Stoichiometry and mechanism of protonation of alkali metal salts of benzophenone radical anions by weak proton donors and its relevance to the base-catalyzed decomposition of benzopinacol

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The stoichiometry of the protonation of lithium and potassium salts of benzophenone radical anions and of the lithium salt of the fluorenone radical anion by methanol has been measured and found to be $[(Ar_2C{=}O)^{\cdot -}]/[MeOH] = 2 : 1$. This result, which was obtained by the method of magnetic titration, implies that paramagnetism decays by the reaction between a ketyl anion and a ketyl radical (*i.e.*, a protonated ketyl anion). The reactivities of alkali metal salts of fluorenone radical anions in relation to methanol exhibit a pronounced dependence on the nature of the counterion. No kinetic deuterium isotope effect has been found for the protonation of the lithium salt of the benzophenone radical anion in tetrahydrofuran (THF) by *tert*-pentyl alcohol. The lithium salt of the benzophenone radical anion in *N,N,N',N'*-tetramethylethylenediamine (TMEDA) behaves markedly differently. Namely, its protonation by methanol exhibits 1 : 1 stoichiometry and it reacts considerably more slowly with *sec*-butyl alkohol, k(THF)/k(TMEDA) = 2.5. Benzopinacol undergoes decomposition by an alkoxide base to diphenyl ketyl, which decays into an equimolar mixture of benzophenone and benzhydrol. The reaction follows second-order kinetics and the specific rate constants exhibit an inverse relationship with respect to the initial concentration of the alkoxide. With a very strong base benzopinacol decomposes into two diphenyl ketyl anions. On the basis of this information as well as on studies of products, relevant mechanisms are proposed for the protonation of ketyl anions and for the decomposition of aromatic pinacols in basic media.

Key words: benzophenone, radical anion; benzopinacol; protonation, stoichiometry, mechanism.

In our continuing effort to understand the structure and reactivity of radical anions at high concentrations, we have undertaken the elucidation of the mechanism of the protonation of alkali metal salts of aromatic ketone radical anions. By employing NMR spectroscopy, we have been successful in measuring kinetics[1] and equilibria[2] involving stable radical anions either as reactants or products at concentrations up to 1 mol L^{-1}. The basis of the method is the linearity between the formal concentration of the radical anion and the corresponding paramagnetic solvent NMR shift.

We have chosen to study the protonation of the benzophenone radical anion because this reaction is of both practical and theoretical interest. Protonation by a strong acid of a solution of an alkali metal salt of an aromatic ketone radical anion in THF affords aromatic pinacols.[3] At the same time, aromatic pinacols characteristically exhibit pronounced thermal instability in the presence of bases even at −78 °C and undergo fragmentation through the intermediacy of the blue ketyl.[4] It appears, therefore, interesting to examine the reasons for the *formation and fission of the same* C—C *bond in* $Ar_2C(OH)—C(OH)Ar_2$ *in acidic and basic media, respectively* (Eq. (1)).

$$2\ Ph_2C{=}O^{\cdot -} \underset{-2H^+\ \text{(strong base)}}{\overset{2H^+\ \text{(strong acid)}}{\rightleftharpoons}} Ph_2C(OH)—C(OH)Ph_2 \quad (1)$$

According to Schenk *et al.*,[5] in a <0.01 *M* solution of alcoholate, fragmentation of benzopinacol leads to benzophenone and benzhydrol, apparently without formation of the ketyl radical, whereas, in concentrations of an alcoholate base >0.2 mol L^{-1} fragmentation leads to the benzophenone radical anion, supposedly by homolytic cleavage of the benzopinacol dianion. Benzopinacol in neutral media in the presence or in the absence of oxygen undergoes a markedly more difficult thermal decomposition, than in basic media, to form a mixture of benzophenone and benzhydrol with an activation energy of 36.9 kcal mol^{-1} in both cases.[5] The decomposition of benzopinacol in boiling methanol in the presence of paraquat, PQ^{2+}, was followed by the ap-

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pearance of $PQ^{\cdot+}$, whose rate of formation was assumed to be equal to the rate of the thermal decomposition of benzopinacol itself.[6]

All previous studies have involved protonation of *in situ* generated aromatic ketone radical anions by photolysis,[7] electrochemical reduction[8] or by pulse radiolysis.[9] In this work we report equilibrium and kinetic measurements of: a) the reaction between alkali metal salts of radical anions of benzophenone and fluorenone and simple alcohols; b) the base catalyzed decomposition of benzopinacol by bases. We also report the distribution of products in the above mentioned reactions.

Results and Discussion

Benzophenone radical anion

Stoichiometry of protonation. We measured the stoichiometry of the reaction between lithium and potassium salts of the benzophenone radical anion and methanol ($pK_a^w = 16$)[10] in THF by the magnetic titration[1b,c,2] method. The addition of increments of methanol to a given amount of the radical anion in THF leads to its gradual destruction, and this is accompanied by the corresponding decay of the paramagnetic solvent NMR shift. Figure 1 shows the change of the paramagnetic solvent NMR shift referred to the low field signal of THF when methanol is added to solutions of lithium and potassium salts of the benzophenone radical anion with respect to the ratio of the concentrations of methanol and the radical anion, $[MeOH]/[Ph_2C{=}O^{\cdot-}]$. It can be seen that a well defined break occurs at a ratio of 0.5. This means that it takes one molecule of methanol to destroy two molecules of the ketyl anion. Namely, the protonation exhibits a stoichiometry $[MeOH]/[Ph_2C{=}O^{\cdot-}] = 1 : 2$. An interesting solvent effect was encountered when THF was replaced by TMEDA. In this solvent, the reaction between the lithium salt of the benzophenone radical anion and methanol exhibited a stoichiometry of 1 : 1 (Fig. 2).

Reaction products. We investigated the reaction products of the protonation of the lithium salt of the benzophenone radical anion by methanol under various conditions. Protonation with a stoichiometric amount of methanol, *i.e.*, 0.5 equiv., and hydrolytic workup after 24 h gave an equimolar mixture of benzophenone and benzhydrol. Protonation with 2.5 equiv. of methanol and hydrolysis after 0.25 h gave, besides benzophenone and benzhydrol, a 19 % yield of benzopinacol. When the latter experiment was repeated but the mixture was hydrolyzed 24 h after the reagents were mixed, the product was a 50—50 % mixture of benzophenone and benzhydrol. In contrast to the above results, protonation of the lithium salt of the benzophenone radical anion in TMEDA with 1.0 equiv. of methanol followed by a hydrolytic workup after 24 h gave benzopinacol in 27 % yield while the rest of the product was an equimolar mixture of benzophenone and benzhydrol. Acidification of a solution of the lithium salt of the benzophenone radical anion in THF with 6*N* HCl, afforded benzopinacol in 81 % yield.

