(b) **The Role of the Solvent.**—The experiments shown in Table I indicate that pyridine as solvent has a catalytic influence on the condensation too, and not only on the decarboxylation.[8,9] Substitution of pyridine by cyclohexanone as the solvent almost exactly halves the rates of condensation. It is interesting to note that the relative rates of decarboxylation *versus* condensation are practically the same with pyridine alone (Table I, no. 1) and with a mixture of 10% pyridine and 90% cyclohexanone (no. 3). Substitution of the last 10% of pyridine by cyclohexanone (no. 4) lowers the condensation rate only slightly, while practically stopping the decarboxylation, thus showing the essential role of pyridine in the decarboxylation, while experiment no. 2 shows that a mixture of 40% pyridine with 60% cyclohexanone gives much higher relative decarboxylation rates than pyridine alone.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Relative Sensitivity of Triphenylmethyl Chloride to Electrophiles and Nucleophiles in Benzene Solution

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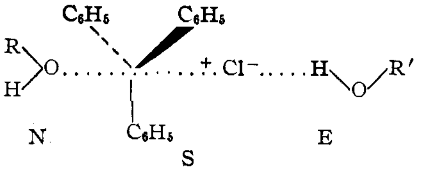
The benzolysis of triphenylmethyl chloride in the presence of trimethylamine in benzene solution has been investigated employing five benzyl alcohols (p-CH_3O–, p-CH_3–, p-H–, p-Cl– and p-NO_2– substituted). Kinetic studies revealed the reactions to be first order in the chloride and second order in the alcohols through at least the first 50% of the reaction. Addition of phenol to the reaction medium enhanced the over-all rate of substitution through the addition of a new *competing* reaction (also leading to the benzyl ether) that appeared to be first order in both chloride and alcohol. The effects of the *para*-substituents of the benzyl alcohols on the rate of the above two independently occurring reactions indicate that the sensitivity of triphenylmethyl chloride to the electrophilic component of these termolecular reactions is significantly greater than to the nucleophilic component. The reaction of equimolar phenol, triphenylmethyl chloride and triethylamine in benzene was found to be second order over-all, a fact which suggests that phenol and triethylamine are completely complexed in benzene solution.

The investigations of Swain[3] on the mechanism of the substitution reactions of triphenylmethyl (trityl) chloride in benzene solution stimulated the present study. As had been demonstrated earlier in other, but similar, systems,[4] solvolyses involving a termolecular mechanism were demonstrated to occur. For instance in the methanolysis of trityl chloride in benzene solution, the reaction was demonstrated to be first order in trityl chloride and second order in methanol, whereas in the presence of added phenol, the reaction rate was enhanced and found to be first order in trityl chloride and in methanol. Swain interpreted these observations in terms of a transition state (I) involving both a displacing nucleophile and an anion-solvating electrophile. More recently these concepts were put on a more quantitative basis through the agency of the linear free-energy relationship (equation 1) which



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correlates the rates of a number of substitution reactions in terms of four parameters. Thus n measures the nucleophilic reactivity of N, e the electrophilic reactivity of E, and s and s' the sensitivity of the substrate (S) to different N and E reagents, respectively, while k represents the rate constant of the reaction

$$\log (k/k^0) = sn + s'e \qquad (1)$$

being compared to the rate constant (k^0) of the reaction of the same substrate under the same conditions but with water as both N and E.

The present investigation reports a kinetic study of the benzolysis of trityl chloride in the presence of trimethylamine in benzene solution in which five benzyl alcohols (p-CH_3O–, p-CH_3–, p-H–, p-Cl– and p-NO_2–substituted) have played the role of both N and E. The results of a second series of kinetic experiments are also recorded which deal with the same reactions carried out in the presence of added phenol, which for the most part assumed the role of E in the mechanism. The objective of these studies was to evaluate as quantitatively as possible the relative sensitivity in this medium of trityl chloride to the N and E components of these termolecular processes.

Results

The first set of kinetic experiments was conducted at 30° in a benzene solution saturated with triethylamine hydrochloride, with triethylamine present in concentrations about equal to that of the trityl chloride. The reaction was followed acidimetrically essentially by a method previously reported.[4b] Under these conditions, third-order kinetics of the form of equation 2 were observed in all

$$-\frac{d[(C_6H_5)_3CCl]}{dt} = k_3[ROH]^2[(C_6H_5)_3CCl] \qquad (2)$$

cases, the constants being calculated for each point by the integrated equation of Swain.[3a] The third-order rate constants (k_3) were reproducible to within

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[3] (a) C. G. Swain, THIS JOURNAL, **70**, 1121 (1948); (b) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

[4] (a) N. T. Farinacci and L. P. Hammett, *ibid.*, **59**, 2542 (1937); (b) P. D. Bartlett and R. W. Nebel, *ibid.*, **62**, 1345 (1940).

