

The Free-radical Addition of Thiols to Hexachloronorbornadiene

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THE free-radical addition of *p*-thiocresol to hexachloronorbornadiene (II) was shown by Cristol, Brindell, and Reeder¹ to give *exo*-norborn-5-en-2-yl *p*-tolyl sulphide (III) *via* 1,2-addition and 3-nortricyclyl

¹ 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- ω -thiol (d) with hexachloronorbornadiene (I) are reported in the table below:

are consistent with the work of Williamson³⁻⁵ on *endo*-substituted hexachloronorbornenes. The n.m.r. data for (VIIa—VIIId) are consistent with the structures postulated. The absence of a coupling constant of about 12 c./sec. rules out any structure with geminal protons; H₅ must be *exo* since coupling between H₄ and H₅, if *endo*, would have been approximately zero.⁶ The presence of the chlorine-substituted double bond is indicated by infrared absorption at 6.27 μ . This rules out any nortricycylene structure.

The results are consistent with *endo*-attack of a thiyl radical to give (IX) which may rearrange *via* a 1,2-shift to give (X). Chain transfer of (IX) with

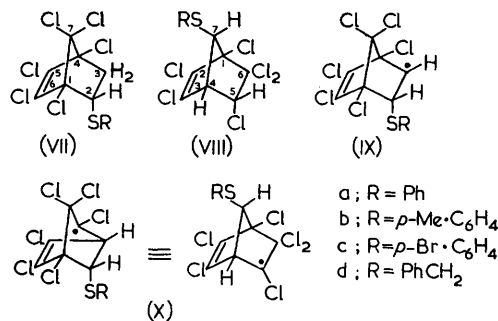
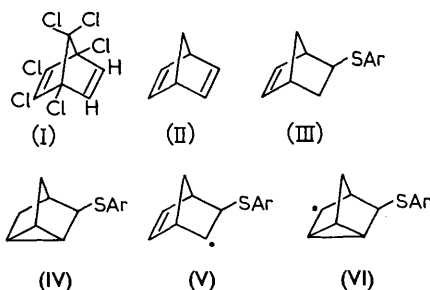
TABLE

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

Compound	M.p.	Yield (%)	N.m.r. data					
			H _{2(exo)}	τ -Values H _{3(exo)}	H _{3(endo)}	J _{2,3(exo)}	J-Values (c./sec.) J _{2,3(endo)}	J _{3(exo), 3(endo)}
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 ₄	H ₅	H ₇	J _{4,5}	J _{4,7}	
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	
VIIIId	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.² 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 $>\dot{\text{C}}\text{H}$.⁷ The rate of chain



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

³ K. L. Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 516.

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

⁵ K. L. Williamson, *J. Amer. Chem. Soc.*, 1964, **86**, 5712.

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

⁷ 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- ω -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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