Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Potassium Fluoride on Alumina: A Convenient Synthesis of O-Alkyl Methyldithiocarbonates. Pyrolysis of O-Benzyl-S-Methyldithiocarbonates

Didier Villemin [a] & Messaoud Hachemi [a]

[a] Ecole Nationale Supérieure d' Ingénieurs de Caen, I.S.M.R.A., Groupe Catalyse et Modélisation , (U.R.A. 480) F-14050, Caen Cedex, France

To cite this article: Didier Villemin & Messaoud Hachemi (1996) Potassium Fluoride on Alumina: A Convenient Synthesis of O-Alkyl Methyldithiocarbonates. Pyrolysis of O-Benzyl-S-Methyldithiocarbonates, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:13, 2449-2459, DOI: 10.1080/00397919608004557

To link to this article: http://dx.doi.org/10.1080/00397919608004557

SYNTHETIC COMMUNICATIONS, 26(13), 2449-2459 (1996)

POTASSIUM FLUORIDE ON ALUMINA: A CONVENIENT SYNTHESIS OF O-ALKYL METHYLDITHIOCARBONATES. PYROLYSIS OF O-BENZYL-S-METHYLDITHIOCARBONATES

Didier Villemin* and Messaoud Hachemi

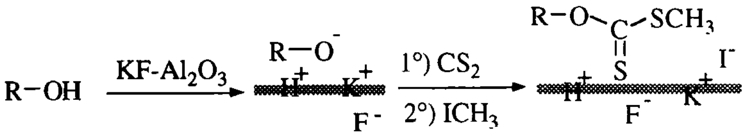
Ecole Nationale Supérieure d' Ingénieurs de Caen,
I.S.M.R.A., Groupe Catalyse et Modélisation (U.R.A. 480)
F-14050 Caen Cedex, France.

Abstract: *Xanthates were easily prepared by adsorption of alcohol on KF-*Al_2O_3 *followed by treatment of carbon disulfide and iodomethane at room temperature. Pyrolysis of benzyl xanthate affords to a complex mixture of products. A radical process was proposed to explain the nature of products obtained.*

O-Alkyl-S-methyldithiocarbonates (xanthates) are a versatile source of radicals [1], versatile intermediates in the synthesis of thiols [2], thiocarbonates [3], alkenes [4], alkanes [5], S-activated carbanion [6] and photosensitivers [7] for polymerization of vinyl monomers. Xanthates are used in the synthesis of natural products [8], Claisen rearrangement [9], and are also important for their biological properties. The O-Alkyl S-methyldithiocarbonates are generally prepared from alcohol in a three step process [10]. The reaction involves use of strong base such

---

* To whom correspondence should be addressed



Scheme 1: Synthesis of O-alkyl-S-methyldithio-carbonates on KF-alumina.

as sodium hydride, sodium amide or potassium t-butoxide in polar aprotic solvent like DMSO [11], DMF [12] or diglyme [13]. Phase transfer catalysis and crown ether has also been used with unfunctionalised alcohols [14].

● Synthesis of O-alkyl-S-methyldithiocarbonates on KF-alumina.

We report herein the synthesis of O-alkyl-S-methyldithiocarbonates simply by adsorption of alcohol on potassium fluoride on alumina, followed by a treatment with carbon disulfide and alkylation with iodomethane at room temperature according to scheme 1.

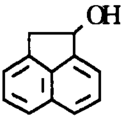
This synthesis is very simple, fast and convenient. Moreover, this synthesis did not use an anhydrous solvent, and a laborious preparation of the alcoholate was not necessary (Eg: menthol alcoholate was obtained with sodium only after 32 h in refluxing toluene [15]. This new method also gave gave pure O-alkyl-S-methyldithiocarbonates with better thermal stability than those obtained by a classical way that contain radical precursors which are responsible for the formation of olefins (Chugaev's reaction). The elimination of radical precursors is carried out with a ferrous salt [16]. Contrary to the use of the phase transfer reaction [14], only a trace of the trithiocarbonate was formed and can be easily separated from the products by filtration on silica.