TABLE I

PRODUCTS AND RATES OF REACTION OF *p*-SUBSTITUTED BENZYL ALCOHOLS WITH TRITYL CHLORIDE IN BENZENE AT 30.00 ± 0.05°

		Rate data Initial concentrations (mole liter^{-1})					Product data			
Run no.	*p*-X	*p*-XC_6H_5-CH_2OH	$(C_6H_5)_3CCl$	Et_3N	Mean $k_3 \times 10^2$ (l.^{2}/mole^2 min.)	$\log \frac{k_3}{k^\circ_3}$	Rate run analyzed	Yield of ether, %	M.p., °C. Product	Pure ether
1	H–	0.0708	0.0554	0.0493	10.4 ± 0.6					
3	H–	.1459	.0491	.0525	10.2 ± .7[a]	0.00	3	64[b]	97–100	100–102
4	H–	.1980	.0937	.0525	9.7 ± .3					
6	NO_2–	.0781	.0516	.0531	27.4 ± 2.3					
8	NO_2–	.0700	.0536	.0560	27.8 ± 1.8	.486	6	96	154–158	166–167
15	NO_2–	.1321	.0612	.0560	31.2 ± 1.6[a]					
7	CH_3O–	.0537	.0539	.0575	11.4 ± 1.9					
9	CH_3O–	.1470	.0535	.0565	11.1 ± 0.5[a]	.037	9	91	120–130	132–134
13	CH_3O–	.210	.0544	.0546	11.9 ± 0.5					
10	Cl–	.142	.0539	.0575	18.1 ± 1.6[a]					
14	Cl–	.202	.0561	.0559	22.2 ± 1.8	.248	10	93	135–136	136–137
12	CH_3–	.0726	.0570	.0553	8.5 ± 0.5					
11	CH_3–	.1419	.0544	.0553	8.3 ± .2[a]	– .089	16	90.5	114–116	117–117.5
16	CH_3–	.215	.0552	.0555	8.7 ± .3					

[a] These values were used in calculating log k_3/k_3° which is plotted *vs.* sigma in Fig. 1. [b] This low yield is no doubt due to the high solubility of the product in pentane.

±5% where the initial alcohol concentrations were varied from about 0.07 to 0.21 *M* when ROH was benzyl, *p*-methylbenzyl or *p*-methoxybenzyl alcohol. However, when ROH was either *p*-nitrobenzyl or *p*-chlorobenzyl alcohol, the rate constants increased noticeably when the initial alcohol concentrations were about doubled. Since these latter molecules are rather polar, this rate increase might be due to an increase in the dielectric constant of the medium. Accordingly, only rate constants which were determined at comparable alcohol concentrations will be compared. Every rate determination was carried to at least 50% completion of the reaction based on the consumption of the trityl chloride present. In no case could any evidence of reaction of the trityl chloride with triethylamine be detected (product analyses were made in representative cases). Table I reports the conditions and results of each experiment, Table II records the data taken from a typical kinetic run, and Table III, the results of the analyses of the benzyl trityl ether products.

TABLE II

REACTION OF 0.0612 *M* TRITYL CHLORIDE WITH 0.1312 *M* *p*-NITROBENZYL ALCOHOL IN BENZENE CONTAINING 0.0560 *M* TRIETHYLAMINE AT 30.00 ± 0.05° (RATE RUN 15)

Point	Time, min.	Titer, ml.[a]	$(C_6H_5)_3CCl$ reacted, %	$k_3 \times 10^2$, (l.^{2}/mole^2 min.)
1	0	8.60	0.0	
2	23	7.56	11.1	32.8
3	35	7.15	15.4	30.4
4	47	6.75	19.7	30.2
5	56	6.42	23.2	30.9
6	71	6.03	27.4	30.7
7	94	5.45	33.5	30.3
8	104	5.18	36.4	30.9
9	123	4.76	39.8	29.6
10	146	4.30	45.8	32.1
11	163	4.00	38.9	32.0
12	190	3.60	53.2	31.6
13	∞ Calcd.	–0.80	100.0	
				Mean 31.2 ± 1.6 × 10^{-2}

[a] 2.440-ml. aliquot titrated with 0.01585 *N* pyridinium chloride in acetone.