Kinetic measurements. Since the reaction involves a proton, *i.e.*, a particle of small mass, we investigated the possibility of the involvement of tunnelling.[11] We measured the kinetics of the protonation of the lithium salt of

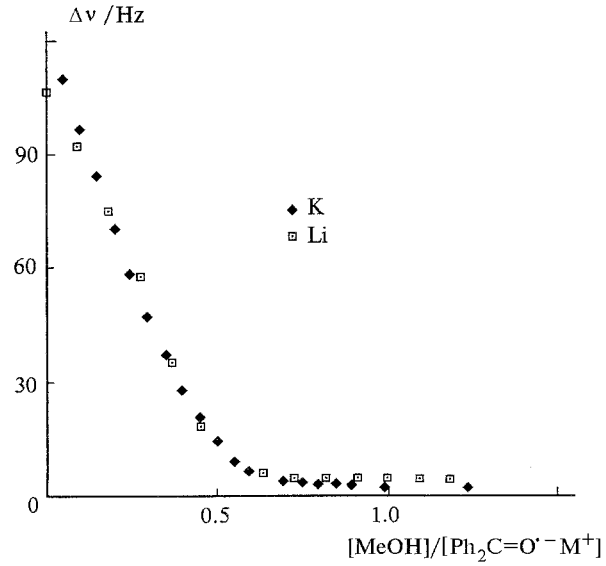


Fig. 1. Magnetic titration of lithium and potassium salts of the benzophenone radical anion in THF against methanol, *i.e.*, a plot of solvent NMR shift (the low field signal of THF) *vs.* the ratio of concentrations of reactants.

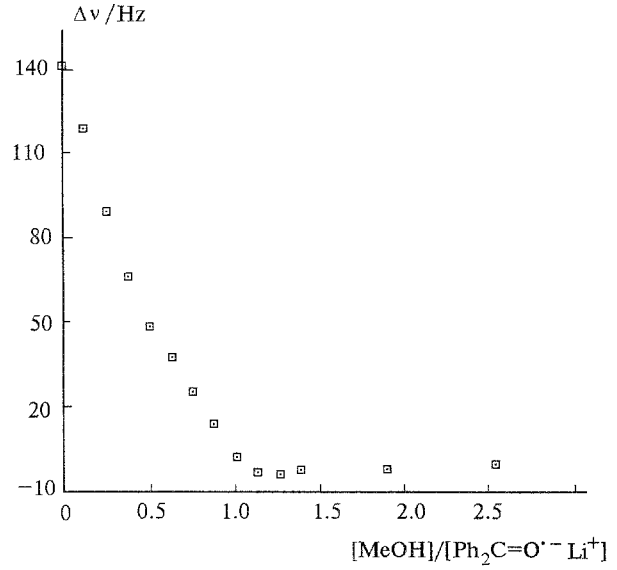


Fig. 2. Magnetic titration of lithium salt of the benzophenone radical anion in TMEDA against methanol. The deviation from linearity of the shift *vs.* ratio of reactants line is due to the coalescence of the two proton signals of TMEDA (see Experimental).

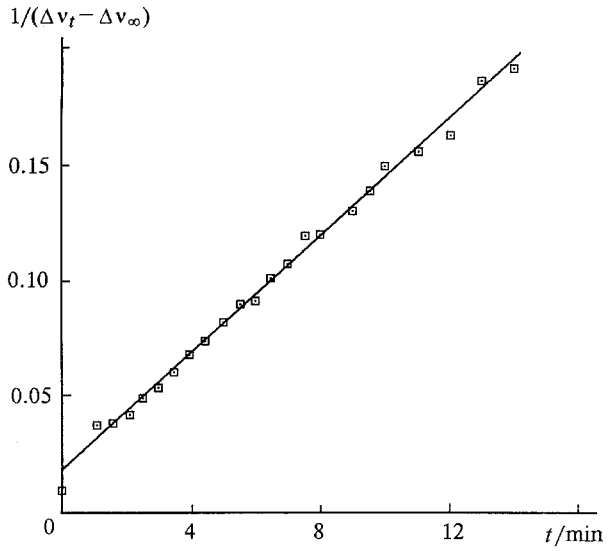


Fig. 3. Second-order decay of paramagnetic solvent NMR shift in a mixture of lithium salt of the benzophenone radical anion and *tert*-pentyl alcohol at *ca.* 34 °C ([benzophenone]$_0$ = 0.94 mol L^{-1}, [*t*-$C_5H_{11}OH$]$_0$ = 1.267 mol L^{-1}).

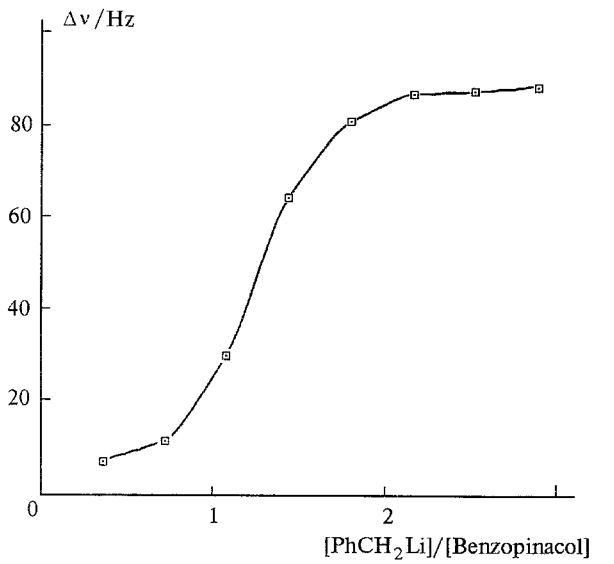


Fig. 4. Paramagnetic solvent NMR shift increase during addition of benzyllithium to a solution of benzopinacol in THF (plotted in the form of a magnetic titration).

the benzophenone radical anion with 2-methylbutan-2-ol and its oxygen-deuterated analog. The latter alcohol (pK_a^w = 19)[10] is less acidic than methanol by three orders of magnitude, giving rates of protonation that can be followed very conveniently by the present NMR method. The reaction obeys simple second-order kinetics,[12] indicating that paramagnetism decays by the reaction of two species of equal concentrations (Fig. 3). No deuterium kinetic isotope effect was found, k_H = 1.7(±0.1) · 10^{-6} L mol^{-1} s^{-1}, *vs.* k_D = 1.6(±0.1) · 10^{-6} L mol^{-1} s^{-1} at 34 °C. Thus the proton is not involved in the rate determining step. A comparative kinetic study of the reaction between the lithium salt of the benzophenone radical anion and *sec*-butanol in THF and TMEDA was carried out. The corresponding specific rate constants at 34 °C are: *k*(THF) = 1.9(±0.1) · 10^{-6} L mol^{-1} s^{-1} and *k*(TMEDA) = 7.6(±1.0) · 10^{-7} L mol^{-1} s^{-1}. It can be seen that paramagnetism in TMEDA decays markedly more slowly, than in THF, *i.e.*, *k*(THF)/*k*(TMEDA) = 2.5.

