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A Preparative Route to 2-Substituted 1,1-Diphenylthio Cyclobutanes[1a)]

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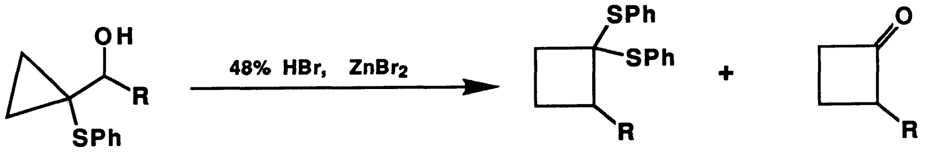
Treatment of 1-phenylthiocyclopropylcarbinyl alcohols with thiophenol and $HBr/ZnBr_2$ gives 2-alkyl (and 2-aryl) 1,1-diphenylthiocyclobutanes.

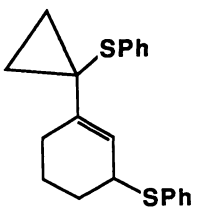
Previous work showed that amines and organocuprates attack the cyclopropane ring of cyclopropylcarbinyl halides to give the homoallylic substitution product. The reaction with amines was second order and shown to be an homoallylic S_N2' but the organocuprate ring opening was a metal mediated radical reaction.[3)] Our synthesis of functionalized vinyl sulfides via homoallylic substitution[4)] required the preparation of 1-phenylthio-1-cyclopropyl halides from the corresponding alcohol, **1**.



1 *2* *3*

We anticipated that **1** would give the bromide, cyclobutanone **3** or the β-ketosulfide observed by Miller.[6)] To our surprise, reaction with $HBr/ZnBr_2$ converted **1a** to a 1:1 mixture of **3a** and the unprecedented **2a**. Addition of excess thiophenol led to synthetically useful yields of **2**, as shown in Table 1. The conjugating phenyl group in **1d** was expected to give sulfides such as **4**, analogous to products obtained by Trost[7a)] and Gadwood.[7b)] $HBr/ZnBr_2$ with thiophenol converted **1d** to 63% of bis-sulfide **5** and 27% of **2d** but 25 equivalents of thiophenol and heating (65 ℃) increased the yield of **1d** to 67%, with only 23% of **5**.

Thiols other than thiophenol can be added to the reaction medium, giving unusual 'mixed' dithioketals (SPh, SR). Reaction of **1a** with excess propanethiol



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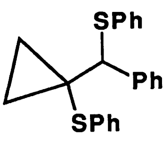

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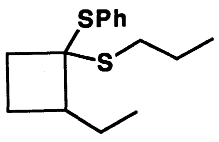

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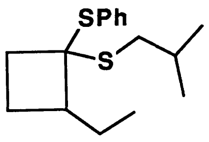

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(25 ℃, 10 $ZnBr_2$, 25 RSH) gave **6** in 72% and excess 2-methylpropanethiol gave **7** in 65%. The ability to form cyclobutane dithioketals is a new and interesting addition to the rich chemistry of cyclopropylcarbinyl alcohols.

Table 1. Conversion of 1-Phenylthiocyclopropylcarbinyl Alcohols to 1,1-Diphenylthiocyclobutanes with Aq. $HBr/ZnBr_2$

Alcohol	R	Dithioketal	% 2	% 5
1a[8)]	Et	**2a**	95[a)]	0
			45[c,e)]	0
1b	iPr	**2b**	92[a)]	0
			59[c,f)]	0
1c	c-C_6H_{11}	**2c**	92[a)]	0
1d	Ph	**2d**	27[d)]	63
			36[a)]	54
			67[b)]	23

[a)] RT, 5 PhSH. [b)] 65 ℃, 25 PhSH. [c)] RT, no PhSH. [d)] RT, 1 PhSH.
[e)] 48% **3a**. [f)] 10% **3b**.

References

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6) R.D. Miller and D.R. McKean, Tetrahedron Lett., 1979, 583; R.D. Miller, D.R. McKean, and D. Kaufann, ibid., 1979, 587.

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8) Addition of 2.70 g (12.4 mmol) of **1a** to 4.0 g of $ZnBr_2$ in 3.5 mL of 48% HBr at -10 ℃ was followed by stirring for 2 h at 0 ℃. The slurry was overlaid with 100 mL of pentane and poured onto 250 mL of ice cold water, overlaid with 500 mL of pentane. Drying ($MgSO_4$), removal of solvents and chromatography (SiO_2/pentane) gave 3.54 g (11.8 mmol, 95%) of 2-ethyl-1,1-diphenylthiocyclobutane, **2a**: ^1H NMR ($CDCl_3$): δ 0.6 (t, 3H), 1.3-2.0 (m, 6H), 2.3 (m, 2H), and 6.8-7.5 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): δ 11.6 (t), 23.2 (t), 24.2 (t), 32.7 (t), 50.2 (d), 66.3 (s), 127.2 (s), 128.6 (s), 128.7 (s), 134.0 (s), and 136.0 ppm (s); Mass spectrum (m/z, Rel. intensity): 300 (5,P), 244 (2), 223 (15), 191 (100), 135 (75), and 81 (70).

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