to those minor absorptions in the spectra of the product mixtures. The infrared spectra of VII and VIII were nearly superimposable except for slight differences in wavelength for absorptions between 11 and 14 μ.

The nmr spectrum of a CCl_4 solution of VIII showed no peaks downfield of 178 cps. The cyclohexyl ring protons absorbed continuously throughout the region 59–178 cps, while the *t*-butyl protons had a shift of 53 cps.

Competitive Addition of HBr to 1-Chloro-4-*t*-butylcyclohexene (I) and 1-Chlorocyclohexene (IX).[13]—1-Chloro-4-*t*-butylcyclohexene (17.25 g, 0.100 mole), 1-chlorocyclohexene (11.65 g, 0.100 mole), and 88 ml of pentane were placed in a quartz flask. A Dry Ice condenser was attached and flask was immersed in a −78° bath. Hydrogen bromide (8.4 g, 0.10 mole) was condensed in the cold pentane solution and this stirred solution was irradiated for 1 hr using a medium-pressure mercury lamp. Analysis of the product mixture by vpc (fluorosilicone column at 125° with programming at approximately 2.5°/min) indicated that the area of the *cis*-1-bromo-2-chlorocyclohexane (X)[15] peak was 58.3% of the combined area of the two adduct peaks (II and X). Using the same vpc conditions as above, the relative response of the adducts was determined by analysis of a mixture of known composition of II and X. Applying this correction to the area measurement of the product mixture, it was found that the molar ratio, X/II, was 1.63/1.0.

Assuming complete reaction of HBr, the ratio of rate constants for reaction of each olefin with HBr can be calculated from the expression

$$\frac{k_{IX}}{k_I} = \frac{\log \frac{[IX]_i}{[IX]_f}}{\log \frac{[I]_i}{[I]_f}} = \frac{\log \frac{0.1}{0.038}}{\log \frac{0.1}{0.062}} = 2.0$$

(13) 1-Chlorocyclohexene was prepared by a procedure which was essentially that of Mousseron and Jacquier.[12] A 45% yield of IX was obtained: bp 77.0–78.3° (98 mm), $n^{25}D$ 1.4783 [lit. bp 50° (20 mm),[11] 63–65° (61 mm);[13] $n^{25}D$ 1.4772,[11] 1.4784[13]].

(14) H. L. Goering, D. I. Relyea, and D. W. Larsen, *J. Am. Chem. Soc.*, **78**, 348 (1956).

(15) *cis*-1-Bromo-2-chlorocyclohexane, bp 64–66° (1 mm), $n^{25}D$ 1.5230, was prepared by the ultraviolet-initiated addition of HBr to 1-chlorocyclohexene in pentane [lit.[2b] bp 87.5–88° (7 mm), $n^{25}D$ 1.5238].

Determination of Rate Constants for Alkaline Dehydrohalogenation. A. Dehydrobromination of *trans*-3-Bromo-*trans*-4-chloro-*t*-butylcyclohexane (II).—A solution of adduct II (0.0647 *M*) and 80% ethanol (0.1012 *M* in NaOH) was prepared in a volumetric flask which was placed in a bath at 24.92 ± 0.04°. Aliquots were removed periodically and pipetted into dilute nitric acid. After extraction of the resulting mixture with CCl_4, analysis of the aqueous layer for bromide was accomplished using the Volhard procedure. Eleven determinations involving 8–46% reaction gave $k_2 = (6.74 \pm 0.16) \times 10^{-4}$ l./mole sec.

B. Dehydrobromination of *cis*-4-Bromo-*trans*-4-chloro-*t*-butylcyclohexane (VII).—A solution of adduct VII (0.0496 *M*) and 80% ethanol (0.0973 *M* in NaOH) was apportioned among ampoules which were sealed and placed in an oil bath at 75.90 ± 0.02°. After the desired intervals of time, the ampoules were removed and plunged into ice–water. Aliquots were added to dilute nitric acid and analysis for bromide was accomplished as above. Eight determinations involving 14–63% reaction gave $k_2 = (24.2 \pm 1.6) \times 10^{-4}$ l./mole sec. The values of the rate constants showed a downward trend with increasing reaction more than likely indicating contamination by the less reactive adduct (VIII).

