lithium to give **3**, $[\alpha]_D$ +1.4°, $[\alpha]_{350}$ +15.4° ($CHCl_3$), confirms this conclusion.[25b]

The stereochemical course of the organolithium displacement reaction parallels that of the analogous sulfoxide[26] and phosphine oxide[8] syntheses. Retention of configuration in the reduction of arsine sulfides by organolithium reagents is easily rationalized by assuming attack of the carbanionic species on sulfur, followed by extrusion of the arsine and formation of mercaptide ion. Perhaps, by analogy between this reaction and the reduction of phosphine sulfides by hexachlorodisilane, which proceeds with retention of configuration at phosphorus,[27] the reaction takes place by way of an intermediate of type $[R_3As{=}SR]^-$. Indeed, reduction of (+)-**5** with hexachlorodisilane under the conditions previously described for the reduction of the phosphorus analogs[27] gives **3**, $[\alpha]_D$ +1.4°, $[\alpha]_{350}$ +15.6° ($CHCl_3$), *i.e.*, the reaction proceeds with retention at arsenic.

Displacements of menthoxide from thioarsinate esters with lithium reagents proceeds with some degree of racemization, as was previously observed for reactions of organolithium reagents with analogous phosphinate esters.[8c] Since the enantiomeric purities of (+)-**4** obtained directly from reaction of **1a** (76% de) with *n*-propyllithium and of (+)-**4** obtained by sulfurization of (+)-**2** (from 76% de **1a**) are identical, the loss of stereospecificity does not occur in the desulfurization step.

Although the sequences described above have been restricted to only one precursor, thioarsinate **1**, it is anticipated that, by analogy with comparable phosphinates,[8] the method here described is a general one.

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A New Convenient Method of Producing Radical Anions Involving One-Electron Transfer from Trimethylsilylsodium[1-3]

Sir:

In the course of a survey of the reactions of trialkylsilyl anions,[2,4] we found that trimethylsilylsodium was excellent as an electron-transfer reagent to produce radical anions from a variety of compounds.

In typical examples 0.5–1.0 ml of a 0.5 *M* solution of trimethylsilylsodium in hexamethylphosphoramide (HMPA)[4a] was added from a hypodermic syringe under argon to 10–100 μg of naphthalene in a glass tube constructed with a 6 × 60 mm upper portion and a 0.5 × 80 mm thin-walled lower portion. The tube was then sealed off after three freeze–thaw cycles on a vacuum line.

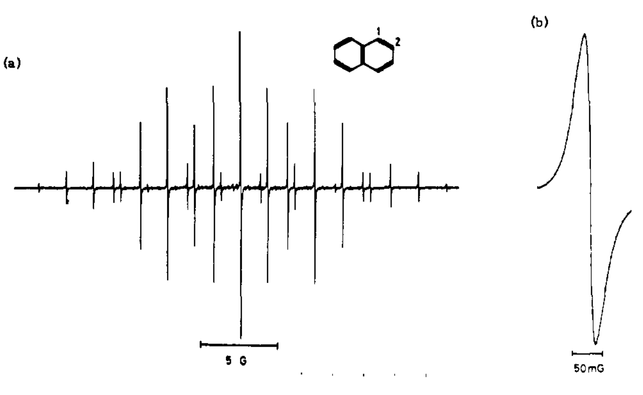

Figure 1. Esr spectra of the naphthalene radical anion in HMPA at room temperature, scan time 2 hr, modulation frequency 10 kHz, modulation amplitude 10 mG: (a) full spectrum, range 40 G, a_1 = 4.92 G, a_2 = 1.79 G; (b) an expanded spectrum of the center part, range 1 G.

An exceptionally well-resolved esr spectrum with the line width of 27 mG was recorded at room temperature as shown in Figure 1.[5] The spectrum was unchanged after storing this solution for 1 month at about −5°. Similar successful results were obtained from a wide variety of compounds including aromatic compounds, substituted benzenes, aromatic ketones, and olefins.

The reaction apparently involved one-electron transfer from trimethylsilylsodium to substrates. The trimethylsilyl radical thus formed can attack either HMPA or methoxytrimethylsilane[4a] to give finally hexamethyldisiloxane.

$$\mathrm{Me_3Si^-} + \mathrm{ArH} \longrightarrow \mathrm{Me_3Si\cdot} + [\mathrm{ArH}]^-$$

$$\mathrm{Me_3Si\cdot} \xrightarrow[\text{or Me}_3\text{SiOMe}]{\text{solvent}} (\mathrm{Me_3Si})_2\mathrm{O}$$

Although organic radical anions have been prepared successfully by reduction with alkali metals,[6,7] electrolytic reduction,[8-10] and photolytic reduction,[11] the following points can be made about the usefulness of the present new method.

(a) Preparation of the sample for esr measurement requires only simple injection of a small amount of the reagent from a stock solution to a substrate, no special technique being required. We have recently found a very simple method to prepare hexamethyldisilane, the requisite precursor to trimethylsilylsodium.[2]

(b) Only very small amounts of both substrates and solvent are required in the operation.

