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Preliminary communication

PREPARATION OF BENZYL ANIONS BY METALATION WITH TRIMETHYLSILYLMETHYLMETAL COMPOUNDS

ALAN J. HART, DANIEL H. O'BRIEN and CHARLES R. RUSSELL

Department of Chemistry, Texas A and M University, College Station, Texas 77843 (U.S.A.)

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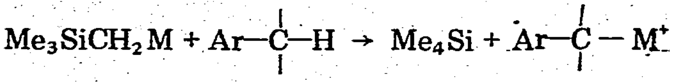
Several methods have been employed to prepare benzylmetal compounds. Benzyllithium has been obtained by reduction of benzyl methyl ether [1—3], by reduction of dibenzylmercury [4, 5] and by metalation of toluene with alkyllithium complexes of tetramethylethylenediamine [6]. Metal—halogen exchange between n-butyllithium and benzyl halides fails to give benzyllithium and yields only coupling products [7, 8]. Benzylsodium has been prepared by metal reduction of dibenzylmercury [9] and by metalation of toluene with either phenyl- or amylsodium [10—12]. These methods are not entirely satisfactory for the preparation of solutions of benzyl anions for magnetic resonance studies. Proton spectra of benzyl anions prepared by reduction of benzyl methyl ether showed interfering resonances due to the benzyl methyl ether, toluene and coupling products [1]. Further, reduction of benzyl methyl ether gives solutions containing methoxide ion. Metalation of toluene does not give high yields of benzylsodium unless toluene is in large excess. Without this large excess, dimetalation and coupling dominates [11, 12]. The method of choice appears to be the reduction of dibenzylmercury. This reduction gives solutions which are free of other anions such as alkoxide and chloride, which might influence chemical shift values. However, for the magnetic resonance study of substituted benzyl anions, each individual dibenzylmercury compound would have to be synthesized.

We wish to report the reduction of bis(trimethylsilylmethyl)mercury to give trimethylsilylmethylmetal compounds and the use of these precursors for the metalation of a variety of alkylbenzenes (eqn. 1). Metal sand (~12 mg-atom in a typical preparation) is prepared by heating the alkali metal in mineral oil in a septum-capped, argon-flushed centrifuge tube. The mineral oil is replaced by washing with several portions of dry cyclohexane (~5 ml). Bis(trimethylsilylmethyl)mercury (1 ml, 4.4 mmol) [13] is then added. Reduction is rapid with potassium, rubidium and cesium (~ one half hour) and it is necessary to cool the tube in an ice bath. The reduction occurs with the formation of the amalgam and a light gray precipitate. Reduction with sodium sand is more difficult and requires several hours of heating at 60°. This difficulty is most probably due to the formation of high melting sodium amalgam at the surface of the sodium sand,

$$[\mathrm{Me_3SiCH_2}]_2\mathrm{Hg} + 2\mathrm{M} \rightarrow 2\mathrm{Me_3SiCH_2M} + \mathrm{Hg}$$

$$\mathrm{M} = \mathrm{Na, K, Rb, Cs} \qquad (1)$$



$$\mathrm{Me_3SiCH_2M} + \mathrm{Ar{-}\overset{|}{\underset{|}{C}}{-}H} \rightarrow \mathrm{Me_4Si} + \mathrm{Ar{-}\overset{|}{\underset{|}{\dot{C}}}{-}M^+}$$

which greatly reduces the available sodium surface. This problem may be solved by employing sodium amalgam of high mercury content which remains liquid throughout the reduction.

After the reduction is complete, a slight excess of the alkylbenzene (~6 mmol) to be metalated is added and the heterogeneous reaction mixture is shaken at room temperature for approximately one hour. The precipitated product is washed several times with cyclohexane. The sample is centrifuged and most of the cyclohexane is syringed away. Addition of THF results in deep red solutions of the anion dissolved in approximately 20% cyclohexane and 80% THF.

The solutions of benzyl anions were examined with Fourier transform carbon-13 magnetic resonance. As an example of the quality of spectra obtained, the proton-decoupled spectrum of α-trimethylsilylbenzylrubidium, prepared by the metalation of benzyltrimethylsilane, is presented in Fig. 1. The chemical shifts and coupling constants are compared in Table 1. This spectrum shows no interfering resonances due to either the starting material or to coupling products. Quenching the solution with water gives only the spectrum of benzyltrimethylsilane.

Compared to benzyltrimethylsilane, the benzylic carbon of the anion shows a downfield chemical shift and an increase in the carbon—hydrogen coupling constant. These changes reflect the combined effect of a change in hybridization

