

CONVERSION OF XANTHATES TO DITHIOLCARBONATES CATALYZED BY 2,4,6-TRINITROALKOXYBENZENE

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Lewis acids¹ and more rarely protonic acids^{1b,2} have been used to cause catalytic rearrangements of thionic esters to thiolic esters. Recently, it was found in our study³ on thermolysis of cholesteryl S-methyl xanthate that phenol might have the same activity too. Therefore, a study was undertaken to investigate the catalytic activities of phenolic compounds in thermal reactions of xanthates. The chemical operation was performed in the following way: A xanthate was heated with a phenolic compound at about 180°C until UV spectrum of the reaction mixture had shown the disappearance of absorption band near 280 nm due to xanthate. Characterizations and quantifications of products were done by aids of GLC⁴ and IR spectroscopy with authentic samples.

Preliminarily, comparative catalytic activity of phenol, *p*-chlorophenol, *p*-nitrophenol, 2,4-dinitrophenol and picric acid was tested using ethyl S-*n*-butyl xanthate as substrate. Of those, picric acid induced 76% conversion of the xanthate to the dithiolcarbonate with use of 0.25 molar equivalent qualifying itself as the most active one. Hence, a series of xanthates were submitted to thermolysis in the presence of picric acid. As Table 1 shows, picric acid exhibited catalytic activity effectively with 0-*prim*-alkyl esters, but not with 0-*sec*-alkyl esters because of preferential elimination. A research group has reported the possible catalytic action of *p*-toluenesulfonic acid in the rearrangement of thionocarbamate^{1b}, nevertheless it was much inferior to the activity of picric acid in the present case (see Table 1, footnote b).

Table 1. Products (RSCOSR') from reactions of xanthates (ROCSSR') with picric acid (0.25 mol. equiv.) at 180°C

	substrate and product ^a		reaction time(hr)	yield(%)
	R	R'		
1	CH ₃	<i>n</i> -C ₄ H ₉	3.0	85
2	CH ₃	C ₆ H ₅ CH ₂	1.5	79
3	C ₂ H ₅	<i>n</i> -C ₄ H ₉	6.0	76 ^b
4	<i>n</i> -C ₃ H ₇	CH ₃	6.0	41
5	<i>iso</i> -C ₃ H ₇	CH ₃	0.5	— ^c
6	<i>n</i> -C ₅ H ₁₁	CH ₃	5.0	60
7	<i>cyclo</i> -C ₆ H ₁₁	CH ₃	0.5	— ^c

a) All compounds are known^{1d,5,6} except xanthate in 1, bp 107°C/22 mmHg, and dithiolcarbonates in 3 and 6, bps 92°C/15 mmHg and 62-64°C/0.8 mmHg⁷. b) Instead, the use of *p*-toluenesulfonic acid (0.5 mol. equiv.) resulted in 22 % yield. c) elimination

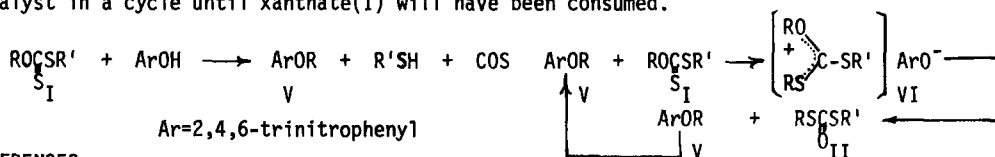
This suggests that actions of both protonic acids may be mechanistically different, though the catalysis of protonic acid has been shown to start with protonation to thiocarbonyl by a example of thionoacetate^{2b}. Incidentally, we found the existence of a small quantity of 2,4,6-trinitro-

Table 2^a

ROCSR' I		2,4,6-trinitroanisole 180°C		RSCSR' + CH ₃ SCSR' + RSR' II III IV		
R	R'	catalyst mol. equiv.	reaction time(hr)	product(%)		
				II	III	IV
CH ₃	C ₆ H ₅ CH ₂	0.1	0.5	78		
C ₂ H ₅	n-C ₄ H ₉	0.2	1.5	69	19	
n-C ₄ H ₉	n-C ₄ H ₉ ^b	0.2	2.5	66 ^b	19	
n-C ₅ H ₁₁	CH ₃	0.1	6.0	68	8 ^c	
C ₆ H ₅ CH ₂	CH ₃ ^c	0.1	0.5	56	4 ^c	29

a) See Table 1 for compounds to which remarks are not given. b) substrate: known compound⁶. product(II): bp 118-120°C/10 mmHg⁷ c) known compounds^{1d}

anisole in the reaction mixture of methyl S-n-butyl xanthate with picric acid. Getting a hint from this finding, picric acid was replaced by 2,4,6-trinitroanisole as an additive in reaction with xanthates. As be seen in Table 2, generally the trial made reaction time short producing dithiolcarbonates (II and III) in higher total yields. Furthermore, it showed intermolecular character of this reaction that thermolysis of a mixture of ethyl S-n-butyl and n-butyl S-methyl xanthates with picric acid gave ethyl methyl, ethyl n-butyl, n-butyl methyl and di-n-butyl dithiolcarbonates. These observations afforded a base for the mechanistical consideration of the catalytic rearrangement concerned as follows: The reaction starts from alkylation of picric acid with xanthate(I) producing 2,4,6-trinitroalkoxybenzene(V). The ether (V) works as alkylating agent⁸ on xanthate to form an unstable intermediate, alkoxy-di(alkylthio)carbonium ion(VI). Immediately, the cleavage of O-alkyl bond follows to convert VI to dithiolcarbonate(II) accompanying regeneration of ether V. Thus, ether V works as the real catalyst in a cycle until xanthate(I) will have been consumed.



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