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Potassium Fluoride on Alumina: One-Pot Synthesis of S-Allyl-S-Methyldithiocarbonates by Tandem Condensation-Alkylation-Sigmatropic Rearrangement

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**POTASSIUM FLUORIDE ON ALUMINA: ONE-POT
SYNTHESIS OF S-ALLYL-S-METHYLDITHIOCARBONATES
BY TANDEM CONDENSATION-ALKYLATION-SIGMATROPIC
REARRANGEMENT**

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Abstract:

Allyl alcohols adsorbed on Al_2O_3 -KF at room temperature reacted with carbon disulfide and iodomethane and gave S-allyl-S-methyldithiocarbonate. Linalool did not give a rearrangement product. With chrysanthemyl alcohol, opening of the cyclopropane ring was observed.

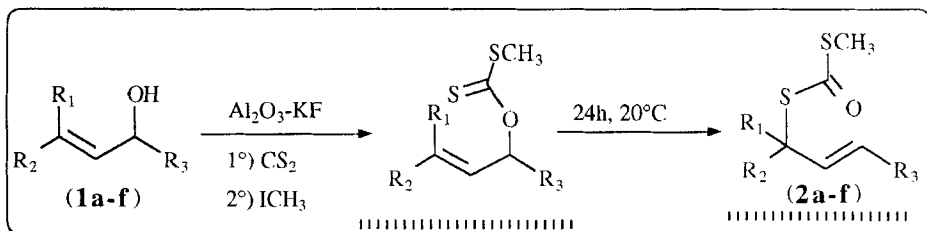
Adsorption on the surface can increase the ease of sigmatropic rearrangement. Claisen or Cope rearrangements were observed simply by adsorption on alumina or silica ¹. Pursuing the use of solid support for the catalysis of sigmatropic rearrangement ², we report herein the tandem condensation-alkylation-sigmatropic rearrangement of allylic alcohols into S-allyl-S-methyldithiocarbonates. The reaction takes place at room

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temperature simply by adsorption of the allylic alcohol with carbon disulfide and iodomethane on potassium fluoride on alumina.

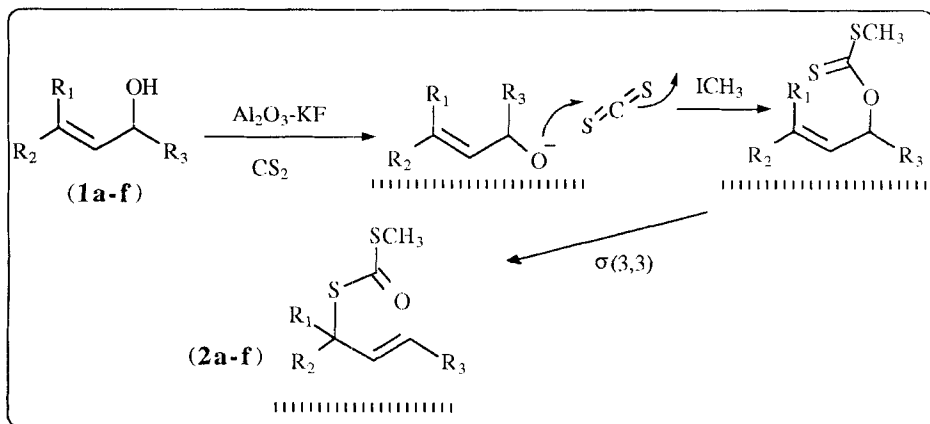
In a first step the alcohol adsorbed with the solid base, potassium fluoride on alumina, gives the corresponding alkoxide ³. The alkoxide then reacts with carbon disulfide, and the dithiocarbonate obtained is alkylated to the xanthate (Scheme 1).

Scheme 1:



This adsorbed xanthate was rearranged slowly at room temperature into the S-allyl-S-methyldithiocarbonate (Scheme 2).