The results obtained are presented in table 1.

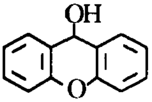
Table 1

starting product **ROH**	product **$ROCSSCH_3$**	Yield %
n-Butanol	**1**	97
sec-Butanol	**2**	60
ter-Butanol	a	0
1- Acenaphthenol	**6**	78
Xanthydrol	**7**	53
Fluorenol	**8**	78
Cedrol	a	0
Menthol	**9**	53
Cholesterol	**10**	50
Lanosterol	**11**	42

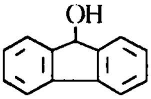
a : no reaction



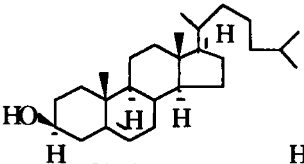
1-Acenaphthenol



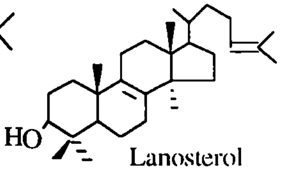
Fluorenol



Xanthydrol



Cholesterol



Lanosterol

Cedrol

With a primary alcohol, the reaction was easy. With hindered a secondary alcohol like the lanosterol, the reaction was slow and the addition of small amount of DMSO increases the yield of the reaction. With a tertiary alcohol like cedrol and t-butanol no reaction was observed.

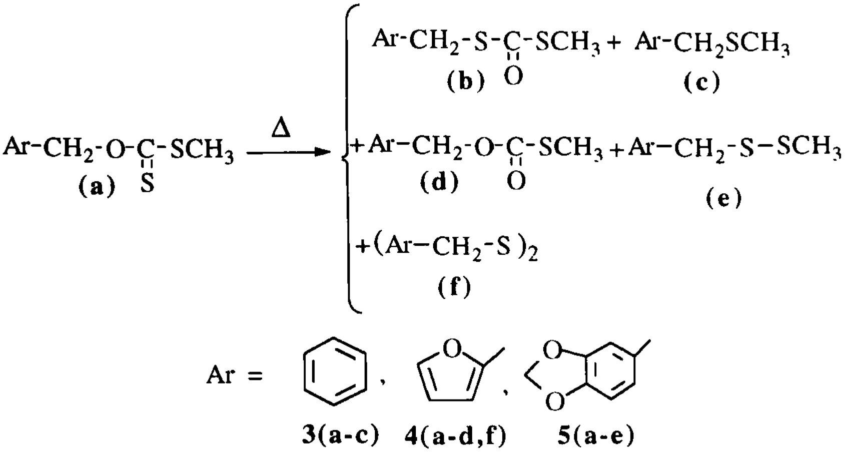
Pure xanthates are more thermically stable. The xanthates obtained with our method were sufficiently pure to be distiled under vacuum without decomposition. It is known in the literature that xanthates were transformed into alkenes under pyrolytic conditions [4] (Chugaev's reaction). The decomposition of xanthate is easy in particular when impurities formed during the classical preparation of xanthate were present [4b,16].

