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ALUMINUM-CHLORIDE CATALYZED REACTION OF ALLYLIC SULFIDES WITH METHYL PROPIOLATE· A NOVEL ADDITION REACTION VIA AN IONIC [3 3] SIGMATROPIC REARRANGEMENT

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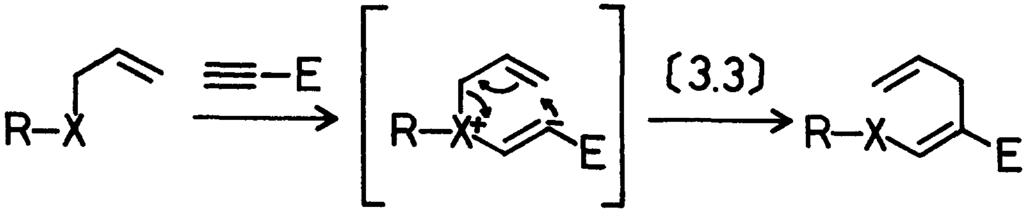
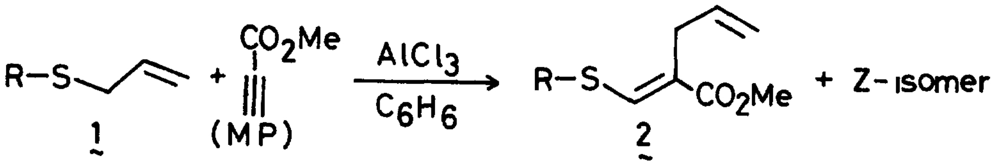
Abstract The aluminum-chloride catalyzed reaction of allylic sulfides with methyl propiolate resulted in the clean formation of novel 1 1 adducts via ionic [3 3] sigmatropic rearrangements.

Pericyclic reactions of organosulfur compounds have become increasingly important as a general synthetic method for the carbon-carbon bond formation.[1] Especially, allylic sulfides are of great utility because of their ability to undergo a variety of rearrangements including the well-known name reactions such as the Stevens ([1 2]) rearrangement,[2] the Wittig ([1 2]) rearrangement,[3] the Sommlet-Hauser ([2.3]) rearrangement,[4] and the thio-Claisen ([3.3]) rearrangement.[5] Although ionic (or zwitterionic) species are often involved in these pericyclic reactions due to the unique properties of sulfur,[6] no ionic [3 3] sigmatropic rearrangement of the organosulfur compounds is known We now report a novel Lewis-acid catalyzed addition reaction of allylic sulfides to methyl propiolate (MP) via an ionic [3.3] sigmatropic rearrangement which is generally illustrated in eq 1 (X=S) The idea originated in our recent finding of the facile reaction of thebaine with MP in polar solvents which could be regarded as the nitrogen case of eq 1 (X=NMe) [7] Extension of this reaction to the organosulfur compounds would enhance its synthetic utility because of the unusual versatility of vinyl sulfides to be formed[8]



(1)

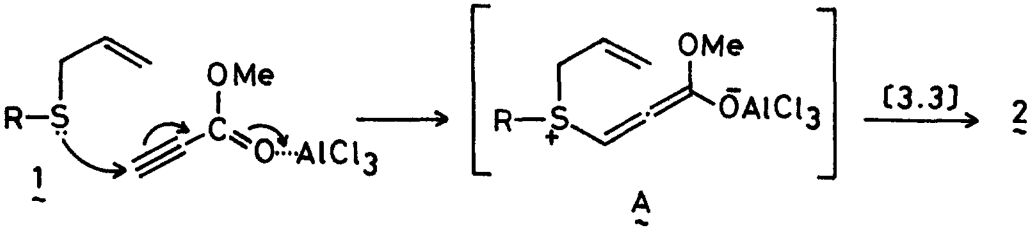
However, the treatment of allyl phenyl sulfide 1 (eq 2; R=Ph) with MP in various solvents led to only the recovery of starting materials even under drastic conditions. It is now found that the use of aluminum chloride as a catalyst causes a dramatic change in their reactivities and results in the smooth formation of addition product 2 (R=Ph) under mild conditions (eq 2)