In order to develop our mechanistic scheme, which we feel can explain the experimental evidence for the protonation of the benzophenone radical anion, it is necessary to consider the closely related base catalyzed decomposition of benzopinacol.

Base catalyzed decomposition of benzopinacol. Reaction products. The addition of lithium *tert*-butoxide to benzopinacol in THF at a molar ratio of [Bu^{t}OLi]/[benzopinacol] = 12.36 : 1.0 at −70 °C afforded the lithium salt of the benzophenone radical anion in a quantitative yield, judging from the paramagnetism of the solution. The ketyl, however, decayed at room temperature in about 48 h to an equimolar mixture of benzophenone and benzhydrol. By employing the much stronger base, benzyllithium, in THF we carried out a magnetic titration of benzopinacol against $PhCH_2Li$ (Fig. 4). In this case the stoichiometry of the reaction was also determined and found to be [$PhCH_2Li$]/[benzopinacol] equal to 2 : 1. On the basis of the maximum paramagnetic solvent NMR shift, *i.e.*, at the equivalence point and beyond, an 84 % yield of the lithium salt of the benzophenone radical anion can be estimated. The descrepancy of 16 % from the theoretical yield can be reasonably attributed to the decay of the ketyl initially formed at the early stages of the titration. Indeed, in these stages of titration the [benzopinacol]/[ketyl] ratio was large, a condition which favors a rapid reaction between ketyl and benzopinacol (see the relevant discussion on the kinetics of the alkoxide-induced decomposition of benzopinacol). Thus, the above-determined stoichiometry, as well as the yield of the lithium salt of the benzophenone radical anion, indicate that one molar equivalent of benzopinacol reacts with two molar equivalents of benzyllithium to afford two molar equivalents of the lithium salt of the benzophenone radical anion. It is of relevance to note that the decomposition of aromatic pinacols by methyllithium has been employed as a method for preparing the lithium salts of aromatic ketone radical anions.[13]

Kinetics. As has already been mentioned, the decomposition of benzopinacol by an alkoxide base takes place through an intermediate benzophenone radical anion.[5] This then makes this reaction very relevant to the protonation of the benzophenone radical anion by alcohols. Indeed, the decomposition of benzopinacol by, *e.g.*, lithium *tert*-butoxide in THF leads to the formation of the benzophenone radical anion, which decays accord-

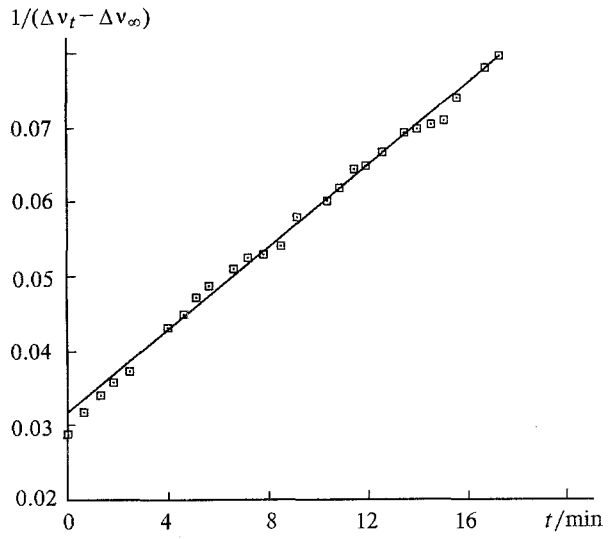


Fig. 5. Second-order decay of the paramagnetic solvent NMR shift in a mixture of benzopinacol and lithium *tert*-butoxide ([benzopinacol]$_0$ = 0.167 mol L^{-1}, [Bu^{t}OLi]$_0$ = 0.80 mol L^{-1}).

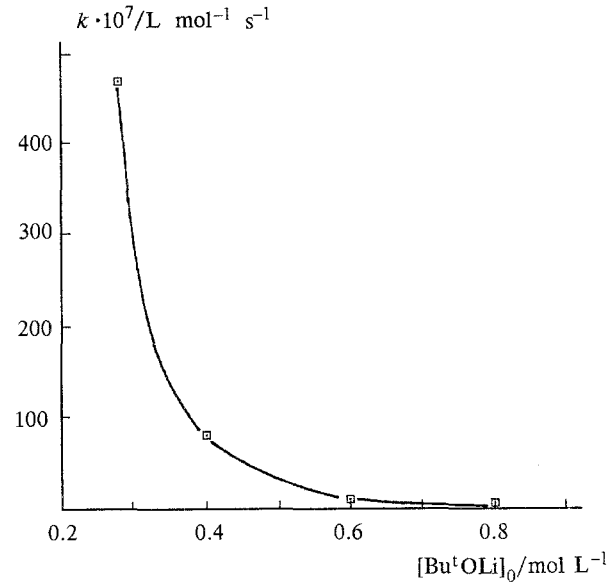


Fig. 6. Specific rate constants of the reaction between benzopinacol and lithium *tert*-butoxide plotted against initial concentration of lithium *tert*-butoxide at [benzopinacol]$_0$ = 0.167 mol L^{-1}.

ing to second-order kinetics, just as protonation of the benzophenone radical anion by an alcohol does (Fig. 5). Changing the initial concentration of base while keeping the benzopinacol concentration constant revealed an inverse relationship between [base]$_0$ and the specific rate constant (Fig. 6). Changing the initial concentration of benzopinacol while keeping the [base]$_0$ constant indicated that the specific rate constants increase very rapidly as the initial concentration of benzopinacol increases (Fig. 7).

