or a mixture of labels, neither of which is consistent with the results obtained here.

It is therefore clear that in the formation of imides by the thermal dehydration of amic acids, the amide function serves as the nucleophilic component in the ring closure reaction and that the nature of the steric inhibition to imide formation previously observed does not reflect a partitioning of a species such as **7** between the formation of anhydride and the isomide **4** based on the relief of steric interactions in such an intermediate. Furthermore, on the basis of the results obtained here, we cannot distinguish between imide formation by paths A or B or a combination of these. We can, however, state that if path A is operative in this reaction, the rearrangement of the isomide **3** must occur with specific nucleophilic assistance proceeding by attack of water at the carbonyl carbon of the isoimide. This observation is consistent with the previously proposed mechanism for this reaction.[8,9] It has also been suggested that isoimides rearrange to imides under "substantially anhydrous" conditions;[10] however, a consideration of this possibility does not alter the conclusions drawn in this work.

Experimental Section

Melting points were determined on a Melt-Temp apparatus and are uncorrected. Mass spectral analyses were performed on a Varian MAT 731 field desorption mass spectrometer.

Materials. All glassware was dried in vacuo at 140 °C and assembled under a dry nitrogen atmosphere. THF was freshly distilled from lithium aluminum hydride. *N*-Butylbenzamide and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were distilled prior to use and stored over activated molecular sieves. ^{18}O-labeled carbon dioxide (Stohler 99.9% ^{18}O by mass spectral analysis) was used as purchased immediately after its mass spectral analysis.

Preparation of Labeled *N*-*n*-Butylphthalamic Acid (2). To a solution of 0.861 g (4.86 mmol) of *N*-butylbenzamide and 1.232 g (10.40 mmol) of TMEDA in 25 mL of dry TFH at 0 °C under a nitrogen atmosphere was added 6.5 mL (10.30 mmol) of a 1.6 molar solution of *n*-butyllithium in hexane. The *n*-butyllithium was added at a rate sufficient to maintain the reaction temperature between 0 and 10 °C. The reaction mixture was then allowed to stir at 0 °C for 4 h. The three-neck flask containing this reaction mixture was connected by means of a vacuum transfer line to a 250-mL round-bottom flask coontaining 0.500 g (11.3 mmol) of carbon dioxide (99.9% ^{18}O), which was cooled in liquid nitrogen to solidify the gas. The reaction mixture was then cooled to −78 °C in a dry ice–acetone bath and subsequently transferred to the flask containing the solid carbon dioxide. The reaction mixture was held at −78 °C overnight and then allowed to warm slowly to ambient temperature the next morning. Small aliquots (2 mL) were added to 25 mL of isooctane to precipitate the dilithium salt of the phthalamic acid. The precipitated salts were acidified in aqueous HCl to pH 3 at 5 °C and water was removed under vacuum at 0–5 °C. The solid residue was then extracted with cold acetone and filtered. Removal of the acetone solvent under vacuum at 0–10 °C provided the phthalamic acid **2**: mp 103 °C (lit.[2] mp 103 °C); field-desorption mass spectrum, *m/e* 226 (M + H). Thermolysis of the phthalamic acid on the emitter at 200 °C gave exclusively *N*-*n*-butylphthalimide, *m/e* 205 (M^+). Thermolysis of the phthalamic acid on the solids probe and analysis by electron-impact mass spectrometry gave the same result.

Acknowledgment. We express our gratitude to Professor Samuel Danishefsky, Dr. D. M. White, and Dr. H. M. Relles for many helpful discussions.

Registry No. 2, 78371-58-1; *N*-butylbenzamide, 2782-40-3.

