₂C₆H₄CO₂	Carbon, %		Hydrogen, %	
Compound	Present	Lit.		Calcd.	Found	Calcd.	Found
C₆H₅CHXC₆H₅	66–68	69[c]	131–133[i]				
m-CH₃C₆H₄CHXC₆H₅	45–52[a]	52[d]	114–116.5	72.61	72.57	4.93	5.15
p-CH₃C₆H₄CHXC₆H₅	50–52	52–53[e]	90–93	72.61	72.58	4.93	4.94
m-CH₃OC₆H₄CHXC₆H₅	Oil[b]	41[f]	90–91.5	69.41	69.61	4.72	4.49
p-CH₃OC₆H₄CHXC₆H₅	66–68	66–67[g]	79–82	69.41	69.68	4.72	4.75[j]
m-ClC₆H₄CHXC₆H₅	38–40.5	39–40[d]	121–122	65.31	65.71	3.84	4.19
p-ClC₆H₄CHXC₆H₅	61–63	57–59[h]	120–123	65.31	65.32	3.84	4.14

[a] Low melting solid, difficult to purify. [b] Could not be induced to solidify. [c] J. U. Nef, *Ann.*, **298**, 202 (1897). [d] J. F. Norris and J. T. Blake, THIS JOURNAL, **50**, 1808 (1928). [e] E. Fischer and O. Fischer, *Ann.*, **194**, 242 (1878). [f] R. Stoermer, *Ber.*, **41**, 321 (1908). [g] M. P. Balfe, M. A. Doughty, J. Kenyon and R. Poplett, *J. Chem. Soc.*, 605 (1942). [h] J. F. Norris and C. Banta, THIS JOURNAL, **50**, 1804 (1928). [i] Lit. m.p. 131–132°; J. Meisenheimer and W. Schmidt, *Ann.*, **475**, 177 (1929). [j] Calcd. N 3.86. Found N 3.97.

solvolyses, let us focus on the Hammett correlations of Table IV. Each tabulated ρ for the acid-catalyzed reactions is the sum of two negative ρ's and therefore represents a maximum (absolute) value for the heterolysis step[17] of the positively-charged species. There thus appears to be an appreciable difference between the size of ρ for the heterolysis of the neutral and the positively-charged molecules. The limited data of Table IV suggest that this difference is not an artifact and that it will probably persist over a variation in reaction conditions. It therefore appears that, in this particular case, the acid-catalyzed reaction, proceeding without ion-pair formation, is less sensitive to substituent effects than is the uncatalyzed solvolysis, proceeding with ion-pair formation. One is tempted to speculate that the larger absolute value of ρ for the uncatalyzed reaction indicates that relatively more positive charge is developed on the incipient diphenylmethyl cation in the transition state for this reaction,[18] but one must exert considerable caution in attempting to interpret the significance of ρ-values.[8,10]

Acknowledgment.—The author is indebted to several individuals for helpful discussions.

Experimental[19]

Materials.—The alcohols were either commercial samples or were synthesized by conventional procedures from the

(17) The solvolysis of compounds such as substituted benzhydryl-sulfonium salts would avoid the complication introduced by the protonation step. Unfortunately, so far we have had little success in synthesizing these compounds.

