yields obtained in this and the preceding experiments are probably the result of not including a reagent to reoxidize Rh(I).

Bis(*p*-anisyl) Ketone from *p*-Anisylmercuric Chloride and a Rhodium Chloride Catalyst. In a heavy-walled Pyrex bottle with a magnetic stirring bar was placed 10 mmol of *p*-anisylmercuric chloride and 0.1 mmol of rhodium trichloride trihydrate. The bottle was capped and flushed with carbon monoxide and 10 ml of acetonitrile was injected. The reaction mixture was stirred under 50 psig of carbon monoxide at 100° overnight. Analyses by glpc showed the solution to be 0.32 *M* in bis(*p*-anisyl) ketone. No *p*-anisyl chloride was detected.

3,3′-Bis(carbomethoxy)benzophenone from 3-Carbomethoxyphenylmercuric Chloride. A reaction was carried out as in the preceding example using 10 mmol of 3-carbomethoxyphenylmercuric chloride in place of *p*-anisylmercuric chloride. Evaporation of the reaction mixture and recrystallization of the product from a mixture of benzene and hexane gave 0.23 g of 3,3′-bis(carbomethoxy)benzophenone, mp 129–130° (lit.[14] mp 130°).

4,4′-Dichloro-3,3′-dinitrobenzophenone from 4-Chloro-3-nitrophenylmercuric Chloride. A reaction was carried out as in the above experiment using 10 mmol of 4-chloro-3-nitrophenylmercuric chloride instead of 3-carbomethoxyphenylmercuric chloride. Isolation of the product in the same manner and two recrystallizations from aqueous acetic acid gave 0.22 g of product, mp 129.5–130.5° (lit.[15] mp 133–134°).

Benzophenone from Phenylmercuric Chloride and Rh(CO)Cl-(PR_3)$_2$ Catalysts. A. In a gasometric apparatus were placed 1.0 mol of $RhCl(CO)[P(C_2H_5)_3]_2$[16] and 10 mmol of phenylmercuric chloride. The air in the apparatus was replaced by carbon monoxide at atmospheric pressure and 10 ml of toluene was added. In 4 hr at 50°, 46 ml of gas was absorbed and a slow absorption continued. After reacting overnight, analyses by glpc showed the solution to be 0.25 *M* in benzophenone with only a trace of biphenyl.

B. In a heavy-walled Pyrex bottle containing a magnetic stirring bar was placed 10 mmol of phenylmercuric chloride and 0.1 mmol of $RhCl(CO)[P(n\text{-}Bu)_3]_2$.[16] The bottle was capped and flushed with carbon monoxide. After the injection of 10 ml of toluene, the reaction mixture was pressured to 50 psig with carbon monoxide and stirred for 2.5 hr at 100°. After cooling, analyses by glpc showed the solution to be 0.24 *M* in benzophenone.

Di-*p*-anisyl Ketone from *p*-Anisylmercuric Chloride and $RhCl(CO)[P(n\text{-}Bu)_3]_2$ as Catalyst. A reaction was carried out as in B using 10 mmol of *p*-anisylmercuric chloride in place of phenylmercuric chloride. Analysis showed the solution to be 0.15 *M* in di-*p*-anisyl ketone. Evaporation of solvent and recrystallization of the product from aqueous ethanol gave 0.23 g of di-*p*-anisyl ketone, mp 140.5–141.5° (lit.[17] mp 143–144°).

Acknowledgment. Most of the experimental work was carried out with the assistance of Mr. Joseph Keelins.

(14) R. W. Beattie and R. H. F. Manske, *Can. J. Chem.*, 42, 223 (1964).
(15) J. Forrest, O. Stephenson, and W. A. Waters, *J. Chem. Soc.*, 333 (1946).
(16) R. F. Heck, *J. Amer. Chem. Soc.*, 86, 2796 (1964).
(17) K. Auwers, *Chem. Ber.*, 36, 3900 (1903).

The Synthesis of Olefins and Ketones from Carbonyl Compounds and Sulfinamides

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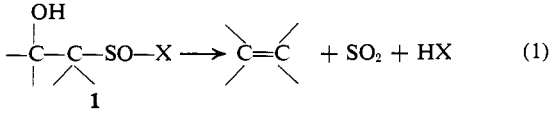
Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received April 18, 1968*

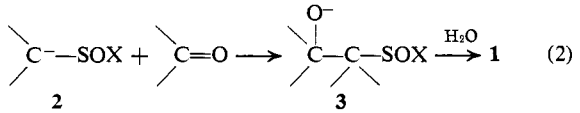
Abstract: The reaction of α-lithio sulfinamide derivatives with aldehydes and ketones affords β-hydroxy sulfinamides by carbonyl addition. These adducts undergo smooth thermolysis in the range 80–110° to form olefins along with sulfur dioxide and the appropriate amine. These reactions constitute a new synthetic route to olefins. A new and useful one-step synthesis of ketones from esters and α-lithio sulfinamide derivatives is also described.

