labilization of phosphorus to nucleophilic attack by the β-oxygen function.[8]

(8) We thank the National Institutes of Health for generous financial aid in the form of a research grant and postdoctoral fellowship.

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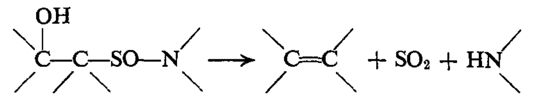
The Synthesis of Olefins and Ketones from Carbonyl Compounds and Sulfinamides

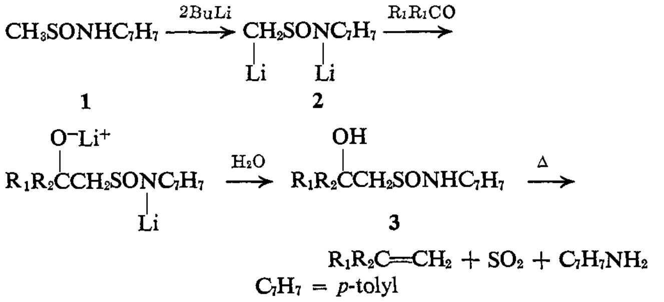
Sir:

A number of considerations led to the hypothesis that olefins might be produced from β-hydroxy sulfinic acid amides by an elimination of the form



We now report the observation of such reactions and a method of synthesis of the β-hydroxy sulfinyl system from carbonyl compounds and lithium salts of sulfinamides; together, these reactions constitute a new synthesis of olefins. Lithium salts of sulfinamides also react with carboxylic esters to form ketones in a one-step process.

Reaction of N-methanesulfinyl-*p*-toluidine (**1**)[1] in tetrahydrofuran at −78° with 2 equiv of *n*-butyllithium afforded a dilithio derivative (**2**)[2] in less than 20 min, as determined by deuteration with D_2O and nmr analysis. Treatment of the dilithio derivative **2** with 1 equiv of benzophenone afforded after hydrolysis the carbonyl addition product **3**, $R_1 = R_2 = C_6H_5$, in 97% yield.[3] The adduct **3**, $R_1 = R_2 = C_6H_5$, 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.



$$CH_3SONHC_7H_7 \xrightarrow{2BuLi} \underset{Li}{CH_2}SO\underset{Li}{N}C_7H_7 \xrightarrow{R_1R_2CO}$$

$$\mathbf{1} \qquad \mathbf{2}$$

$$R_1R_2\overset{O^-Li^+}{C}CH_2SO\underset{Li}{N}C_7H_7 \xrightarrow{H_2O} R_1R_2\overset{OH}{C}CH_2SONHC_7H_7 \xrightarrow{\Delta}$$

$$\mathbf{3}$$

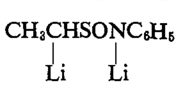
$$R_1R_2C{=}CH_2 + SO_2 + C_7H_7NH_2$$

C_7H_7 = *p*-tolyl

The dilithio derivative **2** 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 **2** is accompanied significantly (*ca.* 40%) by proton transfer to give an 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 **2** and cyclohexanone and cyclopentanone upon heating in benzene furnished methylenecyclohexane and methylenecyclopentane in *ca.* 90% yield.

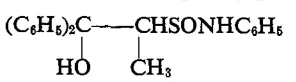
The conversion of aldehydes to olefins has also been demonstrated. Thus, benzaldehyde, Δ^3-cyclohexenecarboxaldehyde, and dodecanal react with the reagent **2** to form β-hydroxy sulfinamides in 98, 73, and 68% yield, respectively; these adducts are decomposed by heating in *dry* toluene at reflux for 5 hr to afford, respectively, styrene (76%), 4-vinylcyclohexene (90%), and 1-tridecene (83%).[4]

