

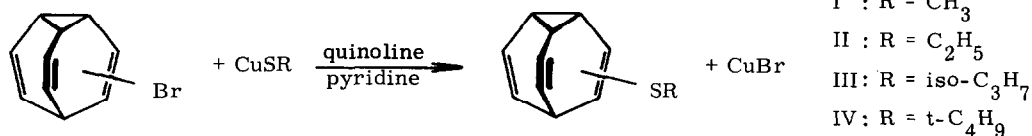
SYNTHESIS AND SPECTRAL PROPERTIES OF BULLVALYL THIOETHERS.

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We report on the synthesis of a series of thioethers of bullvalene, $C_{10}H_9SR$, in which R represents methyl, ethyl, isopropyl or t-butyl. The synthesis was achieved by refluxing bromobullvalene ¹⁾ with cuprous mercaptides in a mixture of quinoline and pyridine according to the equation:



The cuprous mercaptides were prepared according to literature procedures: CH₃SCu from methanethiol and cuprous chloride in aqueous ethanolic ammonia ²⁾, C₂H₅SCu from ethanethiol and cuprous oxide in ether ³⁾ and the other cuprous mercaptides from the corresponding thiols and cuprous oxide in ethanol by analogy with the procedure described in ref. 4.

The general experimental procedure was as follows:

5.0 g (24 mmoles) of bromobullvalene were dissolved in a mixture of 25 ml of quinoline and 8ml of pyridine; 32 mmoles of cuprous mercaptide ^{2, 3, 4)} were added to this solution and the resulting dark brown liquor was refluxed for 4 hrs. in an oil bath at 175-180°C. After cooling to about 100° the syrupy liquor was poured on ice and stirred for 1 hr. Then 30 ml of conc. HCl were added and stirring was continued for 15 min. The water layer was filtered off and extracted twice with ether. The residue was triturated with ether and the ether fractions were washed successively with dilute hydrochloric acid, ammonia and water. The total ether extract was then dried over Na₂SO₄ and evaporated. In the case of the methyl (I) and ethyl (II) derivatives the crude oil solidified and was recrystallized from methanol giving I (colourless crystals of m. p. 45-46°, yield 68%) and II (m. p. 46-47°, 77%). The crude oils of the other two thioethers III and IV did not crystallize and were purified by distillation in a small molecular still. III and IV were obtained as colourless oils (III distilled at 65°/0.05 mm, yield 80%; IV distilled at 78°/

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0.05 mm, yield 74%). After distillation IV was still contaminated by 2 other products in minor amount and was thus further purified by preparative VPC (silicone 20% - chromosorb in a glass column). During the study of the temperature dependence of the NMR spectra it was observed that IV was thermally less stable than the other bullvalene thioethers; there are strong indications that naphthalene derivatives are formed at high temperature. All bullvalyl thioethers gave correct elemental analyses.

UV spectra

The alkylthiobullvalenes I-IV have a UV absorption extending to 300 nm and show two weak but distinct shoulders at the wavelengths indicated in Table I, the shoulder at ca. 260 nm being most pronounced for II and III. On the other hand, the corresponding alkoxybullvalenes exhibit only end absorption (up to 270 nm); the ϵ values at $\lambda = 235$ nm ($\log \epsilon_{235}$) for the compounds of each series are given in Table I for comparison.

Table I: UV spectra of bullvalyl thioethers in n-hexane.

Compound	λ_{\max} (nm)	$\log \epsilon$	λ_{\max} (nm)	$\log \epsilon$	$\log \epsilon_{235}$	$\log \epsilon_{235}$ ^{a)}
I	220	3.90	260	3.53	3.74	3.38
II	220	3.91	259	3.52	3.63	3.48
III	220	3.92	261	3.44	3.62	3.48
IV	220	4.09	270	3.25	3.65	3.40

a) Values from ref. 1 for corresponding alkoxybullvalenes.

Analogous differences in the UV spectra are reported for the open chain O- and S-vinyl ethers: e. g. n-butyl vinyl ether has no absorption maxima above 200 nm ⁵⁾ whereas methyl vinyl sulfide has maxima at 230 nm ($\log \epsilon = 4.2$) and 240 nm ($\log \epsilon = 4.0$) ⁶⁾; furthermore absorptions at 224 nm ($\log \epsilon = 3.81$) and 249 nm (sh., $\log \epsilon = 3.4$) for cyclohexenyl methyl sulfide (a cyclic vinyl thioether) were reported ⁷⁾.