(18) (a) For the solvolysis of dimethylphenylcarbinyl chlorides in 90% acetone at 25°, ρ = −4.62; for diphenylmethyl chlorides in ethanol at 25°, ρ = −4.05; for triphenylmethyl chlorides in 40% ethanol–60% ether at 25°, ρ = −2.34. Crudely, considering that a total charge of +1 is developed in the transition state for all the reactions, in the first example about a full +1 is delocalized into the aromatic ring, in the second, +1/2 and in the third, +1/3 is so delocalized. See N. C. Deno and W. L. Evans, THIS JOURNAL, **79**, 5804 (1957). In the case of the present work, the number of aromatic rings is constant; the amount of charge in the transition state may vary and be reflected in ρ. (b) Van Bekkum, Verkade and Wepster [*Rec. Trav. Chim.*, **78**, 815 (1959)] recently have critically reëvaluated the concept of dual σ constants. The reason the σ⁺ values correlate the data in the present research so well is probably because they are derived⁹ for a reaction that is quite similar to these ester solvolyses. Unfortunately the nature of the substituents chosen in our study precludes accurate treatment by the procedure of van Bekkum, Verkade and Wepster. However, a crude estimate of the *para* interaction-energy difference (ΔΔ*F*ₚ) for the acid-catalyzed reaction in 90% acetone and for the uncatalyzed reaction in 75% acetone was made. The quantity ΔΔ*F*ₚ was larger in the *uncatalyzed* reaction for *para* substituents CH₃, CH₃O and Cl. This is in general accord with our suggestions which are founded on the σ⁺ treatment of the data.

literature. The conversion of the alcohols to the *p*-nitrobenzoate esters followed the method of Goering and Blanchard,[20] and the esters were purified by recrystallization from heptane. The properties of the alcohols and esters are given in Table V.

Reagent grade perchloric acid and anhydrous sodium perchlorate were used without further purification. The solvent for the kinetic runs was prepared by measuring the desired volume of water,[21] containing either sodium perchlorate or perchloric acid, into a volumetric flask and diluting to the mark with pure[22] acetone. Thus 90% acetone is 200 ml. of water diluted to 2000 ml. All volumes were measured and all dilutions were carried out at 25°.

Kinetic Experiments.—Ampule technique was used with titration by standard sodium hydroxide of the total acid present (*p*-nitrobenzoic acid plus any perchloric acid). This method has been described by Goering and Silversmith.[7] Initially, considerable difficulty was encountered in obtaining reproducible results. The solvent itself was found to produce appreciable acid titer[23] at temperatures above 100°. Experimentation showed that this decomposition was greatly diminished by sealing the ampules under nitrogen and by adding 0.1 g. of hydroquinone per 50 ml. of solvent before each run. Reproducible blanks were then determined for the solvent decomposition, which was not entirely surpressed, and these blanks were applied to each run. For instance, 5 ml. of 90% acetone, [HClO₄] = 0.0078 *M*, required an additional 0.64 ml. of 0.01375 *M* sodium hydroxide after 50 hr. at 114.6°. The corrections for solvent decomposition represented a significant fraction of the total acidity developed only in the slowest runs. Thus, in an

TABLE VI

RATE OF HYDROLYSIS OF 0.0329 *M* *m*-CHLOROBENZHYDRYL *p*-NITROBENZOATE IN 90% ACETONE AT 114.6°, [HClO₄] = 0.0078 *M*

Time, sec.	0.01375 *M* NaOH,[a] ml.	Blank,[b] ml.	10^5k, sec.⁻¹
0	2.90		
58680	6.55	3.10	0.579
87420	7.95	3.29	.565
108200	8.88	3.43	.563
137280	9.90	3.51	.556
173400	11.11	3.54	.578

Av. 0.568 ± 0.008

[a] Amount of base required to titrate a 5.0-ml. aliquot. [b] Determined by heating the solvent in absence of ester, with precautions as described in text.

(19) All melting points are uncorrected. Analyses are by Drs. Weiler and Strauss, Oxford, England. All concentrations are for 25°.

(20) H. L. Goering and J. P. Blanchard, THIS JOURNAL, **76**, 5405 (1954).

(21) Purified according to W. J. Blaedel and V. W. Meloche, "Elementary Quantitative Analysis," Row, Peterson and Co., Evanston, Ill., 1957, p. 96.