Treating N-ethanesulfinylaniline with 2 equiv of *n*-butyllithium at −40 to −45° for 30 min afforded the dilithium salt **4**, as evidenced by reaction with benzophenone to give the β-hydroxy sulfinamide **5** in 55% yield. Thermal decomposition of the adduct **5** at reflux in benzene for 5 hr produced 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 **4** and benzaldehyde.



$$CH_3\underset{Li}{C}HSO\underset{Li}{N}C_6H_5$$

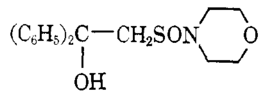
4



$$(C_6H_5)_2\underset{HO}{C}{-}\underset{CH_3}{C}HSONHC_6H_5$$

5

Adducts from N,N-disubstituted sulfinamides and aldehydes or ketones, *e.g.*, the morpholide **6**, decompose cleanly to olefins at 80° in dry benzene (96% 1,1-diphenylethylene from **6**). However, the generation of α-lithio N,N-disubstituted sulfinylamides is complicated by the tendency of these intermediates to decompose to sulfines. Thus, reaction of methanesulfinylmorpholine with *t*-butyllithium[5] (added rapidly) at −78° in tetrahydrofuran led to the formation of the desired reagent **7**, X = morpholide, and the undesirable by-product **7**, X = *t*-butyl (presumably from $H_2C{=}SO$ and *t*-butyllithium), in a ratio of *ca.* 8:1 and a total yield of only *ca.* 50%, as determined by isolation of the corresponding adducts with benzophenone. As expected from this result, the α-lithio derivatives of alkanesulfinic acid esters are too unstable to be prepared by the techniques described here.[6] The presence of electron-withdrawing groups at C_α should facilitate the generation of α-anions from sulfinic acid N,N-disubstituted amides and esters; however, this has not been studied as yet.



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$LiCH_2SOX$

7

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 **8** and **9**, the former being easily accessible because of the

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[1] Prepared from *p*-toluidine and methanesulfinyl chloride; the acid chloride was obtained by the procedure of I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, 26, 1996 (1961).

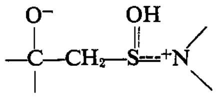
[2] See R. L. Gay, S. Boatman, and C. R. Hauser, *Chem. Ind.* (London), 1789 (1965), for an analogous metalation of acetanilide.

[3] The new compounds reported herein have been characterized satisfactorily by elemental analysis and/or spectroscopic (nmr, infrared) measurement.

[4] The rates of elimination of the β-hydroxy sulfinamides from **2** 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.

[5] This is a more satisfactory reagent than *n*-butyllithium in this case.

[6] In contrast, 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%).



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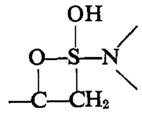


9

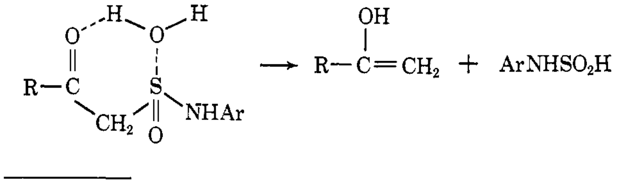
enhancement of basicity of the sulfinyl group by nitrogen. The same effect of nitrogen operates to prevent olefin-forming elimination from O-lithium salts of β-hydroxy sulfinamides. Close similarities between the β-hydroxy sulfinamide and β-hydroxy phosphonamide[7] systems are apparent.

We have also discovered that certain β-hydroxy sulfoxides can be converted to olefins by an elimination of the vicinal hydroxyl and sulfinyl functions. Thus, the β-hydroxy sulfoxide from benzophenone and methylsulfinylcarbanion[8,9] is converted to 1,1-diphenylethylene in 45% yield by heating to *ca.* 160° at 0.3 mm. Furthermore, acid catalysis of this elimination has been noted in the case of the β-hydroxy sulfoxide from benzophenone and phenylsulfinylcarbanion which decomposes with 10% sulfuric acid in 95% ethanol at 25° for 15 hr to give 1,1-diphenylethylene in 65% yield. Olefin formation from β-hydroxy sulfoxides is potentially an extremely important reaction, and this too is being pursued.