C. Dehydrohalogenation of *cis*-3-Bromo-*trans*-4-chloro-*t*-butylcyclohexane (VI).—A solution of adduct VI (0.0388 *M*) and 80% ethanol (0.101 *M* in NaOH) was prepared in a 25-ml volumetric flask. This solution was transferred to an alkali-resistant flask which was placed on a steam bath. The solution was refluxed (temperature approximately 82°) for the desired length of time and then cooled to room temperature for removal of an aliquot. Analysis for halide after 230, 545, and 2090 min indicated 7 to 23% reaction, assuming loss of 1 equiv of HX. The second-order rate constant was calculated, $k_2 = 3 \times 10^{-5}$ l./mole sec (average of three values, 4.9, 2.5, and 1.9×10^{-5}).

Acknowledgment.—Direct financial support from the Air Force Office of Scientific Research and fellowships (P. D. R.) from the National Science Foundation (Cooperative) and the Ethyl Corporation are acknowledged with thanks. The A-60 Varian proton resonance spectrometer was purchased with a grant from the National Science Foundation to our Department of Chemistry.

Stereochemistry of the Free-Radical Addition of Methyl Mercaptan to 1-Chloro-4-*t*-butylcyclohexene

P. D. READIO AND P. S. SKELL

Department of Chemistry, the Pennsylvania State University, University Park, Pennsylvania

Received April 20, 1965

The major product from radical-chain addition of methyl mercaptan to 1-chloro-4-*t*-butylcyclohexene is *trans*-3-methylmercapto-*trans*-4-chloro-*t*-butylcyclohexane (II), the result of diaxial addition; the other three isomers have been identified as minor products (12% total). The role of 1,2-sulfur bridging is discussed.

Free-radical thiol additions are generally less stereospecific than the additions of hydrogen bromide involving analogous systems. Additions to cyclic systems (except bridged bicyclic) show a preference for *trans* addition, although complete stereospecificity has not been reported. The reactions with acyclic molecules are essentially nonstereospecific. For the most part, the stereochemical results are rationalized by a mechanism involving classical radicals, with the lack of specificity attributed to the slow chain-transfer step. Isomerizations of alkyl radicals and even conformational changes in cyclic intermediate radicals are presumed to occur before the hydrogen-abstraction process is completed. The absence of complete specificity in thiol reactions has created little enthusiasm for a mechanism involving bridged sulfur radical intermediates. Those investigations of thiol additions completed before 1940 were summarized by Mayo and Walling,[1] while the more recent results have been described by Walling.[2] Work involving the stereochemical aspects have also been well reviewed by Bohm and Abell.[3]

More recently, Le Bel and Czaja have investigated the radical additions of thiophenol, hydrogen sulfide, and thiolacetic acid to 2-chloro-4-*t*-butyl-cyclohexene.[4] The product of *trans*-diaxial addition was the predominant adduct observed in each case, although products

(1) F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940).

(2) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(3) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962).

(4) N. A. Le Bel and R. F. Czaja, in press.

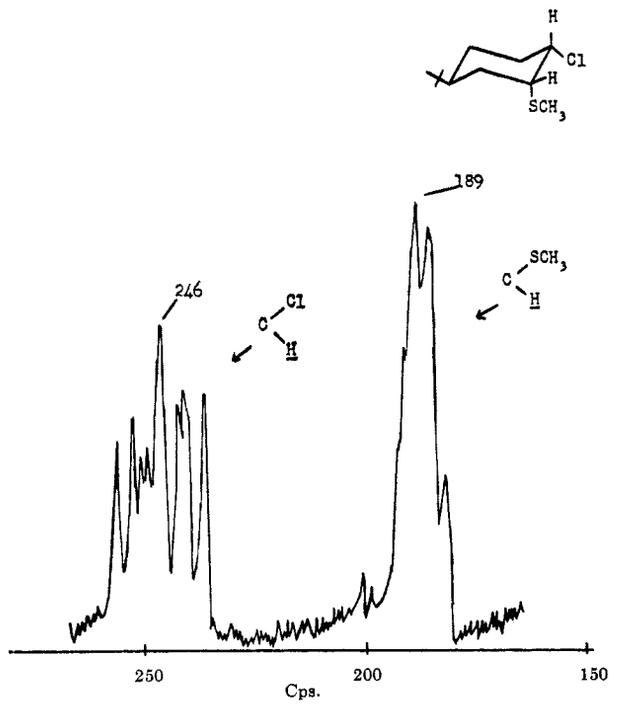
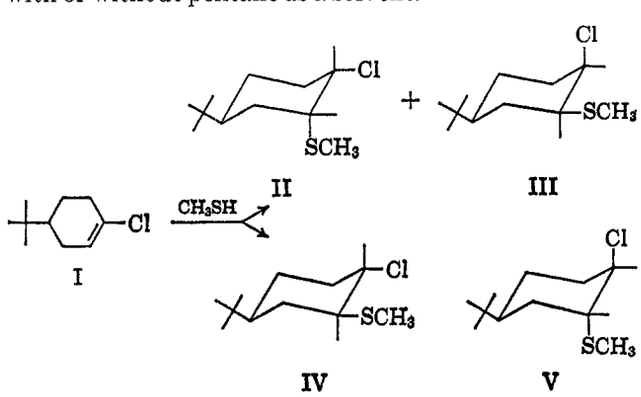