The investigations reported herein originated from the hypothesis that olefins might be produced from β-hydroxy sulfinyl derivatives by the elimination process outlined in eq 1, and additionally from the possibility that the required intermediate **1** might be accessible



(1)

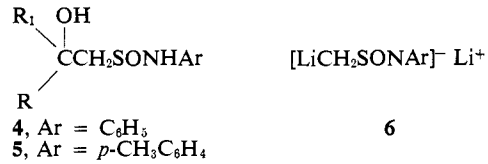
by the reaction of an α-sulfinylcarbanion of type >C⁻–SOX (**2**) with an aldehyde or ketone (eq 2).



(2)

Transformations 2 and 1 in sequence would constitute an interesting and possibly useful alternative to the Wittig reaction, one based on a key role for sulfur rather than phosphorus in the carbon-bond-forming and elimination steps. It was clear from previous work that β-alkoxy sulfoxide derivatives, represented by **3** with, *e.g.*, X = alkyl or aryl are not particularly susceptible to olefin-forming elimination under mild conditions.[1,2] However, little was known about the possibility of effecting elimination from *hydroxy* sulfinyl compounds of type **1** either with sulfoxides or other sulfinyl derivatives such as X = NR_1R_2 or X = OR. Most of our studies to date have been concerned with β-hydroxy sulfinamides and, more specifically, with β-hydroxy sulfinanilides and β-hydroxy sulfin-*p*-toluidides of general formula **4** and **5**, respectively, these being the most readily available sulfinamide–carbonyl adducts. As described in a preliminary publication[3] these adducts which are accessible from the

(1) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 84, 866 (1962); 87, 1345 (1965).
(2) For a special case of olefin formation from an intermediate of type **3** under forcing conditions see, E. J. Corey and M. Chaykovsky, *J. Org. Chem.*, 28, 254 (1963), and also C. Walling and L. Bollyky, *ibid.*, 28, 256 (1963).
(3) E. J. Corey and T. Durst, *J. Am. Chem. Soc.*, 88, 5656 (1966).

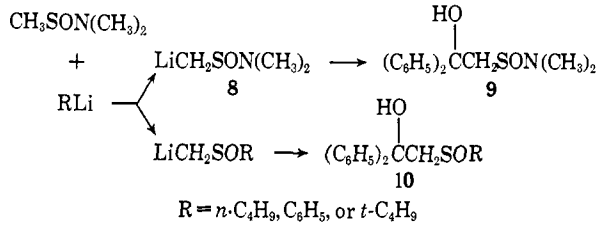


4, Ar = C_6H_5
5, Ar = p-$CH_3C_6H_4$

6

reaction of lithio reagents of type **6** with aldehydes and ketones, do indeed undergo ready thermal decomposition to form olefins in accordance with eq 1. Thermolytic olefin formation from β-hydroxy sulfinamides is very much more facile than from β-hydroxy sulfoxides, a fact which is responsible for the present focus on the sulfinamide series. This paper also describes another novel and potentially useful reaction of the lithio sulfinamide derivatives **6** which allows the conversion of esters to methyl ketones with high efficiency in a single step.

The first task which we faced was the development of a method for preparing α-metallated sulfinamide derivatives, a problem which turned out to be much more difficult than the metallation, for example, of sulfoxides. The reaction of N,N-disubstituted methanesulfinamides, *e.g.*, the dimethylamide **7**, with alkyllithium reagents in tetrahydrofuran at −78 to −95° under conditions which are generally very effective for the generation of sulfur-stabilized carbanions did not lead cleanly to the lithio derivative **8** as was apparent from the fact that at least two different products were generally obtained after the addition of benzophenone and hydrolysis. One was the expected adduct **9** and another invariably was the adduct **10** of benzophenone with the sulfoxide derived by displacement of dimethylamine by an alkyl group originating in the alkyllithium reagent. In a typical experiment with *n*-butyllithium at −78° the

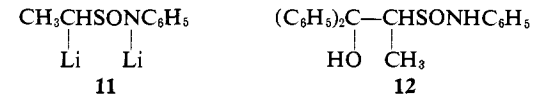


adducts **9** and **10**, R = *n*-C_4H_9, were produced in 50% yield in a 2:1 ratio. The best results were obtained using the morpholide of methanesulfinic acid at −78° in tetrahydrofuran with rapid addition of *t*-butyllithium as base, under which conditions a 50% yield of sulfinamide and sulfoxide adducts were formed with benzophenone in a ratio of *ca.* 8:1. The replacement of amine by alkyl in these metallations, which might involve either a nucleophilic displacement by alkyl at sulfur or an elimination–addition mechanism *via* the sulfine ($H_2C{=}S{=}O$), could not be circumvented and so attention was directed toward the use of N-monosubstituted methanesulfinamides based on the precedent that acetanilide undergoes facile metallation by butyllithium (2 equiv) in tetrahydrofuran to form a C_α, N-dilithio derivative.[4] It was found that the dilithio derivative **6** could be generated smoothly from methanesulfin-*p*-toluidide **5** by treatment with 2 equiv of *n*-butyllithium in tetrahydrofuran at −78° for *ca.* 20 min. Deuteration of **6** by D_2O followed by quantitative nmr analysis and also reaction of **6** with benzophenone to afford the carbonyl adduct **5**, $R_1 = R_2 = C_6H_5$, in 97% yield, both indicated the high degree of efficiency of this metallation process. The adduct **5**, $R_1 = R_2 = C_6H_5$, decomposes cleanly when heated alone at 137–139° (melting point) or at reflux in dry benzene (5 hr) to form 1,1-diphenylethylene (99%), *p*-toluidine (96%), and sulfur dioxide.

