and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (to W.J.E.).

Registry No. 1,5-C_8H_{12}, 1552-12-1; $K_2C_8H_8$, 34480-05-2; K, 7440-09-7; UCl_4, 10026-10-5; 1,3,5,7-C_8H_8, 629-20-9; $U(C_8H_8)_2$, 11079-26-8; O_2, 7782-44-7; $CdCl_2$, 10108-64-2; dichlorophenylphosphine, 644-97-3; azobenzene, 103-33-3; *cis*-bicyclo[3.3.0]oct-2-ene, 930-99-4; 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, 13887-07-5.

Synthesis of Aromatic Ketones from Carboxylic Acids and Phenyllithium. Destruction of the Excess Phenyllithium

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We required aromatic ketones for photochemical studies[1] and were using the reaction of phenyllithium with carboxylic acids[2] when we read the excellent papers[3,4] by Levine and co-workers in which they show that the often low yields of ketones from these reactions are principally due to the reaction of excess phenyllithium with the ketone produced during hydrolysis. Yields can be improved by using a stoichiometric ratio of phenyllithium and the lithium carboxylate of the acid, but it was not possible to simplify the procedure by using 2 equiv of phenyllithium and the free acid as carbinols were again formed.[4] While the yields reported were excellent, the procedure requires the transfer and use of solutions of phenyllithium of known concentration (which must be measured) and the preparation and drying of the lithium salt of the acid to be used. This entails an extra synthetic step and is considerably more complicated then the preparation (or use) of an excess of phenyllithium to which the organic acid is added in the same flask.

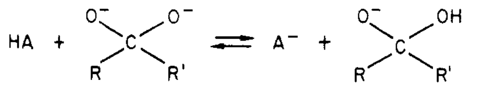
Since an excess of phenyllithium is only detrimental during hydrolysis, we felt that if the excess was removed after reaction with the carboxylic acid but before hydrolysis, a simple modification of the normal procedure might result in a significant improvement in yield without the necessity of preparing lithium salts or titrating the phenyllithium. Using the reaction of phenyllithium with benzoic acid to generate benzophenone as a model, we tested the capacity of various potential reagents for the destruction of excess phenyllithium. The results are presented in Table I.

Table I. Reagents Used To Eliminate Excess Phenyl Lithium from the Reaction with Benzoic Acid

reagent used	% yield of benzophenone[a]	% yield of benzpinacol[a]
water[b]	42	36
water[c]	26	57
tert-butyl alcohol	55	29
formaldehyde	79	6
aniline	64	18
acetone	48	21
acetic acid	49	41
sodium formate	42	41

[a] Yields are the average of at least two determinations. The agreement between analyses was ±10%. [b] Water added to the reaction mixture. [c] The reaction mixture added to water and ice.

From Table I it can be seen that the addition of any reagent to the reaction mixture results in an improvement in the yield of ketone relative to the usual procedure of pouring the reaction mixture onto water and ice. The best reagents were formaldehyde and aniline. Formaldehyde gives a better yield of ketone and less carbinol but requires the generation of formaldehyde from paraformaldehyde and generates benzil alcohol. The yields of ketone are lower when aniline is used but aniline is easier to add and does not form any other products. It is also easily removed from the resulting reaction mixture by acid–base extraction. In our experience the reagent chosen must be anhydrous. It should be either an aprotic acid (Lewis acid) or a very weak Brönsted acid such that the conjugate base is stronger than the ketone hydrate dianion. For success the equilibrium shown in eq 1 must favor reagents. A suggested procedure for the destruction of excess phenylltihium is presented in the Experimental Section.



(1)

Experimental Section

Phenyllithium was prepared from bromobenzene and lithium in ether in the normal manner[5] and was used as needed. Benzophenone and triphenylcarbinol were analyzed by temperature-programmed VPC on a $^1/_8$ in. × 4 ft column, using 10% Se-30 on Chromosorb G as the stationary phase and using *n*-butylphthalate and 4-phenylbenzophenone as internal standards to quantify the results. A Model 900 Perkin-Elmer gas chromatograph with a flame ionization detector was used.

Analytical studies were carried out by the following procedure. Dry ether (1.5 mL) was distilled into a 50-mL round-bottom blask containing 240 mg of benzoic acid. After the acid had dissolved with magnetic stirring, 20 mL of 1.0 M phenyllithium was added and the mixture was refluxed for 2 h with a spiral condenser and calcium chloride drying tube to protect the mixture. The excess phenyllithium was then destroyed with the reagents listed in Table I which were added until the brown color of phenyllithium disappeared. Water was added, the phases were separated, the aqueous phase was extracted with ether, and the combined ether fractions were washed with bicarbonate solution and then water. The ether solution was dried and concentrated and then adjusted to 20.00 mL and mixed with a mixture of internal standards for VPC analysis.

For preparative use the following hydrolysis procedure is suggested. After the reaction between acid and phenyllithium is complete (about 24 h[6]), the excess phenyllithium is destroyed by adding dry distilled aniline or by bubbling dry formaldehyde (prepared by heating paraformaldehyde[7] until the brown color of phenyllithium is eliminated and then adding water and following the normal workup procedure.[8]

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[6] A longer time is needed here due to the smaller excess of phenyllithium used in preparative reactions.