Figure 1.—The nmr spectrum of *trans*-3-methylmercapto-*trans*-4-chloro-*t*-butylcyclohexane (II).

from *trans*-diequatorial and from *cis* addition were also obtained.

Results

The free-radical addition of methyl mercaptan to 1-chloro-4-*t*-butylcyclohexene (I) proceeded readily to give good yields of 3-methylmercapto-4-chloro-*t*-butylcyclohexanes. The additions were initiated with ultraviolet irradiation and found to go equally well with or without pentane as a solvent.



The major product was *trans*-3-methylmercapto-*trans*-4-chloro-*t*-butylcyclohexane (II). This substance was obtained on distillation of crude product either as a liquid or as a partially crystallized material. Low-temperature recrystallization from pentane yielded solid II, mp 35–36°. This adduct amounted to about 88–91% of the products. By analogy to the hydrogen bromide addition[5] to I and the methyl mercaptan addition to 1-chlorocyclohexene,[6] a *trans* addition of thiol was anticipated. The *cis* relationship of the chloro and methylmercapto groups was verified by the inertness of the product to solvolysis by 80% ethanol; $k_1^{100} = 5.4 \times 10^{-7}$ sec^{-1} (see Table I for summary of rate constants). The *trans* relationship of these groups to the *t*-butyl was then established by the nmr spectrum (Figure 1, the *H*–C–SCH_3 and *H*–C–Cl region). The *H*–C–SCH_3 proton is equatorial (δ = 189 cps *vs.* TMS) whereas the hydrogen on C-4, *H*–C–Cl, is axial (δ = 246 cps).[7]

cis-3-Methylmercapto-*cis*-4-chloro-*t*-butylcyclohexane (III) was the second isomer with a *cis* relationship of methylmercapto and chloro groups. This material was slightly higher boiling than II and was initially observed in distillation fractions by its absorption in the infrared spectrum (14.3 μ). Low-temperature recrystallization of distillate containing II and III concentrated III (about 80% as estimated by nmr) in the mother liquor. The small quantity of concentrate precluded any further separation by distillation, but was sufficient for solvolytic and nmr studies. This minor adduct was estimated to be about 2% of the total product. This product likewise solvolyzed at a very slow rate; its first-order rate constant, $k_1^{100} = 6 \times 10^{-6}$ sec^{-1}, was somewhat larger than that for II, possibly owing to the axial position of the chlorine atom. The structure was assigned on the basis of the nmr spectrum (Figure 2). The *H*–C–SCH_3 absorption (δ = 160 cps) was split, indicating an axial hydrogen whereas the *H*–C–Cl absorption (δ = 262 cps) was indicative of an equatorial proton.

cis-3-Methylmercapto-*trans*-4-chloro-*t*-butylcyclohexane (IV) was also initially formed on addition, accounting for 7–10% of the radical products. This adduct was not isolated, but its presence was deduced from several observations. The product mixture before distillation contained a substance which solvolyzed in 80% ethanol with a first-order rate constant, $k_1^{25.2} = 4.8 \times 10^{-5}$ sec^{-1}. Comparison of this rate with that of *trans*-2-chlorocyclohexyl methyl sulfide,[10] $k_1^{34.7} = 5.04 \times 10^{-4}$ sec^{-1}, provides an indication of the relationship of the mercapto and chloro groups in the solvolyzable adduct. Accounting for the difference in temperature (factor of 2) and assuming the *trans*-2-chlorocyclohexyl methyl sulfide to be 50% in the reactive diaxial conformation, one obtains an estimated rate, $k_1^{25} = 5 \times 10^{-4}$ sec^{-1}, for the adduct having substituents in a *trans*-diaxial relationship. This structure is therefore not consistent with the slow rate observed, and the *trans*-diequatorial arrangement appears more likely. Further, a slow, careful vacuum distillation of the addition products through a spinning-band column allowed partial separation of the adducts, giving rise to a relatively low-boiling, fast-solvolyzing substance, $k_1^{24.9} = 7.3 \times 10^{-4}$ sec^{-1}, with infrared absorptions not found in the initial prod-