The dilithio derivative **6** adds similarly to 4-*t*-butylcyclohexanone to give an adduct (94% based on reacted ketone) which undergoes elimination at reflux in benzene to 4-*t*-butylmethylenecyclohexane (84%) and *p*-toluidine (92%). However, the reaction of this ketone with **6** is accompanied significantly (*ca.* 40%) by proton transfer to give enolate which affords after work-up the starting ketone, 4-*t*-butylcyclohexanone; this is easily separated from the β-hydroxy sulfinamide by treatment with pentane, in which the latter is insoluble. Similarly, the adducts from **6** and cyclohexanone and cyclopentanone upon heating in benzene furnished methylenecyclohexane and methylenecyclopentane in *ca.* 90% yield.

The conversion of aldehydes to olefins has also been demonstrated. Thus, benzaldehyde, Δ^3-cyclohexenecarboxaldehyde, and dodecanal react with the reagent **6** to form β-hydroxy sulfinamides in 98, 73, and 68% yields, respectively; these adducts are decomposed by heating in *dry* toluene at reflux for 5 hr to afford, respectively, styrene (76%), 4-vinylcyclohexene (90%), and 1-tridecene (83%).[5]

Treating ethanesulfinanilide with 2 equiv of *n*-butyllithium at −40 to −45° for 30 min afforded the dilithium salt **11** as evidenced by reaction with benzophenone to give the β-hydroxy sulfinamide **12** in 55% yield. Thermal decomposition of the adduct **12** at reflux in benzene for 5 hr produces 1,1-diphenylpropene in >98% yield. Similarly, 1-phenyl-1-propene was



obtained as a mixture of *trans* and *cis* isomers (ratio 1.6:1) in two steps from **11** and benzaldehyde.

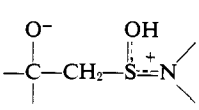
The thermal decomposition of β-hydroxy sulfinamides appears to be a general reaction which leads to olefins in good to excellent yields. It should be noted that carbonyl adducts of N,N-disubstituted sulfinamides, *e.g.*, **9**, yield olefins, if anything, more cleanly than do the corresponding *p*-toluidides or anilides. The real limitation of the sulfinamide route to olefins at present, therefore, is in that part of the process involving the generation of α-metallated sulfinamide reagents. The development of a method for the formation of these reagents in high yields and with broad applicability to any α-substituted sulfinamide would constitute an important advance. The techniques described here would appear adequate for the preparation of α-lithiosulfinamides possessing electron-withdrawing substituents at C_α, but inadequate for the generation of those carrying one or two bulky alkyl groups.

(4) R. L. Gay, S. Boatman, and C. R. Hauser, *Chem. Ind.* (London), 1789 (1965).

(5) The rates of elimination of the β-hydroxy sulfinamides from **6** and aldehydes are considerably slower than those for the adducts from ketones and, consequently, the higher boiling solvent, toluene, is more suitable for the formation of olefins derived from aldehydes. In addition, in these cases it is important that no water be present, since this leads to side reactions which diminish the yield of olefin.

It is worthy of mention that the α-lithio derivatives of alkanesulfinic acid esters are too unstable to be prepared by the techniques described here.[6]

With regard to the mechanism of formation of olefins from β-hydroxy sulfinamides, it is attractive to suppose that elimination occurs *via* intermediates of type **13** and **14**, the former being easily accessible because of the



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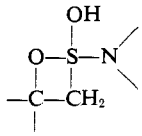


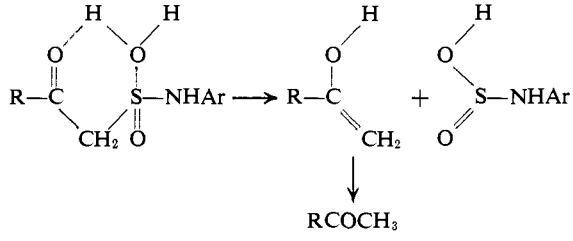
14

enhancement of basicity of the sulfinyl group by nitrogen. The same effect of nitrogen operates to prevent olefin-forming elimination from O-lithium salts of β-hydroxy sulfinamides. The supposition that elimination occurs *via* **13** and **14** is consistent with the demonstration of a preferred *cis* pathway for the elimination[7] and the much greater ease of such elimination from β-hydroxy sulfinamides than from the corresponding sulfoxides. Close similarities between the β-hydroxy sulfinamide and β-hydroxy phosphonamide[8] systems are apparent.

