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Registry No. 1, 3074-03-1; 3, 479-79-8; 4, 5693-33-4; 1-indanone, 83-33-0; phthalaldehyde, 643-79-8; 11*H*-benzo[*b*]fluorene, 243-17-4; 11*H*-benzo[*a*]fluorene, 238-84-6.

Preparation of β-Keto Sulfones from [(Phenylsulfonyl)methylene]dilithium and Acid Chlorides

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As a class of compounds β-keto sulfones provide a range of synthetic versatility.[1-5] The β-keto sulfone moiety may be prepared from a variety of precursors; e.g., from cyano sulfones via the Thorpe reaction,[6] by oxidation of sulfides or sulfoxides,[7] or from esters through Claisen condensations.[8] We have prepared several new β-keto sulfones by a significantly more convenient method. We describe this method herein and report for the first time reactions that yield β-keto sulfones from acid chlorides and [(phenylsulfonyl)methylene]dilithium (Scheme I).

Scheme I

$$C_6H_5SO_2CHLi_2 \xrightarrow{RCOCl} \xrightarrow{NH_4Cl} C_6H_5SO_2CH_2COR$$

R = cyclopropyl, isopropyl, ethyl, methyl, cyclohexyl, phenyl

The dianion of methyl phenyl sulfone is prepared by treating the sulfone with 2.2 equiv of *n*-butyllithium in dry tetrahydrofuran (THF) at −30 °C.[9] The resulting yellow suspension is stirred for 30 min, after which the acid chloride is added slowly to the dianion. The resulting enolate is subsequently quenched with saturated ammonium chloride solution and then extracted with chloroform. The organic extract is dried, filtered, and evaporated. The crude β-keto sulfone is recrystallized from a suitable solvent. The yields and melting points for the products of a series of representative reactions are given in the Experimental Section.

The reactions of acid chlorides with the monoanion of the sulfone were not efficient. Once the β-keto sulfone is formed under these conditions it presumably is quickly deprotonated by any unreacted [(phenylsulfonyl)methyl]lithium; therefore, the maximum yield of β-keto sulfone would be 50%. Since the reaction of the sulfone dianion with acid chloride directly gives the enolate, this undesirable internal quenching is avoided.

Although geminal dilithio derivatives of alkyl sulfones do react with esters to produce β-keto sulfones,[10-12] the analogous reactions performed with acid chlorides are simpler and cleaner. When esters are used in this type of reaction, the use of either tetramethylethylenediamine (TMEDA) or hexamethylphosphoramide (HMPA) is often required. The use of these cosolvents is not necessary when acid chlorides are employed. Additional advantages of our method over others include higher yields, greater ease of product isolation, and minimal synthetic steps. For example, the average yield of β-keto sulfone from Claisen condensations is only 27%,[8] while the present method affords yields from 36% to 74%.

Experimental Section

General Procedure. Infrared (IR) spectra were recorded as KBr pellets or mineral oil mulls on either a Perkin-Elmer 983 or a Perkin-Elmer 1310 spectrophotometer. Nuclear magnetic resonance (NMR) experiments were performed by using a JEOL FX-90Q for ^{13}C at 22.45 MHz and ^1H at 89.55 MHz by using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the reference. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points are uncorrected.

All acid halides were distilled prior to use. THF was distilled from sodium benzophenone ketyl under nitrogen immediately before use. Methyl phenyl sulfone (Parish Chemical) was used without further purification. Butyllithium (1.6 M in hexane) was obtained from Aldrich Chemical Company.