TABLE III

CHARACTERIZATION OF *p*-X-SUBSTITUTED BENZYL TRIPHENYLMETHYL ETHERS

p-X	M.p., pure, °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H$^-$	100–102	89.11	88.98	6.33	6.12
NO_2^-	166–167	78.97	78.67	5.35	5.28
CH_3O^-	132–134	85.23	85.52	6.36	6.63
Cl$^-$	136–137	81.13	81.29	5.50	5.61
CH_3^-	117–117.5	88.96	88.83	6.64	7.03

The results of those benzolyses carried out in the presence of 0.0521 *M* phenol in benzene are recorded in Table IV, while Table V presents a typical sample of the kinetic data. The concentration of triethylamine was initially the same in each run and comparable to the phenol concentration, whereas the alcohol concentrations were significantly varied. The kinetics of these reactions were complicated for two reasons. First, examination of the kinetic data indicates that each run fits the second-order rate law within each run. However, in those runs where *p*-chloro or *p*-nitrobenzyl alcohols were used, when the initial alcohol concentration was increased, the mean second-order rate constant increased significantly more than experimental error. This anomaly was set aside through the successful application of equation 3 for mixed second- and third-order kinetics. Table IV therefore records the average second-order rate constant

$$\frac{-d[(C_6H_5)_3CCl]}{dt} = k_2[ROH][(C_6H_5)_3CCl] + k_3[ROH]^2[(C_6H_5)_3CCl] \quad (3)$$

observed within the run (k_2') along with k_2 and k_3 obtained by solving the integrated form of equation 3 by the successive approximation method of Bartlett and Nebel.[4b] Justification for this procedure is found in the near equivalence of the values of k_3 obtained in this manner for the *p*-chlorobenzyl

TABLE IV

PRODUCTS AND RATES OF REACTION OF *p*-SUBSTITUTED BENZYL ALCOHOLS WITH TRITYL CHLORIDE IN BENZENE AT 30.00 ± 0.05° IN PRESENCE OF PHENOL

		Initial concn.[a]		Rate data					Product data[b]		
Run No.	*p*-X	*p*-XC_6H_4-CH_2OH	$(C_6H_5)_3$-CCl	Av. 2nd[c] order k_2' obsd. × 10^2, l./mole min.	k_2 × 10^2, l./mole min.	k_3, l.^{2}/mole min.	log k_2/k_2^0	Rate run analyzed	Yield of ether, %	M.p., °C. Product	M.p., °C. Pure ether
31	H–	0.0660	0.0540	6.25 ± 0.25							
32	H–	.1330	.0503	6.10 ± .25	6.2 ± 0.3	Not obsd.	0.000	32	75.5	86–88	100–102
33	NO_2–	.0565	.0507	9.05 ± .10							
34	NO_2–	.0919	.0505	9.85 ± .20	7.5 ± .3	0.315	.086	33	94.5	140–153	166–167
35	CH_3O–	.0520	.0505	7.30 ± .10							
36	CH_3O–	.1110	.0503	7.55 ± .20	7.5 ± .3	Not obsd.	.083	36	90.5	110–115	132–134
37	Cl–	.0705	.0503	6.60 ± .20							
38	Cl–	.1421	.0510	8.25 ± .20	6.0 ± .3	0.182	– .009	38	75.5	132–135	136–137
39	CH_3–	.0685	.0507	5.90 ± .25							
40	CH_3–	.1154	.0505	5.95 ± .10	5.9 ± .3	Not obsd.	– .020	40	96.5	98–107	117

[a] All runs were initially 0.0521 *M* in phenol and 0.0546 *M* in triethylamine. [b] All products were contaminated with phenyl triphenylmethyl ether, m.p. 102–103°. [c] Calculated for each point up to at least 50% reaction by the second-order integrated equation.

and *p*-nitrobenzyl alcohol runs with those obtained in comparable runs in the absence of phenol (compare runs 33–34 and 37–38 of Table IV with runs 6 and 10 of Table I, respectively). In the cases of the runs utilizing the other three alcohols and involving phenol, the additional third-order term was no doubt present but its effect on the kinetic data was always within experimental error (k_3 associated with these alcohols are somewhat smaller than those involving the *p*-chloro and *p*-nitrobenzyl alcohols).

TABLE V

REACTION OF 0.0503 *M* TRITYL CHLORIDE WITH 0.0565 *M* *p*-NITROBENZYL ALCOHOL IN THE PRESENCE OF 0.0546 *M* TRIETHYLAMINE AND 0.0521 *M* PHENOL IN BENZENE AT 30.00 ± 0.05° (RATE RUN 33)

Point	Time, min.	Titer,[a] ml.	$(C_6H_5)_3CCl$ reacted, %	k_2 × 10^2[b] l./mole min.
1	0.0	8.40	0.0	
2	25.0	7.52	11.3	9.00
3	37.5	7.15	16.0	9.00
4	52.8	6.79	20.6	8.65
5	68.5	6.36	26.2	9.05
6	91.3	5.90	32.1	9.00
7	112.0	5.54	36.7	8.95
8	131.5	5.22	40.8	9.00
9	153.3	4.91	44.8	9.00
10	176.0	4.63	48.4	9.10
11	200.0	4.36	51.8	9.10
12	∞	Calcd. 0.66	100.0	
		Obsd. 0.47		
				Av. 9.05 ± 0.10

[a] 2.440-ml. aliquot titrated with 0.01585 *N* pyridinium chloride. [b] Second-order constant calculated by integrated equation.