The reaction of 2 equiv of the dilithio derivative **2** with esters affords, after addition of water, methyl ketones in good yield. For example, ethyl benzoate,

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

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 **3**, $R_1 = C_6H_5$, $R_2 = H$, 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[10]



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(7) E. J. Corey and G. T. Kwiatkowski, *J. Am. Chem. Soc.*, **88**, 5653 (1966).

(8) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962); **87**, 1345 (1965).

(9) E. J. Corey and M. Chaykovsky, *J. Org. Chem.*, **28**, 254 (1963).

(10) This work was supported by the National Institutes of Health.

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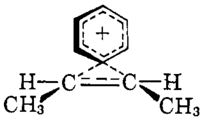
The Behavior of the 3-Phenyl-2-butanols in SO_2–FSO_3H–SbF_5[1]

Sir:

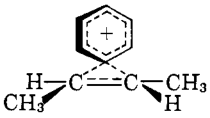
Having recently reported the direct observation of the aryl-bridged anthrylethyl cation,[2] we were very interested in the possibility of observing simpler analogs of this species. In this connection, Olah and Pittman[3] have recently reported the direct observation of phenonium ions from β-arylalcohols in SO_2–FSO_3H–SbF_5 at −60°. In particular, they reported that both *threo*- and *erythro*-3-phenyl-2-butanols (I-OH and II-OH) give an equimolar mixture of *cis*- and *trans*-phenonium ions III and IV in this medium. The spectrum from either alcohol was reported to show methyl doublets at δ 1.37 and 1.68, a methine multiplet assigned to the C_2 and C_3 protons at δ 3–3.5, and a quartet at δ 8.02 and a doublet at δ 9.54 assigned to the aromatic protons. It was reported that the areas were in accord with theory, and quenching of the solution led to a good yield of monomer alcohols and olefins.

threo-$CH_3CH(C_6H_5)CH(OH)CH_3$
I-OH



III

erythro-$CH_3CH(C_6H_5)CH(OH)CH_3$
II-OH



IV

There are several troublesome features of the report of Olah and Pittman. On mechanistic grounds it was very difficult to understand a lack of stereospecificity in the formation of phenonium ions and yet no accompanying major production of benzylic ion from hydride shift. As regards their reported nmr spectrum, the δ 8.02 signal which appeared as an AB-like quartet seemed more appropriate for the A_2B_2 pattern of a *para*-disubstituted benzene than for a phenonium ion.[4] Our own examination of this system has shown that phenonium ions are not generated from I-OH and II-OH in SO_2–FSO_3H–SbF_5.

In SO_2–FSO_3H–SbF_5 medium, the *threo*- and *erythro*-I-OH and -II-OH do not give rise to identical spectra. When *threo*-I-OH was extracted from pentane into HSO_3F–SbF_5–SO_2 at −78°, the nmr[5,6] at −52° showed five signals at chemical shifts approximately as reported by Olah and Pittman. These were

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(1) Research supported in part by the National Science Foundation.

(2) L. Eberson and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3506 (1965).

(3) G. A. Olah and C. U. Pittman, Jr., *ibid.*, **87**, 3509 (1965).

(4) The methyl signals for the assumed *cis*- and *trans*-phenonium ions would be expected to be more complex than those reported: F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961).

(5) All chemical shifts (δ) are reported in parts per million downfield from TMS using internal CH_2Cl_2 (δ 5.30) as the secondary standard.

(6) Viscosity broadening of peaks is observed in some cases, and this depends on the ratio of reagents used. Sharp spectra were obtained with mole ratios of FSO_3H–SbF_5–SO_2–ROH of 1:1:4:0.2 and 6.5:1:5:0.5. Severe viscosity broadening occurred below −45° with 3.5:1:4.5:0.5 mole ratios.