Typical Procedure. 1-Cyclopropyl-2-(phenylsulfonyl)-ethanone. Butyllithium (18 mL of 1.6M solution, 28 mmol) was added slowly with efficient stirring under dry nitrogen to a solution of methyl phenyl sulfone (2.0 g, 13 mmol) in 40 mL of anhydrous THF at −30 °C. After 30 min, cyclopropanecarboxylic chloride (1.6 g, 15 mmol) was slowly added by syringe so as to minimize the temperature increase that results from the exothermic reaction. Subsequently, the reaction mixture was poured into 150 mL of saturated NH_4Cl solution and stirred. The β-keto sulfone was extracted with chloroform and the organic phase was washed with saturated NaCl solution, dried with anhydrous magnesium sulfate, filtered, and evaporated. The 1-cyclopropyl-2-(phenylsulfonyl)ethanone was recrystallized from CCl_4: recrystallized yield 74%; mp 58 °C (lit.[13] mp 56 °C). [Alternatively, this β-keto sulfone may be recrystallized from water.] ^1H NMR ($CDCl_3$), ppm: 0.6–1.0 (m, 4 H), 1.8–2.2 (m, 1 H), 4.0 (s, 2 H), 7.0–8.0 (m, 5 H). ^{13}C NMR ($CDCl_3$), ppm: 13.2 (t), 22.0 (d), 68.0 (t), 128.2 (d), 129.2 (d), 134.1 (d), 138.7 (s), 198.2 (s). IR (cm^{-1}) 3012, 1695, 1585, 1477, 1445, 1384, 1323, 1155, 1087, 1060, 1024, 898. Anal. Calcd for $C_{11}H_{12}SO_3$: C, 58.91; H, 5.39; S, 14.30. Found: C, 58.67; H, 5.43; S, 14.61.

3-Methyl-1-(phenylsulfonyl)-2-butanone: recrystallized yield from CCl_4 43%; mp 66.5–67 °C. ^1H NMR ($CDCl_3$), ppm: 1.1 (d, 6 H), 2.9 (septet, 1 H), 4.3 (s, 2 H), 7.5–8.0 (m, 5 H). ^{13}C NMR ($CDCl_3$), ppm: 17.2 (q), 41.7 (d), 64.2 (t), 128.0 (d), 129.0 (d), 133.9 (d), 138.8 (s), 201.7 (s). IR (cm^{-1}) 3040, 2935, 1680, 1450, 1375, 1290, 1140, 740, 680. Anal. Calcd for $C_{11}H_{14}SO_3$: C, 58.38; H, 6.24; S, 14.17. Found: C, 58.46; H, 6.25; S, 14.58.

1-(Phenylsulfonyl)-2-butanone: recrystallized yield from CCl_4 60%; mp 44–45 °C. ^1H NMR ($CDCl_3$), ppm: 1.1 (t, 3 H), 2.7 (q, 2 H), 4.2 (s, 2 H), 7.7–7.9 (m, 5 H). ^{13}C NMR ($CDCl_3$), ppm: 6.7 (q), 37.1 (t), 65.7 (t), 127.6 (d), 128.8 (d), 133.7 (d), 138.4 (s), 198.4 (s). IR (cm^{-1}) 3045, 3000, 2960, 2920, 1705, 1575, 1445, 1300, 1140, 740, 680. Anal. Calcd for $C_{10}H_{12}SO_3$: C, 56.59; H, 5.70; S, 15.10. Found: C, 56.79; H, 5.75; S, 15.32.

1-(Phenylsulfonyl)-2-propanone: recrystallized yield from CCl_4 36%; mp 52–54 °C. ^1H NMR ($CDCl_3$), ppm: 2.4 (s, 3 H), 4.2 (s, 2 H), 7.7–7.9 (m, 5 H). ^{13}C NMR ($CDCl_3$), ppm: 31.6 (q),

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67.5 (t), 128.5 (d), 129.8 (d), 134.7 (d), 138.8 (s), 196.0 (s); IR (cm^{-1}) 3010, 2920, 2900, 1700, 1300, 1160, 700. Anal. Calcd for $C_9H_{10}SO_3$: C, 54.53; H, 5.08. Found: C, 54.76; H, 5.01.

1-Cyclohexyl-2-(phenylsulfonyl)ethanone: recrystallized yield from CCl_4 63%; mp 83–84 °C. ^1H NMR ($CDCl_3$), ppm: 1.1–2.0 (m, 10 H), 2.6 (m, 1 H), 4.3 (s, 2 H), 7.5–8.1 (m, 5 H). ^{13}C NMR ($CDCl_3$), ppm: 25.2 (t), 25.6 (t), 27.8 (t), 51.5 (d), 64.6 (t), 128.3 (d), 129.2 (d), 134.1 (d), 139.0 (s), 201.2 (s). IR (cm^{-1}) 3010, 2990, 2960, 1680, 1420, 1275, 1140, 1110, 730, 660. Anal. Calcd for $C_{14}H_{18}SO_3$: C, 63.13; H, 6.81; S, 12.04. Found: C, 63.43; H, 6.69; S, 12.29.