The other complicating factor in the kinetic picture is the fact that phenol, triethylamine and trityl chloride react to give phenyl trityl ether under the conditions of the above experiments at a second-order rate which is approximately one-tenth as fast as the accompanying pseudo-second-order alcohol reactions. This source of error was not eliminated, but was at least kept constant from run to run by using the same concentrations of triethylamine and phenol. This effectively reduced the phenol reaction to a nearly constant error since the alcohols all have k_2 constants of the same magnitude.

The analyses of the products of representative runs (Table IV) revealed the presence of small amounts of the phenyl ether which lowered and widened the melting point range of the major benzyl ether product. Again no evidence of quaternary ammonium product was found.

The reaction of phenol, triethylamine and trityl chloride in benzene saturated with triethylammonium chloride at 30° was also investigated, each of the three components having the same initial concentration. Phenyl trityl ether was produced at a velocity governed by a second-order rate law. For purposes of comparison both the second- and third-order rate constants were calculated for each point by the usual integrated rate expression (equation 4), and the results for a typical run are recorded in Table VI.

$$k_n = \frac{1}{(n-1)t}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] \qquad (4)$$

n = order of over-all reaction

$a = [(C_6H_5)_3CCl] = [(C_2H_5)_3N] = [C_6H_5OH]$

TABLE VI

REACTION OF 0.0503 *M* PHENOL, 0.0503 *M* TRITYL CHLORIDE AND 0.0503 *M* TRIETHYLAMINE IN BENZENE AT 30.00 ± 0.05°

Point	Time, min.	Titer,[a] ml.	$(C_6H_5)_3CCl$ reacted, %	3rd order constant k_3, l.^{2}/mole^2 min.	k_2 × 10^2 l./mole min.
1	0.0	7.80	0.0		
2	101	7.52	3.6	0.15	(0.90)
3	353	6.92	11.3	.15	.74
4	683	6.18	20.6	.17	.78
5	1075	5.63	27.9	.17	.73
6	1368	5.25	32.6	.18	.71
7	1830	4.65	40.4	.20	.74
8	2790	3.84	50.8	.23	.74
9	2935	3.68	52.9	.24	.76
10	3244	3.45	55.8	.25	.78
11	∞	Calcd. 0.00	100.0		
					Av. 0.76 ± 0.03 × 10^{-2}

[a] 2.440-ml. aliquot titrated with 0.0158 *N* pyridinium chloride in acetone.

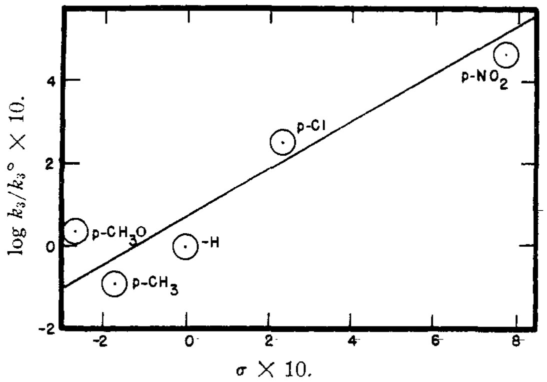
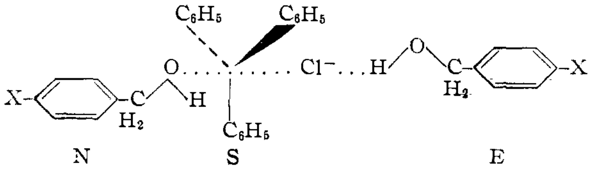


Fig. 1.—Plot of log k_3/k_3° *vs.* σ.

