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CATIONIC POLAR CYCLOADDITION WITH CHLOROMETHYL PHENYL SULFIDES

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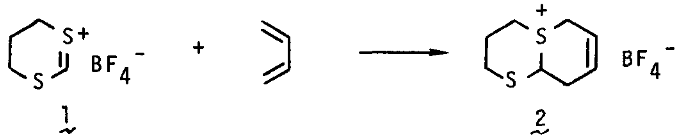
Summary: Chloromethyl phenyl sulfides 3 underwent $[4^{+}+2]$type polar cycloadditions with styrene, *trans*-stilbene, and phenylacetylene in the presence of stannic chloride to afford the thiochroman 4, 5 and thiochromen derivatives 6. Under the same reaction conditions, N-allyl-α-chloro-α-(phenylthio)acetamide (7) gave the intramolecular cycloaddition product 8.

Cycloadditions with positively charged ionic components are known as "cationic polar cycloadditions".[1] A number of polar systems capable of cycloadditions have been described in the literature. In particular, the polar systems containing nitrogen-stabilized carbocation have been extensively investigated.[2] However, the cycloaddition with the system containing sulfur-stabilized carbocation has received scant attention; the only reported example is the reaction of 1,3-dithienium fluoroborate (1) with cojugated dienes giving the $[2^{+}+4]$ type polar cycloaddition products 2.[3] We have now found that chloromethyl phenyl sulfides 3a,b,c undergo $[4^{+}+2]$ type polar cycloaddition with nucleophilic multiple bonds in the presence of stannic chloride ($SnCl_4$) to afford the thiochroman and thiochromen derivatives 4-6.



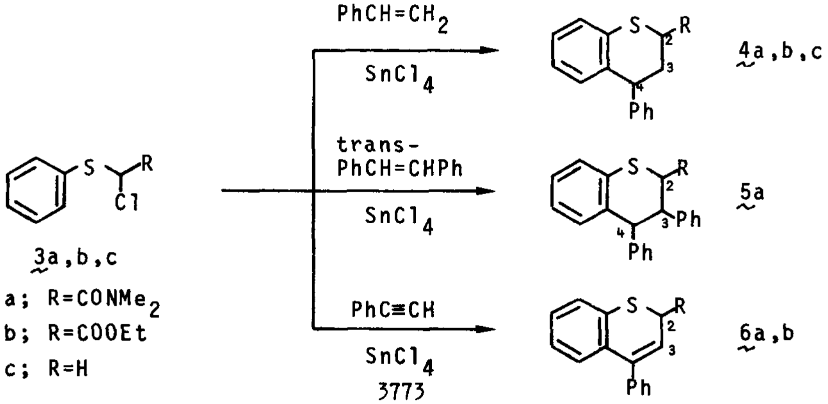


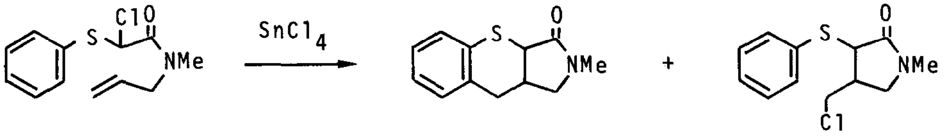
Table. Yields and Physical Data for 4, 5, and 6.

Product	Yield (%)	mp (°C)	^{1}H-NMR (CDCl$_3$) δ, J in Hz H-2	H-3	H-4
4a	72	110-111	4.37(dd,J=10,5)	2.4-2.9(m)	4.03(dd,J=10,6)
4b	60	oil	3.9-4.5*	2.3-3.0(m)	3.9-4.5*
4c	60	oil	2.7-3.2(m)	2.2-2.45(m)	4.20(dd,J=9.5,4)
5a	39	174-175	4.52(d,J=9)	3.88(dd,J=10,9)	4.30(d,J=10)
6a	27	164-165	4.79(d,J=4.8)	6.14(d,J=4.8)	—
6b	31	oil	4.43(d,J=6)	6.09(d,J=6)	—

* multiplet

Reactions of 3a, 3b, and 3c with styrene (1 eq) were carried out in methylene chloride at 0° in the presence of SnCl$_4$ (1 eq) to give the 4-(phenyl)thiochroman derivatives 4a, 4b, and 4c in good yields, respectively. The yields and physical data are given in Table. Similar reaction of 3a with *trans*-stilbene gave the adduct 5a, and the reactions of 3a and 3b with phenylacetylene afforded the thiochromen derivatives 6a and 6b, respectively (see Table).

The present polar cycloadditions are also applicable to the intramolecular cyclization. Thus the sulfide 7, upon treatment with one equivalent of SnCl$_4$ in methylene chloride at 0°, gave the polar cycloaddition product 8 in 27% yield together with the 1,2-addition product 9 (20%), whose cyclization into 8 in the presence of SnCl$_4$ was attempted, but unsuccessful.[4]



7 8 9

Scope and stereochemistry of these inter- and intra-molecular polar cycloadditions are currently investigated.

REFERENCES AND NOTES

1 For an excellent review and classification of polar cycloadditions, see R. R. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 12, 212 (1973).

2 C. K. Bradsher, *Adv. Heterocyclic Chem.*, 16, 289 (1974).

3 E. J. Corey and S. W. Walinsky, *J. Am. Chem. Soc.*, 94, 8932 (1972).

4 8: mp 163-164°, δ 2.7-3.1 (m, 3H), 2.91 (s, 3H, NMe), 3.23 (t, 1H, J=9 Hz), 3.45-3.8 (m, 2H), and 6.9-7.2 (m, 4H, arom.); 9: oil, δ 2.45-3.0 (m, 1H), 2.80 (s, 3H, NMe), 3.18 (d, 2H, J=7 Hz, CH$_2$Cl), 3.5-3.7 (m, 3H), and 7.1-7.7 (m, 5H, arom.).

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