1-Phenyl-2-(phenylsulfonyl)ethanone: recrystallized yield from CCl_4 63%; mp 90–91 °C (lit.[14] mp 93–94 °C). ^1H NMR ($CDCl_3$), ppm: 4.7 (s, 2 H), 7.6–7.9 (m, 10 H). ^{13}C NMR ($CDCl_3$), ppm: 63.4 (t), 128.6 (d), 128.9 (d), 129.2 (d), 129.3 (d), 134.2 (d), 134.4 (s), 135.7 (d), 138.7 (s), 187.9 (s). IR (cm^{-1}) 3040, 3000, 2880, 1690, 1330, 1160, 755, 695. Anal. Calcd for $C_{14}H_{12}SO_3$: C, 64.60; H, 4.65. Found: C, 64.24; H, 4.77.

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Selective C-Alkylation of β-Diketones[1]

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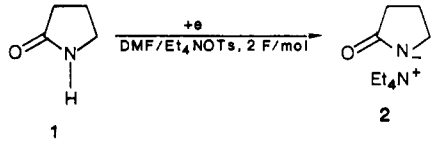
The C-monoalkylation of β-diketones are not always selectively achievable by using usual bases[2-5] since some undesirable side reactions such as O-alkylation,[6] dialkylation,[7] and cleavage of β-diketones may take place together with the C-monoalkylation. Although a method using thallium enolates has been reported,[8] it is suggested to be effective for only methylation.[9] Tetraalkylammonium enolates of β-diketones have also been shown to be useful to overcome such difficulty; however, the preparation[10] of these enolates under anhydrous conditions is not necessarily easy.

We have previously reported[11-13] that the electroreduction of 2-pyrrolidone (1) in DMF using Et_4NOTs as a supporting electrolyte yielded the corresponding anionic species **2** having tetraethylammonium cation (Et_4N^+) as a counterion.



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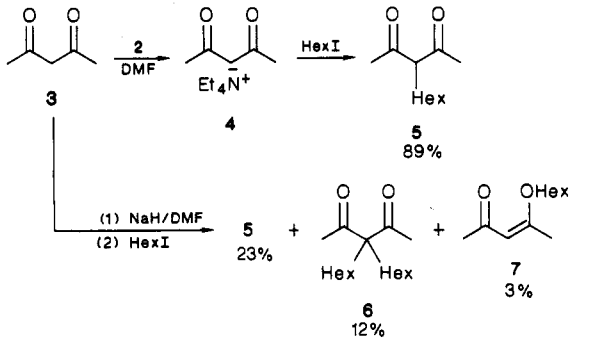
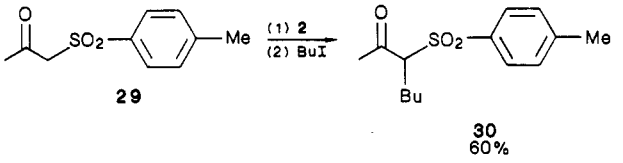
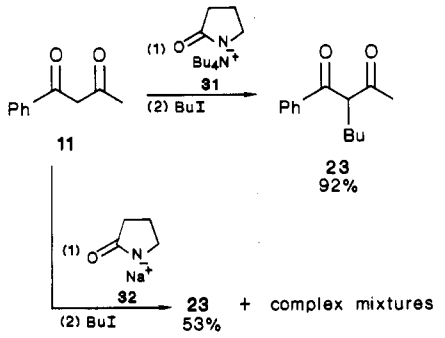
Scheme I



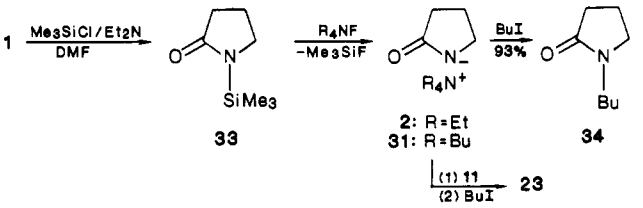
Scheme II



Scheme III



Scheme IV



In this paper, we wish to report that the reaction of **2** with β-diketones gave the corresponding tetraethylammonium enolates under anhydrous conditions and the reaction of these enolates with alkyl halides led to the selective C-monoalkylation of β-diketones.

As shown in Scheme I, the addition of a solution of **2** in DMF to a DMF solution of 2,4-pentanedione (**3**) at room temperature followed by the trapping of the resulting ammonium enolate **4** with hexyl iodide gave the corresponding C-alkylated product **5** in excellent yield, whereas the alkylation of **3** using NaH as a base gave a mixture of

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