❷ Pyrolysis of benzylxanthates

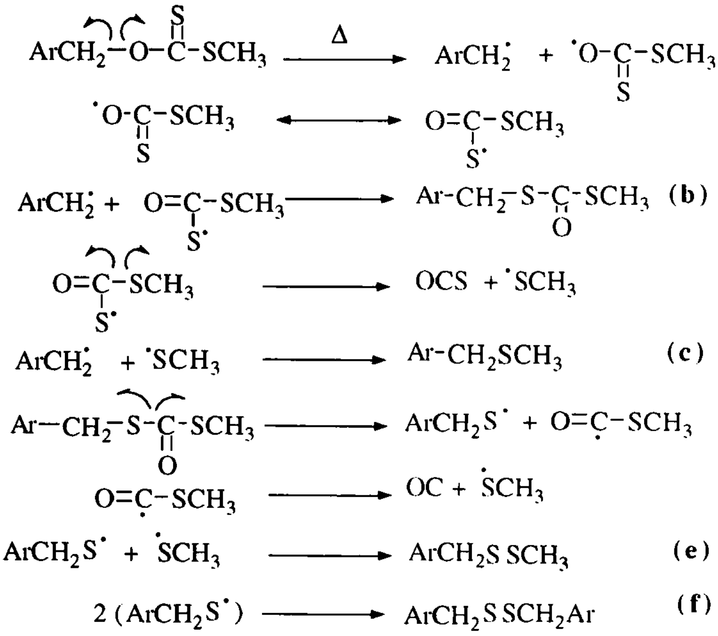
We have recently reported the sigmatropic rearrangement of allylic xanthate adsorbed on KF-Alumina at room temperature [17]. By analogy with allyl alcohols, we studied the case of benzyl alcohols. The O-Benzyl -S-methyl dithiocarbonate can be obtained in pure form without rearrangement, while the furfuryl and methylenedioxybenzyl alcohol gave a mixture of products (scheme 2).

In fact, we have decided to examine the behaviour of these benzylxanthates under pyrolytic conditions. We have identified all the products of the mixture which are: the S-dithiocarbonate (**b**), the methylthio derivative (**c**), the methylthiocarbonate (**d**), the disulfides (**e**) and (**f**). Remark: The methylthiocarbonate (**d**) was an oxidation product of xanthate (**a**) and only traces are present if the pyrolysis and the synthesis of (**a**) was conducted under a nitrogen atmosphere.

The formation of these different products (**b,c,e,f**) can be explained by a radical mechanism rather than a sigmatropic rearrangement. We proposed a radical mechanism according the following process (Scheme 3).



Scheme 2: Pyrolysis of benzyl xanthates



Scheme 3: Proposed mechanism for pyrolysis of benzyl xanthates

In conclusion, the use of KF on alumina allow the convenient synthesis of xanthate from primary and secondary alcohols. In the case of benzyl alcohols a radical process of decomposition of the xanthate had occured. The temperature of decomposition depended on the substrates

Experimental

Proton NMR spectra (PMR) and ^{13}C NMR recorded in ppm downfield from internal Me_4Si were recorded on a Brucker AC 250 instrument from a solution in ($CDCl_3$) of the product.

Infrared spectra were recorded (cm^{-1}) on a Perkin Elmer 16PC FT IR. Pyrolysis and distillations were performed with a Kugelrohr Büchi GKR-50. KF on alumina was prepared according reference. Melting point (°C) and boiling point(°C) were uncorrected .

❶ Synthesis of O-alkyl-S-methyldithiocarbonates on KF-alumina.

General procedure

To a solution of alcohol (10 mmol) in THF (15 ml), we added potassium fluoride on alumina (6 g) and then carbon disulfide (11 mmol) under nitrogen. After 3 h of stirring at room temperature, iodomethane (11 mmol) was added. After 4 h of stirring, the mixture was filtered on Celite and solvent was distillated under vacuum.

O-n-Butyl-S-methyl dithiocarbonate:(1)

Yellow liquid, yield 97%

PMR: 1.0 (t, 3H, CH_3), 1.50 (m, 2H, CH_2), 2.55 (s, 3H, SCH_3), 4.6 (t, 2H, OCH_2).

O-sec-Butyl-S-methyl dithiocarbonate: (2)

Yellow liquid, yield 60%

PMR: 0.9 (t, 3H, CH_3CH_2), 1.2 (d, 3H, CH_3CH), 1.6 (m, 2H, CH_2), 2.55 (s, 3H, SCH_3), 5.50 (m, 1H, CH).

O-Benzyl-S-methyl dithiocarbonate: (3a)

Yellow liquid, yield 98%.