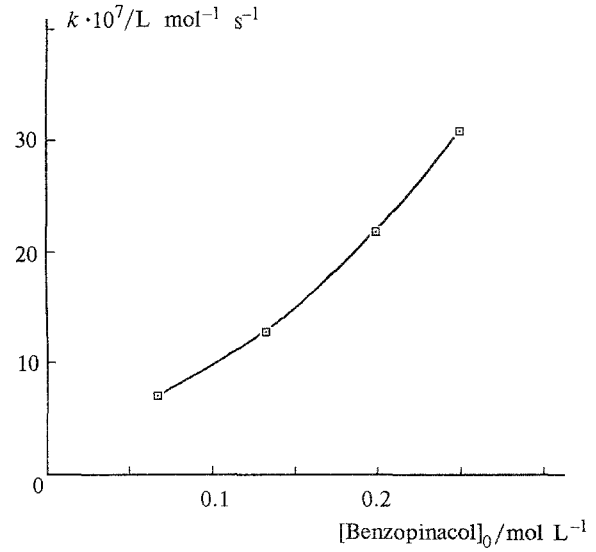


Fig. 7. Specific rate constants of the reaction between benzopinacol and lithium *tert*-butoxide plotted against the initial concentration of benzopinacol at [Bu^{t}OLi] = 0.58 mol L^{-1}.

These results indicate that the stability of the paramagnetic species depends on the relative concentration of benzopinacol and the base, rather than on [base]$_0$ alone. Thus, the reported[5] decomposition of benzopinacol by a <0.01 *M* solution of alkoxide without formation of blue ketyl was most probably due to the use of a high [benzopinacol]/[alkoxide] ratio that led to the destruction of the benzophenone radical anion at the moment of its production.

We found that by mixing Bu^{t}OLi and benzopinacol in THF at a molar ratio of [alkoxide]/[benzopinacol] = 12.36 : 1.0 at *ca.* −70 °C, the lithium salt of the benzophenone radical anion was produced almost *instantly* and *quantitatively*, judging from the paramagnetic solvent NMR shift. It was also observed that in the latter solution the paramagnetism decayed very slowly; it took more than 48 h for the complete disappearance of the blue color of the solution. These observations can be readily understood on the basis of the observed inverse relationship between the specific rate constant and the initial concentration of the alkoxide base.

The lithium salt of the benzophenone radical anion that forms can decompose benzopinacol in THF, but in this case the paramagnetic intermediate decays according to first-order kinetics (Fig. 8). The latter indicates that different mechanisms are operable in the decomposition of benzopinacol by $Ph_2C{=}O^{\cdot -}Li^+$ and Bu^{t}OLi. Obviously, the reason for the different behavior of the benzopinacol—$Ph_2C{=}O^{\cdot -}Li^+$ system is the presence of an unpaired spin in the paramagnetic base.

Reaction mechanisms. We feel that there is an analogy between the base catalyzed decomposition of benzopinacol and its decomposition in boiling methanol and in the presence of PQ^{2+}.[6] The observed reduction of paraquat by benzopinacol may have occurred by an

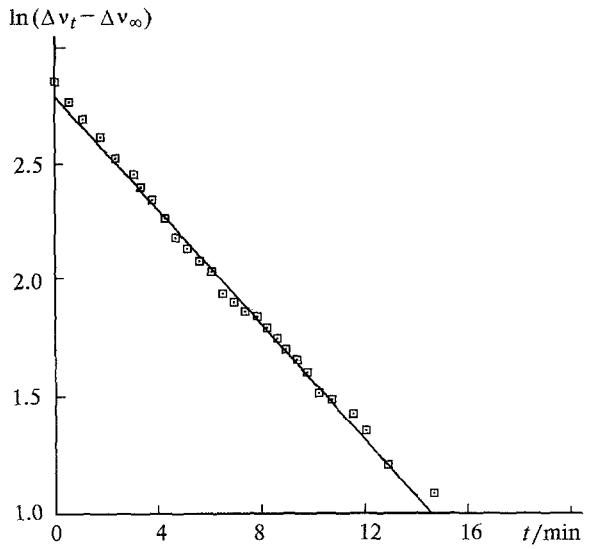


Fig. 8. First-order decay of the paramagnetic solvent NMR shift in the THF solution of the lithium salt of the benzophenone radical anion and benzopinacol ([benzophenone]$_0$ = 0.47 mol L^{-1}, [benzopinacol]$_0$ = 0.25 mol L^{-1}).

alternative pathway, namely, by oxidation of benzopinacol by PQ^{2+}. Abstraction of an electron from the lone pair of an OH group of pinacol would lead to the formation of the O-centred radical **1**, which by undergoing β-scission[14] can give benzophenone and a diphenyl ketyl radical. The latter is transformed to benzophenone by reducing a second molecule of PQ^{2+} (Scheme 1). In support of this hypothesis, we showed that 9-fluorenol in *neutral* methanol reduces PQ^{2+} to $PQ^{\cdot+}$. Moreover, refluxing benzopinacol in a 50 : 50 (v/v) methanol and THF mixture for 6 h did not cause any noticeable fragmentation of benzopinacol.

Scheme 1

$$Ph_2C(OH)C(OH)Ph_2 + PQ^{2+} \xrightarrow{\text{slow}} Ph_2C(O^{\cdot+}H)C(OH)Ph_2 + PQ^{\cdot+}$$

$$Ph_2C(O^{\cdot+}H)C(OH)Ph_2 \xrightarrow{\text{rel. fast}} \underset{\mathbf{1}}{Ph_2C(O^{\cdot})C(OH)Ph_2} + H^+$$

$$Ph_2C(O^{\cdot})C(OH)Ph_2 \xrightarrow{\text{fast}} Ph_2C{=}O + Ph_2C^{\cdot}{-}OH$$

$$Ph_2C^{\cdot}{-}OH + PQ^{2+} \xrightarrow{\text{very fast}} Ph_2C{=}O + PQ^{\cdot+} + H^+$$

It is important to recall that diaryl ketyl alkali metals exist in solution in the form of paramagnetic clusters,[2c] and, therefore, protonation of a ketyl anion in the cluster should cause the resulting $Ph_2C^{\cdot}{-}OH$ to be in close proximity to a ketyl anion, $Ph_2C{=}O^{\cdot-}$. Perhaps it is for this reason that the decomposition of benzopinacol by a base becomes relevant to the protonation of an aromatic ketone radical anion by a weak proton donor.