(5) *trans*-3-Bromo-*trans*-4-chloro-*t*-butylcyclohexane is the major adduct (95%) resulting from HBr addition to I. P. D. Readio and P. S. Skell, *J. Org. Chem.*, **31**, 753 (1966).

(6) The radical addition of methyl mercaptan to 1-chlorocyclohexene was investigated. Depending upon the conditions, the relative quantity of the *cis* adduct varied from 8.4 to 18%. P. S. Skell and P. D. Readio, in press.

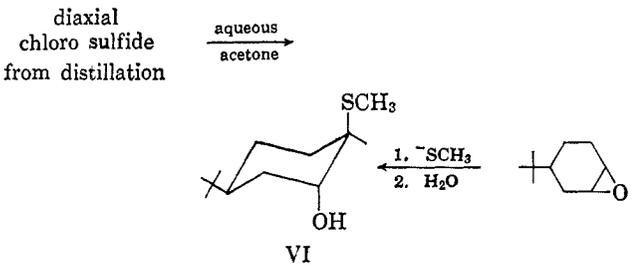
(7) As a consequence of the greater coupling constants between axial protons[8,9] the cyclohexyl X–C–*H* proton absorptions vary depending upon whether the protons are equatorial or axial. Equatorial hydrogens show absorptions which are fairly sharp, essentially unsplit, and relatively narrow at the base, whereas the axial protons are characterized by absorptions with a significant degree of splitting, often a multiplet of seven or eight peaks, and a greater base width.

(8) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 2237 (1958).

(9) N. O. Brace, *ibid.*, **84**, 3020 (1962).

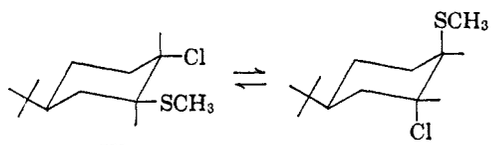
(10) Prepared by reaction of PCl_5 with *trans*-2-hydroxycyclohexyl methyl sulfide.

uct mixture. Since the nmr spectrum (Figure 3) indicated a *trans*-diaxial arrangement of substituents and since the rate of solvolysis is consistent with that estimated above for such a structure, this product was first thought to be *trans*-3-methylmercapto-*cis*-4-chloro-*t*-butylcyclohexane (V). However, refluxing this material with acetone containing 10% water yielded a hydroxy sulfide (isolated by elution with methanol from neutral alumina) which was identical (mixture melting point) with *trans*-3-hydroxy-*cis*-4-methylmercapto-*t*-butylcyclohexane (VI) prepared from methyl mercaptide addition to *trans*-4-*t*-butylcyclohexane oxide.[11] The chloro sulfide from distillation was thus identified as *trans*-3-chloro-*cis*-4-methylmercapto-*t*-butylcyclohexane (VII). Heating at 130–140° for 4



VI

hr results in nearly complete conversion of IV to VII. Since VII could not have formed on addition, rearrangement of the initially formed IV is suggested. Such rearrangements are reasonable in light of the facile



IV VII

rearrangements of 1,2-dibromides and bromohydrin tosylates.[12] Diaxial–diequatorial rearrangements of phenylmercapto and chloro groups are also known.[13] The rate data and evidence for rearrangement give support to a *trans*-diequatorial structure for the solvolyzable adduct, IV.

The *trans*-diaxial chloro sulfide, V, was not isolated, nor was its presence in the product mixture definitely established. Adduct V, if formed, would be expected to solvolyze rapidly, $k_1^{25} = 7 \times 10^{-4}$ sec^{-1}. On the basis of the high initial rate of solvolysis of a product mixture (not distilled), it was inferred that V was present; the maximum amount of this isomer was estimated to be 2.5% the total adduct. The ratio of IV to V in this case was about 3 to 1. For the above conclusion to be valid, the absence of other fast-solvolyzing materials is required. Solvolysis of a sample of product (not distilled) failed to produce any 4-*t*-butylcyclohexanone (infrared and gc), thus indicating at least that no 4-chloro-4-methylmercapto product was present.