(22) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

(23) The development of acid by aqueous dioxane and acetone solvents at elevated temperatures has been commented upon by M. C. Caserio, D. L. Glusker and J. D. Roberts, *ibid.*, **81**, 336 (1959),

acid-catalyzed run of *m*-chlorobenzhydryl *p*-nitrobenzoate at 114.6° in 90% acetone, for one point 0.6 ml. of a total 7 ml. of developed titer was attributed to solvent decomposition. The largest relative correction applied was in the uncatalyzed hydrolysis of benzhydryl *p*-nitrobenzoate at 114.6° in 90% acetone, where 0.15 ml. out of 0.85 ml. of developed titer was attributed to solvent decomposition.

In the runs in 75% acetone, the solubility of the ester was often a limiting factor in the amount of ester to be solvolyzed. Despite the problems presented by solvent decomposition and limited solubility, rate constants calculated for individual points within a run showed no detectable trend and the mean deviation from the average of these points was generally ±2% or better. The individual points in the very fast reactions, such as *p*-methoxybenzhydryl *p*-nitrobenzoate in 75% acetone at 114.6°, showed deviations of about ±4% from the average. Rates were reproducible from run to run. In general, a run was studied to about

70% reaction, or to 50 hr. if the run was a slow one. Infinity titers were not usually determined. An example of a run requiring large blank corrections (and in which several ampules exploded) is shown in Table VI.

The formation of *p*-nitrobenzoic acid during a run had no detectable effect upon rate constants calculated for various points within that run.[7]

Calculation of Arrhenius Parameters.—The pseudo first-order rate constant for the acid-catalyzed reaction was obtained by subtracting the pertinent uncatalyzed rate constant from the observed rate constant under acid-catalyzed conditions. Second-order rate constants were then calculated by dividing the pseudo first-order rate constant by the acid concentration at the temperature in question[24] and these constants were used in calculating E_a and log A.

(24) The solvent expansions were determined and were similar to that observed for 80% acetone by Goering and Silversmith.[7]

Stereochemical Relations in the Pentachlorophenyl-ethanes, -ethenes and -ethyne[1,2]

BY GEORGE HUETT AND SIDNEY I. MILLER

When either *cis*- or *trans*-ω-bromopentachlorophenylethene is treated with potassium ethoxide, the predominant product is *cis*-ω-ethoxypentachlorophenylethene. The *trans*-ω-ethoxystyrene also found appears to arise from the isomerization of the *cis* compound. It has been shown that pentachlorophenylethyne, which is first formed, adds ethanol in the *trans* sense to give the *cis* ether. In the course of this work several new side-chain bromination products of pentachlorophenylethane were obtained.
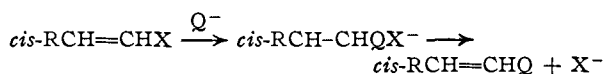
What happens when a haloalkene is treated with a base? The answer to this question must be variable and may be complex.[3]

In 1952, Ross and co-workers found that a haloalkene and ethoxide ion gave rise to a *cis–trans* pair of ethoxyalkenes.[4] We considered that a closer look at the reactions involving these compounds, all pentachlorophenyl derivatives, would have broad mechanistic interest. In addition, we prepared pentachlorophenylethyne and several pentachlorophenylethanes and -ethenes. The presence of a highly modified phenyl substituent raised some unusual problems.

Of the several processes which can occur when a haloalkene undergoes substitution in the presence of a base, only two are relevant here. Briefly, the first, elimination–addition, usually leads to a single product formed by *trans* addition to the acetylenic intermediate:

$$cis\text{- or } trans\text{-RCH=CHX} \xrightarrow{\text{base}} \text{RC≡CH} \xrightarrow{\text{HQ}} cis\text{-RCH=CHQ} \quad (1)$$
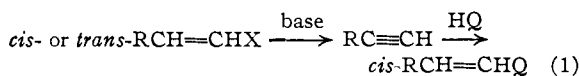
The second, addition–elimination, leads primarily to a product of the same configuration as the reactant[3]; secondary processes involving the carbanions or the

$$cis\text{-RCH=CHX} \xrightarrow{Q^-} cis\text{-RCH–CHQX}^- \longrightarrow$$
$$cis\text{-RCH=CHQ} + X^-$$

$$trans\text{-RCH=CHX} \xrightarrow{Q^-} trans\text{-RCH–CHQX}^- \longrightarrow$$
$$trans\text{-RCH=CHQ} + X^- \quad (2)$$

adduct, RCH_2CHQX, could lead to isomerized products.

