63989-44-6; **24**, 25948-15-6; **20**, 63988-97-6; **22**, 63988-99-8; **5**, 55759-61-0; **11**, 64011-18-3; **1**, 63989-41-3; **16**, 63988-98-7; **17**, 63989-42-4; NFB, 350-46-9; BNFB, 701-45-1; NAEA, 142-26-7; FNBN, 17417-09-3; 5-nitro-2-fluoropyridine, 456-24-6; NMEA, 109-83-1; CNBN, 16588-02-6; [*N*-(β-hydroxyethyl-2-cyano-4-nitroaniline, 63989-40-2; acetyl chloride, 75-36-5; 5-nitro-2-chloropyridine, 4548-45-2.

Supplementary Material Available. Table III and Figures 2, 5, 6, and 7 (6 pages). Ordering information is given on any current masthead page.

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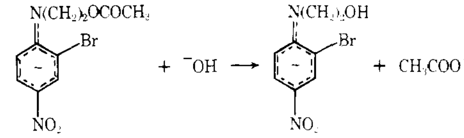

12 12a

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Crown–Cation Complex Effects. 8. Reactions of Crown Ether Activated *tert*-Butoxide Ion

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The effect of catalytic amounts of 18-crown-6 on tetrahydrofuran, *tert*-butyl alcohol, and benzene solutions of potassium *tert*-butoxide has been investigated. In each solvent, the enhanced nucleophilicity of *tert*-butoxide ion was manifested in its reaction with benzyl chloride; i.e., good yields of benzyl *tert*-butyl ether were obtained. In the latter solvent, 18-crown-6 served as phase-transfer agent as well as activator. *tert*-Butoxide ion was found to be most effective as a nucleophile in tetrahydrofuran solution, and, in general, the results of exemplary reactions indicated that nucleophilicity was enhanced more than basicity. Crown-activated *tert*-butoxide, for example, converts isatoic anhydride to *tert*-butyl anthranilate, benzaldehyde and diphenylmethane to benzhydryl phenyl ketone, and, in the presence of oxygen, fluorene directly to 2-carboxybiphenyl.

There has been interest for many years in solvent properties, particularly regarding their effect on the basicity and nucleophilicity of anionic reagents. The difference of 10^{11} in the rates of proton removal from carbon by alkoxide in methanol compared to dimethyl sulfoxide (Me_2SO) is an especially dramatic demonstration of such solvent effects.[1] Other studies conducted in the early 1960's demonstrated the value of *tert*-butoxide as a base, particularly in Me_2SO,[2,3] and it was at about this time that cation effects became clearly recognized.[4] A great deal is now known about the *tert*-butoxide ion[5] and, in general, about the chemistry of ion pairs.[6]

The ability of crown ethers to solvate cations has led to new studies of ion pairs both in the presence and absence of such ligands.[7] In general, in the presence of crown ether, aggregates of ion pairs are broken up and the anionic portion of the ligand separated or dissociated ion pair exhibits enhanced reactivity. This enhanced reactivity has manifested itself in decarboxylation reactions,[8] oxy-Cope rearrangements,[9] and elimination reactions.[10] We were particularly interested in the reactivity of potassium *tert*-butoxide (**1**) in the presence of crown ethers.[11] We felt that in such solvents as Me_2SO the enhanced basicity can be attributed, at least in part, to solvent assistance in carbanion formation.[12] In the presence of crown in a solvent such as tetrahydrofuran where solvent assistance is limited, the reactivity enhancement should be more apparent in the nucleophilic sense than in the basic sense. We have examined several reactions of *tert*-butoxide ion and have indeed found an enhancement of the nucleophilic behavior of this hindered base.

Results and Discussion

The chemistry of potassium *tert*-butoxide has been thoroughly reviewed.[5] This base has been utilized in a variety of media including *tert*-butyl alcohol, dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, and benzene, although **1** is only sparingly soluble in the latter.[13] Benzyl chloride (**2**) has been used in the past as a substrate for studying nucleophile/base balance in systems where the anion behaved more as a base than as a nucleophile.[14] Utilization of this substrate

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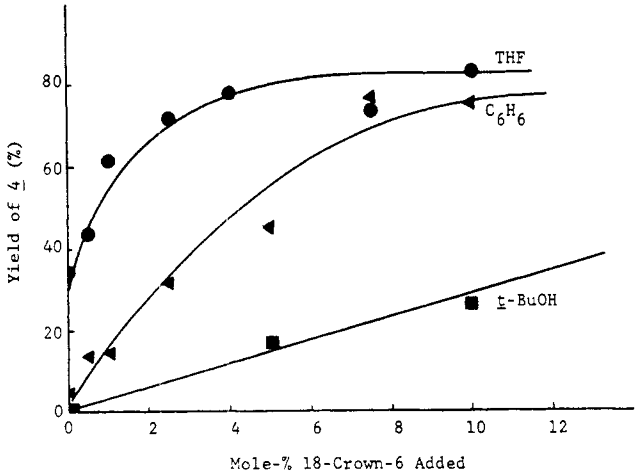


Figure 1. Yield of 4 as a function of added 18-crown-6.

