

The Reaction of Thiols with β -1-Cyanoethyl D

TABLE I. REACTION OF THIOLS WITH PROPYLENE OXIDE AT 80° C FOR SIX HOURS
 Propylene oxide 0.2 mol., Thiol 0.3 mol., Free radical source 0.01 mol.

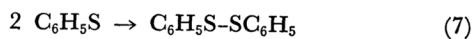
Thiol (RSH)	Free Radical Source (R'-R')	Yields of Products		
		CH ₃ -CH-CH ₂ SR OH % ^{a)}	RS-SR % ^{b)}	R'H % ^{b)}
C ₆ H ₅ SH	None	0	0	0
	(C ₆ H ₅) ₂ N-N(C ₆ H ₅) ₂	92	96	93
	C ₆ H ₅ CO-OC-C ₆ H ₅ O O	9.3	96	93
	(CH ₃) ₂ NCS-SCN(CH ₃) ₂ S S	75	90	
	(CH ₃) ₂ CN=NC(CH ₃) ₂ CN CN	0	99	
	None	0	0	0
C ₆ H ₅ CH ₂ SH	(C ₆ H ₅) ₂ N-N(C ₆ H ₅) ₂	99	98	98
	C ₆ H ₅ CO-OCC ₆ H ₅ O O	18	66	c)
	(CH ₃) ₂ NCS-SCN(CH ₃) ₂ S S	85	99	
	(CH ₃) ₂ CN=NC(CH ₃) ₂ CN CN	0	90	
	None	0	0	0

a) Mole % based on the amount of propylene oxide.

b) Mole % based on the amount of free radical source added.

c) Syrupy oil (2.36 g.) containing sulfur atom.

In these experiments the disulfides corresponding to the thiols were used as free radical sources.



The results presented above suggest that the reaction is not initiated by thiyl radicals derived from the reactions of thiols with free radical sources. The reaction may, then, reasonably explained as follows:

was converted to L-propylenebromohydrin with dry hydrogen bromide, and the bromohydrin was then cyclized to L(+)-propylene oxide with concentrated aqueous potassium hydroxide. The crude material was purified by refluxing it over potassium hydroxide pellets; b. p. 34.5–35°C, $[\alpha]_D^{25} : +16.51^\circ$

to the directions of Schuetz,²⁰⁾ and the 3, 5-dinitrothalate of this product showed no melting-point depression when mixed with an authentic sample (m. p.

ed completely with that of 1-benzylthio-2-propanol (λ_{max} 260.3 $m\mu$, ϵ_{max} 3.40×10^3 and λ_{max} 267.0 $m\mu$, ϵ_{max} 2.03×10^3).