The reaction of 2 equiv of the dilithio derivative **6**, Ar = *p*-tolyl with esters affords, after addition of water, methyl ketones in good yield. For example, ethyl

$$\mathrm{RCOOR'} + 2\,\mathbf{6} \xrightarrow{\mathrm{THF}} \xrightarrow[0^\circ]{\mathrm{H_2O}} \mathrm{RCOCH_3}$$

benzoate, ethyl cyclohexanecarboxylate, and ethyl pivalate gave acetophenone, acetylcyclohexane, and pinacolone in 89, 84, and 93% yield, respectively. Methyl *n*-alkyl ketones and α,β-unsaturated ketones have also been prepared readily. β-Keto sulfinamides, which are reasonable intermediates in these reactions, are evidently extraordinarily unstable in the presence of water. This is also indicated by the observation that the oxidation of the β-hydroxy sulfinamide **5**, R_1 = C_6H_5, R_2 = H, with manganese dioxide in chloroform at 25° afforded directly acetophenone and not the corresponding β-keto sulfinamide. A number of plausible pathways suggest themselves for the remarkably facile conversion of β-keto sulfinamides to ketones, for example.



The results reported here open a new and interesting chapter in organosulfur chemistry. Although it is clear that many problems remain to be solved, it is equally apparent that opportunities abound for the development of a deeper understanding of the reactions of sulfinyl systems and for the discovery of new reactions. We are particularly intrigued with the possibilities for olefin synthesis from sulfoxide-derived carbanions and carbonyl compounds and we are currently investigating this subject in some detail.

Experimental Section

Melting points were determined using a Büchi apparatus with capillary tubes and are corrected. Infrared spectra were taken using a Perkin-Elmer Model 137 Infracord and nmr data were obtained using a Varian Associates Model A-60 spectrometer. Nmr shifts are expressed in parts per million downfield from internal tetramethylsilane. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and A. Bernhardt, Müllheim, Germany.

Tetrahydrofuran was purified just prior to use by distillation from lithium hydride. Alkyllithium reagents were commercial products from the Foote Mineral Co. All reactions involving alkyllithium reagents were carried out under nitrogen atmosphere.

Methanesulfinyl Chloride. Dimethyl disulfide (100 g, 1.06 mol) and glacial acetic acid (127 g, 2.12 mol) were placed in a 1-l., three-necked flask fitted with mechanical stirrer and cooled by means of a Dry Ice–acetone bath. Sulfuryl chloride (430 g, 3.18 mol) was added to this solution at such a rate that the temperature initially remained between −5 and +5°, later between −5 and −15°. The time for addition was about 1.5 hr. Work-up, carried out according to Douglass, *et al.*,[9] yielded 168 g (86%) of methanesulfinyl chloride. The nmr spectrum (CCl_4) showed a single peak at 3.37 ppm.

Ethanesulfinyl Chloride. The preparation was carried out as in the case of methanesulfinyl chloride. Diethyl disulfide (122 g, 1.0 mol), acetic acid (120 g, 2.0 mol), and sulfuryl chloride (405 g, 3.0 mol) gave 185 g (82%) of ethanesulfinyl chloride.[9]

N,N-Dimethylmethanesulfinamide. This compound was prepared in 60% yield by addition of methanesulfinyl chloride to excess dimethylamine in ether. The nmr spectrum (CCl_4) showed two singlets at 2.46 (relative area 1) and 2.69 ppm (relative area 2).[10]

Methanesulfinmorpholide. A stirred solution of 5.20 g (67 mmol) of morpholine and 8 ml of triethylamine in 150 ml of ether was cooled to −20° and treated with 6.58 g (67 mmol) of methanesulfinyl chloride. The reaction mixture was stirred for a further 30 min, then filtered to remove triethylammonium chloride. Evaporation of the ether and distillation of the residue yielded 5.64 g (56%) of methanesulfinmorpholide, bp 94–97° (0.5 mm). Nmr absorptions ($CDCl_3$) were at 2.52 (s, 3 H), 2.8–3.2 (m, 4 H), and 3.5–3.8 ppm (4 H).

Methanesulfin-*p*-toluidide. Methanesulfinyl chloride (9.50 g, 0.097 mol) was added over a 5-min period to a cooled solution of 10.0 g (0.094 mol) of *p*-toluidine and 15 ml of triethylamine in 300 ml of methylene chloride. The reaction mixture was stirred for an additional 30 min, then washed several times with water. The methylene chloride layer was dried and the solvent evaporated. Recrystallization of the residue from methylene chloride–pentane gave 14.4 g (86%) of colorless needles, mp 115–116° dec, with softening at 110° (lit.[11] mp 109–111°). The nmr spectrum ($CDCl_3$) showed singlets at 2.25 (3 H), 2.78 (3 H), 6.96 (4 H), and 7.65 ppm (broad, 1 H). The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ at 3.10 (m) and 9.50 (s) μ.