Scheme 2

$$But O^- + Ph_2C(OH)C(OH)Ph_2 \overset{\text{fast}}{\rightleftharpoons} Ph_2C(O^-)C(OH)Ph_2 + ButOH \quad (2,a)$$

$$Ph_2C(O^-)C(OH)Ph_2 \xrightarrow{\text{rel. fast}} [Ph_2C(O^{\cdot})C(OH)Ph_2 + e^-_{solv}] \quad (2,b)$$

$$[Ph_2C(O^{\cdot})C(OH)Ph_2 + e^-_{solv}] \xrightarrow{\text{fast}} [Ph_2C{=}O^{\cdot-}, Ph_2C^{\cdot}{-}OH] \quad (2,c)$$

$$[Ph_2C{=}O^{\cdot-}, Ph_2C^{\cdot}{-}OH] \xrightarrow{\text{slow}} [Ph_2C{=}O^{\cdot-}, Ph_2CHO^{\cdot}] \quad (2,d)$$

$$[Ph_2C{=}O^{\cdot-}, Ph_2CHO^{\cdot}] \xrightarrow[\text{fast}]{\text{very}} Ph_2C{=}O + Ph_2CHO^- \quad (2,e)$$

On the basis of the above considerations and the results of the equilibrium, kinetic, and product analyses, we propose the mechanism in Scheme 2 for the decomposition of benzopinacol by bases and the protonation of ketyl anions by weak proton donors (see Scheme 3).

Thus, the mono-anion of benzopinacol is produced in a rapid and reversible step, followed by a thermal charge-transfer-to-solvent (CTTS) process which leads to the formation of the respective oxygen centered radical. The latter undergoes β-scission[14] within a cage that includes the fragments, *i.e.*, the ejected solvated electron recaptured by benzophenone, and the diphenyl ketyl radical. The latter species isomerizes[3b,15] to the benzhydryloxyl radical which, by accepting the electron from the radical anion of benzophenone, is converted to a benzhydrolate anion. It is felt that it would be very difficult to explain the fragmentation of benzpinacol by a thermal reaction at a low temperature, such as −70 °C, without invoking CTTS and β-scission processes.

An analogous mechanism has been proposed for the transformation of lithium 9-fluorenolate to the lithium salt of the fluorenone radical anion in THF.[3b] In the presence of a very strong base step (2,d) in Scheme 2 is modified as in (2,d′), in order to account for the results of the magnetic titration of benzopinacol against benzyllithium, *i.e.*, the formation of two benzophenone radical anions from one molecule of benzopinacol.

$$[Ph_2C{=}O^{\cdot-}, Ph_2C^{\cdot}{-}OH] \xrightarrow{PhCH_2Li} 2\ Ph_2C{=}O^{\cdot-} \quad (2,d')$$

The Weissman mechanism[16] for the protonation of a radical anion (see below) requires a stoichiometry of 1 : 1.

$$2\ Ph_2C{=}O^{\cdot-}M^+ + 2\ MeOH \longrightarrow 2\ Ph_2C^{\cdot}{-}OH \longrightarrow Ph_2C(OH){-}C(OH)Ph_2$$

Obviously, the 2 : 1 stoichiometry of lithium and potassium benzophenone radical anion salts does not agree with that predicted on the basis of a Weissman mechanism.

It is felt that the mechanistic scheme that best fits the experimental observation is the one in Scheme 3.

Scheme 3

$$(Ph_2C{=}O^{\cdot -})_2 + ROH \overset{fast}{\rightleftharpoons} \rightleftharpoons [Ph_2C{=}O^{\cdot -}, Ph_2C^{\cdot}{-}OH] + RO^- \quad (3,a)$$

$$[Ph_2C{=}O^{\cdot -}, Ph_2C^{\cdot}{-}OH] \xrightarrow{slow} [Ph_2C{=}O^{\cdot -}, Ph_2CHO^{\cdot}] \quad (3,b)$$

$$[Ph_2C{=}O^{\cdot -}, Ph_2CHO^{\cdot}] \xrightarrow{very\ fast} Ph_2C{=}O + Ph_2CHO^- \quad (3,c)$$

In the proposed mechanism the oligomer[2c] of the diphenyl ketyl anion is shown as a dimer for simplicity. It could also be added that the alkoxide produced in the first step of the reaction could be associated with a benzophenone radical anion cluster.[2c] The mechanism depicted in Scheme 3 can explain the formation of benzopinacol when protonation is carried out by excess alcohol or by a strong acid. Namely, if all of the anions in the ketyl cluster are protonated almost simultaneously, then the ketyl radicals produced will combine rapidly to form benzopinacol (Eq. (3,a′)).

$$(Ph_2C{=}O^{\cdot -})_2 + 2\,H^+ \longrightarrow [2\,Ph_2C^{\cdot}{-}OH] \longrightarrow Ph_2C(OH)C(OH)Ph_2 \quad (3,a')$$

In an analogous manner the thermal decomposition of benzopinacol at its melting point, which leads to the formation of an equimolar mixture of benzophenone and benzhydrol[5] can be visualized as follows (Scheme 4).

Scheme 4

$$Ph_2C(OH)C(OH)Ph_2 \xrightarrow{\Delta} [2\,Ph_2C^{\cdot}{-}OH] \quad (4,a)$$

$$[2\,Ph_2C^{\cdot}{-}OH] \longrightarrow [Ph_2C^{\cdot}{-}OH, Ph_2CHO^{\cdot}] \quad (4,b)$$

$$[Ph_2C^{\cdot}{-}OH, Ph_2CHO^{\cdot}] \longrightarrow Ph_2C{=}O + Ph_2CHOH \quad (4,c)$$

In step (4,c) of the above scheme an H atom transfer process[17] is implied.

In order to explain the results of the protonation of the lithium salt of the benzophenone radical anion in TMEDA it becomes necessary to consider the following: a) the relatively high acidity of $Ph_2C^{\cdot}{-}OH$, pK_a = 9.2;[18] b) the very low acidity of benzopinacol; c) the ionizing power of the basic solvent; d) the ability of TMEDA to form strong chelates with the lithium cation in general,[19] and with $Ph_2C{=}O^{\cdot -}Li^+$, in particular.[2a] We assume that the lithium salt of the benzophenone radical anion and lithium methoxide are in the form of chelates. It also appears reasonable to believe that lithium methoxide in TMEDA is less basic than in THF. In addition, we presume that the protonated ketyl, $Ph_2C^{\cdot}{-}OH$, ionizes to some extent in the basic TMEDA solvent and, most importantly, chelation of the lithium counterion by TMEDA could possibly break down the ketyl clusters into monomeric ketyls. These ideas are incorporated into Scheme 5, which, it is felt, satisfactorily explains the experimental evidence.

