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Synthesis of S-dithiocarbonates with polymer-supported xanthates

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SUMMARY

Polymer-supported ammonium salts of methyl and ethyl xanthates react with alkyl halides to yield S-dithiocarbonates.

INTRODUCTION

Polymer supported reagents have been widely applied in organic synthesis (HODGE, SHERRINGTON 1980) mainly because of the ease of separation of the products. The readily available commercial macroporous anion exchangers, can be used with the same advantages of more sophisticated polymeric material: e.g. simple reaction work-up, an easy product isolation and mild reaction conditions.

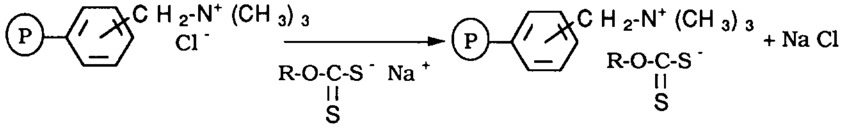
Supported sulfur nucleophiles have been recently described, eg: thioacetate (CAINELLI et al. 1981; 1983), thiophenates (CAINELLI et al.1982), dithiocarboxylates (CAIRON et al. 1988).

Here we describe the reaction of alkyl halides with polymer-supported xanthate anions.

PREPARATION OF SUPPORTED XANTHATES:

Amberlyst A-26, a commercially available† macro-reticular anion-exchange resin containing ammonium groups, is converted into methyl and an ethyl xanthate form by washing with aqueous sodium methyl xanthate and ethyl xanthate respectively.

Scheme I : Preparation of xanthate supported polymer



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EXPERIMENTAL. The chloride form of Amberlyst A-26 (40g) is shaken for 18h with an aqueous solution of methyl or ethyl xanthate sodium salt (0.2mol in 1000 ml of water). The resin is then filtered , washed at first with water (10X100ml), then with ethanol(2X100ml) and finally with ether (3X100ml). The resin is finally dried in vacuum.

The exchange capacity of the resin is found by microanalysis of the polymer to be 3.8 mmol of xanthate/g.

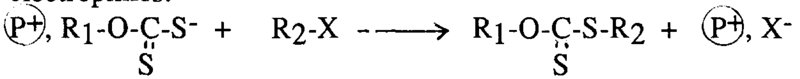
ALKYLATION WITH ALIPHATIC ELECTROPHILES

The alkylation of polymer supported methyl or ethyl xanthate turns out to be very easy and yields S-dithiocarbonates. S-dithiocarbonates are versatile intermediates in the synthesis of thiols(ISOLA et al. 1976), thiocarbonates (MORI et al. 1975; DEGANI et al. 1981), alkenes (NACE 1962), alkanes (BARTON et al. 1975; HARTWIG 1983), S-activated carbanion (DEGANI et al. 1979; TANAKA et al. 1979) and photosensitivers for polymerization of vinyl monomers(OKATAWA 1965).

EXPERIMENTAL

The above polymer-supported xanthate ion dry resin (3g) in cyclohexane (30ml) is stirred with alkyl halide (3mmol) under nitrogen. The resin is filtered off. The solvent is evaporated in vacuum and the residue is purified by Kugelrohr distillation.

Scheme II: Reaction of xanthate supported resin with aliphatic electrophiles:



$$\textcircled{P+}, R_1\text{-O-}\underset{\underset{S}{\|}}{C}\text{-S}^- + R_2\text{-X} \longrightarrow R_1\text{-O-}\underset{\underset{S}{\|}}{C}\text{-S-}R_2 + \textcircled{P+}, X^-$$

RESULTS AND DISCUSSION

Supported xanthates are very active nucleophiles, e.g. methylene chloride reacts with polymer supported xanthates and yield methylene S,S'-bisdithiocarbonates without any reaction observed with the sodium salts in homogeneous conditions. Similar activations were described for the supported carboxylates (DESHMUKH et al. 1987) and supported dithiocarboxylates (CAIRON et al. 1988) on ammonium resins. Supported xanthates appear to be strong nucleophiles and slightly basic reagents,which do not lead to elimination even with very sensitive compounds such as bromophenylethanes (5 to 8).

The products† are identified by their spectral data (IR,^{1}H NMR)(Table II) and by elemental analysis .

Table I: Reaction of Amberlyst A26, xanthate form with alkyl halides (20°C,18h).