Ethanesulfinanilide. Ethanesulfinyl chloride (14.2 g, 0.126 mol) was added slowly to a stirred ice-cold solution of 12.1 g (0.130 mol) of aniline and 15.0 g (0.15 mol) of triethylamine in 300 ml of ether. The reaction mixture was stirred at 0° for a further 30 min and worked up in the usual manner. Ethanesulfinanilide, 16.7 g (77%), was obtained as a pale yellow gum which solidified on standing. Recrystallization from ether–pentane gave colorless needles, mp 71–72.5° (lit.[12] mp 72°). The nmr spectrum showed absorption at 1.21 (t, J = 7.5 cps; 3 H), 3.01 (q, J = 7.5 cps; 2 H), 6.9–7.3 (m, 5 H), and 7.90 ppm (broad singlet, 1 H).

Generation of Lithiodimethylaminosulfinylcarbanide and Reaction with Benzophenone. To a rapidly stirred solution of 610 mg (5.7 mmol) of N,N-dimethylmethanesulfinamide in 20 ml of tetrahydrofuran was added 5.8 mmol of *n*-butyllithium over a 30-sec period. After an additional 1 min, 950 mg (5.2 mmol) of benzophenone

(6) In contrast (see Experimental Section), the α-lithio derivative of methyl methanesulfonate ($LiCH_2SO_2OCH_3$) is formed cleanly with *n*-butyllithium in tetrahydrofuran at −78°, as shown by the isolation of adducts with benzophenone (91%) and cyclohexanone (76%).

(7) E. J. Corey and T. Durst, *J. Am. Chem. Soc.*, 90, 5553 (1968).

(8) E. J. Corey and G. T. Kwiatkowski, *ibid.*, 88, 5652, 5653 (1966).

(9) I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, 26, 1996 (1961).

(10) R. M. Moriarty, *ibid.*, 30, 600 (1965).

(11) I. B. Douglass and B. S. Farah, *ibid.*, 23, 805 (1958).

(12) A. Sonn and E. Schmidt, *Ber.*, 57, 1355 (1924).

was added as a tetrahydrofuran solution. The reaction mixture was stirred for 10 min at −78°, poured into water, and extracted with ether. The ether layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated to give an oily solid. Recrystallization from ether–pentane gave 661 mg of colorless solid which was shown to be approximately a 2:1 mixture of the β-hydroxy sulfinamide **9** and β-hydroxy sulfoxide **10** (R = n-C_4H_9) by nmr analysis. The mixture was placed on a silica gel column. Elution with benzene gave 1,1-diphenylethylene (from decomposition of **9**); with 10% ether in benzene the β-hydroxy sulfoxide **10** was eluted. Recrystallization of **10** from methylene chloride–pentane gave colorless needles, mp 118–120°.

Anal. Calcd for $C_{18}H_{22}O_2S$: C, 71.50; H, 7.33; S, 10.58. Found: C, 71.66; H, 7.37; S, 10.57.

The nmr spectrum ($CDCl_3$) showed absorption at 0.7–2.1 (m, 7 H), 2.70 (t, J = 7.0 cps; 2 H), 3.63 and 3.60 (AB quartet, J = 13.2 cps; 2 H), 5.72 (s, 1 H), and 7.2–7.7 ppm (m, 10 H). The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ at 2.91 (m), 9.50 (s), and 9.92 (s) μ.

Reaction of Methanesulfinmorpholide with *t*-Butyllithium. This reaction was carried out a number of times at −78 and −95° with variations in solvent and in the rate of addition of base. The best results were obtained at −95° using tetrahydrofuran and adding the *t*-butyllithium to the rapidly stirred sulfinamide solution in less than 5 sec. The average of three such runs gave an over-all yield of approximately 50% of an 8:1 mixture of sulfinamide and sulfoxide adducts as determined by nmr analysis. The use of toluene or ether as solvents gave inferior results.

When sulfinamide adduct (95% pure by nmr) was heated in benzene solution for 12 hr a 96% yield of 1,1-diphenylethylene was obtained.

Generation of the Dilithio Salt 5 of Methanesulfin-*p*-toluidide. To a rapidly stirred solution of 370 mg (2.2 mmol) of methanesulfin-*p*-toluidide in 40 ml of tetrahydrofuran at −78° under a nitrogen atmosphere was added dropwise 4.5 mmol of *n*-butyllithium over a 2-min period. Aliquots were removed after 20 and 80 min and quenched with deuterium oxide. The nmr spectra ($CDCl_3$) of the products obtained from both aliquots were identical. They showed absorption at 2.26 (s, 3 H), 2.76 (t, $J \sim 1$ cps; 2 H), 6.97 (s, 4 H), and 7.6 ppm (s, 1 H).

The dilithio salt **5** was stable for at least 3 hr at −78° but had a half-life of approximately 1 hr at 0° as judged by the yield of adduct formed with benzaldehyde (see below).