Scheme 5

$$Ph_2C{=}O^{\cdot -}[Li(TMEDA)]^+ + MeOH \rightleftharpoons \rightleftharpoons Ph_2C^{\cdot}{-}OH + MeO^-[Li(TMEDA)]^+ \quad (5,a)$$

$$Ph_2C^{\cdot}{-}OH + TMEDA \longrightarrow Ph_2C{=}O^{\cdot -}[H(TMEDA)]^+ \quad (5,b)$$

$$Ph_2C{=}O^{\cdot -}[Li(TMEDA)]^+ + Ph_2C{=}O^{\cdot -}[H(TMEDA)]^+ \xrightarrow{very\ slow} Ph_2C{=}O + Ph_2CHOLi \quad (5,c)$$

$$2\,Ph_2C^{\cdot}{-}OH \longrightarrow Ph_2C(OH)C(OH)Ph_2 \quad (5,d)$$

Thus, ionization of the protonated ketyl, (see Scheme 5, step 5,b), no longer permits it to combine with the ketyl anion, $Ph_2C{=}O^{\cdot -}Li^+$, to form diamagnetic products. Therefore, a second proton is now required in order to destroy the magnetism. This explains the observed 1 : 1 stoichiometry. Consequently, in the case of TMEDA the disappearance of paramagnetism takes place by dimerization of the protonated ketyl (see Scheme 5, step 5,d). The lower basicity of MeOLi in TMEDA is apparently responsible for the low rate of ionization of benzopinacol to its mono-anion (a prerequisite for decomposition) and this could explain the survival of benzopinacol in this system. Scheme 5 is further supported by the results of the comparative kinetic study of the reaction between diphenyl ketyl lithium and *sec*-butanol in THF and TMEDA (see above). The markedly slower rate of protonation of the lithium salt of the benzophenone radical anion in TMEDA can be accounted for by step (5,b) in Scheme 5, in which re-ionization of the protonated ketyl becomes an opposing reaction.

Fluorenone radical anion

Although the mechanistic scheme for the protonation of the benzophenone radical anion should be more or

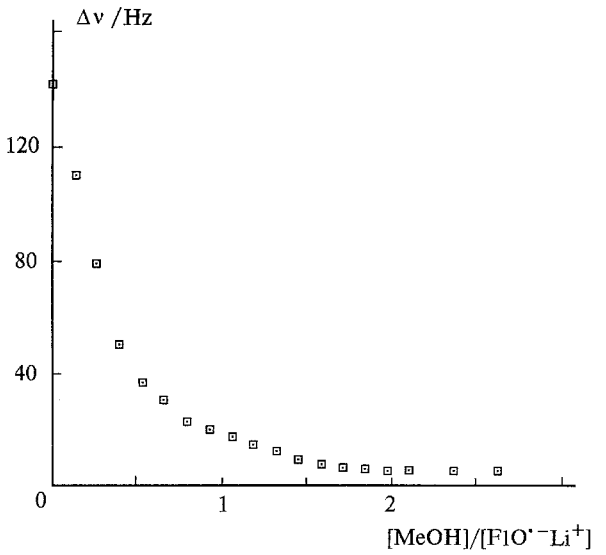


Fig. 9. Magnetic titration of the lithium salt of the fluorenone radical anion in THF against methanol.

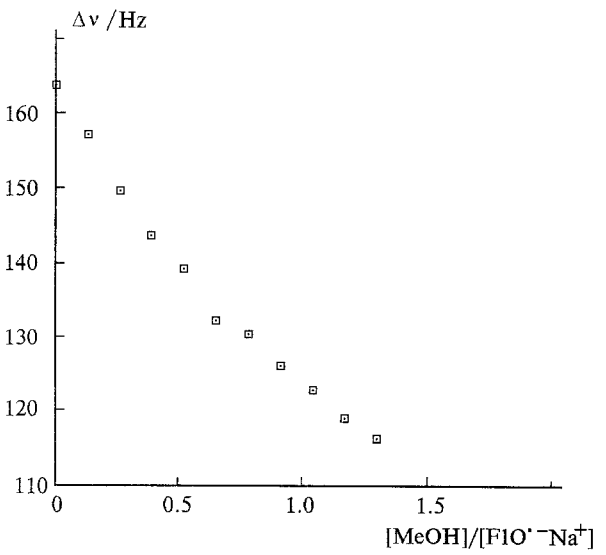


Fig. 10. The sodium salt of the fluorenone radical anion titrated against methanol in THF.

less applicable to protonation of any aromatic ketone radical anion, some differences could arise from factors such as the electron affinity of the neutral aromatic ketone and the involvement of opposing reactions. This situation seems to occur in the protonation of the fluorenone radical anion.

Stoichiometry of protonation. The lithium salt of the fluorenone radical anion in THF appears to react with methanol with a stoichiometry of [FlO·⁻Li⁺]/[MeOH] = 2 : 1 (Fig. 9). We notice, however, that in the latter case the break at the equivalence point is less abrupt and some residual paramagnetism still remains beyond that point. Sodium and potassium fluorenone radical anion salts appear to be resistant to protonation by methanol. Indeed, Fig. 10 shows that in an attempted titration of the sodium salt of the fluorenone radical anion, the addition of methanol at a ratio of [MeOH]/[FlO·⁻Na⁺] up to 1.3 was unable to bring about complete destruction of the ketyl. Only when the latter ratio became 8.75 : 1.0 did we observe complete discharge of paramagnetism. In the case of the potassium salt of the fluorenone radical anion, the addition of methanol at a ratio [MeOH]/[FlO·⁻K⁺] up to 11.22 : 1.0 was insufficient to cause complete destruction of the ketyl. These results are summarized in Tables 1 and 2. Table 1 shows the per cent of ketyl destruction at various ratios of [MeOH]/[FlO·⁻K⁺] and at various time intervals, and Table 2 shows the extent of the reaction at the "theoretical" stoichiometric ratio [MeOH]/[Ar_2C=O·⁻M⁺] = 0.5 : 1.0, where Ar_2C=O is benzophenone or fluorenone and M = Li, Na, or K.