Table I

$$C_6H_5CH_2Cl^{d} + (CH_3)_3CO^-K^{+\,e} \xrightarrow[\text{18C6}]{\text{THF}} \underset{\mathbf{4}}{C_6H_5CH_2OC(CH_3)_3^{f}} + \underset{\mathbf{5}}{C_6H_5CH{=}CHC_6H_5^{g}}$$

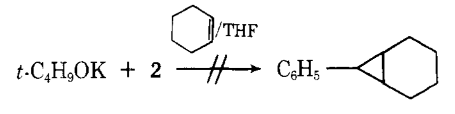
Solvent	mol % added[b] crown ether[h]	Yield, %[c]	
		4	5
THF		34	0
THF	0.5	44	Trace
THF	1.0	62	5.0
THF	2.5	72	5.7
THF	5.0	78	4.4
THF	7.5	74	3.0
THF	10.0	83	1
C_6H_6		5	0
C_6H_6	0.5	14	0
C_6H_6	1.0	15	Trace
C_6H_6	2.5	32	~1
C_6H_6	5.0	45	2
C_6H_6	7.5	77	6.4
C_6H_6	10.0	75	8.6
t-C_4H_9OH		<1	0
t-C_4H_9OH	5.0	17	0
t-C_4H_9OH	10.0	26	0
t-C_4H_9OH	25.0	58	Trace

[a] All reactions were conducted at 30 ± 1 °C for 1 h under an atmosphere of N_2. [b] 18-crown-6; see ref 17. [c] Determined by GLC using a 5 ft × 0.25 in. 10% SE 30 column on NAW Chromosorb P, 60–80 mesh. [d] Registry no.: 100-44-7. [e] Registry no.: 865-47-4. [f] Registry no.: 3459-80-1. [g] Registry no.: 103-30-0. [h] Registry no.: 17455-13-9.

for our purposes seemed particularly advantageous because the products of deprotonation are well known and the condensation product (benzyl *tert*-butyl ether) has always been accessible only with difficulty. Previous syntheses of benzyl *tert*-butyl ether required either long periods of time (e.g., 10 days at ambient temperature in *tert*-butyl alcohol to achieve a 55% yield)[15] or use of a dipolar aprotic solvent (30–40% yield after 18 h at ambient temperature in DMF).[16]

We have found that 1 readily condenses with 2 at 30 °C in tetrahydrofuran solution (see eq 1). In less than 2 h in the presence of 5 mol % 18-crown-6 (3),[17] benzyl *tert*-butyl ether (4) is isolated in 74% yield. The only by-product detected in this reaction is a small amount of stilbene (5). The stilbene apparently arises by deprotonation of 2, followed by nucleophilic substitution and then elimination of HCl. Although this sequence was not confirmed directly, the alternative of carbene dimerization was ruled out by conducting the reaction in a 1:1 mixture of cyclohexene and tetrahydrofuran (see Experimental Section). Any phenylcarbene generated should have been intercepted by the olefin to give 7-phenylnorcarane,[14a,b] none of which was detected (see eq 2).

$$\underset{\mathbf{1}}{t\text{-}C_4H_9OK} + \underset{\mathbf{2}}{C_6H_5CH_2Cl} \longrightarrow \underset{\mathbf{4}}{t\text{-}BuOCH_2C_6H_5} + \underset{\mathbf{5}}{C_6H_5CH{=}CHC_6H_5} \quad (1)$$



(2)

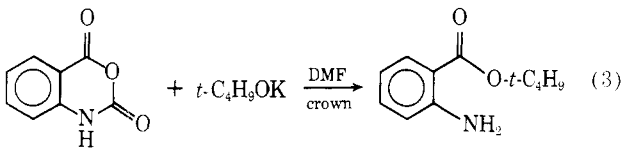
In order to determine whether the benzyl *tert*-butyl ether synthesis was solvent and/or crown concentration dependent, a series of experiments was conducted in which crown concentration was varied systematically in *tert*-butyl alcohol, benzene, and tetrahydrofuran (see Table I and Figure 1). In the latter solvent, the yields of 4 ranged from 34 to 83% when the reaction was conducted at 30 ± 1 °C for 1.0 h in the presence of 0.5–10 mol % 18-crown-6. As the amount of crown ether present was increased, the yield of ether increased as well, but the difference in yield between reactions containing 5 and 10 mol % added crown was negligible. The leveling of the yield curve is obvious in Figure 1. In the absence of any 18-crown-6, a 70% yield of 4 was realized, but only after 24 h. The amount of stilbene produced in each reaction was never more than 6% under any of the conditions utilized.

In contrast, the attempted synthesis of 4 in Me_2SO solution was unsuccessful, even less ether was produced than in the previously reported DMF case.[16] Apparently, 1 is much more basic in Me_2SO than in THF. Under conditions conducive to the formation of 4 (74% in 1 h at 30 °C) in THF, only 15% of this ether (4) could be detected. Although a small amount of 2 remained in the reaction mixture, stilbene was the major (47%) product. It seems very likely that crown or Me_2SO activated 1 is a potent anion, but, where the dipolar aprotic medium can offer solvent assistance in deprotonation, the basic behavior of the anion becomes dominant.

In *tert*-butyl alcohol, a solvent in which potassium *tert*-butoxide is also freely soluble,[13] the crown effect was also evident, although the yields of ether were lower even in the presence of considerably more crown and the yield increase as a function of added crown was nearly linear. Up to 25 mol % 18-crown-6 was added (see Table I and Figure 1) to the reaction mixture (under the conditions described above), and only 58% yield of ether was obtained. We feel that this reflects anion deactivation due to hydrogen bonding between the *tert*-butoxide ion and solvent. It is known that *tert*-butoxide is more basic (in elimination reactions) in the presence of crown than in its absence,[10] so it appears that both the nucleophilicity and basicity of this substance are enhanced by ion pair separation. The lesson seems to be that *tert*-butyl alcohol is not the best solvent for utilizing the potential of this synthetically important[5] reagent.