Reaction of the Dilithio Salt 5 with Ketones and Aldehydes. The reactions were carried out in the following manner. A tetrahydrofuran solution of the dilithio salt was prepared as described above. To this solution, kept at −78°, was added the carbonyl compound as a tetrahydrofuran solution. The reaction mixture was stirred for a further 10 min while warming to 0°. Work-up was effected by adding water and extracting with ether or methylene chloride. The organic extracts were dried over anhydrous magnesium sulfate and the solvent was evaporated. The yields refer to recrystallized material.

Benzophenone. A solution of 2.85 mmol of the dilithio salt **5** in 35 ml of tetrahydrofuran and 515 mg (2.85 mmol) of benzophenone yielded, after recrystallization from methylene chloride–pentane, 915 mg (97%) of β-hydroxy sulfinamide as colorless needles, mp 137–139° dec.

Anal. Calcd for $C_{21}H_{21}NO_2S$: C, 71.78; H, 6.02; S, 9.12. Found: C, 72.03; H, 6.00; S, 9.23.

The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ at 2.95 (m), 3.14 (m), 9.50 (s), and 11.2 (s) μ. Nmr absorption ($CDCl_3$) occurred at 2.25 (s, 3 H), 3.90 (s, 2 H), 5.6 (s, 1 H), and 6.7–7.6 ppm (m, 14 H).

Cyclohexanone. A solution of 3.92 mmol of dilithio salt **5** in 40 ml of tetrahydrofuran and 390 mg (4.0 mmol) of cyclohexanone gave an oily solid which was recrystallized from ether–pentane to give 716 mg (68%) of β-hydroxy sulfinamide adduct as colorless plates, mp 125–127° dec.

Anal. Calcd for $C_{14}H_{21}NO_2S$: C, 62.90; H, 7.92; S, 11.97. Found: C, 62.75; H, 7.81; S, 12.04.

The nmr spectrum ($CDCl_3$) showed singlets at 2.28 (3 H) and 3.15 ppm (2 H).

4-*t*-Butylcyclohexanone. Dilithio salt **5** (9.2 mmol) in 50 ml of tetrahydrofuran and 1.43 g (9.2 mmol) of 4-*t*-butylcyclohexanone gave, after recrystallization of the crude product from chloroform, 1.58 g (53%) of β-hydroxy sulfinamide as colorless plates, mp 158–159° dec. The yield based on recovered ketone was 94%.

Anal. Calcd for $C_{18}H_{29}NO_2S$: C, 66.84; H, 9.04; S, 9.90. Found: C, 66.59; H, 9.10; S, 9.99.

The infrared spectrum ("Kaydol" mull) showed λ_{max} at 3.01 (s), 9.68 (s), and 11.27 (m) μ.

Cyclopentanone. A solution of 1.70 mmol of the dilithio salt **5** in 20 ml of tetrahydrofuran and 143 mg (1.70 mmol) of cyclopentanone gave after recrystallization from methylene chloride–pentane 171 mg (40%) of β-hydroxy sulfinamide as shiny colorless plates, mp 141–143° dec.

Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.64; H, 7.56; S, 12.64. Found: C, 61.41; H, 7.23; S, 12.50.

Benzaldehyde. A solution of 6.36 mmol of **5** in 50 ml of tetrahydrofuran and 668 mg (6.4 mmol) of benzaldehyde yielded 1.64 g (97%) of sulfinamide, mp 127–139° dec (chloroform–pentane).

Δ³-Cyclohexenecarboxaldehyde. Δ³-Cyclohexenecarboxaldehyde (780 mg, 7.1 mmol) was added to 40 ml of tetrahydrofuran containing 6.1 mmol of **5**. The yield of β-hydroxy sulfinamide was 1.26 g (73% based on **5**), mp 160–162° dec.

Anal. Calcd for $C_{13}H_{21}NO_2S$: C, 64.49; H, 7.58; S, 11.46. Found: C, 64.35; H, 7.39; S, 11.60.

Dodecanal. Dilithio salt **5** (17.0 mmol) in 50 ml of tetrahydrofuran and 3.14 g of dodecanal gave 4.06 g (68%) of β-hydroxy sulfinamide, mp 130–145° dec.

Anal. Calcd for $C_{20}H_{35}NO_2S$: C, 67.95; H, 9.98; S, 9.05. Found: C, 67.66; H, 10.14; S, 8.88.

The nmr spectrum ($CDCl_3$) showed absorption at 2.25 (s, 3 H), 3.0 (t, J = 6 cps; 2 H), 6.97 (s, 4 H), and 7.85 ppm (broad singlet, 1 H).