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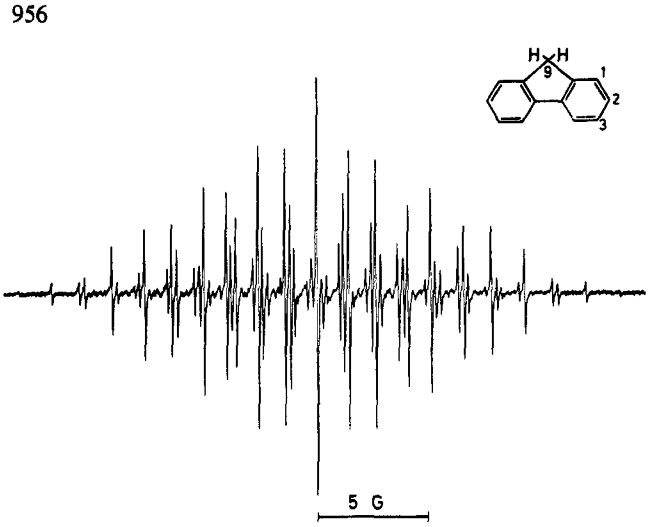

Figure 2. Esr spectrum of the fluorene radical anion in HMPA at room temperature, range 40 G, scan time 16 min, modulation frequency 100 kHz, modulation amplitude 50 mG, a_1 = 1.49 G, a_2 = 5.26 G, a_3 = 1.49 G, a_4 = 2.74 G, a_9 = 2.74 G.

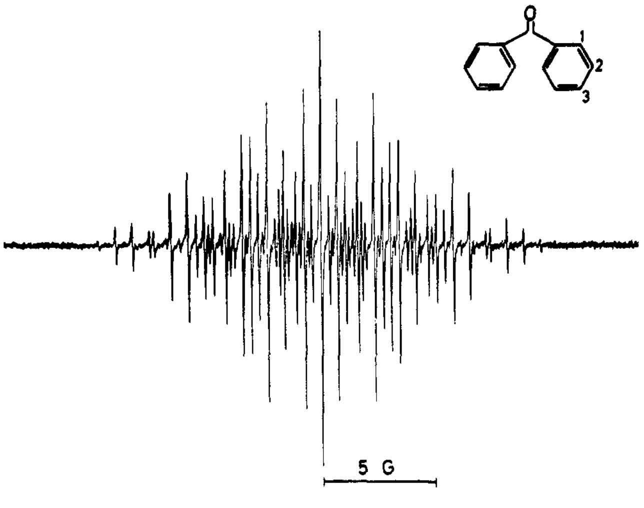

Figure 3. Esr spectrum of the benzophenone ketyl in HMPA at room temperature, range 40 G, scan time 8 min, modulation frequency 100 kHz, modulation amplitude 20 mG, a_1 = 2.38 G, a_2 = 0.73 G, a_3 = 3.49 G.

(c) Since trimethylsilylsodium can be used in large excess to substrates, essentially no neutral molecule is left in the system. Further reduction of radical anions to dianions is seemingly very slow. As a result, well-resolved, strong signals such as those in Figure 1 can usually be observed.

(d) Even though trimethylsilylsodium is very nucleophilic and basic, its rapid electron transfer dominates completely. This is illustrated by the well-resolved spectrum of the fluorene radical anion at room temperature as shown in Figure 2. Fluorene is known to react with alkali metals at room temperature to give the fluorenyl anion. The fluorene radical anion is reportedly only relatively stable at −70°.[12]

(e) For ketyl radicals such as benzophenone ketyl (Figure 3) and for radical anions from nitro compounds such as nitrobenzene,[13] the hyperfine splitting constants of ring protons and nitrogen were smaller than any recorded values. This may indicate minimum interactions of radical anions to the countercation and the solvent[14] because of a strongly basic nature of the solvent.[13,15]

Studies on the scope and limitations of this new reagent are now in progress.

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Synthesis of a Bridged [18]Annulene

Sir:

It has been predicted that the delocalization energy per double bond will decrease with increasing ring size until, somewhere in the range of 22–30 members, such annulenes will become simple polyolefins.[1-3] Sondheimer and his colleagues have demonstrated that both [22]annulene[4] and monodehydro[26]annulene[5] sustain a dimagnetic ring current, thus providing qualitative evidence for delocalization of the π electrons in rings of 22 and 26 members. However, as has been shown in such a striking fashion for [18]annulene,[6] the simple annulenes are subject to conformational flipping which undoubtedly decreases the effective delocalization energy. To test the upper limit for the delocalization energy of $4n + 2$ hydrocarbons it is highly desirable to use as a test molecule one with a rigid, planar annulene skeleton. In the present communication we describe an approach of possibly general application leading to bridged molecules with a rigid, planar annulene skeleton.

Treatment of 2,8-dibromodibenzothiophene[7] (**1**) with *n*-butyllithium followed by *N*,*N*-dimethylformamide gave the corresponding dialdehyde **2**, mp 233–234°, in 68% yield.[8] Reduction of **2** with sodium borohydride proceeded in quantitative yield to give the diol **3**, mp 159–160°. Treatment of **3** with hydrogen bromide in glacial acetic acid then afforded 2,8-bis(bromomethyl)dibenzothiophene (**4**) in 93% yield as white needles, mp 217–218°. When **4** was treated with 1,4-bis(mercaptomethyl)benzene (**5**) in ethanolic base, the paracyclophane **6**, mp 260–261°, formed in 88%

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