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A Simple, Inexpensive Synthesis of Dipotassium Cyclooctatetraenide, $K_2C_8H_8$

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The cyclooctatetraenyl dianion, $C_8H_8^{2-}$, has proven to be important in many areas of chemistry.[2–4] It is of interest as a planar aromatic dianion, as a precursor to C_8 ring systems, and as a ligand in organometallic complexes of the transition, lanthanide, and actinide metals. More extensive use of the cyclooctatetraenyl dianion and the compounds derived from it is often not practical, however, due to the unavailability and/or expense of its precursor, 1,3,5,7-cyclooctatetraene.

As part of our general investigation of the nonaqueous reductive chemistry of the lanthanide metals,[5–9] we discovered that the relatively inexpensive *cis,cis*-1,5-cyclooctadiene (1,5-C_8H_{12}) can be converted to the cyclooctatetraenyl dianion at room temperature by the product of the reduction of $PrCl_3$ with 3 equiv of potassium.[6] To determine the importance of potassium vis-â-vis praseodymium in this reaction, we examined several reactions involving only potassium and 1,5-cyclooctadiene. Although no reaction occurred at room temperature, at higher temperatures the conversion of 1,5-C_8H_{12} to $K_2C_8H_8$ was observed. This reaction has proven to be an excellent synthetic route to $K_2C_8H_8$. We report here the details of this convenient preparation of $K_2C_8H_8$ and its conversion to 1,3,5,7-cyclooctatetraene (1,3,5,7-C_8H_8),[2] 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene ($C_6H_5PC_8H_8$)[10–12] and uranocene ($U(C_8H_8)_2$).[13] Subsequent to our report,[6] an alternate synthesis of $C_8H_8^{2-}$ from 1,5-C_8H_{12} was briefly described using *n*-C_4H_9Li or C_6H_5Na in the presence of tetramethylethylenediamine (TMEDA).[14] Although these reactions are similar, our method is simpler since potassium rather than phenylsodium is required, and since the base free salt, $K_2C_8H_8$, is isolated rather than the TMEDA adduct, $Na_2C_8H_8{\cdot}2TMEDA$.

Results and Discussion

The primary reaction which occurs when potassium and 1,5-cyclooctadiene are heated to 100–150 °C in the absence of solvent is the isomerization of the diene to *cis*-bicyclo-

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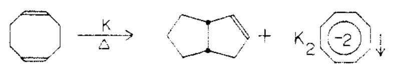
[3.3.0]oct-2-ene (eq 1). This isomerization has previously



(1)

been described in connection with studies of the following reactions: phenylpotassium plus 1,5-cyclooctadiene at 175 °C in an autoclave,[15] potassium hydride plus 1,5-cyclooctadiene at 190 °C in an autoclave,[16,17] and potassium plus 1,3-cyclooctadiene at 199 °C.[15] In our hands, during the course of the rearrangement shown in eq 1, a substantial amount of tan-to-brown solid material is formed, which can be extracted with tetrahydrofuran (THF) to form an intensely colored solution. The powder which ultimately can be isolated from this solution is identified by elemental analysis and infrared[18] and NMR spectroscopy[19] as $K_2C_8H_8$.[19] In the previous rearrangement studies,[15-17] only the liquid reaction products were analyzed; hence no evidence for $K_2C_8H_8$ was presented. However, in the two autoclave reactions, a hydrogenated C_8 product, cyclooctene, was observed, suggesting that some hydrogen-deficient species must have also formed.

The purity and yield of the $K_2C_8H_8$ obtained in reaction 1 is variable depending on several factors. Reaction temperature is one important factor. When the reaction between potassium and 1,5-cyclooctadiene is carried out at reflux temperature, the $K_2C_8H_8$ is frequently contaminated with an impurity that has an infrared absorption at 1530–1560 cm^{-1}. The THF extracts of the reaction solids are frequently green or purple rather than the brown color found for lower temperature reactions. Removal of solvent from this solution forms solids which can vary in color from gray-green to purple rather than the yellow to gray-green powders isolated from lower temperature reactions. Elemental analysis suggests that the amount of contaminant responsible for these color effects is small, and even in these cases, the reaction product is primarily $K_2C_8H_8$.[20,21] However, since the yields of the reactions conducted at reflux are variable and since the purity of this material often reduces yields of subsequent reactions (e.g., oxidation to 1,3,5,7-C_8H_8), lower reaction temperatures are preferred. Although an extensive study of the effects of temperature on this reaction has not been done, we have consistently obtained the best results when the reaction is run at 106–110 °C.