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[8] We have used this method with aniline to eliminate excess phenyllithium, to give a 49% isolated yield of 2-benzoyl-3-phenylbicyclo[2.2.1]hept-2-ene from 2-carboxy-3-phenylbicyclo[2.2.1]hept-2-ene and a 69% isolated yield of 2-benzoylindan from 2-carboxyindan.

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Registry No. Benzophenone, 119-61-9; triphenylcarbinol, 76-84-6; benzoic acid, 65-85-0; phenyllithium, 591-51-5.

Micellar Effects upon the ElcB Mechanism of Ester Hydrolysis

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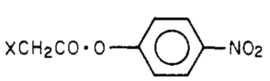
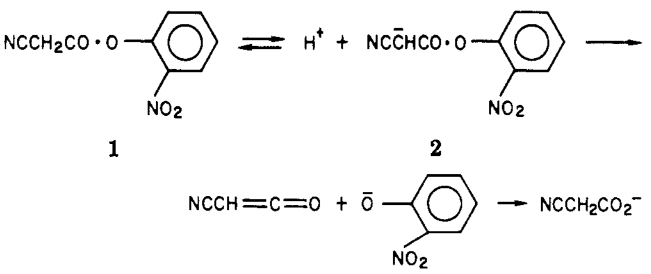
The ElcB mechanism of carboxylic ester hydrolysis is observed with nitrophenyl esters which contain a strongly electron attracting group at the α-carbon atom, as in **1**[1] (Scheme I). The apparent pK_a value of 1 is 8.57, and the reaction rate increases with increase in pH (above 6) to a limiting value at pH >9, which corresponds to rate-limiting decomposition of the preformed carbanion (**2**).[1]

Micellar effects upon ElcB hydrolyses of substituted p-nitrophenyl acetates (**3**), have been reported.[2] The rate enhancements by cationic micelles of $C_{16}H_{33}NMe_3Br$ (cetyltrimethylammonium bromide, CTABr) were larger than those typical of hydrolyses by the $B_{Ac}2$ mechanism,[3,4] and "saturation kinetics" were observed which were consistent with extensive substrate incorporation in the micelles.[2] The rates in the micellar solutions were stated to be the same at pH values of approximately 8 and 10 for reaction of **3** where X = $O_2NC_6H_4$ and PhS, respectively. The micellar catalysis was measured at pH 8.99 (buffer unspecified), so that some, but not all, of the substrates should have been extensively deprotonated under the reaction conditions (cf. ref 1).



3, X = p-$O_2NC_6H_4$, p-$MeOC_6H_4$, PhS, PhO

Scheme I



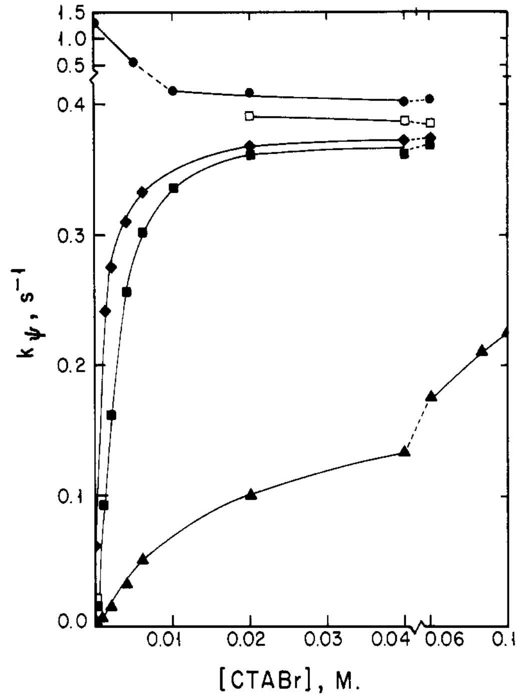


Figure 1. Effect of CTABr on the hydrolysis of o-nitrophenyl cyanoacetate: (●) 0.01 M NaOH; (□) pH 7, phosphate buffer; (◆, ■, ▲) maleate buffer, pH 8, 7, and 6, respectively, with 0.01 M buffer.

Cationic micelles can affect the rate of an ElcB mechanism of a substrate such as **1** by changing the equilibrium constant for deprotonation of **1** or the rate constant for decomposition of the carbanion (**2**). Cationic micelles markedly increase extents of deprotonation,[5-8] and they catalyze E2 eliminations[6] and related deprotonations,[7] but this effect will not be kinetically significant if the substrate is already deprotonated, as at pH ≫ pK_a.

Micelles inhibit S_N1 reactions,[8,9] but cationic micelles catalyze anionic decarboxylations[9,10] and the spontaneous decompositions of aryl sulfate monoanions[11] and aryl and acyl phosphate dianions,[12] so that one can only speculate on their effect on the rate constant for decomposition of **2** (Scheme I).

The aim of our work was to clarify this situation by examining reaction of **1** in CTABr at high pH and at pH < pK_a. At high pH we should follow spontaneous decomposition of the carbanion (**2**), and at low pH both steps could be important.

Experimental Section

Materials. o-Nitrophenyl cyanoacetate (**1**) was prepared by heating a mixture of o-nitrophenol, cyanoacetic acid, and $POCl_3$ at 60 °C for 3 h.[1] The crushed solid was extracted with Et_2O and was recrystallized from Et_2O, mp 71.5 °C (lit.[1] mp 71.5 °C).

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