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The Free-radical Addition of Thiols to Hexachloronorbornadiene

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The free-radical addition of p-thiocresol to and Reeder¹ 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

¹ S. J. Cristol, G. D. Brindell, and J. A. Reeder, J. Amer. Chem. Soc., 1958, 80, 635.

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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-(1,4,5,6,7,7hexachloronorborn-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 hexachloronorbornenes. endo-substituted n.m.r. data for (VIIIa-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 6.27μ . This rules out any nortricyclene 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

		•	N.m.r. data					
			τ-Values			J-Values (c./sec.)		
Compound	М.р.	Yield (%)	$\mathbf{H}_{2(exo)}$	$H_{3(exo)}$	$H_{3(endo)}$	${J}_{2,3(exo)}$	$J_{2,3(\mathit{endo})}$	$\int 3$ (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	$8 \cdot 6$	3.9	13.0
VIIc	66°	22	5.85	6.94	7.94	8.8	4.0	$13 \cdot 2$
VIId	liquid	$5 \cdot 4$	$6 \cdot 25$	7.20	$8 \cdot 25$	$9 \cdot 0$	4.1	13.0
			H_4	$\mathbf{H_5}$	H_7	$J_{4,5}$	$J_{4,7}$	
VIIIa	100°	28	6.63	5.11	6.02	$3 \cdot 9$	1.8	
VIIIb	116°	23	6.57	5.03	6.02	3.8	1.6	
VIIIc	148°	33	6.55	4.96	5.98	3.8	1.9	
VIIId	43°	20	6.95	5.19	$6 \cdot 39$	$3 \cdot 7$	1.7	

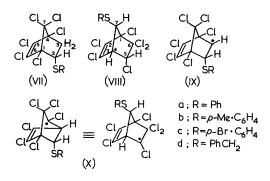
The structure of (VIIa) was confirmed by identity with the Diels-Alder adduct of hexachlorocyclopentadiene and phenyl vinyl sulphide.2 The n.m.r. data quoted for compounds (VIIa-VIId)

thiols must occur exclusively from the exo-side of the molecule. The driving force for rearrangement is presumably the greater stability of radicals >CCl compared with >CH.7 The rate of chain

CI CI CI SAr SAr (IV) (V) (VI)

$$CI CI H (II) (III) (III)$$

$$Ar = p-tolyI$$



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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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