

## The Free-radical Addition of Thiols to Hexachloronorbornadiene

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THE free-radical addition of *p*-thiocresol to      and Reeder<sup>1</sup> to give *exo*-norborn-5-en-2-yl *p*-tolyl norbornadiene (II) was shown by Cristol, Brindell,      sulphide (III) *via* 1,2-addition and 3-nortricyclyl

<sup>1</sup> S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Amer. Chem. Soc.*, 1958, **80**, 635.

*p*-tolyl sulphide (IV) *via* homoconjugative addition. They suggested the radicals (V) and (VI) as intermediates.

An investigation of the free-radical addition of thiols to hexachloronorbornadiene (I) has shown that the sole products are *endo*-(1,4,5,6,7,7-hexachloronorborn-5-en-2-yl) aryl (or alkyl) sulphide (VII) and *syn*-(1,2,3,5,6,6-hexachloronorborn-2-en-7-yl) aryl (or alkyl) sulphide (VIII). The yields and some physical properties of the products formed on reaction with thiophenol (a), *p*-thiocresol (b), *p*-bromothiophenol (c), and toluene- $\omega$ -thiol (d) with hexachloronorbornadiene (I) are reported in the table below:

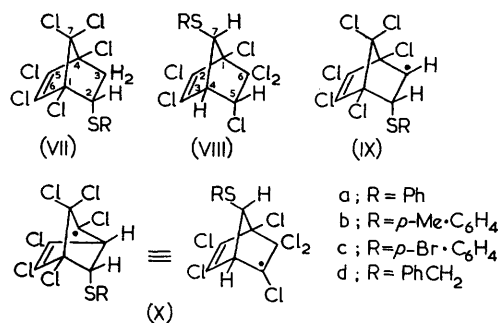
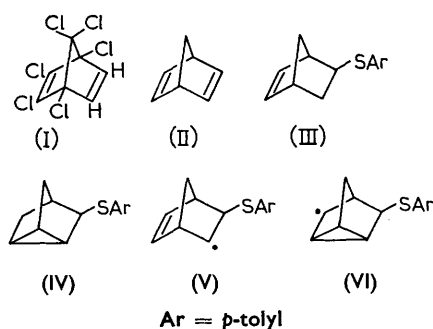
TABLE

% Yield and Properties of the Products from the Reaction of Thiols with Hexachloronorbornadiene

Compound	M.p.	Yield (%)	N.m.r. data						
			$\tau$ -Values		<i>J</i> -Values (c./sec.)				
			H <sub>2</sub> ( <i>exo</i> )	H <sub>3</sub> ( <i>exo</i> )	H <sub>3</sub> ( <i>endo</i> )	<i>J</i> <sub>2,3</sub> ( <i>exo</i> )	<i>J</i> <sub>2,3</sub> ( <i>endo</i> )	<i>J</i> <sub>3</sub> ( <i>exo</i> ), 3( <i>endo</i> )	
VIIa	36°	54	5.84	6.97	7.93	8.8	4.0	13.2	
VIIb	80°	62	5.89	6.96	7.93	8.6	3.9	13.0	
VIIc	66°	22	5.85	6.94	7.94	8.8	4.0	13.2	
VIIId	liquid	5.4	6.25	7.20	8.25	9.0	4.1	13.0	
VIIIa	100°	28	H <sub>4</sub>	H <sub>5</sub>	H <sub>7</sub>	<i>J</i> <sub>4,5</sub>	<i>J</i> <sub>4,7</sub>		
VIIIb	116°	23	6.63	5.11	6.02	3.9	1.8		
VIIIc	148°	33	6.57	5.03	6.02	3.8	1.6		
VIIId	43°	20	6.55	4.96	5.98	3.8	1.9		
			6.95	5.19	6.39	3.7	1.7		

The structure of (VIIa) was confirmed by identity with the Diels-Alder adduct of hexachlorocyclopentadiene and phenyl vinyl sulphide.<sup>2</sup> The n.m.r. data quoted for compounds (VIIa—VIIId)

thiols must occur exclusively from the *exo*-side of the molecule. The driving force for rearrangement is presumably the greater stability of radicals  $>\dot{\text{C}}\text{Cl}$  compared with  $>\dot{\text{C}}\text{H}$ .<sup>7</sup> The rate of chain



<sup>2</sup> M. F. Shostakovskii, A. V. Bogdanova, and T. M. Ushakova, *Proc. Acad. Sci. U.S.S.R. (Chem. Sect.)*, 1958, **118**, 91.

<sup>3</sup> K. L. Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 516.

<sup>4</sup> K. L. Williamson, N. C. Jacobus, and K. T. Soucy, *J. Amer. Chem. Soc.*, 1964, **86**, 4021.

<sup>5</sup> K. L. Williamson, *J. Amer. Chem. Soc.*, 1964, **86**, 5712.

<sup>6</sup> P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1964, **86**, 1171.

<sup>7</sup> A. N. Nesmeyanov, R. Kh. Friedlina, V. N. Kost, and M. Ya. Khorlina, *Tetrahedron*, 1961, **16**, 94.

transfer compared with the rate of rearrangement of (IX) to (X) governs the relative amounts of (VII) and (VIII) formed, and accounts for the larger proportion of rearrangement product formed on reaction with toluene- $\omega$ -thiol. It is noteworthy that in contrast to norbornadiene (II)

where exclusive *exo*-attack of thiyl radicals occurs, with hexachloronorbornadiene (I) attack is exclusively *endo* on account of the steric shielding of the *exo*-side of the molecule by the two bridge chlorine atoms.

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