For an alkylthiobullvalene 4 positional isomers are possible; B, O_b, O_c and C (vide infra). The observed absorptions at ca. 260 nm being at longer wavelengths than those of alkyl and cycloalkyl vinyl sulfides suggests that the preponderant isomer is that (O_b) where the lone electron pairs of the S atom have maximum conjugation with the cyclopropyl vinyl system. This is confirmed by the study of the temperature dependent NMR spectra (vide infra).

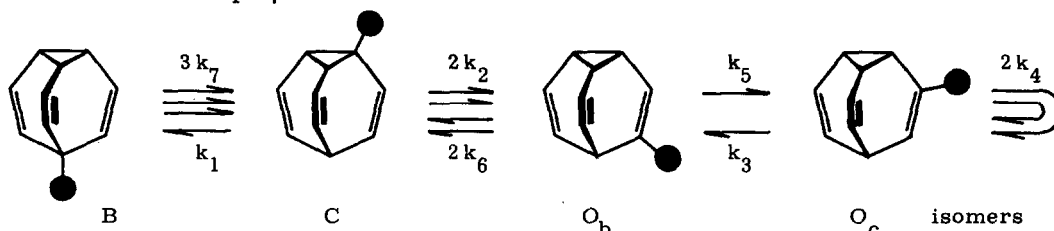
IR spectra

The IR spectra of the alkylthiobullvalenes are similar to those of the corresponding alkoxybullvalenes ¹⁾. However, there are characteristic differences in the C=C stretch region; the alkoxybullvalenes and bullvalene itself (as a liquid film and / or in CCl₄ solution) have one strong band at 1642 cm⁻¹, whereas I-IV all show two well-resolved weak bands at 1623 and 1642 cm⁻¹, the latter being slightly stronger. The C=C stretch mode of the OR substituted double bond

apparently coincides with those of the unsubstituted double bonds in the alkoxybullvalenes. For the alkylthiobullvalenes we therefore attribute the absorptions at 1642 cm^{-1} to the C=C stretching modes of the unsubstituted olefinic bridges and those at 1623 cm^{-1} to the SR substituted olefinic bridge. This assignment is supported by the IR absorption observed in open chain olefins: n-butyl vinyl ether absorbs at 1650 cm^{-1} ⁸⁾ but aliphatic vinyl thioethers of the formula $\text{RSCH}=\text{CHR}'$ (cis and trans) absorb at 1600 cm^{-1} ⁹⁾. Whether the substituent occupies the position O_b or O_c on the double bond cannot be deduced from the IR spectra.

NMR spectra and their temperature dependence

For the alkylthiobullvalenes the $\frac{10!}{3}$ valence isomers are not all identical as it is the case for bullvalene itself, but they are distributed among 4 sets of positional isomers: B, O_b , O_c and C¹⁾. The diagram shows how these positional isomers are related; the seven elementary isomerization rates k_1 - k_7 to be considered, together with their multiplicity are also indicated:



The NMR spectra of the alkylthiobullvalenes are expected to be temperature dependent: all bullvalyl protons are expected to pass through the 21 (=3+6+6+6) possible magnetic sites implied by the 4 positional isomers and to give one single line at high temperatures.

The NMR spectra of methylthiobullvalene (I) recorded at different temperatures are shown in fig. 1. The spectrum at -60°C corresponds to the slow exchange limit and indicates which positional isomer is preferred. This spectrum consists of 3 signals at $\tau = 4.30$ (multiplet), $\tau = 4.85$ (doublet) and $\tau = 7.90$ (complex signal) with relative intensities 4.0 / 1.0 / 7.0. This indicates that the substituent prefers to occupy one of the olefinic positions and therefore that the equilibrium is dominated by either the O_b or the O_c isomer. The doublet at $\tau = 4.85$ has to be attributed to the olefinic bullvalyl proton adjacent to the substituent ($J_{\text{H-H}} = 7.5\text{ Hz}$); the multiplet at $\tau = 4.30$ corresponds to the four other olefinic bullvalyl protons while the signal at $\tau = 7.90$ is the superposition of the signals of the three cyclopropyl, the bridgehead and the three methyl protons.

With increase in temperature, there is a progressive broadening of the bullvalyl proton signals at $\tau = 4.30$ and $\tau = 7.90$; on the contrary, the doublet at $\tau = 4.85$ (olefinic proton adjacent to the substituent) remains very sharp up to $+10^\circ\text{C}$. At higher temperatures the signals of all the bullvalyl protons coalesce into one single line at $\tau = 5.85$ (line width at $+80^\circ\text{C}$: $\Delta\nu = 9.0\text{ Hz}$). At all temperatures the methyl signal remains unaffected.