The purity and yield of the solid product of reaction 1 is also affected by the manner in which the crude product is isolated. Since potassium and 1,5-cyclooctadiene rapidly react at room temperature in the presence of THF to form KC_8H_{11},[22] this solvent and its vapors must be rigorously excluded from the reaction when unreacted potassium and 1,5-cyclooctadiene are present. To avoid this problem, the crude product must be thoroughly washed with pentane before the product is extracted with THF. Another problem which deserves special comment is that finely divided solid byproducts are often formed in reaction 1 and are difficult to remove with a single filtration of the THF extract. Multiple filtrations are necessary to obtained the highest purity.

With the 106–110 °C temperature range and the proper isolation procedures, $K_2C_8H_8$ can routinely be obtained via reaction 1 in high purity based on IR, NMR, and elemental analysis. Yields are typically 7–10% based on 1,5-cyclooctadiene and 60–75% based on potassium. Although the yield of $K_2C_8H_8$ is low based on 1,5-cyclooctadiene, this is not critical since this precursor is readily available and inexpensive. Consequently, this reaction constitutes a much cheaper synthesis of $K_2C_8H_8$ than the previously used reaction of potassium with 1,3,5,7-cyclooctatetraene.[23]

To demonstrate the utility of $K_2C_8H_8$, obtained in this way from potassium and 1,5-cyclooctadiene, we have used this material as a precursor to uranocene[13] and 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene.[10-12] Uranocene can be obtained in 53% yield without extensive Soxhlet extraction using this precursor. In comparison, 60–80% yields are obtained when the $K_2C_8H_8$ is generated from 1,3,5,7-cyclooctatetraene and when the uranocene product is isolated by extensive Soxhlet extraction. Our yield of $C_6H_5PC_8H_8$ (23%) is also lower than the yield reported in the literature (33%),[12] but the reaction has been consistently successful in our hands.

We have also investigated the importance of the $K_2C_8H_8$ obtained from 1,5-cyclooctadiene as an alternative source of 1,3,5,7-cyclooctatetraene. Several oxidants including dry oxygen, $CdCl_2$,[24] SCl_2,[10] CeO_2, Fe^{3+}, and azobenzene[25] have been examined in several solvents including THF, diethyl ether and hexamethylphosphoramide. To date the best method for oxidizing $K_2C_8H_8$ to 1,3,5,7-cyclooctatetraene is the azobenzene oxidation which produces 1,3,5,7-C_8H_8 in 66–69% yield. Dry air oxidation of a THF solution at 0–5 °C forms the tetraene in 52% yield. With $CdCl_2$ as the oxidant in THF at 0 °C, a 42% yield is observed.[26]

Conclusion

A convenient, low-cost synthesis of $K_2C_8H_8$ from 1,5-cyclooctadiene and potassium has been developed which should provide the opportunity for more extensive use of the cyclooctatetraenyl dianion in both organic and organometallic chemistry.