Generation of the Dilithio Salt 11 of Ethanesulfinanilide. Reaction with Benzophenone. Tetrahydrofuran (8 ml) containing 132 mg (0.78 mmol) of ethanesulfinanilide was cooled to −40° and allowed to react with 1.6 mmol of *n*-butyllithium for 30 min. Benzophenone (145 mg, 0.78 mmol) was added and the solution, first green and then yellow, was allowed to warm to room temperature. The usual work-up left a yellow oil which upon addition of 10 ml of 1:1 ether–pentane deposited 148 mg (54%) of β-hydroxy sulfinamide **12**, mp 146–149° dec. The nmr spectrum ($CDCl_3$) showed a doublet at 1.49 ppm (J = 7.0 cps) and a quartet at 4.00 ppm (J = 7.0 cps). The adduct **12** decomposed slowly at room temperature and was not analyzed.

When 219 mg (0.66 mmol) of adduct **12** was heated in 5 ml of benzene and the reaction mixture worked up in the usual manner there was obtained 119 mg (98%) of 1,1-diphenylpropene as an oil which crystallized when scratched, mp 43–46° (lit.[13] mp 48°).

Reaction of 11 with Benzaldehyde. Ethanesulfinanilide (154 mg, 0.91 mmol) was dissolved in 8 ml of tetrahydrofuran and allowed to react with 1.96 mmol (10% excess) of *n*-butyllithium for 30 min at −40°. Benzaldehyde (102 mg, 0.96 mmol) was added, and the solution was slowly allowed to warm to room temperature. Work-up gave a yellow oil which was pyrolyzed by refluxing in dry toluene for 5 hr. Analysis of the pyrolysate by vapor phase chromatography (vpc) showed a 32% over-all yield of 1-phenylpropenes based on ethanesulfinanilide. The *trans*/*cis* ratio was 1.6 to 1.

Pyrolysis of the β-Hydroxy Sulfinamides Derived from Addition of 5 to Ketones. A. Benzophenone Adduct. A solution of 298 mg (0.85 mmol) of adduct in 6 ml of benzene was refluxed for 12 hr. The reaction mixture was washed with 20 ml of 10% hydrochloric acid. The benzene layer was dried and the solvent evaporated yielding 149 mg (99%) of 1,1-diphenylethylene (identified by comparison of the infrared and nmr spectra with those of an authentic sample). The aqueous phase was made basic and extracted with ether. Evaporation of the ether left 87 mg (96%) of an oil whose infrared spectrum (CCl_4) was identical with an authentic sample of *p*-toluidine.

In a second experiment it was shown that the decomposition of the adduct was complete after 5 hr of reflux time.

B. 4-*t*-Butylcyclohexanone Adduct. A solution of 480 mg (1.47 mmol) of adduct in 10 ml of benzene was refluxed for 12 hr. Work-up as above gave 185 mg (84%) of 4-*t*-butylmethylenecyclohexane (ir, nmr) and 142 mg (92%) of *p*-toluidine.

C. Cyclohexanone Adduct. Adduct (19.1 mg) and benzene (585 mg) were heated in a sealed soft glass tube at 85° for 15 hr. The yield of methylenecyclohexane as determined by vapor phase chromatography (vpc) was 84%. There was no evidence of isomerization to 1-methylcyclohexene.

D. Cyclopentanone Adduct. Adduct (16.4 mg) and benzene (553 mg) were heated as above for 15 hr. The yield of methylenecyclopentane (vpc) was 96%.

(13) P. Schoriger, *Ber.*, **41**, 2720 (1908).

Pyrolysis of the β-Hydroxy Sulfinamides Derived from Adducts of 5 with Aldehydes. General Procedure. Toluene was dried by cycling two or three times through a Soxhlet containing molecular sieves (Fisher A-5). The solid adduct was then introduced and the solution was refluxed for approximately 5 hr. The yields of olefin formed were determined by vapor phase chromatography (vpc).

A. Dodecanal Adduct. After a reflux time of 6 hr, the yield of 1-tridecene was 83%. When dry benzene was used as a solvent only 33% of 1-tridecene had formed after a reflux period of 18 hr.

B. Benzaldehyde Adduct. After a reflux time of 5 hr, the yield of styrene was 76%.

C. Δ^3-Cyclohexenecarboxaldehyde Adduct. A yield of 90% of 4-vinylcyclohexene was formed after 5 hr of reflux.

Reaction of the Dilithio Salt 5 with Esters. General Procedure. To a tetrahydrofuran solution of the dilithio salt **5** at −78° was added 0.5 equiv of ester, neat if liquid, or as a tetrahydrofuran solution if solid. The reaction mixture was stirred at −78° for 30 min and then poured into water and extracted with ether. The ether layer was dried over magnesium sulfate, and the solvent was evaporated. The methyl ketones were isolated by (a) triturating the crude reaction product with pentane in which the contaminant, methanesulfin-*p*-toluidide is insoluble or (b) filtering the crude product through a silica gel column; elution with pentane gave the pure ketone.

A. Ethyl Benzoate. The addition of 252 mg (1.68 mmol) of ethyl benzoate to 3.36 mmol of **5** in 30 ml of tetrahydrofuran gave an immediate deep red solution. Work-up according to method a gave 179 mg (89%) of acetophenone. The melting point of the 2,4-dinitrophenylhydrazone (DNPH) derivative was 238–240°.[14]

On another experiment, the crude ether extract was added to DNPH reagent. The yield of acetophenone dinitrophenylhydrazone was 97%. Finally 1 equiv of ester was treated with 1 equiv of **5**. The yield of acetophenone dinitrophenylhydrazone was 42%.