The line shape evolution of the signals of the bullvalyl protons is explicable under the

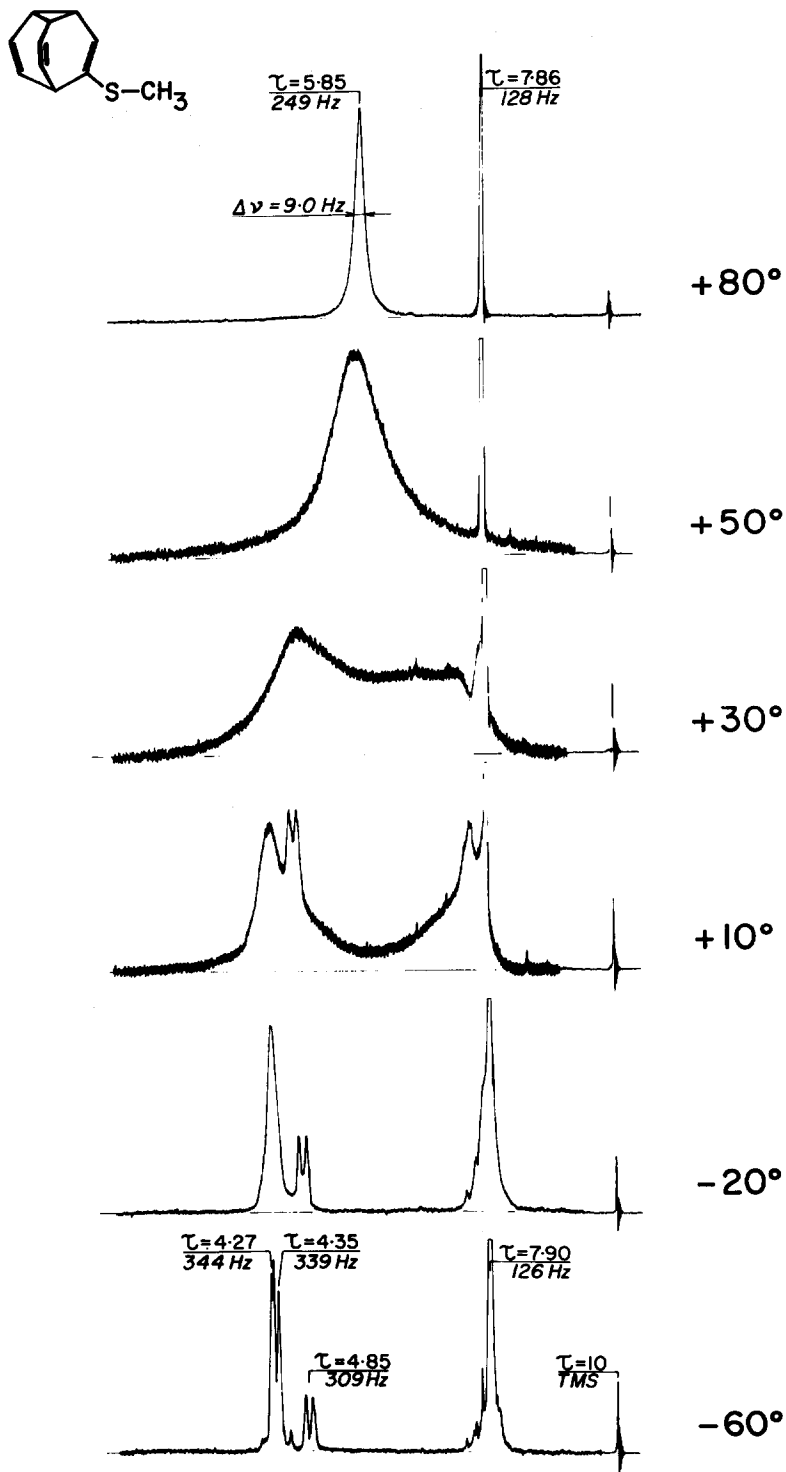
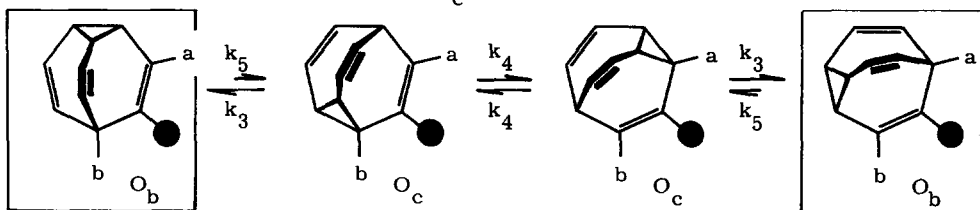