PMR: 2.54 (s, 3H, SCH_3), 5.60 (s, 2H, OCH_2), 7.30 (m, 5H, Ar);

CMR: 13.77; 35.67; 127.14; 128.25; 128.62; 128.76; 129.17; 134.94; 215.78 (C=S); IR (cm^{-1}) : 1059 (v C=S).

O-Furfuryl-S-methyl dithiocarbonate: (4a)

Yellow liquid, yield= 18% in the mixture with (4b), (4c) (4d) and (4d).

PMR: 2.50 (s, CH_3, SCH_3); 5.58 (s, 2H, CH_2O); 6.31-6,32 (d, 1H, Ar, J= 0,73 Hz); 6.33-6.34 (m, 1H, Ar); 7.32-7.33 (d, 1H, Ar, J= 0,89 Hz).

O-Piperonyl-S-methyl dithiocarbonate: (5a)

Yellow liquid, yield= 6% in the mixture with (5b), (5b), (5d) and (5f).

PMR: 2.50 (s,CH_3, SCH_3); 5.58 (s, 2H, CH_2O); 5.86 (s, 2H, CH_2O_2); 6.66-7.18 (m, 3H, Ar).

O-ter-Butyl-S-methyl dithiocarbonate: not formed

O-1-Acenaphthenyl-S-methyl dithiocarbonate: (6)

Brown liquid, yield = 78%.

PMR: 2.55 (s, 3H, SCH_3), 3.50 (dd, 2H, CH_2, $J_{2\text{-}3}$ = 7,8 Hz), 4.0 (dd, 1H, CH, $J_{1\text{-}2}$ = 17.8 Hz, $J_{1\text{-}3}$ = 18 Hz), 7.2-7.9 (m, 6H, Ar).

O-Xanthydryl-S-methyl dithiocarbonate: (7)

Yellow liquid, yield 52% (kugelrohr 130°C (0.15).

PMR: 2.45 (s, 3H, SCH_3), 5.7 (s, 1H, CHO), 7.1-8.4 (m,8H, Ar).

O-Fluorenyl-S-methyl dithiocarbonate: (8)

Yellow liquid, yield 78% (kugelrohr 150°C (0.15).

PMR: 2.45 (s, 3H, SCH_3), 5.6 (s, 1H, CHO), 7.0-7.6 (m,8H, Ar).

O-Menthyl-S-methyl dithiocarbonate: (9)

Yellow liquid, yield 53% (kugelrohr 150°C (0.15).

PMR: 0.8 (d, 3H, CH_3), 0.90 (m, 6H, $2CH_3$), 1.0-2.2 (m, 8H, cycle), 2.50 (s, 3H, SCH_3), 5.50 (m, 1H, CHO).

O-Cholesteryl-S-methyl dithiocarbonate: (10)

Pale yellow solid, yield 50%, Mp 124 (methanol-ether), Mp lit.[5] 126-128

PMR(DMSO): 0.7 (s, 3H, CH_3), 0.9 (d, 6H, $2CH_3$), 1.0 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.2-2.2 (m, 31H, cycle), 2.54 (s, 3H, SCH_3), 3.50 (m, 1H, CHO), 5.50 (m, 1H, CH=C).

O-Lanosteryl-S-methyl xanthate: (11)

Pale yellow prism, yield 42%.Mp 124-126 (CH_3OH-CH_2Cl_2), Mp lit.[5]

PMR: 0.7 (s, 3H, CH_3), 0.8 (s, 3H, CH_3), 0.95 (s, 6H, $2CH_3$), 1.0 (d, 3H, CH_3), 1.1-2.1 (m, 33H), 2.70 (s, 3H, SCH_3), 3.30 (m, 1H, CHO), 5.20 (m, 1H, CH=C).

O-Cedryl-S-methyl dithiocarbonate: not formed.

❷ Pyrolysis of benzylxanthates:

♦ Pyrolysis of O-Benzyl-S-methyl dithiocarbonate (3a).