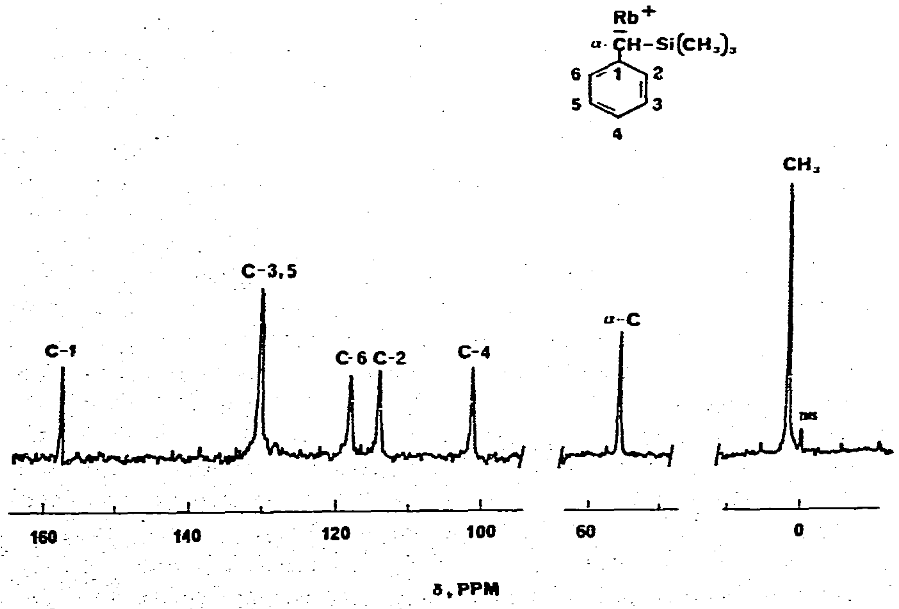


Fig. 1. The proton decoupled carbon-13 spectrum of α-trimethylsilylbenzylrubidium. The solvent resonances are not shown.

TABLE 1

CARBON-13 CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR BENZYLTRIMETHYLSILANE AND α-TRIMETHYLSILYLBENZYLRUBIDIUM [a]

Carbon	$C_6H_5CH_2SiMe_3$	$[C_6H_5CHSiMe_3]^-Rb^+$
CH	δ 27.5 ppm J 121 Hz	δ 55.7 ppm J 130 Hz
C(1)	δ 140.6 ppm	δ 157.5 ppm
C(2,6)	δ 128.6 ppm	δ 118.0 ppm δ 114.0 ppm
	J 158 Hz	J 150 Hz J 150 Hz
C(3,5)	δ 128.6 ppm J 158 Hz	δ 130.0 ppm J 150 Hz
C(4)	δ 124.5 ppm J 158 Hz	δ 101.6 ppm J 160 Hz
$SiMe_3$	δ −1.8 ppm J 120 Hz	δ 1.7 ppm J 117 Hz

[a] Shifts in ppm downfield from TMS (internal).

and the presence of a negative charge. The *ortho* and *para* carbons show a corresponding upfield chemical shift indicating delocalization of the charge into the ring. With different groups on the benzylic carbon, the *ortho* carbons are nonequivalent in the anion. The nonequivalence of the *ortho* positions in the proton resonance of a number of benzyl carbanions has been previously reported [1, 14—18]. This nonequivalence and the chemical shift changes suggest that there is substantial double bond character in the benzylic carbon—aryl carbon bond.

The preparation of benzyl anion solutions by metalation of alkylbenzenes with trimethylsilylmethylmetal compounds satisfies two contrasting requirements: reasonably rapid reduction and metalation reactions in an environment without an interfering coupling pathway. Bis(trimethylsilylmethyl)mercury is very soluble in cyclohexane. This allows the reduction to be rapid with the precipitation of the trimethylsilylmethylmetal compound. In contrast, dibenzylmercury fails to react with sodium or potassium sand in cyclohexane. We have found that no detectable reaction occurs even after 48 h. This is primarily due to insolubility of dibenzylmercury in cyclohexane. If the reduction is carried out in a solvent in which both dibenzylmercury and the anion are soluble, mostly coupling occurs. Reduction of dibenzylmercury with sodium or potassium in THF gave spectra with resonances due mainly to the coupling product, bibenzyl, and due to dibenzylmercury. However, the reduction of dibenzylmercury apparently gives high yields of benzyl anions in THF when lithium is used [4, 5].

The subsequent metalation of alkylbenzenes dissolved in cyclohexane by trimethylsilylmethylmetal compounds occurs with the precipitation of the benzyl anion salt. At this stage, the benzyl anion salt may be washed to remove any unmetalated alkylbenzene. This washing is the key step in obtaining spectra free of interfering resonances. The insolubility of organosodium and organopotassium compounds in hydrocarbons has been used to advantage previously. n-Butyllithium reacts with sodium or potassium t-butoxide in heptane to give precipitates of butylmetal compounds [19]. However, this method was not chosen for the present work because it requires excess organolithium to prevent the formation of insoluble complexes of the organometal and alkoxide. For the preparation of α-trimethylsilylbenzyl anions, the presence of alkoxide ion would be particularly undesirable because of possible trimethylsilyl cleavage by alkoxide.

The procedure described herein provides a convenient technique, especially for magnetic resonance studies, for the rapid preparation of a variety of benzyl anions from a single precursor, bis(trimethylsilylmethyl)mercury. We have used this method to study the magnetic resonance spectra of the anions of toluene, *p*-trimethylsilyltoluene, ethylbenzene, *o*-xylene, benzyltrimethylsilane, and *o*-, *p*- and *m*-methylbenzyltrimethylsilane. These results will be reported in more detail shortly.

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