Potassium *tert*-butoxide is not profoundly soluble in benzene.[13b] This fact makes difficult a direct comparison of the reactivity of 1 in the presence and absence of 3. Nevertheless, in the synthesis of 4 according to eq 1, the yield per unit time of 4 was considerably increased in the presence of 3 (see Figure 1). It appears, in this particular case, that the crown serves as phase-transfer catalyst[18] as well as cation solvator and anion activator.[19]

The reaction of *tert*-butoxide with benzyl chloride to afford a high yield of 4 is, we believe, a convincing demonstration of the nucleophilicity of this ion in the presence of crown. Another such demonstration of this property can be found in the reaction of *tert*-butoxide with isatoic anhydride. Although numerous anthranilate esters have been formed by nucleophilic addition of the appropriate alkoxide to isatoic anhydride (**6**),[20] it is reported that the *tert*-butyl ester cannot be formed by this approach.[21] In DMF solution, crown-activated *tert*-butoxide reacts with isatoic anhydride to afford *tert*-butyl anthranilate (**7**) in 33% yield (see eq 3). In the absence of crown this reaction is not preparatively useful (yield of **7** 8%).



The reactivity of *tert*-butoxide in THF is not enhanced sufficiently for this to afford a useful synthesis of phenyl *tert*-butyl ether from bromobenzene (see eq 4).[1,22] Since it appears that the nucleophilicity of *tert*-butoxide is enhanced more than is the basicity, the failure of eq 4, a reaction which apparently proceeds via a benzyne intermediate,[22] is not so surprising. On the other hand, the direct displacement of chloride by methoxide ion in 1,2-dichlorobenzene under crown catalysis[23] makes the necessity of the benzyne mechanism somewhat less certain.

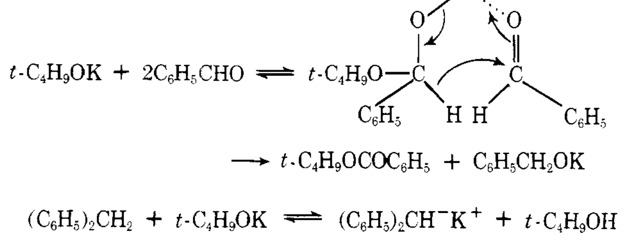
$$t\text{-}C_4H_9OK + C_6H_5Br \rightarrow t\text{-}C_4H_9OC_6H_5 \quad (4)$$

An approximate assessment of *tert*-butoxide ion's basicity under these conditions was obtained by equilibrating several carbon acids with crown-activated *tert*-butoxide ion in THF and then quenching with D_2O. Russell and co-workers showed some years ago that *tert*-butoxide in Me_2SO is basic enough to induce condensation between activated toluenes and benzaldehyde.[2] We have found that metallation of diphenylmethane (**8**) followed by a deuterium oxide quench gave a product which was 8% deuterated after 3 min and 18% deuterated after 4 h (recovery was ca. 90%). Chlorodiphenylmethane was 75% deuterated (by NMR) after only 30 s at 30 °C, although only 41% of the substrate could be recovered, the loss presumably due to ether formation in analogy to eq 1. No H–D exchange was observed for toluene even after 24 h at 30 °C.

Although metallation of **8** was not complete in 4 h, after 22 h in the presence of *tert*-butoxide it condensed with benzaldehyde to give α,α-diphenylacetophenone (**9**) according to eq 5. A more likely product in this reaction seemed to be triphenylethylene, but none was detected. An authentic sample of triphenylethylene survived the reaction conditions, implying that the product could not be accounted for by any process involving this substance as an intermediate.

$$C_6H_5CH_2C_6H_5 + C_6H_5CHO \rightarrow (C_6H_5)_2CHCOC_6H_5 \quad (5)$$

A possible mechanism is shown in eq 6. The sequence envisaged is addition of *tert*-butoxide ion to benzaldehyde to give an intermediate which then takes part in a Cannizzaro-like process to give *tert*-butyl benzoate. Diphenylmethyl anion is acylated by *tert*-butyl benzoate to give diphenylacetophenone in the final step of this reaction sequence. In favor of this mechanism is the fact that if **8** is excluded from the reaction mixture the products isolated are *tert*-butyl benzoate (29%) and benzyl alcohol (65%). We note that this reaction cannot occur by a single process strictly analogous to the Cannizzaro reaction because of the unequal product distribution. Moreover, **9** is produced in 15% yield from lithium diphenylmethide and *tert*-butyl benzoate in THF solution. Contrary to this mechanism, however, is the observation that, under the reaction conditions, diphenylmethane and *tert*-butyl benzoate do not produce detectable amounts of diphenylacetophenone.



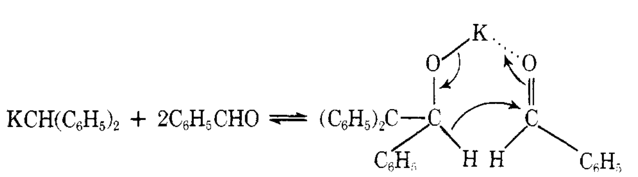
$$\longrightarrow t\text{-}C_4H_9OCOC_6H_5 + C_6H_5CH_2OK$$

$$(C_6H_5)_2CH_2 + t\text{-}C_4H_9OK \rightleftharpoons (C_6H_5)_2CH^-K^+ + t\text{-}C_4H_9OH$$

$$(C_6H_5)_2CH^-K^+ + C_6H_5COO\text{-}t\text{-}C_4H_9 \longrightarrow (C_6H_5)_2CHCOC_6H_5 + t\text{-}BuOK \quad (6)$$