B. Ethyl Cyclohexanecarboxylate. Ethyl cyclohexanecarboxylate (710 mg, 4.15 mmol) and 4.15 mmol of **5** gave, after work-up according to method a, 477 mg (84%) of acetylcyclohexane. The nmr spectrum (CCl_4) showed the $COCH_3$ group at 2.02 ppm.

C. Ethyl Hexanoate. Ethyl hexanoate (288 mg, 1.58 mmol) and 3.16 mmol of **5** gave, after work-up a, 93 mg (52%) of 2-heptanone; DNPH mp 71–73° (lit.[14] mp 74°).

D. Methyl Stearate. Methyl stearate (290 mg, 0.97 mmol) in 10 ml of tetrahydrofuran was added slowly to 1.94 mmol of **5** in 30 ml of tetrahydrofuran at −78°. Much of the methyl stearate precipitated on addition to the cold anion solution. The reaction mixture was stirred for 2 hr at −78° during which time most of the ester dissolved. Purification according to b gave 136 mg (50%) of 2-nonadecanone, mp 50–52° (lit.[15] mp 55°).

E. Δ^1-Cyclohexenecarboxylate Phenyl Ester. Phenyl ester (465 mg, 2.3 mmol) was added to 4.6 mmol of **5** in 25 ml of tetrahydrofuran. The reaction mixture was stirred for 30 min at −78° during which time it became yellow. Purification of the crude product by method b gave 212 mg (75%) of 1-acetylcyclohexene (C=O 5.98 μ). The brick red DNPH had mp 200–202° (lit.[16] mp 204–205°).

F. Methyl Pivalate. Methyl pivalate (348 mg, 3.0 mmol) was added to 5.94 mmol of **5**. The reaction mixture was stirred at −78° for 10 min, poured into water, and extracted with ether. An aliquot of the ether extract was added to DNPH reagent and gave 93% of pinacolone 2,4-dinitrophenylhydrazone, mp 124–125° (lit.[14] mp 125°).

Generation of $LiCH_2SO_2OCH_3$ and Reaction with Benzophenone. Methyl methanesulfonate (770 mg, 7.0 mmol) was dissolved in 20 ml of tetrahydrofuran at −78° and allowed to react with 7.0 mmol of *n*-butyllithium for 1 min. Benzophenone (1.15 g, 6.3 mmol) was added and the reaction mixture stirred for 10 min at −78°. Work-up was effected by addition of water and extraction with ether. The yield of β-hydroxysulfonate ester was 1.67 g (91%), mp 88.5–89°.

Anal. Calcd for $C_{15}H_{16}O_4S$: C, 61.64; H, 5.55; S, 10.97. Found: C, 61.60; H, 5.52; S, 10.98.

The infrared spectrum showed $\lambda_{max}^{CCl_4}$ at 2.80 (m), 7.43 (s), 8.56 (s), and 10.0 (s) μ. The nmr spectrum ($CDCl_3$) showed absorption at 3.60 (s, 3 H), 4.13 (s, 2 H), 4.58 (s, 1 H), and 7.2–7.6 ppm (m, 10 H).

Reaction of $LiCH_2SO_2OCH_3$ with Cyclohexanone. To a solution of 8.0 mmol of the sulfonate ester carbanion in tetrahydrofuran at −78° was added 705 mg (7.2 mmol) of cyclohexanone. The reaction mixture was allowed to warm to room temperature and worked up in the usual manner to give 1.24 g of an oil. Trituration with pentane removed 88 mg of cyclohexanone. The remaining material crystallized when scratched. Recrystallization from ether–pentane gave colorless plates, mp 42–44°; yield of 76%, 86% based on recovered cyclohexanone.

Anal. Calcd for $C_8H_{16}O_4S$: C, 46.13; H, 7.75; S, 15.39. Found: C, 46.07; H, 7.73; S, 15.40.

The infrared spectrum showed $\lambda_{max}^{CCl_4}$ at 2.74 (w), 7.43 (s), 8.46 (s), and 10.0 (s) μ. Nmr peaks ($CDCl_3$) were at 1.4–1.9 (m, 10 H), 3.12 (s, 1 H), 3.31 (s, 2 H), and 3.92 ppm (s, 3 H).

Reaction of Methyl Methanesulfinate with *n*-Butyllithium at −78°. A solution of 445 mg (4.73 mmol) of methyl methanesulfinate in 25 ml of tetrahydrofuran at −78° was allowed to react with 4.8 mmol of *n*-butyllithium for 1 min. Benzophenone (490 mg, 2.8 mmol) was added and the reaction mixture stirred for 30 min at the low temperature. Work-up yielded benzophenone (97%) as the only ether-soluble product.

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