Discussion



The general effect of a *para*-substituent on the N and E functions of the transition state formulated may be easily predicted. If the *para*-substituent has a positive σ-value[5] the hydroxylic hydrogen of the alcohol should be more electrophilic than that of the unsubstituted alcohol, and the oxygen should be less nucleophilic with respect to the substrate. In other words, when X is an electron-withdrawing substituent the E reactivity should increase and N decrease, the reverse being true for electron releasing substituents. Since the substituent influences E and N through the bonding electrons of the O–H bond and the non-bonding electrons of the same oxygen atom, respectively, it is assumed that the parameters n and e of equation 1 for *para*-substituted benzyl alcohols are related to the σ-values[5] of the substituents by the relationships $n = \alpha\sigma$ and $e = \beta\sigma$ in which α and β are proportionality constants (analogous to ρ-values[5]) of opposite sign and approximately equal numerical value.[6] Thus equation 1 may be rewritten as equation 5, and if the above assumptions are correct, the slope of a plot of log k_3/k_3^0 *vs.* σ should be a straight line of slope $\alpha s + \beta s'$. Figure 1 records such a plot (k_3^0 is the

$$\log k_3/k_3^0 = \sigma(\alpha s + \beta s') \qquad (5)$$

third-order rate constant involving benzyl alcohol and k_3 is the similar rate constant for the substituted alcohols), and the points roughly define a linear relationship.

Equation 5 can be adapted to those experiments involving phenol to give equation 6, in which C is a constant equal to the product cs' where c is the electrophilic reactivity of the electrophile operating in the benzene solution of triethylamine and phenol, k_2^0 is the pseudo-second-order rate constant from the integrated form of equation 3 for benzyl alcohol, and

$$\log k_2/k_2^0 = \alpha\sigma s + C \qquad (6)$$

k_2 is the similar rate constant for the substituted alcohols. A plot of log k_2/k_2^0 *vs.* Hammett's[5] σ-values for the five alcohols is found in Fig. 2, and again a crude linear relationship is evident, with the slope of the line (αs) being equal to 0.

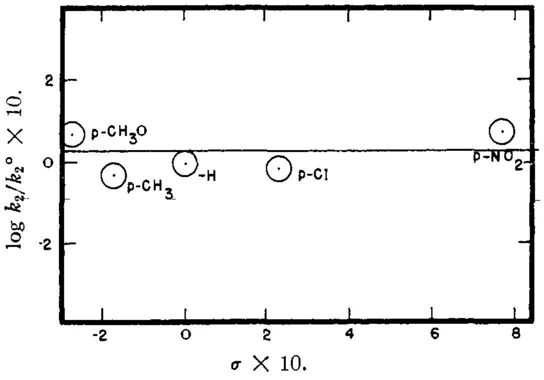


Fig. 2.—Plot of log k_2/k_2° *vs.* σ.

Although some question is associated with the exactness of the values of αs and $\alpha s + \beta s'$ obtained above, it is clear that the latter is considerably greater than the former, and therefore that αs is small compared to $\beta s'$. If α and β are of about equal numerical size, then s' is greater than s. In other words, trityl chloride in benzene is more sensitive to electrophilic than nucleophilic reactivity. This conclusion contrasts with the experimentally unsupported viewpoint of Hughes,[7] that the reaction of methanol with trityl chloride in benzene is an "S$_N$2" reaction.

In light of the work of Winstein, *et al.*,[8] on the evaluation of electrophilic driving forces in functional, polar solvents, trityl chloride might be described as a "limiting" substrate, which the values of s and s' determined here reflect. However, the fact that trityl chloride gives higher rates of reaction with the more nucleophilic of a series of sterically similar nucleophiles[9] indicates that s must have a finite value. In all probability the slope (αs) of the log k_2/k_2° *vs.* σ-plot (Fig. 2) would be slightly negative if the rate constants could have been de-

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(5) L. P. Hammett, "Physical Organic Chemistry," 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184.

(6) This assumption is supported by the following arguments. The electrophilic characters of the alcohols in question depend on the availability of their hydroxylic protons to an atom having a high concentration of valence electrons in much the same way as the corresponding benzoic acids make their protons available to water molecules during ionization. Since the protons of both benzoic acids and benzyl alcohols are effectively insulated from the substituent groups in much the same manner (save for internal charge distribution in the carboxyl group), and since ρ for the complete transfer of a proton from the benzoic acids to water is defined as unity, the similar partial transfer of the alcoholic proton to chlorine in trityl chloride should have a ρ value (β) of the same order of magnitude.

Similarly, the effect of a *para*-substituent on the availability of the non-bonding electrons of the nitrogen atom in benzylamine should provide an adequate model for the effect of a para-substituent on the nucleophilicity of benzyl alcohols. H. H. Jaffe [*Chem. Rev.*, **53**, 191 (1953)] has obtained a ρ-value of -0.723 from measurements made by W. H. Carothers, C. F. Bickford and G. J. Hurwitz [This Journal, **49**, 2908 (1927)] of the K_b values of five substituted benzylamines in water at 25°. Thus it may be inferred that the ρ-value associated with the nucleophilicity of substituted benzyl alcohols (α) is probably also near unity and that α and β are of similar magnitudes but of opposite sign.