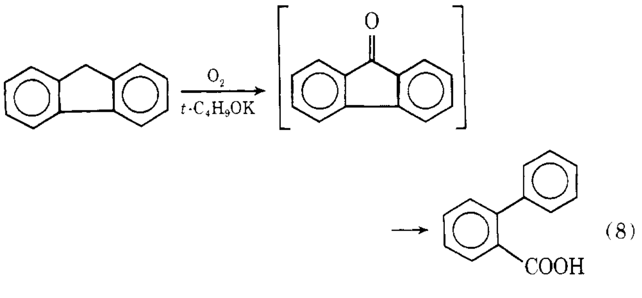
A possible mechanism which does not appear to be contradicted by any of our observations is shown in eq 7. Potassium *tert*-butoxide deprotonates diphenylmethane to give diphenylmethide ion which, in turn, adds to benzaldehyde. The resulting 1,2,2-triphenylethoxide ion then undergoes a Cannizzaro-type reaction as illustrated, resulting in formation of the observed ketone and benzyl alcohol. This second step must occur more rapidly than KOH can be lost because no triphenylethylene is detected in the reaction mixture (see above). When we conduct this reaction, we obtain 29% ketone and 35% alcohol, an approximately 1:1 distribution. When the reaction is carried out with benzaldehyde-α-d, ketone and alcohol are each isolated in 33% yield (slightly different workup) and the benzyl alcohol is, within the limits of detection, dideuterated at the methylene group. A kinetic investigation of this reaction would be interesting, but it is beyond the scope of this work.

$$KO\text{-}t\text{-}C_4H_9 + (C_6H_5)_2CH_2 \rightleftharpoons KCH(C_6H_5)_2 + HO\text{-}t\text{-}C_4H_9$$



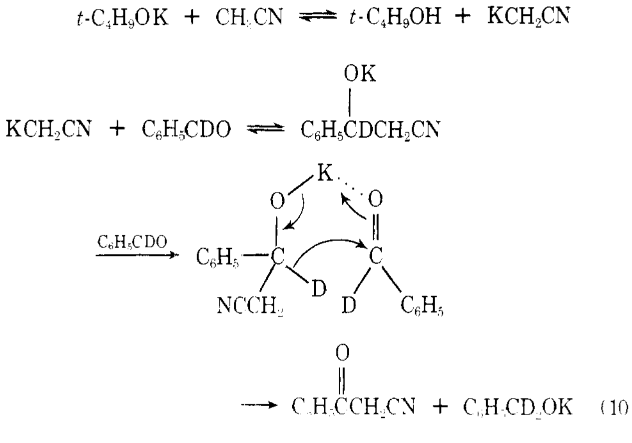
$$\longrightarrow (C_6H_5)_2CHCOC_6H_5 + C_6H_5CH_2OK \quad (7)$$

The crown-activated *tert*-butoxide reagent affords an interesting opportunity to carry out sequential reactions of the type mentioned above. For example, the basic oxidation of fluorene to fluorenone[25] in the presence of crown-activated *tert*-butoxide is rapid at room temperature (see eq 8). This reaction occurs readily under phase-transfer conditions using cryptate-complexed hydroxide,[25a] 18-crown-6-complexed hydroxide,[25b] or quaternary ammonium hydroxides.[25c] A mole of water is produced in this reaction for each mole of hydrocarbon oxidized to ketone. Water is, in turn, deprotonated by excess *tert*-butoxide and Haller–Bauer cleavage[26] of the ketone ensues. In this way, fluorene can be transformed directly into 2-carboxybiphenyl in high yield according to eq 8. We note that in THF solution the crown effect is marginal. Our attempts to conduct this reaction with crown-activated hydroxide have thus far been unsuccessful.



The hoped-for condensation of acetonitrile with benzaldehyde to give cinnamonitrile[27] unadulterated by the β-hydroxynitrile (see eq 9) was less successful. In our particular attempts, the loss of yield was not due to the failure of the dehydration step, but rather due to a process analogous to that described in eq 7. Some cinnamonitrile is obtained in this reaction, but much of the benzaldehyde is lost to a Cannizzaro-type reaction. Specifically, when a THF solution of *tert*-butoxide, acetonitrile, and benzaldehyde-α-*d* was allowed to react, cinnamonitrile-β-*d* was isolated in 22% yield. Benzyl-d_2 alcohol was also isolated by preparative GLC from this same reaction mixture. The conclusion we draw from these observations is that cyanomethyl anion adds to benzaldehyde to give the β-alkoxynitrile. This alkoxynitrile can either lose KOH (or protonate and lose water) or it can undergo a Cannizzaro-type reaction as shown in eq 10. The cyanoacetophenone produced in this reaction is quite acidic and undoubtedly undergoes multiple condensations with benzaldehyde and *tert*-butoxide.

$$C_6H_5CHO + CH_3CN \xrightarrow[\text{crown}]{t\text{-}C_4H_9OK} C_6H_5CH{=}CHCN + C_6H_5CHOHCH_2CN \quad (9)$$


(10)

We note that the condensation of acetonitrile with benzaldehyde to afford cinnamonitrile has been achieved under other conditions which we have reported previously.[28]

Summary. In summary, it appears that potassium *tert*-butoxide in THF in the presence of crown ether is both a powerful nucleophile and base, but the enhancement of nucleophilicity appears to exceed the enhancement of the basicity. The reagent is a potent nucleophile giving hitherto unattainable yields in several exemplary reactions. The system is of value because it appears to compliment the Me_2SO enhanced basicity of *tert*-butoxide. Moreover, the fact that only a catalytic amount of crown appears necessary to observe the enhanced reactivity is of practical value in synthetic applications.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary device and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 and are calibrated against the 1601 cm^{-1} band of polystyrene. NMR spectra were recorded on a Varian Associates A-60A as ca. 15 wt % solutions in CCl_4 or $CDCl_3$. Chemical shifts are reported in ppm (δ) downfield from internal Me_4Si. Mass spectra were determined on an AEI-MS 902 instrument at an ionizing voltage of 70 eV. Gas chromatographic analyses were conducted using either a Varian Associates Model 2720 or 920 analytical gas chromatograph equipped with a thermal-conductivity detector and a 5 ft × 0.25 in. 10% SE-30 column on NAW Chromosorb P. Helium was used as a carrier gas and the flow rate was ca. 60 mL/min.

