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Methylsulfinyl Carbanion

II. Preparation and Decomposition of Xanthates

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Methylsulfinyl carbanion (sodium methylsulfinylmethanide) was utilized in the preparation of xanthates. Alcohols were treated with an equivalent amount of this reagent in dimethyl sulfoxide followed by carbon disulfide and an alkylating or arylating agent. As arylating agents, we used non-aqueous diazonium salts, prepared with dinitrogen tetroxide in dimethyl sulfoxide.

The decomposition temperature of the xanthates is lowered when pyrolysis is carried out in a polar solvent, *e.g.* dimethyl sulfoxide. The ratio of olefins formed is only slightly influenced by substituents on the thiol sulfur. The xanthate of cedrol on pyrolysis gives β-cedrene having an exocyclic methylene group. Sulfur containing impurities are readily removed by filtering the olefin through a silver nitrate impregnated column.

The great synthetic value of methylsulfinyl carbanion (sodium methylsulfinylmethanide) has been demonstrated by Corey and Chaykovsky.[1] In this paper its use in the Chugaev reaction [2] is reported.

Olefins are often conveniently prepared by pyrolysis of xanthates, the Chugaev reaction. The method, however, suffers from some disadvantages,[2] *viz.* xanthates are not always easily prepared and it is difficult to remove impurities containing sulfur from the olefins formed. The decomposition temperatures of xanthates, though lower than those of the corresponding esters [3,4] often are too high to make the reaction attractive.

Xanthates of primary alcohols are easy to prepare, but are more stable to pyrolysis, than those of tertiary and secondary alcohols.[5] For tertiary alcohols the opposite is true; decomposition proceeds at lower temperatures, but it is difficult to prepare the xanthates. Thus there are surprisingly few reports of preparations of olefins from primary and tertiary alcohols by this method.[5]

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Table 1.

Alcohol	Xanthate [a]	Yield of xanthate, %	Decomp. temp. in dimethyl sulfoxide	Decomp. temp. solvent-free	Products after pyrolysis	Analyses	Yield of olefins [b]	Ref.
α-Terpineol	*S*-CH_3	85	20°	40°	Dipentene 95 % Terpinolene 5 %	*d,e,f,g* *e*	72 %	20
α-Terpineol	*S*-$C(C_6H_4)_3$	not isolated	below 20°	—	Dipentene 95 % Terpinolene 5%	*d,e,f,g* *e*	55 %	20
α-Terpineol	*S*-$C_6H_4SO_3H$	not isolated	below 20°	—	Dipentene 95 % Terpinolene 5 %	*d,e,f,g* *e*	68 %	20
Cedrol	*S*-CH_3	86	20°	70°	β-Cedrene 80 % α-Cedrene 20 %	*d,e,f* *d,e,g*	75 %	21
1-Methyl-cyclo-hexanol	*S*-CH_3	82	20°	50°	1-Methylcyclo-hexene 75 % Methylene cyclo-hexane 25 %	*d,e,g* *d,e*	68 %	13[c]
2-Octanol	*S*-CH_3	94	125°	160°	1-Octene 50 % 2-Octene 50 %	*d,e,g* *d,e,g*	69 %	22[c]
2-Octanol	*S*-$C_6H_4SO_3H$	68	50°	85°	1-Octene 50 % 2-Octene 50 %	*d,e,g* *d,e,g*	55 %	22
1-Octanol	*S*-CH_3 [h]	92	no decomp. at 189°	225°	1-Octene	*d,e,g*	74 %	22[c]
1-Octanol	*S*-$C_6H_4NO_2$	63	155°	165°	1-Octene	*d,e,g*	38 %	22[c]

[a] The xanthates were identified by their IR spectra. [b] Yields are calculated on the alcohols. [c] Refers to decomposition of xanthates earlier reported. [d] IR. [e] VPC. [f] NMR. [g] Comparison with authentic sample (IR and VPC). [h] Distilled without decomposition, b.p. 84–86°/0.5 mmHg. (Found: C 54.5; H 9.09. Calc. for $C_{10}H_{20}OS_2$: C 54.5; H 9.15.)

Methods for syntheses of ethers and xanthates from alcohols are closely related. In both cases the alcohol is first converted to its anion. This step is easily accomplished, even for tertiary alcohols, using methylsulfinyl carbanion as a base.[1,6] In general alcohols can conveniently be titrated with a standardised solution of this reagent in dimethyl sulfoxide with triphenylmethane as an indicator.[6] Alkylation of the anions obtained gives ethers, as shown in a previous paper.[7] The xanthates are obtained from the reaction of the anion with carbon disulfide followed by alkylation.