At 150°C, 3 products are observed: **3(a, b, c)** with respective yields **(31, 58, 11%)**. After heating with kugelrohr under vacuum at 250°C, we only obtain the pure product **(3b)**.

S-Benzyl-S-methyl dithiocarbonate (3b):

PMR: 2.36 (s, 3H, SCH_3); 4.18 (s, 2H, CH_2S); 7.30 (m, 5H, Ar).

CMR:13.27; 34.86; 128.05; 128.15; 128.20; 128.48; 137.07; 189.63 (C=O).

Methylbenzylthioether (3c):

PMR: 1.94 (s, 3H, CH_3), 3.62 (s, 2H, CH_2S); 7.30 (m, 5H, Ar).

♦ O-Furfuryl-S-methyl dithiocarbonate (4a): 5 products were formed at room temperature **4 (a-e)** in the respective yields **(18, 21, 34, 15, 12%)**. After heating with kugelrohr [(130°C (0.5)] only the products **(5b)** et **(5e)** were obtained.Finally the pure rearranged product **(4b)** was obtained at high temperature (>250°C).

S-Furfuryl-S-methyl dithiocarbonate (4b)

PMR H^1 : 2.37 (s, 3H, SCH_3); 4.19 (s, 2H, CH_2S); 6.17-6.18 (d, 1H, Ar, J= 0.47 Hz); 6.21-6.23 (m, 1H, Ar); 7.26-7.27 (d, 1H, Ar, J= 0,69 Hz).

CMR :13.25; 27.09; 108.48; 110.76;142.55; 150.01; 189.17 (C=O)

Methylthiofurfurylether (4c):

PMR : 2.05 (s, 3H, CH_3); 3.62 (s, 2H, CH_2S); 6.28-6.29 (d, 1H, Ar); 6.30-6.31 (m, 1H, Ar); 7.45-7.46 (d, 1H, Ar).

O-Furfuryl-S-methyl thiocarbonate (4d):

PMR : 2.68 (s, 3H, SCH_3); 4.60 (s, 2H, CH_2O); 6.24-6.25 (d, 1H, Ar); 6.27-6.27 (m, 1H, Ar) 7.52-7.53 (d, 1H, Ar).

CMR : 20.24, 35.56, 101.23, 109.65, 122.34, 147.93, 189.6(C=O).

Furfurylmethyl disulfide (4e):

PMR : 2.65 (s, 3H, SCH_3); 3.70 (s, 2H, CH_2S); 6.19-6.20 (d, 1H, Ar); 6.22-6.24 (m, 1H, Ar); 7.28-7.29 (d, 1H, Ar).

◆ **O-Piperonyl-S-methyl dithiocarbonate (5).**

A mixture of following products **5 (a-d, f)** was obtained in the respective yield **(6, 27, 14, 27, 20 %).** After heating (140°C), the products **5 (b, c, d, f)** were obtained in the respective proportions (23, 21,13, 43%). By kugelrohr distillation at 160°C, the products **(5b)** and **(5d)**, were obtained in the ratio 77/33.

S-Piperonyl-S-methyl dithiocarbonate (5b):

PMR: 2.41 (s, 3H, SCH_3); 4.22 (s, 2H, CH_2S); 5.86 (s, 2H, CH_2O_2); 6.66-7.18 (m, 3H, Ar); CMR: 13.24; 34.86; 101.23; 108.38; 109.38; 122.34; 130.70; 147.11; 189.60 (C=O). IR (neat): 2894 (ν CH Ar), 1684 (ν C=O), 812 (ν C-S).

Methylthiopiperonyl ether (5c):

PMR: 1.96 (s, 3H, CH_3); 3.64 (s, 2H, CH_2S); 5.86 (s, 2H, CH_2O_2); 6.66-7.17 (m, 3H, Ar).