(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, ref. 123, p. 356.

(8) E. Grunwald and S. Winstein, This Journal, **70**, 846 (1948); **73**, 2700 (1951).

(9) Compare the relative rates of reaction of phenol, p-toluidine and p-thiocresol with trityl chloride in benzene reported in ref. 3b.

termined more accurately and for a larger number of *p*-substituted alcohols.

The fact that phenyl trityl ether is produced many times faster from phenol and trityl chloride in the presence of triethylamine as compared to pyridine[10] indicates that the base strength of the amine employed has a great effect on the rate. This observation, coupled with the fact that in the presence of triethylamine the kinetics were second order over-all suggests two conclusions: (1) the phenol and triethylamine are essentially completely in the form of a triethylamine phenolate ion-pair in benzene; (2) the transition state whose formation controls the rate of reaction is composed of one molecule of trityl chloride and one molecule of triethylammonium phenolate (ion-pair).

The above proposal at once raises the question of the identity of the kinetically invisible electrophile which provided the pseudo-second-order terms in the reactions of the *p*-substituted alcohols with trityl chloride in the presence of triethylamine and phenol. Since the amine and phenol were present in nearly equivalent concentrations at the outset of each rate determination, they would be in the form of triethylammonium phenolate ion-pairs. As the reaction proceeded phenol would be liberated, and if the electrophilic reactivities of phenol and triethylammonium phenolate were different, a drift in k_2 as the reaction proceeded would be observed. If indeed the electrophilic species did change in the course of reaction, the reactivity associated with each electrophile appears to be about the same since no drift was observed in the k_2's of the runs in question.

Experimental

Reagents.—Trityl chloride was prepared from Eastman White Label trityl alcohol to give material, m.p. 110–111° (uncor.).[11] The melting point remained unchanged during the course of the studies, and titrations of hydrolyzed samples gave a minimum of 99.5% the theoretical amount of chlorine. The substance was stored in a vacuum desiccator over phosphorus pentoxide and weighed out as used.

Baker C.P. reagent grade benzene dried over calcium hydride was employed as solvent.

Pyridinium and triethylammonium chlorides were prepared by passing pure, dry hydrogen chloride into ethereal solutions of the pure amines. The pyridinium chloride was separated, triturated with dry ether and quickly transferred to a desiccator which was evacuated. The triethylammonium chloride was collected, washed with dry ether and recrystallized from methanol. It was then dried and stored over phosphorus pentoxide in an evacuated desiccator.

The acetone employed as solvent in the pyridinium chloride standard solution (see below) and as the trituration solvent was C.P. grade dried several days over Drierite and then distilled. The acetone used as the trituration solvent was stored over Drierite in a large dispensing buret and withdrawn as needed.

Eastman white label triethylamine was allowed to stand over calcium hydride for 24 hours and then distilled (b.p. 88°) and stored over calcium hydride.

Baker C.P. grade phenol was recrystallized three times from ligroin–benzene and stored over Drierite in an evacuated desiccator.

Eastman white label benzyl alcohol was purified by distillation (b.p. 204–205°), the same grade *p*-nitrobenzyl alcohol by recrystallization from aqueous alcohol (m.p. 93°), and the same grade *p*-methoxybenzyl alcohol by distillation (b.p. 260°).

The *p*-methylbenzyl alcohol was prepared as follows. A mixture of 46 g. of *p*-toluic acid, 40 ml. of thionyl chloride and 300 ml. of benzene was held at reflux for eight hours. The more volatile material was then allowed to escape, and the residual oil was distilled at 20 mm. of pressure to give 34 g. of *p*-toluoyl chloride. This material in 100 ml. of dry ether was added to a stirred mixture of 9.0 g. of lithium aluminum hydride in 300 ml. of dry ether. The resulting mixture was held at reflux for one hour and worked up the usual way. The product was purified by four recrystallizations from ether–pentane, wt. 12 g., m.p. 59.5–60.0°.[12]

The *p*-chlorobenzyl alcohol was prepared as follows. A mixture of 30 g. of pure *p*-chlorobenzyl chloride, 20 g. of potassium acetate (anhydrous) and 70 ml. of glacial acetic acid was held at reflux for 20 hours, cooled and poured into 500 ml. of water. The ester was extracted with two 100-ml. portions of ether, the resulting solution was dried, and the solvent was evaporated. The residual oil was heated at reflux for eight hours with 20 g. of potassium hydroxide in 200 ml. of 80% aqueous ethanol, the solution was cooled and drowned in 1 liter of water and the oil that separated was extracted into ether. The resulting solution was dried, the solvent was evaporated and the residue was recrystallized once from benzene–pentane to give 18 g. of product. m.p. 70°.[13]