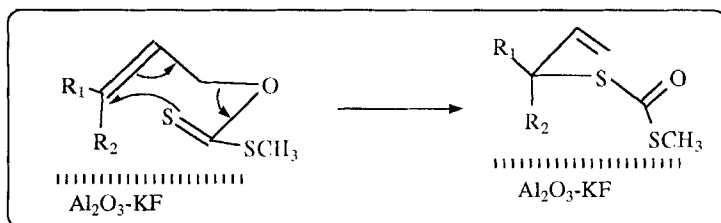
Scheme 2



A possible explanation for this easy rearrangement is that adsorbed xanthate has a conformation very close to the transition state of Claisen rearrangement (chair conformation).⁴

If the product is extracted after 30 mn of contact between the alcohol, carbon disulfide and iodomethane, a mixture of xanthate and S-allyl-S-methyldithiocarbonate is obtained.

Scheme 3



In the case of tertiary allylic alcohol such as 3-methyl-2-butenol or linalool, the addition of alkoxide on carbon disulfide is very slow and the addition of some DMSO improves this step. We noticed that at room temperature the rearrangement is very slow with 3-methyl-2-butenol and doesn't occur with linalool even after two days of stirring. With chrysanthemyl alcohol, we observed at room temperature a rearrangement of xanthate with opening of the cyclopropane (Scheme 4)

Scheme 4

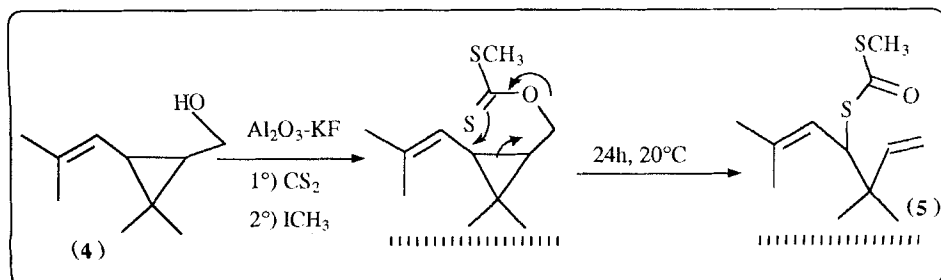


Table 1

alcohol	N°	yield(%)	product N
2-methyl-3-buten-1-ol	1a	50	2a
3-methyl-2-buten-1-ol	1b	90 ^a	2b
cinnamyl alcohol	1c	75	2c
geraniol	1d	55	2d
linalool ^b	1e	55 ^a	3e
farnesyl alcohol	1f	40	2f
chrysanthemyl alcohol ^c	4	55	5

a) dmsO added; b) no sigmatropic rearrangement; c) opening of the cyclopropane

Results obtained are reported in table I.

The thiocarbonates can be easily saponified [1°) KOH, 2°) HCl] to allylic thiols, and hence the tandem reactions described above constitute a procedure for the transformation of allylic alcohols into allylic thiols.

Experimental

Infrared spectra were recorded on Perkin Elmer 684 IR spectrometer in KBr with absorptions in cm^{-1} . Proton NMR spectra (PMR) and ^{13}C NMR spectra (CMR) in ppm downfield from internal Me_4Si were recorded on a Bruker AC 250 instrument from a solution in $\text{d}^6\text{-DMSO}$ of the product. Mass spectra were recorded on Nermag R10.10H spectrometer.

General procedure:

A mixture of allylic alcohol (10 mmol) in acetonitrile (10 ml) and carbon disulfide (1 ml) was adsorbed on potassium fluoride on alumina (6 g). After 4h

at room temperature iodomethane (1 ml) was added at 20°C. After 4h at room temperature, the solid was extracted with methylene chloride (20 ml, 5 ml, 5 ml, 5 ml). The solution after filtration on Celite was evaporated in a vacuum and the residue was purified by chromatography on silica.

Remarks: concerning the following alcohols (linalool and the 2-methyl-3-buten-1-ol), after carbon disulfide addition, the characteristic colour (brick red) obtained with the others alcohols was not observed. Consequently, 0.5 ml of DMSO was added, and the mixture was stirred overnight.

S-Methyl S-[1-(3-methyl-2-butenyl)] dithiocarbonate (2a).

Obtained from 2-methyl-3-buten-1-ol (50%).