The total amount of rapidly solvolyzable adducts formed (7%) was unaffected by a change in the concentration of methyl mercaptan from 2.8 to 14 *M*.

(11) Kindly provided by Dr. N. A. LeBel

(12) J. F. King, R. G. Pews, and R. A. Simmons, *Can. J. Chem.*, **41**, 2187 (1963).

(13) R. G. Pews, private communication.

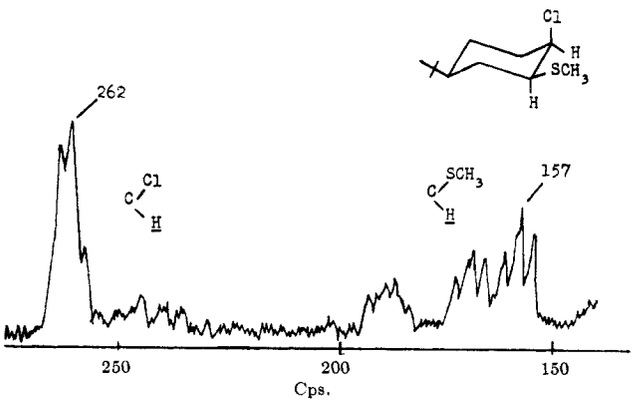


Figure 2.—The nmr spectrum of *cis*-3-methylmercapto-*cis*-4-chloro-*t*-butylcyclohexane (III).

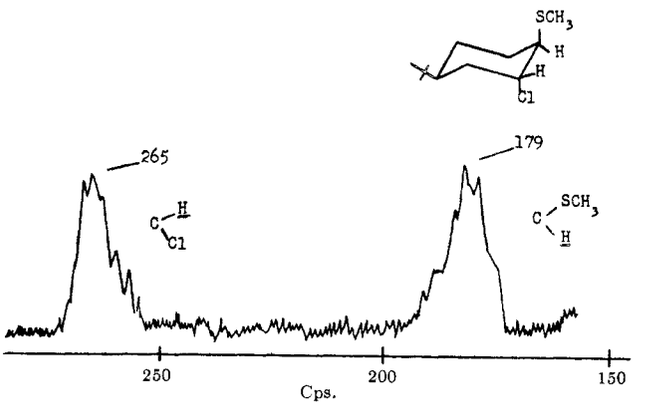
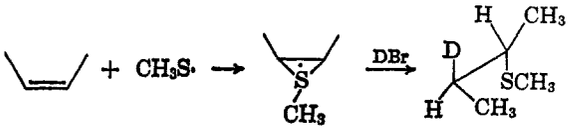


Figure 3.—The nmr spectrum of *trans*-3-chloro-*cis*-3-methylmercapto-*t*-butylcyclohexane (VII).

The relative quantity of these adducts showed a tendency to increase (from 7 to 10%) with increasing temperature.

Discussion

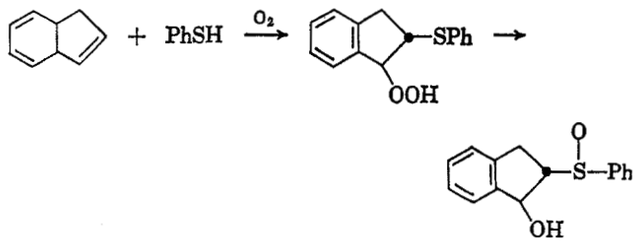
The absence of stereospecificity in radical thiol–olefin reactions has not generated a need for a mechanism involving bridged sulfur radical intermediates. However, the observation of Skell and Allen[14] that methyl deuteriomercaptan undergoes photoinitiated addition in a stereospecific *trans* manner to *cis*- and *trans*-2-butane *in the presence of deuterium bromide* indicated a high degree of steric control, suggesting the intermediacy of a bridged sulfur radical. The earlier results



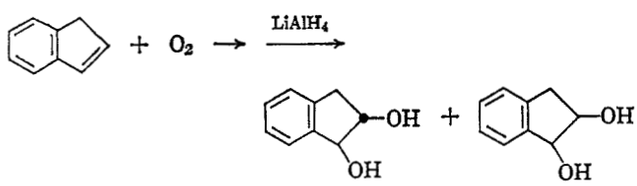
of Ford, Pitkethly, and Young[15] (which they interpreted with classical radical structures) also strongly suggest the existence of bridged sulfur radical species. They studied the cooxidation of thiophenol and indene and found the major product to be *trans*-2-phenylmercapto-1-indanyl hydroperoxide, which rearranges to the two diastereomeric *trans*-2-phenylsulfinyl-1-indanols. Careful analysis of the products indicated that the phenyl-

(14) P. S. Skell and R. G. Allen, *J. Am. Chem. Soc.*, **82**, 1511 (1960).

