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A NOVEL SYNTHESIS OF VICINALLY N,S-DISUBSTITUTED OLEFINS FROM LITHIO SULFENYLTRIMETHYLSILYLMETHANE AND AMIDE

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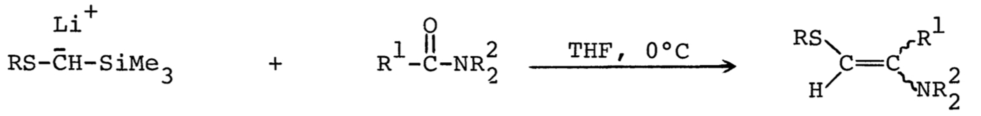
Vicinally N,S-disubstituted olefins are synthesized in good yields from amides by treating with lithio sulfenyltrimethylsilylmethanes.

Vicinally N,S-disubstituted olefins (β-sulfenylenamines) 3 are expected to be very versatile synthetic reagents. They will have chemical property of either or both of an enamine and a vinyl sulfide, and products arising from this reagent will include more than one functional groups which must be applicable to further synthetic reactions. These will make this class of compounds valuable as a "multi-functionalized" reagent. However, such olefins can not readily be prepared from amines or thiols and thus the chemistry of this olefin has not been well studied.1)

We found a facile preparative method for the vicinally N,S-disubstituted olefins, treating amides 2 with carbanions 1 stabilized by a silyl group and sulfur.



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Olefin-forming reactions of the carbanions with ketones are well-known,2) but only a few reports mention this type of reaction with amides.3) The present method affords the olefins 3 in good yields under mild conditions and the results are summarized in Table. The (E)-olefins were predominant over the corresponding (Z)-isomers except when R^1 was a tert-butyl group. The structures of these products were determined on the basis of spectral data and elemental analyses.4)

A typical procedure is as follows. To a THF solution (10 ml) of phenylthiotrimethylsilylmethanes5) treated with 7 ml (10 mmol) of butyllithium (15% in hexane)

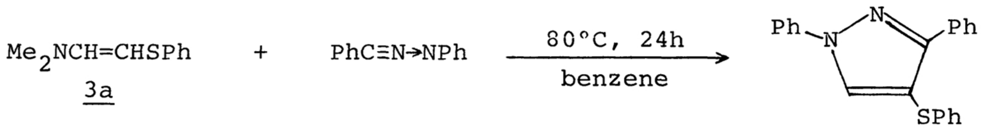
Table. Reaction of Lithio Sulfenyltrimethylsilylmethanes $\underline{1}$ and Amides $\underline{2}$

$RS\text{-}\bar{C}HSiMe_3\cdot Li^+$ ($\underline{1}$)	$R^1CONR^2_2$ ($\underline{2}$)		$RSCH{=}C(R^1)NR^2_2$ ($\underline{3}$)	
R	R^1	R^2_2	Yield (%)	E : Z*
Ph	H	Me_2	64	100: 0
Ph	t-Bu	Me_2	40	20:80
Ph	Ph	Me_2	44	96: 4
Ph	Ph	$-(CH_2)_2-$	87	80:20
Ph	Ph	$-(CH_2)_5-$	55*	100: 0
Me	Ph	$-(CH_2)_5-$	72*	87:13

*Determined by nmr

at 0°C, 0.64 g (10 mmol) of N,N-dimethylformamide in 10 ml of THF was added dropwise at the same temperature. The solution became colorless and was allowed to stand overnight at room temperature. The cooled reaction mixture was washed with 10 ml of water and the separated organic layer was dried over $CaSO_4$. Distillation under reduced pressure gave 1.14 g (64%) of 1-dimethylamino-2-phenylthioethylene (3a).

The olefins prepared in this way have been found to react with several reagents as enamines: for example, the reaction of the N,S-disubstituted olefin $\underline{3a}$ with a nitrile imine gave a pyrazole derivative (yield 40%).[6] Thus, this type of olefins



is a good reagent which incorporates a sulfenyl substituent to heterocycles and the further application of the olefins to organic syntheses is in progress.

References and Notes

1) H. Matsuda, K. Hirai and Y. Kishida, Ann. Sankyo Res. Lab., 24, 96 (1972).
2) D. J. Peterson, J. Org. Chem., 33, 780 (1968).
3) a) D. Seebach, M. Kolb, and B. Thomasbröbel, Chem. Ber., 106, 2277 (1973).
b) R. P. Woodbury and M. W. Rathke, Tetrahedron Lett., 709 (1978).
4) The spectral and analytical data, for example, of the olefin $\underline{3a}$ are as follows: ir (neat) 1630 cm^{-1} (C=C); nmr ($CDCl_3$) δ 2.77 (s, 6H), 4.63 (d, 1H, J = 13 Hz), 6.63 (d, 1H, J = 13 Hz), 6.8-7.4 (m, 5H, Ph) [the configuration of the olefin was decided by the coupling constant]; mass spectrum m/e 179 (M^+), 134 ($M^+ - HNMe_2$); elemental analysis, Found C, 66.88; H, 7.43; N, 7.52; S, 18.15 (Calcd. C, 67.02; H, 7.31; N, 7.82; S, 17.86).
5) These methanes are prepared by silylation of corresponding sulfides in TMEDA-THF; D. J. Peterson, J. Org. Chem., 32, 1717 (1967).
6) The spectral and analytical data of the product are as follows: nmr ($CDCl_3$) δ 6.8-8.2 (all protons); mass spectrum m/e 328 (M^+). Elemental analysis: Found C, 76.78; H, 4.75; N, 8.52; S, 9.66 (Calcd. C, 76.81; H, 4.91; N, 8.53; S, 9.75).

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