Yellow liquid; $^1\text{H NMR}(\text{CDCl}_3)$ δ : 1.7 (s, 6H, CH_3) 2.5 (s, 3H, SCH_3) 3.7 (dd, 2H, SCH_2) 5.4 (m, 1H, $\text{CH}=\text{}$); $^{13}\text{C NMR}$: 17.78, 17.85, 25.90, 37.61, 118.33, 134.93, 189.85, 225.06; IR: 816 (δ CH) 960 (δ CH_2) 1072 (ν C-S) 1418 (δ CH_2) 1716 (ν CO) 2914 (ν CH); MS m/s (%) 176(M^+ , 28.64) 155(4.31) 101(5.1) 69(98.82).

S-Methyl S-[3-(3-methyl-1-butenyl)] dithiocarbonate (2b).

Obtained from 3-methyl-2-buten-1-ol (90%) (DMSO).

Yellow liquid; $^1\text{H NMR}(\text{CDCl}_3)$ δ : 1.6 (d, 6H, 2CH_3) 2.5 (s, 3H, SCH_3) 4.8-5.1 (dd, 2H, $\text{CH}_2=\text{CH}$) 6.1 (m, 1H, $\text{CH}=\text{CH}_2$); $^{13}\text{C NMR}$: 13.40, 25.60, 25.63, 35.71, 116.07($\text{CH}_2=\text{CH}$), 137.36($\text{CH}=\text{CH}_2$), 192.32(CO); IR: 894 (δ CH) 966 (δ CH_2) 1062 (ν C-S) 1426 (δ CH_2) 1650(ν C=C) 1712(ν CO) 2970 (ν CH); MS m/s (%) 176(M^+ , 13.79) 130(12.54) 116(18.14) 91(14.24) 69(100).

S-Methyl-S-[1-(1-phenylprop-2-enyl)] dithiocarbonate (2c).

Obtained from cinnamyl alcohol (75%).

Yellow liquid; $^1\text{H NMR}(\text{DMSO})$ δ : 2.4 (s, 3H, SCH_3) 5.2 (dd, 2H, $\text{CH}_2=\text{CH}$) 6.0 (m, 1H, $\text{CH}-\text{CH}_2$) 7.4 (m, 5H, Ar); $^{13}\text{C NMR}$: 13.04, 33.15, 117.43, 127.82, 128.22, 128.50, 128.60, 133.63, 138.94, 193.74; IR: 830 (δ CH) 868

(δ CH₂) 1026 (ν C-S) 1452 (δ CH₂) 1644 (ν C=C) 1712 (ν C=O) 3060 (ν CH Ar); MS *m/s* (%) 224(M⁺ 4.29) 208(2.57) 196(10.86) 149(3.64) 117(100).

S-Methyl-S-[3-(3,7-dimethyl-1,6-octadienyl)] dithiocarbonate (2d).

Obtained from geraniol (55%).

Yellow liquid; ¹H NMR(CDCl₃) δ : 1.56 (s, 3H, CH₃) 1.80 (d, 6H, 2CH₃) 2.0-2.2 (m, 4H, CH₂-CH₂) 2.5 (s, 3H, SCH₃) 5.2-5.4 (m, 2H, CH₂=CH) 6.0 (m, 1H CH=CH₂) ¹³C NMR: 13.43, 17.59, 20.0, 26.22, 27.78, 39.55, 40.21, 115.99, 118.0, 132.10, 139.37, 189.90; IR: 856 (δ CH) 1142 (ν C-S) 1148 (δ CH₂) 1646 (ν C=C) 1716 (ν CO) 2928 (ν CH); MS *m/s* (%) (M⁺, 0.39) 227(0.49) 169(18.87) 136(14.95) 93(12.03).

S-Methyl-O-[3-(3,7-dimethyl-1,6-octadienyl)] dithiocarbonate (2e).

Obtained from linalool (55%) (DMSO).

Yellow liquid; ¹H NMR(CDCl₃) δ : 1.20 (s, 3H, CH₃) 1.56 (d, 6H, 2CH₃) 2-2.2 (m, 4H, CH₂-CH₂) 2.5 (s, 3H, SCH₃) 5-5.1 (m, 2H, CH₂-CH) 5.9 (m, 1H, CH=); ¹³C NMR: 13.40, 17.67, 20.09, 26.55, 27.73, 40.66, 111.34, 114.34, 131.66, 143.44, 225.59(C=S); IR: 820 (δ CH) 920 (δ CH₂) 1026 (ν C=S) 130 (δ CH) 1452 (δ CH₂) 1642 (ν C=C) 2924 (ν CH Ar) MS *m/s* (%) 244 (M⁺ 3.66) 230(2.13) 199(2.27) 169(3.89) 153(6.41).