Tetrahydrofuran was distilled from $LiAlH_4$ through a 30-cm Vigreux column just prior to use. The potassium *tert*-butoxide was sublimed and stored thereafter under dry nitrogen in a desiccator. All other solvents were purified according to literature procedures and stored under dry nitrogen and in contact with 4-Å molecular sieves.

Preparation of Benzyl *tert*-Butyl Ether (in Tetrahydrofuran). A 100-mL, three-necked, round-bottomed flask equipped with an addition funnel and magnetic stirring bar was charged with resublimed potassium *tert*-butoxide (5.61 g, 0.05 mol), 18-crown-6 (0.66 g, 0.0025 mol), and dry THF (40 mL). The solution was placed in a 30 °C bath and the solution was maintained under an inert atmosphere (N_2). Benzyl chloride (6.32 g, 0.05 mol) in THF (10 mL) was added dropwise over 5 min. After the addition was complete, stirring was continued for 1 h, the mixture was quenched with water (5 mL), diluted with an equal volume of ether and filtered, and the filtrate was dried over sodium sulfate and evaporated in vacuo. Benzyl *tert*-butyl ether (6.1 g, 74%) was obtained after distillation (bp 90–92 °C/15 mm) as a colorless oil: NMR (CCl_4, ppm) 1.2 (ψs, 9 H) $-C(CH_3)_3$, 4.3 (ψs, 2 H) $ArCH_2$, 7.2 (ψs, 5 H) aromatic protons. Recrystallization of the pot residue from ethanol/benzene gave (*E*)-stilbene as an off-white solid: 220 mg; 5%; mp 120–121 °C; NMR ($CDCl_3$, ppm) 7.0 (ψs, 2 H) $ArCH{=}CHAr$, 7.1–7.5 (m, 10 H) aromatic protons.

Reaction of Benzyl Chloride with Crown-Activated Potassium *tert*-Butoxide in 1:1 THF/Cyclohexene. A 50-mL, three-necked, round-bottomed flask equipped with a magnetic stirring bar, addition funnel, and nitrogen inlet was charged with THF (5 mL), cyclohexene (10 mL), potassium *tert*-butoxide (1.12 g, 0.01 mol), and 18-crown-6 (0.132 g, 0.0005 mol). The solution was brought to 30 °C and a solution of benzyl chloride (1.26 g, 0.01 mol) in THF (5 mL) was added dropwise over a period of 5 min. After the addition was complete, stirring was continued for 1 h, the mixture was quenched with water (5 mL) and separated, and the organic phase was washed with water (20 mL). The aqueous phase was extracted with ether (20 mL), and the combined organic phase was dried over sodium sulfate and analyzed (GLC) to show benzyl *tert*-butyl ether (93%), stilbene (~1%), and a small amount of unreacted benzyl chloride. No 7-phenylnorcarane could be detected.

Reaction of Benzyl Chloride with Potassium *tert*-Butoxide in Me_2SO. A 100-mL, three-necked, round-bottomed flask equipped with an addition funnel and magnetic stirring bar was charged with potassium *tert*-butoxide (1.12 g, 0.01 mol) and dry Me_2SO (15 mL). The solution was brought to 30 °C under a nitrogen atmosphere and a solution of benzyl chloride (1.26 g, 0.01 mol) in Me_2SO (5 mL) was added dropwise over a period of 5 min. After the addition was complete, stirring was continued for 1 h, and the mixture was quenched with water (5 mL) and diluted with an equal volume of ether. The resulting mixture was washed with water (3 × 20 mL) and the aqueous phase backwashed with ether (20 mL). The combined organic phase was dried over sodium sulfate and analyzed by GLC (see above). Stilbene (47%), benzyl *tert*-butyl ether (15%), and a small amount of unreacted benzyl chloride were detected.

Reaction of Benzyl Chloride with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol. A 100-mL, three-necked, round-bottomed flask equipped with an addition funnel and magnetic stirring bar was charged with potassium *tert*-butoxide (1.12 g, 0.01 mol), 18-crown-6 (0.66 g, 0.0025 mol), and dry *tert*-butyl alcohol (15 mL). The solution was brought to 30 °C under a nitrogen atmosphere and a solution of benzyl chloride (1.26 g, 0.01 mol) in *tert*-butyl alcohol (5 mL) was added dropwise over a period of 5 min. After the addition was complete, stirring was continued for 1 h, and the mixture was quenched with water (5 mL), diluted with an equal volume of ether, and filtered. The filtrate was dried over sodium sulfate and analyzed by GLC (see above). Benzyl *tert*-butyl ether (58%), unreacted benzyl chloride (28%), and stilbene (<1%) were detected.