Let us now examine the reasons for which sodium and potassium salts of fluorenone radical anions appear to react sluggishly with methanol. It can be seen from the data in Table 1 that equilibrium is established rather rapidly. For example, the addition of 3.74 equiv. of methanol to 1.00 equiv. of the potassium salt of the fluorenone radical anion caused 42 % destruction of the ketyl at equilibrium (24 h), compared to 35 % after 2 min. Thus 83 % of the total reaction took place within two minutes. If one considers the pK_a values of the acids FlO·⁻H⁺ and MeOH, 6.3[20] and 16[10] respectively, one is led to the conclusion that protonation of FlO·⁻M⁺ by methanol should be improbable, simply because the acid FlO·⁻H⁺ is approximately 10 orders of magnitude more acidic than methanol. Thus, in the reaction FlO·⁻M⁺ + MeOH $\rightleftharpoons$ FlO·⁻H⁺ + MeOM the equilibrium should lie on the left of the equation. Of course, the latter argument should be valid irrespective of the M in FlO·⁻M⁺. The experimental results, however (see Table 2), indicate that protonation of the fluorenone radical anion exhibits a very marked dependence on the counterion as far as the extent destruction of ketyl by methanol is concerned, and that when M = Li protonation goes almost to completion with just 0.5 equiv. of methanol. Therefore, the apparent reluctance exhibited by the sodium and potassium salts of the fluorenone radical anions to be protonated by methanol must be due to some other factors. The simplest explanation that one can provide is the regeneration of the fluorenone radical anion by the transfer of an electron

Table 1. Extent (η) of the reaction of the potassium salt of the fluorenone radical anion with methanol at various methanol/substrate ratios and time intervals

[MeOH]/[FlO·⁻K⁺]	η (%)		
	2 min	24 h	48 h
3.74 : 1.0	35	42	42
7.48 : 1.0	70	77	77
11.22 : 1.0	80	88	88

Table 2. Extent (η) of the reaction of the alkali metal salts of aromatic ketone radical anions with methanol at a [MeOH]/[$Ar_2C{=}O^{\cdot -}M^+$] ratio equal to 0.5

Substrate	η (%)
$Ph_2C{=}O^{\cdot -}Li^+$	100
$Ph_2C{=}O^{\cdot -}K^+$	100
$FlO^{\cdot -}Li^+$	95.5[a]
$FlO^{\cdot -}Na^+$	14.8[b]
$FlO^{\cdot -}K^+$	5.0[b]

[a] The estimate was obtained from the residual paramagnetism and the molar paramagnetic solvent NMR shift of $FlO^{\cdot -}Li^+$, *i.e.*, 150±2 Hz mol^{-1} at 80 MHz.

[b] The estimate was obtained from the paramagnetic solvent NMR shift which, in turn, was estimated by interpolation. The appropriate data, *e.g.*, Fig. 3, were fitted to a second degree polynominal with $r^2 \geq 0.99$. The molar paramagnetic shifts of $FlO^{\cdot -}Na^+$ and $FlO^{\cdot -}K^+$ are 215±2 and 240±4 Hz mol^{-1}, respectively, at 80 MHz and *ca.* 35 °C and with respect to the low field signal of the THF solvent.

from the alkoxide to fluorenone,[3b] *i.e.*, one of the reaction products (see below). The marked increase in the residual paramagnetism at the theoretical equivalence point, *i.e.*, 0.5 : 1.0 (see Table 2) varies in the order Li < Na < K. It appears then that the methoxide anion functions as a single electron donor in cooperation with the counterion. Given that the ionization potentials of alkali metals increase in the opposite order [*IP*(M) : Li, 5.392; Na, 5.139; K, 4.341 eV[21]] we are tempted to propose that *electron transfer takes place through the mediation of the cation* (Eq. (6)).

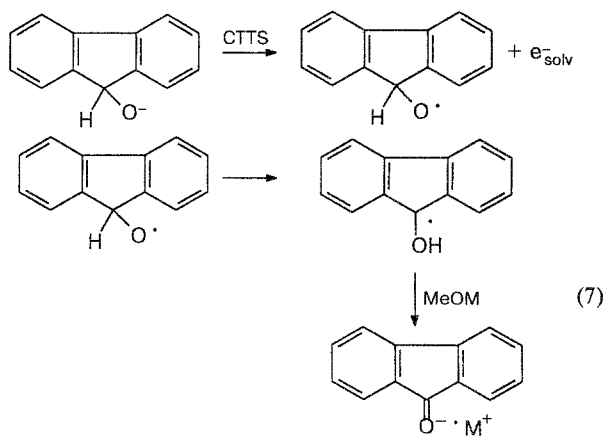
$$\begin{aligned} FlO + MeO^-M^+L_n \longrightarrow\ & [MeO^-M^+L_{n-1}(FlO) \longleftrightarrow \\ \longleftrightarrow\ & MeO^{\cdot}M^{\cdot}L_{n-1}(FlO)] \longrightarrow \\ \longrightarrow\ & (FlO^{\cdot -})M^+L_{n-1} + [MeO^{\cdot}] \end{aligned} \qquad (6)$$

L = MeOLi and/or THF

This inner sphere[22] type mechanism is analogous to the one proposed for the transfer of electrons from the radical anions[1e] to the substrate.

An alternative sourse of the fluorenone radical anion in mixtures of sodium and potassium salts of the fluorenone radical anion and methanol is the 9-fluorenolate anion, which is formed in the initial stages of the reaction and can be transformed into the respective ketyl according to Eq. (7).[3b]

The marked difference in behavior between potassium benzophenone and fluorenone radical anions toward methanol (see Table 2) is readily attributable to the considerable difference between the electron affinities of the respective neutral ketones. Even MeOK is not capable of reducing benzophenone to the corresponding ketyl to an extent measurable by NMR, hence the most complete decay of the paramagnetic solvent NMR shift in mixtures of diphenyl ketyl potassium and methanol takes place at the equivalence point.