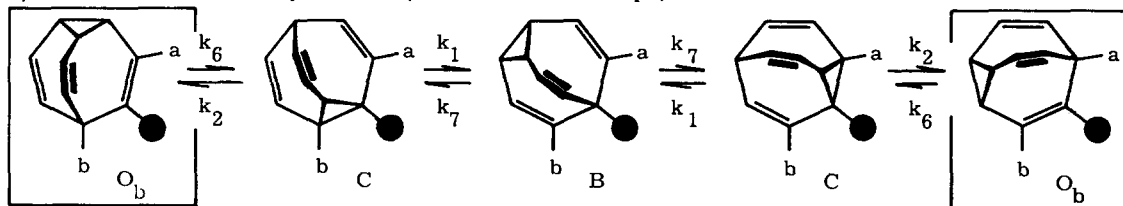
Figure 1 : NMR spectra of methylthiobullvalene at different temperatures.

assumption that the O_b isomer is the dominant species. In this case the doublet at $T = 4.85$ should indeed broaden at much higher temperature than do all the other bullvalyl signals. The reason is that at least three isomerization steps are required to exchange the magnetic environment of the olefinic proton on the same double bond as the substituent (proton a in the schemes below) while two steps ($O_b \xrightarrow{k_6} C \xrightarrow{k_2} O_b$) suffice to exchange the magnetic sites of the other bullvalyl protons:

1) either the molecule isomerizes via two O_c structures (3 isomerization steps):



2) or via the isomers C, B and C (4 isomerization steps):



That the O_c isomer cannot be the predominant one is explained with a similar argument: would O_c be the preferred isomer, then the isomerization $O_c \xrightleftharpoons{k_4} O_c$ would produce immediate exchange of the magnetic environment of the olefinic proton in question (cf. ref. 1).

As can be seen from fig. 1, all the bullvalyl protons of I become magnetically equivalent above 50°C and give one single NMR line. It should be noted that this complete magnetic equivalence of all the bullvalyl protons implies that O_c and C isomers are necessarily passed, whereas B isomers also are most probably but not necessarily passed.

All the other alkylthiobullvalenes II - IV show the same behaviour as I, i. e. :

- in all cases the O_b isomer is preferred,
- all the bullvalyl protons are magnetically equivalent at high temperatures (above 50°C).

This behaviour was also observed in the case of the alkoxybullvalenes with the exception of t-butoxybullvalene for which both isomers O_b and O_c are present in the same concentration. The steric effect invoked to explain this exceptional behaviour ¹⁾ does not arise in the case of t-butylthiobullvalene since the C-S bond is appreciably longer than the C-O bond (1.82 \AA versus 1.43 \AA). The NMR data in absence of exchange for the alkylthiobullvalenes are summarized in table II. In table III we compare the NMR data at 80° (condition of fast exchange) of the alkylthio- and alkoxybullvalenes. As can be seen from the line widths which are smaller for the alkylthio- and alkoxybullvalenes, the former isomerize much faster than the latter, but the sequence in each series remains the same.

Table II: NMR parameters in τ at -60° for alkylthiobullvalenes^{*)}

Substituent	Bullvalyl protons ^{**)}		Protons of substituents ^{**)}		
	olefinic	aliphatic	-CH ₃	-CH ₂	-CH
-SCH ₃	4.30 (4H, m) 4.85 (1H, d)	7.90 (4H)	7.90 (3H, s)		
-SCH ₂ CH ₃	4.32 (4H, m) 4.51 (1H, d)	7.88 (4H, m)	8.80 (3H, t)	7.48 (2H, q)	
-SCH(CH ₃) ₂	4.32 (4H, m) 4.51 (1H, d)	7.70 (2H, m) 7.87 (2H, m)	8.83 (6H, d)		7.05 (1H, sept)
-SC(CH ₃) ₃	3.83 (1H, d) 4.29 (4H, m)	7.43 (2H, m) 7.82 (2H, m)	8.78 (9H, s)		

*) Spectra were taken in CS₂ solution with TMS as internal standard at 60 MHz on DP-60 Varian apparatus.

**) In parentheses: number of protons and multiplicity: s=singlet, d=doublet, t=triplet, q=quadruplet, sept=septuplet and m=multiplet.

Table III: Position and line width of the signal of the bullvalyl protons of bullvalyl O- and S-ethers at 80°C (values for bullvalene and alkoxybullvalenes taken from ref. 1).

Substituent	H	-SMe	-SEt.	-S-iPr	-S-tBut.	-OMe	-OEt	-O-iPr.	-O-tBut.
τ	5.78	5.85	5.86	5.81	5.76	6.02	6.00	6.00	5.97
$\Delta\nu$ (Hz)	2.8	9.0	6.8	7.0	5.6	72.0	55.0	41.0	19.1
preferred isomer	-	O _b	O _b	O _b	O _b	O _b	O _b	O _b	O _b =O _c

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