Preparation of *tert*-Butyl Anthranilate. A 250-mL, three-necked, round-bottomed flask equipped with addition funnel, nitrogen inlet, and magnetic stirring bar was charged with isatoic anhydride (8.2 g, 0.05 mol) and dry DMF (50 mL). After the anhydride had dissolved, a solution of potassium *tert*-butoxide (6.1 g, 0.051 mol) and 18-crown-6 (0.66 g, 0.0025 mol) in DMF (25 mL) was added dropwise. The dark solution was stirred for 24 h, quenched with distilled water (100 mL), and extracted with ether (4 × 100 mL). The combined organic material was washed with distilled water (100 mL) and brine (100 mL), dried over sodium sulfate, and evaporated in vacuo. After distillation (bp 82–90 °C/0.35–0.45 mm), *tert*-butyl anthranilate was obtained (3.12 g, 33%) as a pale-yellow oil: NMR (CCl_4, ppm) 1.56 (s, 9 H) $-C(CH_3)_3$, 6.6 (m, 2 H) $-NH_2$, 6.45 (m, 2 H), 7.0 (m, 1 H), 7.6 (m, 1 H) aromatic protons; IR (neat) $\nu_{C=O}$ 1690 cm^{-1}. High-resolution mass spectrum, calcd: 193.1099; found: 193.1102. (NB: An identical reaction in the absence of 18-crown-6 produced *tert*-butyl anthranilate in only 8% yield.)

Attempted Synthesis of Phenyl *tert*-Butyl Ether. A 200-mL pressure reaction bottle equipped with a magnetic stirring bar was charged with potassium *tert*-butoxide (2.80 g, 0.025 mol), 18-crown-6 (0.33 g, 0.00125 mol), bromobenzene (3.9 g, 0.025 mol), and THF (50 mL). The contents were then sealed under a nitrogen atmosphere, immersed in a 100 °C oil bath, and stirred for 2 h. The reaction mixture was then allowed to cool to room temperature, quenched with water (2 mL), diluted with ether (10 mL), and filtered. The filtrate was reduced in vacuo to give a brown oil from which all volatile material was distilled (bp 45–50 °C, ~15 mm). The distillate was analyzed by NMR and found to consist largely of unreacted bromobenzene with a small amount of phenyl *tert*-butyl ether (NMR).

Metallation of Diphenylmethane with *tert*-Butoxide. A 100-mL, round-bottomed flask equipped with a magnetic stirring bar and nitrogen inlet was charged with THF (40 mL), potassium *tert*-butoxide (2.80 g, 0.025 mol), and 18-crown-6 (0.33 g, 0.00125 mol), and then immersed in a bath maintained at 30 °C. Diphenylmethane (4.1 g, 0.025 mol) in THF (10 mL) was added dropwise, and the solution was stirred for 4 h, quenched with D_2O (2 mL), and diluted with ether (20 mL). The precipitated salts were removed by filtration and the filtrate was reduced in vacuo to a pale-yellow oil. After distillation (bp 132 °C, ~10 mm), diphenylmethane, 18% deuterated (NMR integration), was obtained as a colorless oil (3.6 g, 87% recovery): NMR (CCl_4, ppm) 3.83 (s, 1.64 H) $(Ar)_2C\mathbf{H}d$, 7.08 (s, 5 H) aromatic protons.

Metallation of Chlorodiphenylmethane with *tert*-Butoxide. Chlorodiphenylmethane was added in a stream and metallated as above for 30 s, and D_2O (2 mL) was then added. After distillation (bp 164–165 °C, ~20 mm) chlorodiphenylmethane [75% deuterated at C-1 (NMR integration)] was obtained as a colorless oil (41% recovery): NMR (CCl_4, ppm) 5.95 (ψs, 0.25 H) $(Ar)_2ClC\mathbf{H}(D)$, 7.18 (m, 10 H) aromatic protons.

Attempted Metallation of Toluene with Crown-Activated *tert*-Butoxide. A 100-mL, round-bottomed flask equipped with a magnetic stirring bar and nitrogen inlet was charged with THF (40 mL), potassium *tert*-butoxide (2.80 g, 0.025 mol), and 18-crown-6 (0.33 g, 0.00125 mol), and then immersed in a bath maintained at 30 °C. Toluene (2.30 g, 0.025 mol) in THF (10 mL) was added dropwise, and the solution was stirred for 24 h, quenched with D_2O (2 mL), and diluted with ether (20 mL). The precipitated salts were removed by filtration and the filtrate was reduced in vacuo (bath temp ca. 35 °C) to a pale-yellow oil. Analysis of the crude recovered toluene (NMR integration) indicated no deuteration.

***tert*-Butoxide-Catalyzed Reaction of Diphenylmethane with Benzaldehyde.** A 100-mL, round-bottomed flask equipped with a magnetic stirring bar and nitrogen inlet and maintained at 30 °C was charged with THF (40 mL), potassium *tert*-butoxide (2.80 g, 0.025 mol), and 18-crown-6 (0.33 g, 0.00125 mol). Diphenylmethane (4.10 g, 0.025 mol) in THF (5 mL) was then added in a stream. After allowing 30 min for metallation, benzaldehyde (2.65 g, 0.025 mol) in THF (5 mL) was added dropwise, and the resulting mixture was stirred overnight (22 h). The α,α-diphenylacetophenone which precipitated upon addition of water (100 mL) was collected by filtration and the residue crystallized from hexane. The ketone was obtained (2.0 g, 29% based on diphenylmethane) as a white solid: mp 134–135 °C; lit.[29] mp 136 °C, mmp 132 °C; NMR ($CDCl_3$, ppm δ) 6.03 (ψs, 1 H) $ArCOC\mathbf{H}Ar_2$, 7.28 (ψs, 11 H), 7.45 (ψd, 2 H), 8.0 (m, 2 H) aromatic protons; IR (mull) $\nu_{C=O}$ 1685 cm^{-1}.