To obtain key compounds, pentachlorophenylethane (I) was brominated. As in previous work,[5] the chief products were 1-pentachlorophenyl-1-bromoethane (II) and 1-pentachlorophenyl-1,2-dibromoethane (IV).

cis- and *trans*-ω-bromopentachlorostyrene (V) and 1-pentachlorophenyl-1,2,2-tribromoethane (VI) were novel products of the bromination. Chart 1 gives one of many possible schemes to account for all of the identified products.[6]

CHART 1

BROMINATION OF PENTACHLOROPHENYLETHANE

$$C_6Cl_5C_2H_5 \longrightarrow C_6Cl_5CHBrCH_3 \longrightarrow C_6Cl_5CHBrCHBr$$
$$\text{I} \qquad\qquad\qquad \text{II} \qquad\qquad\qquad\qquad \text{IV}$$

$$\longrightarrow (C_6Cl_5CH=CH_2) \longrightarrow$$
$$\text{III}$$

$$C_6Cl_5CHBrCHBr_2 \longleftarrow C_6Cl_5CH=CHBr$$
$$\qquad\qquad\qquad\qquad\qquad \text{Va, low m.p.}$$
$$\qquad\qquad\qquad\qquad\qquad \text{Vb, high m.p.}$$

The transformations depicted in Chart 2 were carried out to establish gross structure. To differentiate the ω-bromostyrenes V the rates of ethoxide-catalyzed
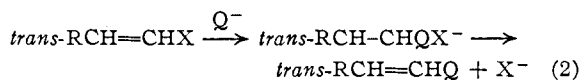
(1) Supported in part by the Office of Ordnance Research, U. S. Army, and in part by the Research Corporation.

(2) In partial fulfillment of the Ph.D. requirements of G. Huett.

(3) (a) S. I. Miller and P. K. Yonan, THIS JOURNAL, **79**, 5931 (1957); (b) S. I. Miller and W. G. Lee, *ibid.*, **81**, 6313 (1959); (c) F. Montanari, *Boll. sci. fac. Chim. ind. (Bologna)*, **16**, 31 (1958); (d) D. E. Jones, R. O. Morris, C. A. Vernon and R. F. M. White, *J. Chem. Soc.*, 2349 (1960).
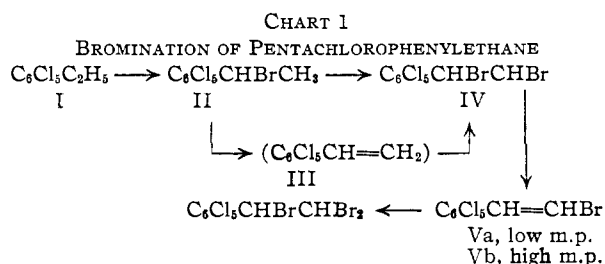
(4) S. D. Ross, W. A. Leach and I. Kuntz, THIS JOURNAL, **74**, 2908 (1952).

(5) S. D. Ross, M. Markarian and M. Nazzewski, *ibid.*, **69**, 2468 (1947).

(6) Ross, *et al.*, suggested that the 1-bromide II dehydrobrominates at 180° to give the styrene from which the 1,2-dibromide is formed.[5] Since we have prepared dibromide in the temperature range 70–130°, it is probable that direct bromination of II also occurs. Elimination–addition steps, however, do account plausibly for the ω-bromostyrenes and the tribromide.