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A $[2^+ +4]$ POLAR CYCLOADDITION OF α-CHLOROSULFIDES WITH CONJUGATED DIENES: ONE-POT SYNTHESIS OF 1-ACYL- AND 1-CYANO-1-METHYLTHIO-2-VINYLCYCLOPROPANES

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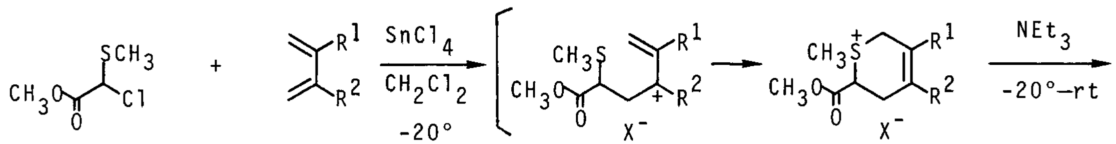
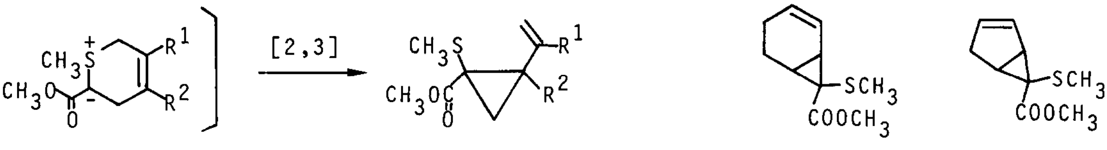
Summary: In the presence of $SnCl_4$, methoxycarbonyl-, acetyl-, benzoyl-, or cyano-substituted chloromethyl methyl sulfide (1-4) undergoes $[2^+ +4]$ polar cycloaddition with conjugated dienes to afford the cycloadducts of type 7, which, on treatment with base, are converted into the 1-acyl- or 1-cyano-1-methylthio-2-vinylcyclopropanes 9-10 *via* the ylide intermediates of type 8.

In the last few years, increasing interest has been generated to a study of Lewis acid promoted cationic polar cycloaddition with α-chlorosulfides. Phenylthiomethyl chlorides afford $[4^+ +2]$ polar cycloaddition products by reaction with alkenes,[1,2] alkynes,[1] or nitriles,[3] and α-acyl-α-chlorosulfides undergo $[3^+ +2]$ cycloaddition with alkenes[2] or alkynes[4] to give furan derivatives. In the present communication, we wish to report that the α-acyl- or α-cyano-α-chlorosulfides 1-4 react with conjugated dienes in a $[2^+ +4]$ fashion to give the cycloadducts of type 7, which are converted, with base *in situ*, into the vinylcyclopropane derivatives 9-12 *via* the ylide intermediates of type 8.



1 5a,b 6a,b 7a,b

a: $R^1=R^2=CH_3$, b: $R^1=H$, $R^2=CH_3$



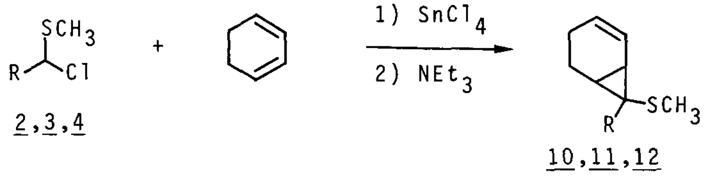
8a,b 9a,b 9c 9d

The following procedure for preparation of the vinylcyclopropane 9a ($R^1=R^2=CH_3$) is representative. A solution of methyl α-chloro-α-(methylthio)-acetate (1) (6.5 mmol) and 2,3-dimethyl-1,3-butadiene (5a: $R^1=R^2=CH_3$) (7.2 mmol) in dry CH_2Cl_2 (24 ml) was treated with $SnCl_4$ (6.5 mmol) at -20°C for 10 min. The reaction was quenched by addition of triethylamine (35 mmol) and the resulting mixture was allowed to warm to room temperature, and then poured into dry ether. The precipitated salts were removed by filtration and the filtrate was distilled *in vacuo* to give 9a[5] in 71% yield (based on 1).

By the same procedure as above, isoprene (5b: $R^1=H$, $R^2=CH_3$), 1,3-cyclohexadiene, and cyclopentadiene gave 9b ($R^1=H$, $R^2=CH_3$), 9c, and 9d in 75, 57, and 39% yields, respectively.

The formation of the vinylcyclopropanes 9 may be best explained as follows. The chloride 1 attacks with the aid of $SnCl_4$ on the olefinic bond of the diene 5 to form a new cationic intermediate 6, which undergoes cyclization by nucleophilic attack of its sulfur atom to an olefinic bond in an S_N1'-like manner giving the $[2^+ +4]$ cycloadduct 7. Subsequent deprotonation of the adduct 7 with triethylamine forms the sulfonium ylide 8, which undergoes [2,3] sigmatropic rearrangement to give 9.[6]

The reactions of α-chloro-α-(methylthio)acetone (2), ω-chloro-ω-(methylthio)acetophenone (3), and α-chloro-α-(methylthio)acetonitrile (4) with 1,3-cyclohexadiene under almost the same conditions as described above afforded the corresponding vinylcyclopropanes 10 (43%), 11 (53%), and 12 (57%), respectively.



2 and 10: $R=COCH_3$
3 and 11: $R=COC_6H_5$
4 and 12: $R=CN$

Cyclopropanes bearing acyl and/or vinyl groups are versatile intermediates in organic synthesis, and hence the present one-pot synthesis of this class of compounds is of great preparative value.

References and Notes

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2) M. Wada, T. Shigehisa, H. Kitani, and K. Akiba, *Tetrahedron Lett.*, 24, 1715 (1983).
3) D. K. Thakur and Y. D. Vankar, *Synthesis*, 1983, 223.
4) H. Ishibashi, S. Akai, H.-D. Choi, H. Nakagawa, and Y. Tamura, *Tetrahedron Lett.*, 24, 3877 (1983).
5) bp 65-66°C/1 mmHg, IR: 1720 cm^{-1}, ^1H-NMR: δ 1.24 (s, 3H, $-\overset{|}{\underset{|}{C}}-CH_3$), 1.55-1.9 (m, 5H, $=\overset{|}{C}CH_3$ and CH_2), 2.10 (s, 3H, SCH_3), 3.75 (s, 3H, OCH_3), 4.80-5.05 (m, 2H, $=CH_2$). All new cyclopropane derivatives were obtained as single stereoisomer, whose stereochemistry is unknown.
6) An anologous $[2^+ +4]$ type polar cycloaddition, which consists of treating of 1,3-dithienium fluoroborate with 1,3-dienes, has been reported; E. J. Corey and S. W. Walinsky, *J. Am. Chem. Soc.*, 94, 8932 (1972).

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