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The Kinetics of the Darzens Reaction of *p*-Substituted Benzaldehydes and Phenacyl Chloride

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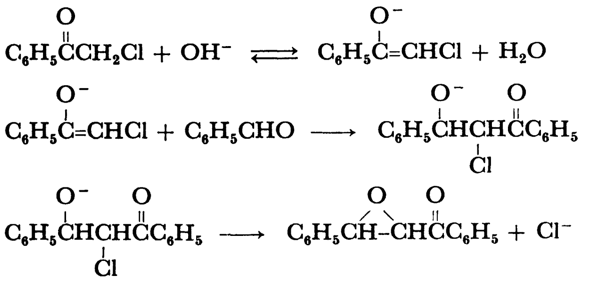
Synopsis. The rate constants for the base-catalyzed Darzens reaction of *p*-substituted benzaldehydes and phenacyl chloride have been measured at two temperatures in aqueous dioxane. Enthalpies and entropies of activation have been evaluated. The reactivity of the *p*-substituted benzaldehydes was found to follow the order p-NO$_2$>p-Cl>p-Br>H>p-CH$_3$>p-OCH$_3$. The kinetic data can be correlated with ρ values according to the Hammett equation.

The Darzens reaction often involves the condensation between aldehyde or ketone and α-halogenomethylene compound to produce an oxirane containing derivative. The mechanism of the reaction between benzaldehyde and phenacyl chloride catalyzed by sodium hydroxide to form an epoxy ketone appears to be established from the work of Bartlett.[1] It is generally agreed that the following sequence of reactions is involved:



$$C_6H_5\overset{O}{\overset{\|}{C}}CH_2Cl + OH^- \rightleftharpoons C_6H_5\overset{O^-}{\overset{|}{C}}{=}CHCl + H_2O$$

$$C_6H_5\overset{O^-}{\overset{|}{C}}{=}CHCl + C_6H_5CHO \longrightarrow C_6H_5\overset{O^-}{\overset{|}{C}H}\underset{Cl}{\underset{|}{C}H}\overset{O}{\overset{\|}{C}}C_6H_5$$

$$C_6H_5\overset{O^-}{\overset{|}{C}H}\underset{Cl}{\underset{|}{C}H}\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow C_6H_5CH\overset{O}{-}CH\overset{O}{\overset{\|}{C}}C_6H_5 + Cl^-$$

Furthermore, it is argued from non-kinetic methods that the second step is the rate-determining step of the reaction.[2]

A brief study of the methoxide ion catalyzed reaction between benzaldehyde and substituted phenacyl chlorides was made[3] to evaluate the effect of substituents on rate. There is no kinetic investigation, however, on the rate of the reaction when the substituents are located on benzaldehyde. In our continuing study[4] of the various aspects of the Darzens reaction we have measured the rates of the reaction between *p*-substituted benzaldehydes and phenacyl chloride using sodium hydroxide in dioxane–water solvent mixture. We have also examined the application of the Hammett equation in this reaction.

Experimental

Materials. All liquid aldehydes were purified by fractional distillation and stored under nitrogen: benzaldehyde, bp 62—62.5 °C/10 mmHg, *p*-methoxybenzaldehyde, (E. Merck), bp 88—89 °C/2 mmHg, *p*-methylbenzaldehyde (Fluka, A. G.), bp 72—73 °C/3 mmHg. *p*-Nitrobenzaldehyde (BDH) mp 105.5—106 °C (hexane), *p*-bromobenzaldehyde mp 67—67.5 °C (aq ethanol), phenacyl chloride (Fluka, A. G.), mp 56—57 °C (petroleum ether) were all purified by recrystallization. Analar grade dioxane was purified by refluxing with sodium metal followed by distillation.[5]