Standard Pyridinium Chloride in Acetone Solution.—Approximately 7.0 g. of dry, crystalline pyridinium chloride was placed in a 5-liter three-necked flask which was warmed gently with a burner while being evacuated to 2 mm. pressure. This pressure was maintained with a vacuum pump for five hours, and then dry air was admitted to the flask. The flask was then attached as a receiver to a distillation apparatus, and 3 liters of anhydrous acetone was distilled onto the dry salt. After the salt had dissolved, the flask was fitted with a large Drierite tube through which air could be passed by means of a rubber compression bulb, and with a delivery tube (center neck) attached to a 10-ml. microburet. The third neck was well-stoppered.

Solutions prepared as above (approximately 0.015 *N* acid) remained dry and standard for several months. The solution was standardized against weighed samples of pure, dry triethylamine dissolved in acetone with brom phenol blue as an indicator.

Triethylamine–Phenol Stock Solution.—To 1.9 liters (at 30°) of anhydrous benzene was added 9.842 g. of pure phenol and approximately 15 ml. of pure, dry triethylamine, and the resulting solution was brought to a volume of 2 liters at 30° with more benzene. The amount of triethylamine present was determined by titration of aliquots of this solution with standard pyridinium chloride in acetone. The phenol present did not interfere with the brom phenol blue end-point. This stock solution was 0.0546 *M* in triethylamine and 0.0521 *M* in phenol at 30°.

Kinetic Measurements.—All the rates were run at 30.00 ± 0.05°, and the analysis technique was essentially that employed by Bartlett and Nebel[4b] in their study of the rate of methanolysis of *p*-methoxybenzhydryl chloride in nitrobenzene solution. These investigators followed their reaction by titrating the unconsumed triethylamine in acetone solution with a standard solution of dry hydrogen chloride in ether. In spite of the location of our laboratory, the temperature was too high, and a standard solution of pyridinium chloride in anhydrous acetone was substituted as the standard acid solution. Brom phenol blue was employed as indicator, and control experiments demonstrated that added phenol did not alter the end-points.

The rate runs were carried out in oven-dried, 125-ml. glass-stoppered erlenmeyer flasks. Aliquots were taken at various times with automatic pipets calibrated with benzene at 30°. The aliquot was diluted with 25 ml. of anhydrous acetone, a few drops of 0.010% indicator solution was added, and the mixture was rapidly titrated to a green-yellow end-point. The presence of solid triethylammonium chloride in the reaction mixture did not interfere with the sampling since it settled on the walls of the flask and the aliquot was taken from the surface of the solution.

The alcohol to be used in a rate run was weighed into the

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[10] Swain, *et al.*,[3a] report $k_3 = 4 \pm 2 \times 10^{-3}$ l.^{2}/mole^2 min. for the reaction in the presence of pyridine at 25°. Since their data was not calculated as a second-order constant, the third-order constants have to be compared.

[11] W. E. Bachmann, *Org. Syntheses*, **23**, 98 (1943).

[12] S. Cannizarro (*Ann.*, **124**, 255 (1862)) reports 60°.

[13] W. H. Carothers and R. Adams (THIS JOURNAL, **46**, 1681 (1924)) report m.p. 71–72.5°.

tared reaction flask, and about 1.0 g. of triethylammonium chloride was added as well as 100 ml. (30°) of freshly prepared triethylamine–benzene solution or triethylamine–phenol–benzene stock solution. The resulting mixture was held in the thermostat for six hours to allow the solution to become saturated with the amine hydrochloride. The proper amount of trityl chloride was rapidly weighed and added to the solution (zero time), complete solution of the halide occurring within one minute. An aliquot was immediately taken and analyzed for triethylamine. The reaction flask was held in the thermostat and its contents sampled at appropriate intervals. In runs where the initial amine concentration exceeded that of the trityl chloride, an aliquot was added to a few drops of water and allowed to stand while stoppered for one hour. Acetone was then added to give 25 ml. of homogeneous solution which was titrated for triethylamine to obtain the infinity titer. In the cases where the triethylamine was not present in excess, the calculated infinity titer was used in the calculation of the percentage reaction. The change in titer between zero and infinity time obtained by the hydrolysis method agreed with the calculated change within 2%.

In the runs that utilized no alcohol but only phenol, the same procedure was used.

In one run 0.0278 *M* triethylamine was allowed to react with 0.0278 *M* trityl chloride in dry benzene at 30°. After 10,080 minutes only 6.2% of the halide had been consumed.

