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A SIMPLE, HIGHLY VERSATILE SYNTHESIS OF CYCLOPROPYL PHENYL SULFIDES

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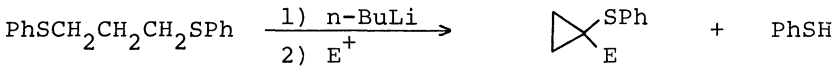
1,3-Bis(phenylthio)propane reacted readily with 2-2.2 equiv. of n-butyllithium in THF at 0°C to afford 1-lithiocyclopropyl phenyl sulfide. Treatment of the substituted 1,3-bis(phenylthio)propanes with 1.1 equiv. of n-butyllithium afforded the corresponding cyclopropanes in good yields.

1-Lithiocyclopropyl phenyl sulfide is a useful reagent for the synthesis of cyclobutanone derivatives,[1] γ-ketosulfides, β-bromoethyl vinyl sulfides.[2] Recently, Cohen found an efficient route to the lithium derivatives of cyclopropanes.[3] We now wish to report an extremely facile method for the preparation of 1-lithiocyclopropyl phenyl sulfide. Treatment of 1,3-bis(phenylthio)propane[4] (I) with 2-2.2 equiv. of n-butyllithium in THF at 0°C followed by addition of electrophilic trapping reagents gave the cyclopropanes (II) in good yields (Table 1).



(I) (II)

Reaction of a variety of alkyl substituted 1,3-bis(phenylthio)propanes with 1.1 equiv. of n-butyllithium gave the corresponding cyclopropanes in good isolated yields.

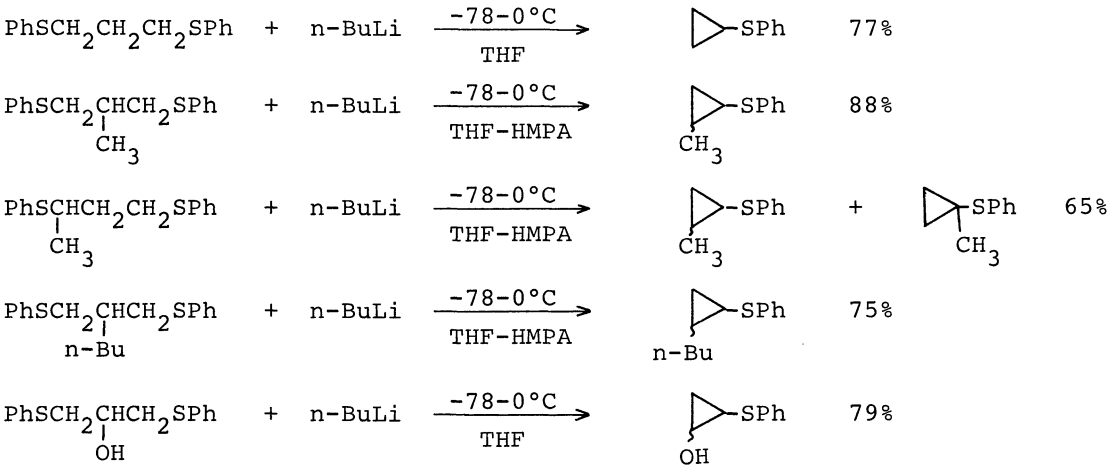
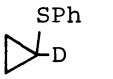
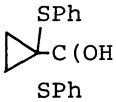
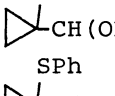
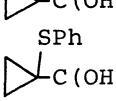
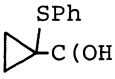
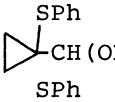
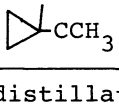
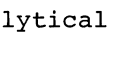


Table I. Preparation of cyclopropanes (II) from 1,3-bis(phenylthio)propane (I)

(I) mmol	n-BuLi mmol	Electrophile[a]	Product (II)[b]	Yield (%)	b.p. °C/Torr
20	44	D_2O		65	84-87/3.5
20	44	4-Heptanone		71	140/0.9
20	44	Benzaldehyde		67	c
20	44	Cyclohexanone		60	c
20	44	3-Pentanone		69	126-128/0.9
20	40	3-Pentanone[d]		85	126-128/0.9
20	40	Heptanal[d]		59	151-152/0.8
20	40	2-Hexanone[d]		65	129/0.6

a) 10 mmol scale. b) Isolated by distillation or chromatography on silica gel and adequately characterized by analytical and spectral data. c) Oil. d) CuI (20 mmol) was added.

This approach can be extended to the preparation of cyclopropanol. Thus, reaction of 2-hydroxy-1,3-bis(phenylthio)propane with 2.2 equiv. of n-butyllithium followed by quenching with saturated aqueous ammonium chloride solution gave 2-hydroxycyclopropyl phenyl sulfide.

The experimental simplicity and use of readily available 1,3-bis(phenylthio)-propanes make the present method highly advantageous for the synthesis of cyclopropane derivatives.

References

1) a) B. M. Trost, Acc. Chem. Res., 7, 85 (1974). b) B. M. Trost, D. Keeley, and M. J. Bogdanowicz, J. Am. Chem. Soc., 95, 3068 (1973). c) B. M. Trost and D. E. Keeley, *ibid.*, 96, 1252 (1974). d) B. M. Trost and D. E. Keeley, *ibid.*, 98, 248 (1976). e) B. M. Trost, D. E. Keeley, H. C. Arndt, and M. J. Bogdanowicz, *ibid.*, 99, 3088 (1977).

2) a) R. D. Miller and D. R. McKean, Tetrahedron Lett., 1979, 583. b) R. D. Miller, D. R. McKean, and D. Kaufmann, *ibid.*, 1979, 587. c) S. Halazy and A. Krief, *ibid.*, 1979, 4233.

3) a) T. Cohen and W. M. Daniewski, Tetrahedron Lett., 1978, 2991. b) T. Cohen, W. M. Daniewski, and R. B. Weisenfeld, *ibid.*, 1978, 4665.

4) 1,3-Bis(phenylthio)propane was prepared in 93% yield from 1,3-dibromopropane and sodium benzenethiolate.[5]

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