O-Piperonyl-S-methyl thiocarbonate (5d):

PMR: 2.70 (s, 3H, SCH_3); 4.5 (s, 2H,CH_2O);5.86(s,2H,CH_2O_2); 6.66-.7.18 (m, 3H, Ar).CMR : 20.24; 41.63; 101.29; 108.44; 109.64; 122.81; 130.84; 147.93; 189.62 (C=O). IR (neat): 2776 (ν CH Ar), 1716 (ν OC=O), 812 (ν CS).

Bi-piperonyl sulfide (5f):

PMR: 3.5 (s, 2H, CH_2S); 5.86 (s, 2H, CH_2O_2); 6.66-7.18 (m, 3H, Ar).

Acknowledgement: The authors thank Dr. Ben Alloum for preliminary experiments and Dr. Monika Puciova for the preparation of a sample of lanosteryl xanthate.

References

1. Barton D.H.R., Mi Chen , Jaszberenyi J.Cs., Rattigan B. and Tang D., *Tetrahedron Lett.*, **1994**, *35*, 6457; Barton D.H.R., Jang D.O. and Jaszberenyi J.C., *Tetrahedron Lett.*, **1990**, *31*, 4681; **1991**, *32*, 2569; Hartwig W., *Tetrahedron* ,**1983**, 2609; Barton D.H.R.and Motherwell W.B., *Pure Appl. Chem.*, **1981**, 1.

2. Isola M., Ciuffarin E. and Sagromora L., *Synthesis* , **1976**, 326.

3. Degani I., Fochi R.and Regondi V., *Synthesis* , **1981**, 149; Baker R., O' Mahony M.and Swain C.J., *J. Chem. Soc. Perkin Trans I*, **1987**, 1623.

4. a) Chugaev L., *Ber.*, **1899**, *32*, 3332 ; b) Nace H.R., *Org. Reac.*, **1962**, *12*, 57.

5. Barton D.H.R. and Mc Combie S.W., *J. Chem.Soc. Perkin Trans, I* , **1975**, 1574.

6. Degani I., Fochi R. and Regondi V., *Synthesis* , **1979**, 178.; Tanaka K., Yamagishi N., Tanikaga R. and Kaji A., *Bull. Soc. Chem. Japan* , **1979**, 52, 3619.

7. Okatawa M., Nakai T., Otsuji Y. and Imoto E., *J. Org. Chem.*, **1965**, *30* , 2025.

8 Curren D. P., *Synthesis*, **1988**, 417 and 489.

9. Ferrier R. J. and Vethavisar N., *J. Chem. Soc., Chem. Commun.*, **1970**, 1385; Baldwin J. E. and Holfe G. A., *J. Am. Chem. Soc.*, **1971**, *93*, 6307; Harano K. and Taguchi T., *Chem. Pharm. Bull.*, **1971**, *20*, 2348; Harano K. and Taguchi T.,*Chem. Pharm. Bull.*, **1972**, *20*, 2357; Nakai T. and Ari-Izumi A., *Tetrahedron Lett.*, **1976**, 2335.

10. Dunn A.D.and Rudorf W. in "Carbon Disulfide in Organic Chemistry", Ellis Horwood , Chichester, 1989, 316-367 and references cited.

11. Meurling P., Sjoberg K., Sjoberg B., *Acta Chem. Scand.*, **1972**, *26*, 279.

12. Mori T., Taguchi T., *Synthesis*, **1975**, 469.

13 Degani I., Forki R. and Sunti M., *Synthesis*, **1977**, 873.

14. Chênevert R., Paquin R.and Rodrigue A., *Synth. Commun.*, **1981**, *11*, 817.

15. Hueckel W., Tappe W. and Legutke G., *Liebigs Ann. Chem.*, **1940**, *543*, 191.

16. Mc Alpine I.M., *J. Chem. Soc.*, **1931**, 114; O' Connor G.L. and Nace H.R., *J. Amer. Chem. Soc.*, **1953**, *75*, 2118.

17. Villemin D. and Hachemi M., *Synth. Commun.*, **1995**, *25*, 2305.

(Received in the UK 9th Jan 1996)