The aqueous phase was extracted with ether which was then dried (Na_2SO_4) and reduced in vacuo to a pale-yellow oil. Column chromatography (80–325 mesh alumina) using 2% ether–hexane as solvent gave diphenylmethane (1.73 g, 42%). Elution with 1:1 (v/v) ether/hexane gave benzyl alcohol (0.97 g, 35%). (NB: No *tert*-butyl benzoate was detected in this experiment.)

Reaction of Benzaldehyde with Crown-Activated Potassium *tert*-Butoxide. A 100-mL, round-bottomed flask equipped with a magnetic stirring bar and nitrogen inlet and maintained at 30 °C was charged with THF (40 mL), potassium *tert*-butoxide (2.80 g, 0.025 mol), and 18-crown-6 (0.330 g, 0.00125 mol). A solution of benzaldehyde (2.65 g, 0.025 mol) in THF (10 mL) was added dropwise, and the resulting highly colored mixture was stirred for 2 h, quenched with water (2 mL), diluted with ether (20 mL), and filtered. The filtrate was dried over sodium sulfate and reduced in vacuo to a pale-yellow oil. Purification by column chromatography as above gave benzyl alcohol (1.87 g, 65%) and *tert*-butyl benzoate (1.28 g, 29%): NMR (CCl_4, ppm) 1.58 (s, 9 H) $-C(CH_3)_3$, 7.4 (m, 3H), 7.95 (m, 2 H) aromatic protons; IR (neat): $\nu_{C=O}$ 1710 cm^{-1}.

Acylation of Lithium Diphenylmethide by *tert*-Butyl Benzoate. A 100-mL, three-necked, round-bottomed flask equipped with a magnetic stirring bar, serum cap, addition funnel and nitrogen inlet was charged with THF (40 mL) and diphenylmethane (1.68 g, 0.01 mol). The solution was cooled to 0 °C and 2.4 M *n*-butyllithium (4.16 mL, 0.01 mol) was syringed in, and the solution was stirred for 30 min. *tert*-Butyl benzoate (1.78 g, 0.01 mol) in THF (10 mL) was then added dropwise, and the solution was stirred for 1 h, quenched, and diluted with water (5 and 100 mL, respectively). The α,α-diphenylacetophenone which precipitated was collected by filtration and the residue crystallized from hexane. The ketone was obtained (0.41 g, 15%) as a white solid, mp 134–135 °C.

Reaction of Diphenylmethane with Benzaldehyde-*d*. A 100-mL, three-necked, round-bottomed flask equipped with a magnetic stirring bar, nitrogen inlet, and addition funnel was charged with THF (15 mL), potassium *tert*-butoxide (1.12 g, 0.01 mol) and 18-crown-6 (0.132 g, 0.0005 mol). Diphenylmethane (1.68 g, 0.01 mol) was syringed in. After allowing 30 min for metallation, benzaldehyde-*d* (1.07 g, 0.01 mol) in THF (5 mL) was added dropwise, and the resulting mixture stirred overnight (22 h) and then quenched with water (5 mL). The mixture was diluted with water (50 mL) and extracted with ether (3 × 25 mL), and the combined organic phases were dried over sodium sulfate. Column chromatography (80–325 mesh alumina, hexane solvent) gave diphenylmethane (1.01 g, 60%). Elution with 5% ether–hexane gave α,α-diphenylacetophenone (0.86 g, 33% based on diphenylmethane), mp 130–132 °C, mmp 133–134 °C, containing no deuterium (NMR). Further elution with 1:1 (v/v) ether–hexane gave benzyl-α,α-d_2 alcohol (0.36 g, 33% based on diphenylmethane) identified by NMR.

Attempted *tert*-Butoxide-Catalyzed Acylation of Diphenylmethane with *tert*-Butyl Benzoate. A 100-mL, three-necked, round-bottomed flask equipped with a magnetic stirring bar, addition funnel, and nitrogen inlet was charged with potassium *tert*-butoxide (1.12 g, 0.01 mol), 18-crown-6 (0.132 g, 0.0005 mol), and dry THF (40 mL). The solution was brought to 30 °C under a nitrogen atmosphere and a solution of diphenylmethane (1.64 g, 0.01 mol) in THF (5 mL) was added dropwise and allowed to react for 10 min. A solution of *tert*-butyl benzoate (1.78 g, 0.01 mol) in THF (5 mL) was then added dropwise over a period of 5 min. After the addition was complete, stirring was continued for 24 h, and the mixture was quenched and diluted with water (5 and 10 mL, respectively). Any α,α-diphenylacetophenone present failed to precipitate after 24 h. The resulting oil was extracted with dichloromethane (2 × 25 mL), dried over sodium sulfate, filtered, and reduced in vacuo to a brown oil. No α,α-diphenylacetophenone could be detected by NMR (benzhydryl proton at δ 6.03), although unreacted diphenylmethane and *tert*-butyl benzoate were readily detected. The same result was obtained when the reaction was conducted for 48 h.