Experimental Section

Except where noted, all reactions are performed under dry, oxygen-free nitrogen by using standard Schlenk and glovebox techniques.[27] Glovebox experiments are performed in the recirculated nitrogen atmosphere of a Vacuum Atmospheres HE-43 Dri-Lab (hereafter called the Dri-Box). 1,5-C_8H_{12} (Aldrich) is dried by passing it through a 1 × 8 in. column of neutral alumina, using alumina previously heated to 50 °C. The diene is then vacuum degassed on a Schlenk line and stored in the Dri-Box under nitrogen. Potassium is used as chunks cut *with caution* from rods which had previously been scraped free of the oxide coating and rinsed with pentane to remove residual oil. UCl_4 is prepared from UO_2 (Alfa) and hexachloropropene (Aldrich) according to the literature procedure.[28] Dichlorophenylphosphine (Aldrich) is purifed by distillation. $CdCl_2$ (Baker) is dried by heating at 110 °C on a high vacuum line for 20 h. Pentane is washed with sulfuric acid, dried over $MgSO_4$, heated at reflux over finely divided

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$LiAlH_4$, vacuum transferred, and stored under nitrogen in the Dri-Box. THF is distilled from potassium benzophenone ketyl under nitrogen and stored in the Dri-Box.

Infrared, visible, and NMR spectra are obtained on a Perkin-Elmer 283, a Cary 14, and a Bruker HX 270 spectrometer, respectively. Infrared samples are stable for at least 0.5 h in the air as Nujol mulls betweeen NaCl plates held in a Presslok holder (Barnes Engineering). The Cary 14 spectrometer is calibrated with K_2CrO_4 immediately before use. Gas chromatography is done on a Hewlett Packard 5830A instrument equipped with a 6 ft × $^1/_4$ in. stainless-steel column containing 20% tricresyl phosphate on 60/80 mesh DMCS-AW Chromosorb W at 105 °C. 1,3-C_8H_{12} is used as the internal standard.

Elemental analyses are performed by Bernhardt Analytical Laboratories, Postfach 1249, 5250 Engelskirchen, Germany.

Caution: Dry $K_2C_8H_8$ will explode in the air. Residual $K_2C_8H_8$ on filter frits, glassware, etc. should be kept wet with solvent until it can be decomposed with ethyl acetate upon removal from the Dri-Box.

$K_2C_8H_8$. A three-neck, 250-mL, round-bottom flask equipped with a glass-encased magnetic stir bar, condenser (as a precautionary measure), a nitrogen inlet, and a thermocouple well is charged with 1,5-C_8H_{12} (108 g, 1 mol) and K (4.7 g, 0.120 mol) in the Dri-Box. The apparatus is then removed to the Schlenk line where the reaction mixture is stirred under nitrogen at 108 ± 2 °C for 4–5 days or until little or no molten K remains. The reaction mixture initially turns orange and, as the reaction progresses, becomes a cloudy tan or brown. After heating is terminated, the assembly is removed to the Dri-Box for workup and product isolation. Filtration of the reaction mixture through a fine frit gives a brown precipitate and a yellow solution which consists of approximately 50% 1,5-C_8H_{12}, 40% *cis*-bicyclo[3.3.0]oct-2-ene, and a trace of 1,3-C_8H_{12} (by gas chromatography). The brown precipitate is washed with pentane to remove residual 1,5-C_8H_{12} and transferred to a separate flask. THF (150–300 mL) is added to this flask, forming a brown solution. This mixture is agitated briefly and allowed to stand several hours before filtering in order to allow the finely divided insolubles, which tend to clog filter frits, to settle. The solution is decanted from the insolubles into a fine filter frit and filtered. THF is removed from this solution by rotary evaporation in the Dri-Box to form damp solids. For maximum purity, two additional extractions in which these solids are redissolved in a minimum of THF, the solutions filtered through a fine frit, and the THF removed should be carried out. After the final removal of THF, the resultant solids are washed with pentane and dried by rotary evaporation until a constant weight is achieved. The product, $K_2C_8H_8$ (7.5 g, 0.041 mol, 68% based on K), is obtained free from THF as a yellow to green-gray air- and moisture-sensitive powder.

Anal. Calcd for $K_2C_8H_8$ (found): K, 42.88 (42.74); C, 52.70 (52.43); H, 4.42 (4.52). IR (cm^{-1}): 1800 (w), 1675 (w), 1535 (w), 1428 (m), 1295 (w), 880 (s), 810 (w), 680 (s); ^1H NMR (THF-d_8) δ 5.76 (s).