(15) (a) J. F. Ford, R. C. Pitkethly, and V. O. Young, *Tetrahedron*, **4**, 325 (1958); (b) see also A. A. Oswald, *et al.*, *J. Org. Chem.*, **24**, 443 (1959); **26**, 842 (1961); *J. Am. Chem. Soc.*, **86**, 3791 (1964).

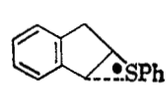


thiyl radical adds exclusively at the 2-position (±5%) and that attack of oxygen in the second step occurs *trans* (only 0.25% *cis* product detected) to the phenylmercapto group. By contrast, the copolymerization of indene and oxygen investigated by Russell[16] yielded a polymeric peroxide product which on reduction with

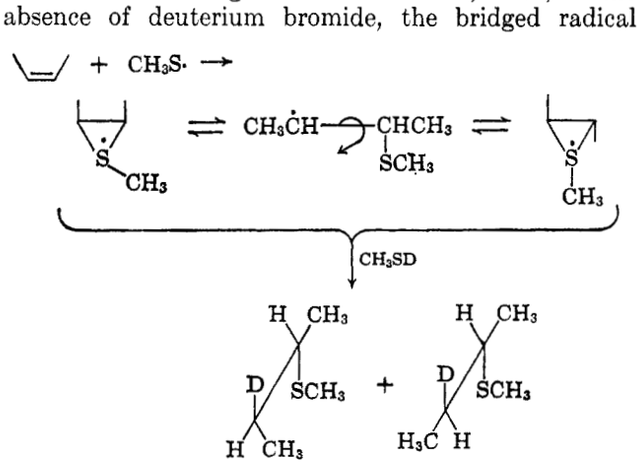


lithium aluminum hydride gave nearly equal amounts of the *cis*- and *trans*-indene glycols. In terms of processes involving the classical radical below, it is difficult to reconcile the high degree of specificity of oxygen addition in the cooxidation reaction with the

very low specificity of oxygen addition in the copolymerization. The following bridged species is required to explain the high degree of stereospecificity observed in the cooxidation process.

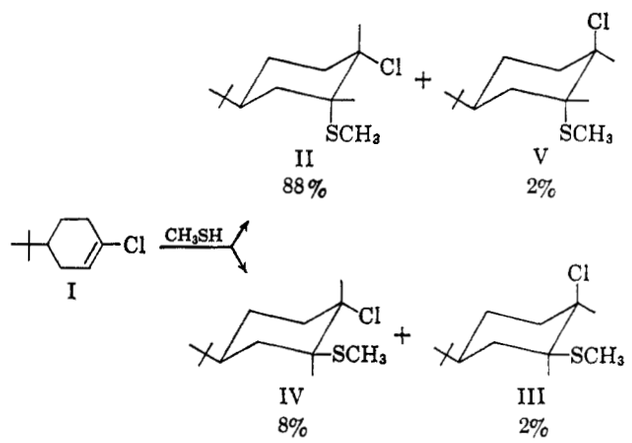


These experiments make a strong case for 1,2-sulfur bridging; this bridging is effective in controlling the steric course of the complete addition reaction only if the bridged radical is trapped by highly reactive reagents, such as DBr or O_2. With less reactive reagents loss of steric control is the rule, as illustrated[14] by the nonstereospecific addition of CH_3SD alone to *cis*- or *trans*-2-butene. Methyl deuteriomercaptan (CH_3SD) is considerably less reactive than deuterium bromide in transferring a deuterium atom; thus, in the absence of deuterium bromide, the bridged radical