The xanthates listed in Table 1 can be readily prepared by the methylsulfinyl carbanion method in a few minutes at 20°. This means a reduction in reaction time from hours or even days at reflux, using methods described previously.[2]

S-Aryl xanthates are obtained from sodium xanthates and aqueous diazonium salts.[9] However, we obtained much better yields by running the reaction under anhydrous conditions. This can be achieved using non-aqueous diazonium salts prepared from atomatic amines and dinitrogen tetroxide in dimethyl sulfoxide according to Nilsson and Sjöberg.[10]

Xanthates are reported[11] to decompose at lower temperatures in polar solvents. This is in agreement with our findings. In dimethyl sulfoxide the xanthates of tertiary alcohols decompose below 20°. However, when washed free from dimethyl sulfoxide the *S*-methyl xanthate of 1-methylcyclohexanol is stable up to 50° and α-terpineyl *S*-methyl xanthate up to 40°. The *S*-methyl xanthate of the secondary alcohol 2-octanol decomposes at 160° in the absence of solvent and at 125° in the presence of dimethyl sulfoxide. The *S*-methyl xanthate of 1-octanol decomposes in the absence of solvent at 225°; no decomposition took place in boiling dimethyl sulfoxide at 189°.

Most studies on xanthates have been carried out on the *S*-methyl derivatives.[5] We have studied the influence of different *S*-substituents on the molar ratio of olefins formed and on the temperature of decomposition. The decomposition products of the *S*-methyl-, *S*-triphenylmethyl-, and *S*-(*p*-sulfophenyl) xanthates of α-terpineol were compared. No significant difference in olefin ratio was noticed; *cf.* Table 1. The temperature of decomposition is lowered by an *S*-aryl substituent. 2-Octyl *S*-(*p*-sulfophenyl) xanthate decomposes at 85° when free from solvent and below 50° in dimethyl sulfoxide; *cf.* 160° and 125°, respectively, for the *S*-methyl derivative. Refluxing 1-octyl *S*-(*p*-sulfophenyl) xanthate in dimethyl sulfoxide does not give complete decomposition within 48 h. On the other hand 1-octyl *S*-(*p*-nitrophenyl) xanthate decomposes at 165° when free from solvent and at 155° in dimethyl sulfoxide solution.

To investigate if the molar ratio of olefins formed is affected by the decomposition temperature, pyrolysis of 1-methylcyclohexyl *S*-methyl xanthate was studied. It has been previously reported[13,14] that when 1-methylcyclohexyl *S*-methyl xanthate decomposes at 200°, 1-methylcyclohexene and methylenecyclohexane are formed in a ratio of 4:1. We obtained the same ratio on decomposition at 200° and at 70°, as well as in dimethyl sulfoxide at 20°. In this case, the difference in temperature did not affect the ratio of olefins.

On pyrolysis of xanthates of cyclic alcohols, formation of the thermodynamically most stable olefin is generally favoured.[13] For xanthates of α-terpineol and 1- methylcyclohexanol this was found to be so, dipentene and 1-methyl-

cyclohexene being the major products. The formation of β-cedrene as the major product from cedrol is surprising. This olefin has an *exo*-methylene group attached to a six-membered, saturated ring, a configuration that is thermodynamically disfavoured.[13] When cedrol is dehydrated with iodine according to Mosher,[15] mainly the *endo* cyclic olefin, α-cedrene, is obtained.

Olefins formed by pyrolysis of xanthates are often contaminated with sulfur-containing impurities.[16] These were found to be easily removed by passing the olefin dissolved in petroleum ether through a column of silica impregnated with silver nitrate.[17] Sulfur-containing impurities were retained near the top of the column.

The xanthates prepared all have strong IR absorption bands in the region of 1070 – 1035 cm^{-1} and 1270 – 1230 cm^{-1}, *cf.* Table 2. For the *S*-methyl xanthates of tertiary alcohols the data indicate a shift to 1035 cm^{-1} of the reported [18] band at 1070 – 1050 cm^{-1}.

Table 2. Characteristic IR-frequencies of xanthates prepared.[a]

Alcohol	Xanthate	Characteristic bands at cm^{-1}		
α-Terpineol	*S*-CH_3	1265 (v.s.)		1035 (v.s.)
Cedrol	*S*-CH_3	1235 (v.s.)		1035 (v.s.)
1-Methylcyclohexanol	*S*-CH_3	1230 (v.s.)	1145 (m)	1035 (v.s.)
2-Octanol	S-CH_3	1230 (v.s.)	1115 (m)	1050 (v.s.)
2-Octanol	*S*-$C_6H_4SO_3H$	1270 (v.s.)	1120 (m)	1020 (v.s.)
1-Octanol	*S*-CH_3	1230 (v.s.)		1070 (v.s.)
1-Octanol	*S*-$C_6H_4NO_2$	1245 (v.s.)		1045 (v.s.)