Product Analysis. Procedure Used in Absence of Phenol.—Approximately 40 ml. of the reaction mixture which had been allowed to stand at room temperature for several weeks was thoroughly washed with water and dried. The benzene was evaporated, the residue was dissolved in boiling pentane, and the solution was allowed to cool slowly. The crystals that separated were collected, washed, weighed and the melting point determined. This material was recrystallized from pentane to constant m.p.

Product Analysis. Procedure Used in Presence of Phenol.—The procedure was the same as above except that after the benzene was evaporated, the low molecular weight compounds were removed from the residue by distillation at 100–125° at 5 mm.

Phenyl Trityl Ether.—A benzene solution of 0.0546 *M* triethylamine, 0.0521 *M* phenol and 0.0507 *M* trityl chloride was allowed to react at 30° until titration of the triethylamine indicated that the reaction was 67% complete. A 40-ml. aliquot of the solution was then washed with water, dried and the solvent was evaporated to give a 10-ml. residue. This solution was absorbed on a 30 × 3 cm. column of activated neutral alumina and eluted with 750 ml. of a 4:1 pentane–benzene solution. The column filtrate produced 374 mg. (82% yield) of phenyl trityl ether, m.p. 101–102° (pentane), lit. m.p. 103°.[3b]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WYOMING]

The *para*-Claisen Rearrangement. I. The Preparation and Rearrangement of the α- and γ-Ethylallyl Ethers of Methyl *o*-Cresotinate. A Reinvestigation[1,2]

BY SARA JANE RHOADS, REBECCA RAULINS AND ROSALIE D. REYNOLDS[3]

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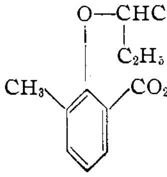
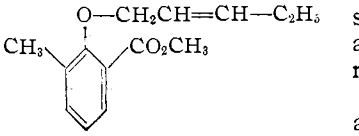
The preparation and rearrangement of the α- and γ-ethylallyl ethers of methyl *o*-cresotinate have been restudied. Evidence is presented which establishes that both ethers undergo the *para*-Claisen rearrangement *without* inversion.

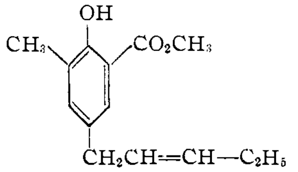
The original report of Mumm, Hornhardt and Diederichsen[4] that the isomeric α- and γ-ethylallyl ethers of methyl *o*-cresotinate (I and II) rearranged to the same *p*-allylated phenol (III) led to the postulation of two mechanisms which would permit equilibration of the migrating allylic system in the *para*-Claisen rearrangement, a free radical process[4] and a "pi complex" mechanism.[5] The "double-cyclic, semi-ionic" picture proposed by Hurd and Pollack[6] in analogy to the well-established mechanism for the *ortho*-rearrangement received scant attention since it required non-inversion in all cases.



I



II



III

Dissatisfied with the evidence offered by Mumm, Hornhardt and Diederichsen for the structures of their isomeric ethers[4,7,8] and dissuaded of the idea that the *ortho*- and *para*-rearrangements should show such differences in mechanism, we undertook a complete reinvestigation of the preparation and rearrangement of this pair of ethers.

Preparation and rearrangement of the γ-ethylallyl ether, II, according to the procedure of the earlier workers gave results essentially in agreement with their report, although we were unable to duplicate their yields of ether or to succeed with their purification method. The reaction mixture from the ether preparation, consisting of unreacted

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[1] Taken from the dissertations of Rebecca Raulins and Rosalie D. Reynolds submitted in partial fulfillment of the requirements for the Ph.D. degree, May, 1953. A preliminary announcement of this work appeared in THIS JOURNAL, **75**, 2531 (1953).

[2] Presented before the Division of Organic Chemistry of the American Chemical Society, March, 1954, in Kansas City, Missouri.

[3] Soroptimist Fellow, Rocky Mountain Region, 1952–1953.

[4] O. Mumm, H. Hornhardt and J. Diederichsen, *Ber.*, **72**, 100 (1939); O. Mumm and J. Diederichsen, *ibid.*, **72**, 1523 (1939).

[5] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 230.

[6] C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

[7] The sole distinction noted between the two ethers lay in their strikingly different behavior toward methanolic potassium hydroxide; the γ-ether saponified normally while the α-ether underwent rearrangement and saponification.

[8] Serious doubt concerning the homogeneity of the α-ether preparation was prompted by the recent recognition of the prevalence of abnormal products in displacement reactions of allylic halides. *Cf.* (a) R. E. Kepner, S. Winstein and W. G. Young, THIS JOURNAL, **71**, 115 (1949); (b) W. G. Young, I. D. Webb and H. L. Goering, *ibid.*, **73**, 1076 (1951).