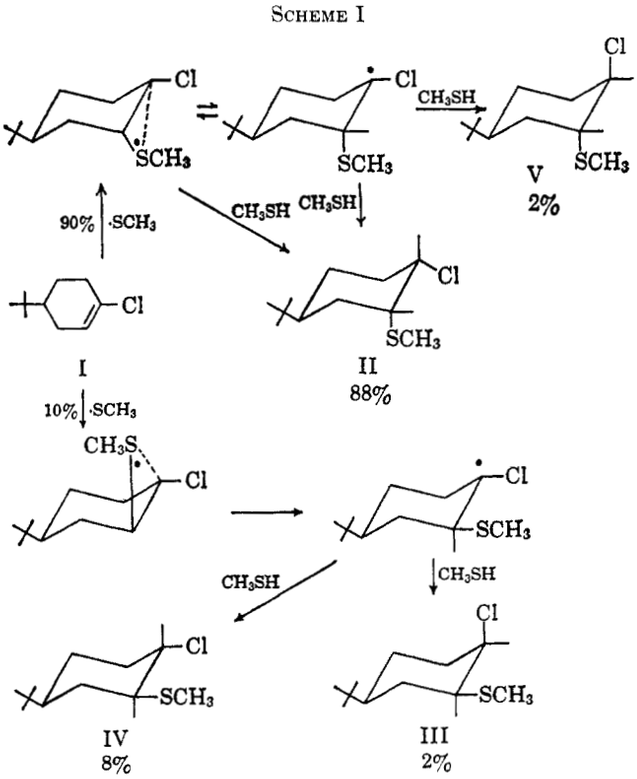
is converted to the 3-methylmercapto-2-butyl radical which undergoes rotational equilibration, resulting in nonstereospecific addition.[14] It is reasonable to assume that RS· additions to olefins which are not stereospecific follow the same course: initial formation of a bridged radical with conversion to the open-chain radical preceding the product-forming steps.

The radical addition of methyl mercaptan studied in this work proceeded to give the following primary products. As anticipated, this is an example in



which bridged intermediates participate but have a limited effect on the course of the second step of the additions. The results can be rationalized with Scheme I.

SCHEME I



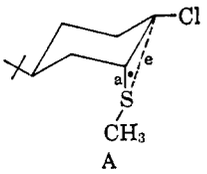
Although RS· additions to olefins are often reversible, this step is not indicated to be reversible in Scheme I, since at −78° the closely analogous 2-chloro-2-butenes are isomerized only 3% in the presence of thiolacetic acid while the additions were nonstereospecific.[17]

(16) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1035 (1956).

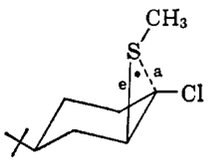
(17) N. P. Neuriter and F. G. Bordwell, *ibid.*, **82**, 5354 (1960).

The 90:10 preponderance of axial methylmercapto groups over equatorial is the same as observed with HBr additions to this olefin[5], 97:3. This reflects a preference for formation of the bridge *trans* to the *t*-butyl substituent, probably the result of activation energy difference, since at higher temperatures the proportion of rapidly solvolyzable products increases relative to the less reactive product (mainly II).

Asymmetry in bridged species was discussed for HBr additions[5] and the same considerations apply here, providing an explanation for B being the higher energy isomer. In A the stronger binding of the sulfur from axial orientation at C-2 leaves a larger free-



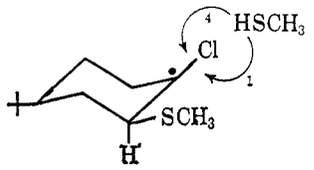
A



B

electron density on C-1 where the stabilizing effect of the chloro substituent operates. In B these effects are in opposition. Both A and B undergo ring opening to classical radicals by cleavage of the sulfur bond to C-4, leading to 3-methylmercapto products only; no 4-derivatives are obtained.

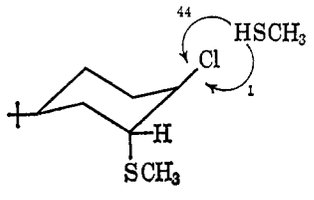
The major product derived from B is IV, requiring the classical radical intermediate B′. This cyclohexyl radical follows the well-documented behavior with preference for reaction from the axial direction.[18]



B′

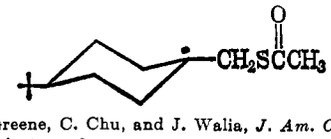
It is unlikely that III is the result of interaction of the bridged radical with methyl mercaptan, since this would require a high-energy boat-form transition state.[5]

Products II and V are derived from A; V clearly is derived from the open-chain radical A′. If both II