Formation of $U(C_8H_8)_2$ from $K_2C_8H_8$. In the Dri-Box, $K_2C_8H_8$ (1.34 g, 7.3 mmol), obtained by the above route, is dissolved in 25 mL of THF in a 100-mL Schlenk flask equipped with a glass encased magnetic stir bar. UCl_4 (1.4 g, 3.7 mmol) dissolved in 25 mL of THF is quantitatively transferred to a Schlenk addition funnel. The funnel is attached to the Schlenk flask, the assembly is removed to the Schlenk line, and the flask is cooled to −78 °C under nitrogen. The UCl_4 solution is then added dropwise to the stirred $K_2C_8H_8$ solution. During addition, a rapid color change from brown to green occurs accompanied by formation of a green precipitate. The reaction is allowed to warm to room temperature and stirred for 2 h. After removal of the THF by pumping on the Schlenk line, the green residue is removed to the Dri-Box where the solids are washed with pentane to remove residual THF. Spectrophotometric analysis of a THF solution of the solids indicated the presence of $U(C_8H_8)_2$ (0.87 g, 2 mmol, 53% based on the 614-nm absorption).

Formation of 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene from $K_2C_8H_8$. A slurry of $K_2C_8H_8$ (9.1 g, 0.05 mol) in 50 mL of diethyl ether (prepared in the Dri-Box) is added from a Schlenk addition funnel to a stirred solution of dichlorophenylphosphine (8.59 g, 0.048 mol) in 50 mL of ether at 0 °C under nitrogen. The addition funnel is rinsed with dry, degassed diethyl ether (3 × 25 mL) and the reaction is stirred for 3 h at room temperature. After the reaction is cooled to 0 °C, 10 mL of H_2O is cautiously added followed by 10 mL of saturated sodium carbonate. Yellow-orange solids are removed by filtration. The flask and filter cake are rinsed with 100 mL of toluene, which is combined with the ether extract. After the organics are dried with $MgSO_4$, the solvents are removed via distillation (ether at atmospheric pressure, toluene at 20 torr). The resultant brown oil is distilled (100–170 °C, 10^{-3} torr) into a receiver thermostatted in a dry ice/2-propanol bath. The product is allowed to warm to room temperature under vacuum to yield a light yellow solid (2.4 g, 0.011 mol, 23%). Recrystallization from methanol forms colorless crystals (mp 82–85 °C, lit.[10] mp 84–86 °C). The NMR spectrum is identical with that reported in the literature.

Conversion of $K_2C_8H_8$ to 1,3,5,7-C_8H_8. a. Azobenzene. $K_2C_8H_8$ (5.56 g, 0.03 mol), obtained by the above route, is dissolved in 75 mL of THF and added to a Schlenk addition funnel in the Dri-Box. The funnel is attached to a 100-mL Schlenk flask containing a previously degassed solution of azobenzene (Aldrich, 5.56 g, 0.03 mol) in 25 mL of THF. The assembly is then removed to the Schlenk line where the flask is cooled to −78 °C under nitrogen. Upon dropwise addition of the $K_2C_8H_8$ solution to the stirred azobenzene solution, a dark brown solution immediately forms. After addition is complete, the stirred reaction mixture is allowed to warm to room temperature over 3 h. The resulting black mixture is cooled to 0 °C and 10 mL of H_2O is added cautiously, turning the reaction mixture red brown. The organics are washed with 1 N HCl (10 mL) and H_2O (3 × 10 mL) and dried with $MgSO_4$. The resulting solution is diluted to 100 mL with THF in a volumetric flask and analyzed by GC for 1,3,5,7-C_8H_8 (2.16 g, 0.021 mol., 69.2%). The solution is vacuum transferred, leaving a brown solid residue. Vacuum transfer or simple distillation of the first 55–60 mL of solution separates THF with a slight loss of 1,3,5,7-C_8H_8 (<4%). An additional 25–30 mL of THF can be separated with loss of an additional 4% of 1,3,5,7-C_8H_8. The remaining volatile fraction (~5 mL) contains approximately 30% THF and 70% 1,3,5,7-C_8H_8 (1.57 g, 0.015 mol, 50.0% yield). 1,3,5,7-C_8H_8 can be isolated by vacuum transfer to a trap cooled to −78 °C which will pass residual THF. The product is identified as 1,3,5,7-C_8H_8 by comparison of the ^1H NMR spectrum and the GC retention time with those of an authentic sample (Aldrich).