Preparation of 2-Carboxybiphenyl. A 100-mL, round-bottomed flask equipped with an addition funnel, magnetic stirring bar, and gas inlet was charged with potassium *tert*-butoxide (2.24 g, 0.02 mol), 18-crown-6 (0.066 g, 0.00025 mol), and THF (40 mL). The solution was placed under an atmosphere of oxygen and a solution of fluorene (0.83 g, 0.005 mol) in THF (10 mL) was added over a period of 5 min. After the addition was complete, stirring was continued under oxygen for 1 h. Then, the reaction was quenched with water (10 mL) and the aqueous phase separated. The organic phase was washed with water (2 × 25 mL) and the combined aqueous phase acidified with concentrated HCl. The acid was then extracted with ether (3 × 20 mL), dried over sodium sulfate, and evaporated in vacuo. There was obtained 2-carboxybiphenyl (0.99 g, 100%) as a yellow solid: mp 109–110 °C; lit.[30] mp 112–112.5 °C; NMR ($CDCl_3$, ppm) 7.23 (ψs, 8 H), 7.72 (m, 1 H) aromatic protons, 11.5 (m, 1 H) -COOH; IR (mull): $\nu_{C=O}$ 1685 cm^{-1}. (NB: An identical reaction in the absence of 18-crown-6 produced 2-carboxybiphenyl in 92% yield.)

Potassium *tert*-Butoxide/Crown Catalyzed Condensation of Benzaldehyde-*d* with Acetonitrile. A 100-mL, three-necked, round-bottomed flask equipped with a magnetic stirring bar, addition funnel, and nitrogen inlet was charged with potassium *tert*-butoxide (1.12 g, 0.01 mol), 18-crown-6 (0.132 g, 0.0005 mol), and THF (15 mL). The solution was stirred at ambient temperature (ca. 27 °C) and acetonitrile (0.41 g, 0.01 mol) was added in one portion. After allowing 10 min for metallation, a solution of benzaldehyde-*d* (1.07 g, 0.01 mol) in THF (5 mL) was added dropwise over a period of 5 min. After the addition was complete, stirring was continued for 3 h, and the mixture was quenched with water (5 mL), diluted with ether (25 mL), and washed with water (3 × 25 mL). The combined aqueous phase was backwashed with ether (25 mL) and the organic phase dried over sodium sulfate. Column chromatography (80–325 mesh alumina) using 1:9 (v/v) ether–hexane as solvent gave cinnamonitrile-β-*d* (0.25 g, 22% *E*/*Z* ~7.1) as a pale-yellow oil: NMR (CCl_4, ppm) *E* isomer, 5.71 (ψt, 1 H) $ArCD{=}C\mathbf{H}CN$, 7.3 (ψs, 5 H) aromatic protons; *Z* isomer, 5.31 (m, 1 H) $ArCD{=}C\mathbf{H}CN$, 7.3 (ψs, 5 H) aromatic protons; IR (neat): $\nu_{C\equiv N}$ 2220 cm^{-1}, elution with 3:7 (v/v) ether–hexane followed by preparative GLC (gas chromatography gave benzyl-α,α-d_2 alcohol identified by NMR).

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Registry No.—Isatoic anhydride, 118-48-9; *tert*-butyl anthranilate, 64113-91-3; diphenylmethane, 101-81-5; deuterated diphenylmethane, 20389-18-8; α,α-diphenylacetophenone, 1733-63-7; benzaldehyde, 100-52-7; *tert*-butyl benzoate, 774-65-2; benzaldehyde-*d*, 3592-47-0; benzyl-α,α-d_2 alcohol, 21175-64-4; 2-carboxybiphenyl, 947-84-2; fluorene, 86-73-7; acetonitrile, 75-05-8; (*E*)-cinnamonitrile-β-*d*, 64113-90-2; (*Z*)-cinnamonitrile-β-*d*, 64113-89-9; deuterated chlorodiphenylmethane, 778-23-40.

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Base-Catalyzed β-Elimination Reactions. 7. Elimination from 4-(Para-substituted-phenoxy)-2-oxobutanoic Acids

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Elimination of para-substituted phenoxides from 4-(para-substituted-phenoxy)-2-oxobutanoic acids in aqueous solution is catalyzed by imidazole, morpholine, diethanolamine, and *N,N*-dimethylethanolamine. The dependence of the pseudo-first-order rate constant on amine concentration is nonlinear, with an initial line of large slope at low amine concentration which changes to a line of smaller slope at high amine concentration. The existence of a carbanion intermediate in the reaction is supported by the result that α-hydrogen exchange at high amine concentration is faster than elimination. These findings, coupled with the results of analysis of Hammett ρ' values for various steps of the elimination reaction catalyzed by morpholine, lead us to conclude that elimination proceeds via spontaneous decomposition of enolates and general-base-catalyzed decomposition of enols.

A considerable body of evidence indicates that many base-catalyzed β-elimination reactions proceed via carbanion intermediates.[1–6] For example, under the experimental conditions employed, β-elimination of para-substituted phenoxides from 4-(para-substituted-phenoxy)-2-butanones is adequately described by the minimal mechanism of Scheme I.[5]

Many biochemical reactions such as aldolization,[7–9] decarboxylation,[10] carboxylation,[8] and elimination[11–13] are thought to occur via proton transfer to form a carbanion intermediate from α-keto acid substrates, and our own interest in carbanion chemistry is related in part to our desire to understand enzyme catalysis. In order to better understand the chemistry of elimination reactions, specifically in compounds capable of stabilizing enols, and to develop potential suicide substrates[14–16] for those enzymes which utilize α-keto acid

Scheme I

$$\mathrm{ArOCH_2CH_2COCH_3} \underset{k_2,\ \mathrm{BH}}{\overset{k_1,\ \mathrm{B}}{\rightleftharpoons}} \mathrm{ArOCH_2CHCOCH_3}^-$$

$$\xrightarrow{k_3} \mathrm{CH_2{=}CHCOCH_3} + \mathrm{ArO}^-$$