Substrat R_1	R_2-X	Yield (%)	Product†	Formula:Mol.Mass
CH_3	CH_3CH_2I	92	1	$C_4H_8OS_2$:136.19
CH_3CH_2	CH_3CH_2I	95	2	$C_5H_{10}OS_2$:150.20
CH_3	$C_6H_5CH_2Cl$	52	3	$C_9H_{10}OS_2$:198.21
CH_3CH_2	$C_6H_5CH_2Cl$	68	4	$C_{10}H_{12}OS_2$:212.22
CH_3	$C_6H_5CH_2CH_2Br$	86	5	$C_{10}H_{12}OS_2$:212.22
CH_3CH_2	$C_6H_5CH_2CH_2Br$	89	6	$C_{11}H_{14}OS_2$:226.23
CH_3	$C_6H_5CHBrCH_3$	86	7	$C_{10}H_{12}OS_2$:212.22
CH_3CH_2	$C_6H_5CHBrCH_3$	85	8	$C_{11}H_{14}OS_2$:226.23
CH_3	CH_2=$CHCH_2I$	98	9	$C_5H_{10}OS_2$:148.19
CH_3CH_2	CH_2=$CHCH_2I$	99	10	$C_6H_{10}OS_2$:162.20
CH_3	$CH{\equiv}CCH_2Br$	86	11	$C_5H_6OS_2$:146.17
CH_3CH_2	$CH{\equiv}CCH_2Br$	87	12	$C_6H_8OS_2$:160.19
CH_3	CH_2Cl_2	1	13	$C_5H_8O_2S_4$: 228.31
CH_3CH_2	CH_2Cl_2	3	14	$C_7H_{12}O_2S_4$:256.34
CH_3	CH_2I_2	78	13	$C_5H_8O_2S_4$:228.31
CH_3CH_2	CH_2I_2	80	14	$C_7H_{12}O_2S_4$:256.34
CH_3Br	CH_2COOCH_3	85	15	$C_5H_8O_3S_2$:132.13
CH_3CH_2	$BrCH_2COOCH_3$	85	16	$C_6H_{10}O_3S_2$:194.11

Table II: **^1H N.M.R. spectra** of S-dithiocarbonates (60Mhz)

Product†	δ / TMS in CCl4
1	1.35(t,3H,CH_3)3.1(q,2H,CH_2S)4.15(s,3H,OCH_3)
2	1.3(t,3H,$C\underline{H}_3CH_2S$)1.4(t,3H,$OCH_2C\underline{H}_3$)3.1(q,2H,CH_2S)4.62(q, 2H,OCH_2)
3	4.1(s,3H,CH_3)4.3(s,2H,CH_2S)7.25(s,5H,C_6H_5)
4	1.4(t,3H,CH_3)4.3(s,2H,CH_2S)4.65(q,2H,OCH_2)7.25(s,5H,C_6H_5)
5	4,05(s,3H,CH_3)7.15 (s,5H,C_6H_5)
6	1.4(t,3H,CH_3)3,25 (m,4H,CH_2)4,6(q,2H,OCH_2) 7.15 (s,5H,C_6H_5)
7	1,7(d,3H,CH_3)4,05(s,3H,OCH_3)4.8(q,1H,CH) 7.25 (s,5H,C_6H_5)
8	1,3(t,3H,CH_3)1,7(d,3H,CH_3)4,05(q,2H,OCH_2)4.8(q,1H,CH) 7.25 (s,5H,C_6H_5)
9	3,8(d,2H,CH_2,J=6Hz)4.2(s,3H,CH_3O)6.3-5.0(m,3H,CH_2=CH)
10	1,4(t,$C\underline{H}_3CH_2$)3,8(d,2H,CH_2)4,65(q,2H,$C\underline{H}_2CH_3$) 6.3-5.0(m,3H,CH_2=CH)
11	2,25(t,1H,CH≡,J=3Hz)3,85(d,2H,CH_2)4.18(s,3H,CH_3O)
12	1,4(t,3H,CH_3)2,25(t,1H,CH≡,J=3Hz)3,85(d,2H,CH_2)4,8(q,2H,CH_2O)
13	4,2(s,6H,CH_3O)4,8(s,2H,CH_2)
14	1,4(t,6H,CH_3)4,7(q,4H,CH_2O) 4,8(s,2H,CH_2)
15	3,8(s,3H,CH_3)3.8(s,2H,CH_2S)4,2(s,3H,CH_3OCS)
16	1,4(t,3H,CH_3)3,8(s,3H,CH_3)3,95(s,2H,CH_2S)4,7(q,2H,CH_2O)

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†**I.R. spectra** (film): all S-dithiocarbonates are characterized by band positions: 2700 cm^{-1} (ν CH,SCH_x),1230 cm^{-1} (ν C-O),1150 cm^{-1}(ν C=S).

In conclusion the synthesis of small quantity of alkyl S-dithiocarbonates is easy and efficiently obtained from supported xanthates ions.

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