(2)

Thus, to a stirred solution of MP (2.4 mmol) and $AlCl_3$ (2.6 mmol) in dry benzene (5 ml), 1 (R=Ph, 2.0 mmol) was added dropwise with ice-cooling (the reaction is *exothermic!*) After stirring at room temperature for 2 h, the reaction mixture was quenched with ice-water, extracted with ether, evaporated in vacuo, and chromatographed on silica gel (hexane-ethyl acetate, 8:1) to give 2 (R=Ph)[9] in 70% yield (E/Z=76:24)[10], bp 145-150° (2 mm, Kugelrohr), IR (neat) 1710 cm^{-1}, ^1H NMR ($CDCl_3$) δ 3.06 and 3.17 (each dm, J=6.0 Hz, 2H, 76:24), 3.71 and 3.88 (each s, 3H, 24:76), 4.95-5.25 (m, 3H), 5.6-6.05 (m, 1H), 6.98 and 7.72 (each s, 1H, 24:76), and 7.2-7.5 (m, 5H), MS m/e 234 (M^+) and 125. Anal. Calcd for $C_{13}H_{14}O_2S$ C, 66.64, H, 6.02 Found C, 66.66, H, 6.00

Table I reveals that the reaction proceeds equally well for the substrate bearing various functional groups with E-stereoselectivity. A slight excess of $AlCl_3$ is required for the optimal yield of these reactions, while the olefin ratio is not affected by the amount of the Lewis acid used. The hydroxyl group needs to be protected in this reaction (entry 7). The benzyl sulfide (entry 5) and a second allyl group of diallyl sulfide (entry 4) do not participate in these reactions. The formation of these novel addition products can be most reasonably explained by a two-step mechanism. The soft sulfur of 1 initially makes an nucleophilic attack on the soft β-carbon of MP activated by $AlCl_3$ to give the zwitterionic intermediate which would be

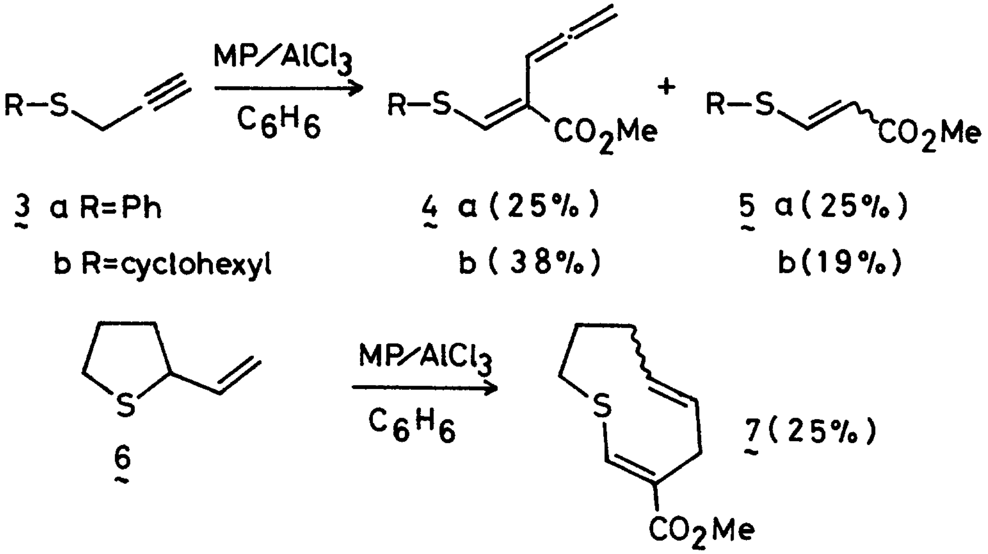


(3)