Caution: The filter cake produced in the following reaction should be kept wet with THF since it is shock sensitive when dry.

b. Dry Oxygen. In the Dri-Box, $K_2C_8H_8$ (1.00 g, 5.5 mmol), obtained by the above route, is dissolved in 40 mL of THF in a 100-mL Schlenk flask equipped with a septum cap. The flask is removed to the Schlenk line and maintained under nitrogen while the brown solution is cooled to 0 °C. Oxygen, dried with a 1 × 6 in. column of Drierite, is slowly passed over the solution entering via a needle through the septum and leaving via the Schlenk stopcock. Within 0.5 h, the solution is cloudy and yellow-orange. The mixture is filtered in air, taking care to keep the filter cake wet with THF, since it is shock sensitive when dry. The filter cake is dissolved in H_2O and discarded. Removal of most of the THF (see section a) from the yellow filtrate leaves a yellow liquid containing 1,3,5,7-C_8H_8 (0.3 g, 2.9 mmol, 52%).

c. $CdCl_2$. In the Dri-Box, a solution of $K_2C_8H_8$ (2.0 g, 0.011 mol) in THF (25 mL) is added to a Schlenk addition funnel and attached to a 100-mL Schlenk flask containing a suspension of $CdCl_2$ (4.0 g, 0.022 mol) in THF (25 mL). The assembly is removed to the Schlenk line where it is cooled to 0–5 °C under nitrogen. Dropwise addition of the $K_2C_8H_8$ solution to the cooled, well-stirred $CdCl_2$ suspension produced a transient red-brown color as a dark brown suspension forms. After addition is complete, the funnel is removed and replaced with a condenser. The reaction mixture is stirred for 3 h at reflux. After heating is terminated and the reaction mixture is cooled, the volatiles are transferred in vacuo on the Schlenk line and combined with THF washes of the residual black solids. Removal of THF (see section a) leaves 1,3,5,7-C_8H_8 (0.49 g, 0.0047 mol, 43%).

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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.

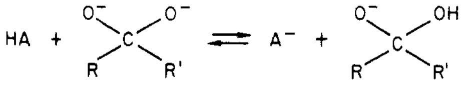
Since an excess of phenyllithium is only detrimental during hydrolysis, we felt that if the excess was removed after reaction with the carboxylic acid but before hydrolysis, a simple modification of the normal procedure might result in a significant improvement in yield without the necessity of preparing 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.

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.

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.



(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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[1] Nicodem, D. E.; Marchiori, M. L. P. F. C. "Abstracts of Papers", 172nd National Meeting of the American Chemical Society, San Francisco, CA, Aug 1976; American Chemical Society: Washington, DC, 1976.

[2] Jorgenson, J. *Org. React.* **1970**, *18*, 1.

[3] Levine, R.; Karten, M. J.; Kadunce, W. M. *J. Org. Chem.* **1975**, *40*, 1770.

[4] Lewine, R.; Karten, M. J. *J. Org. Chem.* **1976**, *41*, 1176.

[5] Adams, R.; et al. *Org. React.* **1967**, *7*, 286.

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

[7] Walter, F. *J. Am. Chem. Soc.* **1933**, *55*, 2821.

[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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