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S-TRIMETHYLSILYL BENZOPHENONE THIOOXIME, $Ph_2C=NSSiMe_3$. A MODERATELY STABLE THIOOXIME PRECURSOR

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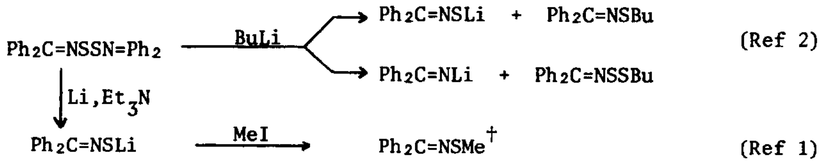
Summary: The title compound, $Ph_2C=NSSiMe_3$, is a useful precursor for thiooximes, including the unstable $Ph_2C=NSH$.

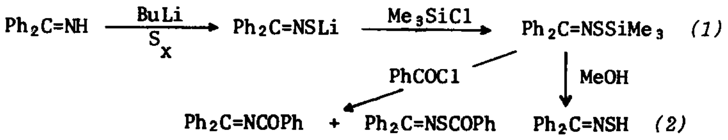
In 1974, simultaneous publications described the generation[1,2] and alkylation[1] of oxygen-sensitive, although otherwise stable, thiooximate ions by two routes (Scheme 1) starting from bis(methylenamine)disulphides. Barton and his colleagues[1] also showed that the thiooximate ion (derived from the bisfluorene-9-ylidene system) could be reversibly protonated at -70°, a result which, taken in conjunction with methylation (diazomethane) experiments, provided strong evidence for the existance of a free thiooxime, $R_2C=NSH$.



Scheme 1

We describe below:

1. An alternative approach to lithium thiooximates (treatment of an imine with BuLi followed by sulphur) which is relatively free from the potentially troublesome byproducts associated with either of the disulphide cleavage methods[1,2];
2. Preparation of a moderately stable *S*-trimethylsilyl derivative of benzophenone thiooxime *(1)* and
3. Reactions of *(1)*, including methanolysis at low temperature which provides an essentially 'neutral' route to free benzophenone thiooxime *(2)*, as illustrated in Scheme 2.



Scheme 2

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† Accompanied by $Ph_2C=NSSMe$, presumably formed by alkylation of $Ph_2C=NSSLi$ resulting from N-S (as opposed to S-S) cleavage.

$Ph_2C{=}NSSiMe_3$ (1)

A suspension of sulphur (70 mmol) in Et_2O (25 cm^3) was added at room temperature to a stirred solution of $Ph_2C{=}NLi$, prepared from $Ph_2C{=}NH$ (50 mmol) and BuLi (70 mmol) in Et_2O (90 cm^3), and a bright orange-red solid formed during 4h. The mixture was then cooled in liquid N_2 and Me_3SiCl (80 mmol) was added. Upon warming to room temperature, LiCl precipitated from the now yellow solution. After 3h further stirring, solvent was removed under reduced pressure and the remaining yellow oil was carefully filtered under N_2 to remove LiCl and unreacted sulphur. The filtrate was held under high vacuum (0.01 mmHg) at room temperature in order to remove $BuSSiMe_3$, the excess of Me_3SiCl and traces of $Ph_2C{=}NH$. The residual yellow oil was shown by t.l.c. to be free from impurities (Yield 95%). (Found: C, 67.5; H, 6.7; N, 5.0. $C_{16}H_{19}NSSi$ calcd.: C, 67.3; H, 6.7; N, 4.9%). N.m.r. (CCl_4): 2.3-3.2τ(m, 10H, C_6H_5), 10.0τ(s, 9H, CH_3). UV λ_{max}(hexane): 240, 290, 328(sh)nm. The product *(1)* was stable for prolonged periods at -25^0 but decomposed at room temperature (half life *ca.* 1 day) with liberation of sulphur. Attempts to prepare *(1)* from samples of $Ph_2C{=}NLi$ made from $Ph_2C{=}NSSN{=}CPh_2$ and Li,Et_3N[1] or BuLi[2] gave the desired product contaminated with significant amounts of $Ph_2C{=}NSiMe_3$, $Ph_2C{=}NSBu$ and $Ph_2C{=}NBu$.

$Ph_2C{=}NSH$ (2)

An n.m.r. tube was charged with a 0.5M solution of *(1)* in $CDCl_3$ with TMS as external lock. The tube was cooled to -50^0 and anhydrous MeOH (1 equiv.) in $CDCl_3$ was added quickly and the spectrum was recorded after 15 min. In addition to existing resonances associated with *(1)* *(vide supra)*, a new resonance of integral 1H appeared at 4τ, which we assign to $Ph_2C{=}NS\underline{H}$ on the basis of a comparison of chemical shifts: *viz.* thiols (SH, *ca.* 8.7τ)[3], MeOH (OH, 6.1τ), oximes (OH, 0.0 to -0.2τ)[4] and $Ph_2C{=}NH$ (NH, 0.32τ)[5]. Upon warming to room temperature, the signal at 4τ collapsed irreversibly and a precipitate of sulphur formed in the n.m.r. tube.

Reaction between *(1)* and PhCOCl

When PhCOCl (10 mmol) in mesitylene (10 cm^3) was added to an ice-cold solution of *(1)* (10 mmol) in the same solvent (10 cm^3), an exothermic reaction ensued and the temperature of the mixture rose to 20^0. After stirring for 1h, the resulting white precipitate was filtered off and fractionally crystallised from CCl_4 to give a 1:1 mixture of $Ph_2C{=}NCOPh$ and $Ph_2C{=}NSCOPh$.

Acknowledgment

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