Experimental Procedure. From several initial preliminary runs it was established that the rate could be conveniently measured in 40% aq dioxane at 15 °C and 25 °C. Appropriate volumes of solutions of the components except phenacyl chloride were transferred to a nitrogen flushed, round bottomed flask fitted with a rubber septum and brought to the desired temperature. The reaction was initiated by injecting a required amount of concentrated solution of phenacyl chloride in dioxane with the help of a hypodermic syringe. The self-condensation of phenacyl chloride was precluded by using 9—15 fold excess of benzaldehyde. Five ml aliquots were withdrawn with the aid of a syringe and run into cold standard sulfuric acid. The remaining sulfuric acid was back-titrated against sodium hydroxide of known strength. The final reading was taken after the reaction flask was allowed to stand for 70 h. The rate constants were calculated from linear plots obtained by using the standard third order equation.[6]

Results and Discussion

All the runs were made at 15 °C and 25 °C in 40% aqueous dioxane (v/v). Sodium perchlorate of 0.01 M strength was employed to maintain a constant ionic strength. Duplicate runs were made in each case. The runs were carried out to about 60—70% completion, the reaction complies to a third order kinetics being first order in the concentration of each reactant. Rate constants were calculated from linear third order plots. Appropriate data are summarized in Table 1.

TABLE 1. THIRD ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS OF BASE-CATALYSED CONDENSATION BETWEEN *p*-SUBSTITUTED BENZALDEHYDES AND PHENACYL CHLORIDE IN AQUEOUS DIOXANE

Compound	*p*-Substituent	$10^{-1}k/l^2$ mol^{-2} s^{-1} 15C°	25°C	ΔH / kcal mol^{-1}	$-\Delta S^{\neq}$ / e.u.
I	OCH$_3$	0.600±0.012	1.296±0.012	12.56±0.191	11.30±0.466
II	CH$_3$	0.676±0.017	1.397±0.029	11.76±0.249	13.97±0.838
III	H	0.764±0.012	1.484±0.010	10.98±0.134	16.33±0.418
IV	Br	0.965±0.019	1.854±0.026	10.47±0.046	17.58±0.150
V	Cl	0.989±0.016	1.878±0.028	10.28±0.070	18.20±0.222
VI	NO$_2$	1.768±0.015	2.890±0.033	7.74±0.042	25.88±0.141

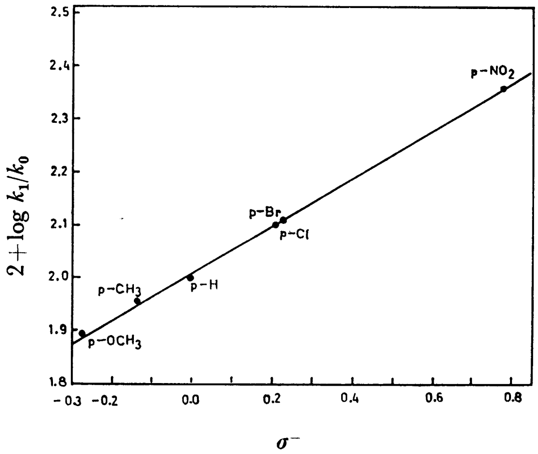


Fig. 1. Hammett plot of condensation of *p*-substituted benzaldehydes with phenacyl chloride.

There is a regular variation in the rates with the nature of the *p*-substituents. The order of reactivity being $NO_2 > Cl > Br > H > CH_3 > OCH_3$ *i.e.* electron-withdrawing groups increase while electron-donating groups decrease the rate. This fact is also borne out by the enthalpies of activation ($\Delta H^{\neq}$) values calculated for these reactions which are 7.8 kcal/mol for the *p*-NO_2 and 12.56 kcal/mol for the *p*-OCH_3 groups.

The sign and magnitude of the reaction constant, ρ in the Hammett equation are often evaluated to assess the charge type of the transition state. The ρ value from the Hammett plot (Fig. 1) has been found to be $+0.446$ ($r=0.998$) by least squares method. The small value reflects a weak interaction between the substituent and the reaction site. It, however, does indicate the transition state has a negative character.

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