S-Methyl S-[3-(3,7,11-trimethyl-1,6,10-dodecatrienyl)] dithiocarbonate (2f).

Obtained from farnesol (40%)

Yellow liquid; ¹H NMR(CDCl₃) δ : 1.4 (s, 3H, CH₃) 1.7 (s, 3H, CH₃) 1.85 (d, 6H, 2CH₃) 2-2.2 (m, 4H, CH₂-CH₂) 2.5(s, 3H, SCH₃) 5.1-5.3 (m, 2H, CH₂=C) 6.0 (m, 1H, CH=CH₂); ¹³C NMR: 15.95, 16.11, 17.64, 17.68, 26.20, 39.64, 40.21, 40.48, 117.90, 123.27, 124.21, 133.13 133.58, 141.58, 192; IR: 856 (δ CH) 1142 (ν C-S) 1448(δ CH₂) 1644 (ν C=C) 1712

(ν CO) 2926 (ν CH); MS m/s (%) 312(M+ 0.16) 296(0.12) 265(0.64) 205(0.8).

**S-Methyl-S-[4-(3,3',6-trimethyl-1,5-heptadienyl)]
dithiocarbonate (2g).**

Obtained from chrysanthemyl alcohol (55%).

Yellow liquid; ^1H NMR(CDCl_3) δ : 1.1 (s, 6H, 2CH₃) 1.7 (s, 6H, 2CH₃) 2.5 (s, 3H, SCH₃) 4.9 (dd, 2H, CH₂=CH) 5.2 (dd, 1H, CH=) 5.8 (dd, 1H, CH=CH₂); ^{13}C NMR: 13.02, 13.18, 18.29, 23.61, 26.94, 38.86, 53.87, 112.92, 118.19, 131.27, 138.01, 190.10; IR: 860 (δ CH) 1064 (ν C-S) 1378 (δ CH₂) 1644 (ν C=C) 1726 (ν CO) 2928 (ν CH); MS m/s (%) 244(M+ 10.82) 229(14.35) 175(40) 143(16.47) 123(98.12).

Saponification

S-Methyl S-[1-(3-methyl-2-butenyl)] dithiocarbonate (5 mmol) was dissolved in dioxane (30 ml) and water (30 ml) with potassium hydroxide(10 mmol) and was reflux for 2h under nitrogen. After cooling the mixture was acidified with hydrochloric acid (pH=1) and extracted with ether (100 ml). After drying on magnesium sulfate the organic phase was distilled. 3-Methyl-2-buten-1-thiol was isolated (bp=124-127°C, lit⁵.125-126°C).

References and notes:

1.Chalais S., Laszlo P. and Mathy A., *Tetrahedron Lett.*, **1986**, 27, 2627; Smith W.A , Pogrebnoy S.V., Kal'yan Y.B. and Krimer M.V., *Izvestia Acad. Nauk SSSR, Ser Khim*, **1987**, 959; Tanoka M., Hotta T. and Takeo S., *Chem.Abs.*, **1987**, 106, 49780a ; Suryawanshi S.N., Rani A. and Bhakuni D.S., *Synth. Commun.*, **1990**, 20 , 625.

2. Ben Alloum A., Labiad B. and Villemin D., *J. Chem. Soc. Chem. Comm.*,**1989**, 3863; Villemin D., Labiad B. and Ouhilal Y.,*Chem. Ind.*,**1989**, 607; Villemin D. and Hachemi M., *Synth. Commun.*, preceding paper.

3. Percolation of methanol on a column of Al_2O_3 -KF gave a solution of potassium methyllate.
4. Doering von E. and Roth W.R., *Tetrahedron*, **1962**, *18*, 67.
5. Obata Y., Koshika M. and Tanaka H., *Nature*, **1961**, *190*, 635.

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