Table I Aluminum-Chloride Catalyzed Reactions of 1 with Methyl Propiolate[a]

entry	compound 1 (R=)	mol equiv of $AlCl_3$	product 2[b] % yield[c]	olefin ratio[d] (E/Z)
1	C_6H_5-	1.3	70	76:24
2	n-C_5H_{11}-	1.3	77	80:20
3	cyclohexyl-	1.3	80	90:10
4	CH_2=$CHCH_2$-	2.6[e]	73	78:22
5	$C_6H_5CH_2$-	1.3	73	86:14
6	MeO_2CCH_2-	1.3	71	77:23
7	$HOCH_2CH_2$-	1.3	complex mixture	
8	$AcOCH_2CH_2$-	1.3	41	71:29
9	$BrCH_2CH_2CH_2$-	1.3	83	79:21

[a] All reactions were carried out in dry benzene at room temperature (2 h) using 1.0 equiv of methyl propiolate (MP) and the given amount of $AlCl_3$. [b] See ref 9 [c] Values reported are isolated yields [d] See ref 10 [e] 2 4 equiv of MP was used



3 a R=Ph
b R=cyclohexyl

4 a (25%)
b (38%)

5 a (25%)
b (19%)

6

7 (25%)

(4)

represented by an aluminate A.[12] The subsequent [3 3] sigmatropic rearrangement of thus formed ionic intermediate (A) gives E- and Z-products (2)[13] (eq 3)

The interesting applications can be seen in the reactions of propargyl sulfides (3) and cyclic sulfide (6)[14] (eq 4). The former afforded allenic products (4)[15] along with the vinyl sulfides (5)[16] which were considered to be formed by depropargylation of the initially formed ionic intermediates. The latter gave the ring-enlargement product 7[17], albeit in modest yield

The facile formation of novel addition products involving the allylic migration is most noteworthy[18] These results are very suggestive of the general applicability of the reaction (eq 1) to other heteroatoms, which is currently under investigation in our laboratory

References and Notes

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10. The olefin ratio was determined by a combination of GLC and ^{1}H NMR analysis with the aid of the characteristic chemical shift of olefinic protons of β-sulfenylated unsaturated esters. The E-isomer was characterized by the downfield absorption of the β-vinyl hydrogen (δ 7 3-7 8), whereas the Z-isomer was characterized by the relative upfield shift of this signal (δ 6 5-6 9) See· (a) K. Isobe, M. Fuse, H Kosugi, H. Hagiwara, H. Uda, Chem. Lett. 785 (1979). (b) J. P. Marino, W. B. Mesbergen, J. Am Chem. Soc. 96, 4050 (1974). Furthermore, the hydrolysis of 2 (R=Ph) by KOH/aq CH$_3$OH followed by recrystallization (n-hexane) gave the pure E-acid, mp 74-74 5 °C, which was again converted to the pure E-ester by CH$_2$N$_2$. The assigned stereochemistry was further confirmed by chemical conversions.
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15 Compound 4a IR (neat) 1940, 1720, and 1250 cm^{-1}, ^{1}H NMR (CDCl$_3$) δ 3.75 (s, 3H), 5 16 (dd, J =7 0, 1.0 Hz, 2H), 6.31 (t, J=7.0 Hz, 1H), 7 20-7 60 (m, 5H), and 7 78 (s, 1H) Compound 4b· IR (neat) 1940, 1720, and 1250 cm^{-1}, ^{1}H NMR (CDCl$_3$) δ 1.15-2 20 (m, 10H), 2.7-3 3 (m, 1H), 3.75 (s, 1H), 5.06 (dd, J=7 0, 1 0 Hz, 2H), 6.21 (t, J=7 0 Hz, 1H), and 7.73 (s, 1H).
16. 5a, E/Z=50.50, 5b, E/Z=83·17. See J.R. Shelton, K. Davis, Int J.Sulfur Chem. 3, 205 (1973).
17. Compound 7: IR (neat) 1720 and 1225 cm^{-1}, ^{1}H NMR (CDCl$_3$) δ 1.6-2.0 (m, 2H), 2.63 (t, J=7.0 Hz 2H), 2 8-3.1 (m, 2H), 3.52 (d, J=7.0 Hz, 2H), 3.77 (s, 3H), 5.13-5 97 (m, 2H), and 7.49 (s, 1H), MS m/e 198 (M$^+$)
18. The similar reactions of crotyl sulfides resulted in simply dealkylation to give 5.

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