[a] The spectra were recorded on a Perkin-Elmer 421 Infrared Spectrophotometer, using liquid films.

It has been shown in this work, that the disadvantages commonly encountered in the Chugaev reaction may sometimes be easily overcome. Olefins have been obtained, free from sulfur, from primary, secondary, and tertiary alcohols, at low decomposition temperatures. Our results indicate that the ratio of olefins formed is independent of decomposition temperature, solvent, and the substituent on the thiol sulfur.

Preliminary experiments [19] show that traces of Lewis acids, especially aluminium chloride in tetramethylene sulfone, drastically lower the decomposition temperature of xanthates. For instance the *S*-methyl xanthate of 2-octanol decomposes in the above mentioned mixture at 80° giving an isomerised product. As Lewis acids are known to isomerise olefins the reaction will be studied further.

EXPERIMENTAL

General procedure. Sodium methylsulfinyl carbanion (sodium methylsulfinylmethanide) was prepared according to Corey and Chaykovsky [1] with the modifications by Sjöberg [8] and standardised with formanilide using triphenylmethane as an indicator.

The alcohol to be dehydrated (0.020 mol) was dissolved in about 5 ml of dry dimethyl sulfoxide in a dry flask. A trace of triphenylmethane was added. An equivalent amount of methylsulfinyl carbanion in dimethyl sulfoxide was introduced from a pipette with stirring and cooling. When a bright red solution had been formed, carbon disulfide (0.025 mol) was added dropwise followed, under maintained stirring and cooling, by an alkylating agent, *e.g.* dimethyl sulfate (0.028 mol).

For arylation of xanthate anions the following procedure was used: A flask with a magnetic stirrer was charged with 10 ml of dry dimethyl sulfoxide and 0.02 mol of dinitrogen tetroxide. The aromatic amine (0.02 mol) in 10 ml of dry dimethyl sulfoxide (using sulfanilic acid) or dry ether (using *p*-nitroaniline) was carefully added with stirring and cooling with cool water. The mother liquor was removed by suction from the precipitated pale yellow diazonium salt. Danger! Do not allow the diazonium salts to become dry. It is not advisable to work with more than 1 g at a time. The precipitate was washed with 5 ml of dimethyl sulfoxide or ether and then suspended or dissolved in 10 ml of dry dimethyl sulfoxide. The freshly prepared sodium xanthate of 0.02 mol of the desired alcohol in 25 ml of dimethyl sulfoxide was then added dropwise with cooling and stirring. Evolution of nitrogen started immediately.

In some cases the xanthates separated as reddish upper layers that could be easily collected. Otherwise the xanthate was isolated by extraction with methylene chloride after addition of water to the reaction mixture. The methylene chloride layer was then washed five times with water. After drying over sodium sulfate, the solvent was removed *in vacuo* leaving the reddish xanthate. When sulfanilic acid is used, it is advisable to add hydrochloric acid when extracting with methylene chloride in order to get a better separation of the layers.

The xanthates of tertiary alcohols started to decompose directly in the reaction medium at 20°, those of secondary and primary alcohols decomposed on heating. The time for complete decomposition of xanthates varied from 1 to 10 h. Temperatures of decomposition are listed in Table 1. The olefins formed were directly distilled from the reaction mixture or extracted with petroleum ether. The olefin in petroleum ether was filtered through a column, which was constructed with silica of a particle size of 0.15–0.30 mm containing about 20 % silver nitrate.[17] After eluting with petroleum ether and removal of solvent the olefins were distilled. For analyses of olefins, see Table 1.

Separation of α-cedrene and β-cedrene was carried out as follows: The distilled mixture from pyrolysis of the xanthate of cedrol was chromatographed on an $AgNO_3$:SiO_2 column.[17] Eluting with diethyl ether: petroleum ether b.p. 40°–60° (1:20) yielded α-cedrene n_D^{22} 1.4978 (lit.[21] n_D^{20} 1.4982), IR identical with authentic sample, and β-cedrene n_D^{22} 1.5022 (lit.[21] n_D^{20} 1.5018).The IR spectrum of β-cedrene shows bands at 3065 cm^{-1} (m), 1640 cm^{-1} (s), and 890 cm^{-1} (s), which are in accordance with reported values.[21]

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