(7)

Experimental

Magnetic titrations and kinetic measurements were carried out with a Varian FT-80A NMR spectrometer. The same instrument was used for recording NMR spectra. Gas chromatographic analyses were performed with a Pye Unicam GCV chromatograph. Tetrahydrofuran was doubly distilled from $LiAlH_4$ under argon shortly before use. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was distilled from barium oxide under argon. Methanol was distilled from magnesium methoxide under argon. The alcohols (*sec*-butanol and *tert*-pentanol) used in the kinetic study were 99 % pure (or better) and distilled under argon shortly before use. *tert*-$C_5H_{11}OD$ was prepared by adding D_2O to the corresponding sodium alkoxide. NMR analysis indicated a purity of at least 95 %. Standard solutions were handled with microsyringes. Alkali metal salts of aromatic ketone radical anions were prepared[2a] in 20 mmol quantities and in concentrations of *ca.* 1 mol L^{-1} under an atmosphere of argon by stirring strictly equivalent amounts of the aromatic ketone and the alkali metal. Any excess of metal causes the formation of the diamagnetic dianion, and for this reason should be avoided. The concentration of the radical anion was determined by reacting an aliquot of the ketyl anion solution with ethylene bromide under argon and titrating the liberated Br^-. This method is not applicable to solutions of ketyl anions in TMEDA. For the benzophenone radical anion in TMEDA *with the lithium counterion only* the concentration of the paramagnetic species can be determined by magnetic titration against a 0.50 *M* solution of $HgCl_2$ in THF, according to the reaction: 2 $Ph_2C{=}O^{\cdot -}Li^+ + HgCl_2 \rightarrow$ 2 $Ph_2C{=}O + Hg^0 + 2$ LiCl. Thus a molar paramagnetic solvent NMR shift was measured in TMEDA and at 34 °C for $Ph_2C{=}O^{\cdot -}Li^+$ and found to be 2.34 ppm mol^{-1}. It should be mentioned that the two NMR signals of TMEDA protons coalesce at high radical anion concentrations. Separate resonances begin to appear at concentrations lower than 0.3 mol L^{-1}.

Magnetic titrations. A 500 μL aliquot of a 1.08 *M* solution of the lithium salt of the benzophenone radical anion in THF was introduced *via* a microsyringe into a 5 mm NMR tube[2a] filled with argon. Increments, 2 μL each, of neat methanol were added with a 10 μL syringe, and the corresponding solvent shifts referred to the low field THF proton signal were recorded. The results are given graphically in Fig. 1.

Kinetic runs. A 1000 μL aliquot of a 0.94 *M* solution of the lithium salt of the benzophenone radical anion in THF was

introduced into the NMR tube as described in the previous paragraph. The tube was placed in the NMR probe which had a temperature of 34 °C, and after a few minutes, 50 μL of *sec*-butanol freshly distilled and saturated with argon, was added to the ketyl solution. Thorough mixing was effected by shaking the NMR tube for a few seconds and placing it again in the probe. The progress of the reaction was followed by observing the solvent shift (low field signal of THF) as a function of time. Points were collected every *ca.* 0.5 min. The data are plotted as $1/[\Delta\nu_t - \Delta\nu_\infty]$ *vs.* time (in minutes), *e.g.*, Fig. 3. Similarly, a 500 μL aliquot of 0.50 *M* benzopinacol in THF was introduced into the NMR tube (see above) followed by the addition of 1000 μL of 1.20 *M* lithium *tert*-butoxide in THF. Data were collected and treated as described in the previous paragraph and they are presented in Fig. 5. The slopes of the $1/[\Delta\nu_t - \Delta\nu_\infty]$ *vs.* time plots were divided by 60 times the molar paramagnetic solvent NMR shift of diphenyl ketyl lithium, *i.e.*, $\Delta\nu_m^\alpha$ = 112 Hz mol^{-1} and $\Delta\nu_m^\beta$ = 103 Hz mol^{-1}, at 80 MHz, in order to convert them from Hz^{-1} min^{-1} to L mol^{-1} s^{-1} units (Table 3).

Reduction of paraquat by 9-fluorenol. Paraquat and 9-fluorenol, 200 mg each, were dissolved in 20 mL of saturated with argon methanol and the reaction mixture was heated to reflux under argon. The blue $PQ^{\cdot+}$ formed as soon as the solvent started refluxing. In a blank experiment, PQ^{2+} failed to react with neutral methanol under argon.

Product analysis. 1. 0.405 mL (*ca.* 10 mmol) of methanol was added to a solution of lithium benzophenone radical anion in THF prepared from 3.64 g (20 mmol) of benzophenone, 0.140 g lithium chips, and 18 mL of THF. This caused an almost instant discharge of the blue color of the solution. The mixture was stirred under argon at room temperature for 24 h. Hydrolysis and extraction with methylene chloride (3×50 mL) gave 3.6 g of product. The NMR spectrum of this product indicated the presence of both benzophenone and benzhydrol. This mixture was completely soluble in absolute ethanol. A 0.5 g portion of the product was treated with 1.0 mL of pyridine and 1.24 mL of acetic anhydride and the resulting mixture was heated with stirring at *ca.* 100 °C for 0.25 h. This process converted benzhydrol to the corresponding acetate ester. The entire acetylation mixture was subjected to gas chromatographic analysis (column: 10 % Apiezon L on Chromosorb GAWBMCS, 6′×18′, argon as carrier gas, v = 42.9 mL min^{-1}, T = 170 °C). Found: [benzophenone]/[benzhydryl acetate] = 1 : 1.

2. Methanol (2.0 mL, *ca.* 50 mmol) was added to 20 mmol of the lithium salt of the benzophenone radical anion in THF at the temperature of a dry ice—acetone bath. Cooling was discontinued and the reaction mixture was stirred for 0.25 h before hydrolysis. Extraction with methylene chloride (3×50 mL) afforded 3.6 g of a solid product. The latter was stirred with 25 mL of warm absolute ethanol for 0.5 h in order to extract benzophenone and benzhydrol. The insoluble benzopinacol was isolated by filtration, dried *in vacuo*, and weighed. Yield 0.7 g (19 %), m.p. 171—173 °C. After two recrystallizations from toluene—hexane it melted at 182—185 °C (Ref. 23: m.p. 182—183 °C).

Table 3. The specific rate constants and the respective initial concentrations for the base catalyzed decomposition of benzopinacol

$[\text{Benzopinacol}]_0$ /mol L^{-1}	$[\text{Bu}^t\text{OLi}]_0$ /mol L^{-1}	$k(\pm 0.1)$ /L mol^{-1} s^{-1}
0.167	0.28	$4.7 \cdot 10^{-5}$
0.167	0.40	$8.2 \cdot 10^{-6}$
0.167	0.60	$1.1 \cdot 10^{-6}$
0.167	0.80	$8.0 \cdot 10^{-7}$
0.067	0.58	$7.1 \cdot 10^{-7}$
0.133	0.58	$1.3 \cdot 10^{-6}$
0.200	0.58	$2.2 \cdot 10^{-6}$
0.250	0.58	$3.1 \cdot 10^{-6}$

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