A′

(18) F. G. Bordwell and G. S. Whitney [Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962, p 64Q] reported a 9:1 preference for axial addition of a hydrogen atom from thiolacetic acid to



See also F. D. Greene, C. Chu, and J. Walia, *J. Am. Chem. Soc.*, **84**, 2463 (1962), and ref 5, footnote 6.

and V are derived from A′ exclusively, there is the problem of explaining an extraordinary preference for axial attack (44:1) for A′, the isomeric B′ showing only a 4:1 preference. A reasonable alternative consistent with these facts is that most of II is the result of methyl mercaptan reaction with the bridged radical A, a preferred reaction mode leading to diaxial addition.[5]

There have been several reports of additions to substituted cyclohexenes which show a dependence of isomer composition on mercaptan concentration, greater stereospecificity resulting from higher mercaptan concentrations. We have not observed this type of effect operating in the systems we have studied. With 1-chloro-4-*t*-butylcyclohexene a change of methyl mercaptan concentration from 2.5 (pentane solvent) to 14 *M* (CH_3SH solvent) gave crude products which contained 7%, respectively, of substances which solvolyzed in 30 min at 100° in 80% ethanol (isomers IV, V, and VII). Thus, there are no indications of conformational equilibrations among the intermediate radicals which are slower than reactions of the radicals with methyl mercaptan.

Experimental Section

Nmr Spectra.—Nmr spectra were obtained with a Varian A-60 nmr high-resolution spectrometer. Spectra were obtained on 24% solutions of adducts in CCl_4 with tetramethylsilane (TMS) as an internal standard. Shifts in cycles per second are referred to TMS. In addition to peaks reflected in Figures 1–3, the spectra of the methyl mercaptochloro adducts also contained the following expected proton absorptions: *t*-butyl (single peak), region 51–54 cps; $-SCH_3$ (single peak), region 124–132 cps; and cyclohexyl ring protons (numerous peaks), region 60–127 cps.

1-Chloro-4-*t*-butylcyclohexene (I), bp 82.5–83.0° (7 mm), $n^{25}D$ 1.4772, was prepared by the previously reported procedure.[5]

***trans*-3-Hydroxy-*cis*-4-methylmercapto-*t*-butylcyclohexane** (VI).—This hydroxy sulfide was prepared according to a procedure provided by Dr. LeBel. Metallic sodium (0.4 g, 0.017 mole) was dissolved in 90 ml of absolute ethanol contained in a 250-ml flask. Cold methyl mercaptan (5 ml, 0.09 mole) was added with *trans*-4-*t*-butylcyclohexane oxide (2.05 g, 0.0133 mole).[11] The reaction mixture was refluxed for 3 hr and then stirred for 16 hr. It was added to 100 ml of benzene and the resultant solution was washed with aqueous acetic acid, $NaHCO_3$, and water. The benzene layer was dried over $MgSO_4$. The benzene was removed by distillation. Attempted distillation of the residue caused solidification of the product. The crude product (87% yield) was recrystallized from pentane at −78°. The hydroxy sulfide VI was obtained, mp 58.5–60.5°. The nmr spectrum of this product was consistent with the assumed diaxial structure.

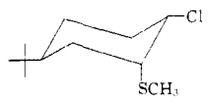
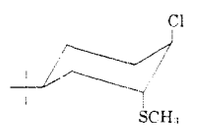
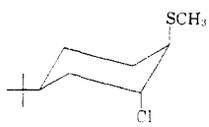
Radical Additions of Methyl Mercaptan to 1-Chloro-4-*t*-butylcyclohexene (I). A.—Methyl mercaptan (11 g, 0.23 mole) was added to a solution of 1-chloro-4-*t*-butylcyclohexene (17.2 g, 0.10 mole) in 100 ml of pentane contained in a quartz flask. The flask was immersed in a Dry Ice–2-propanol bath and the stirred solution was irradiated for 1 hr using a medium-pressure mercury lamp. The pentane was removed by distillation and the material which remained was distilled through a 24-in. spinning-band column (Table I). A 90% yield of products

TABLE I

Function	Wt, g	Head temp, °C	Pressure, mm	$n^{25}D$
1	1.01	75.5–84.0	0.3	1.5023
2	2.43	86.0–86.0	0.3	1.5043
3	3.06	82.0–82.0	0.2	1.5054
4	6.46	82.3–82.0	0.2	1.5053
5	6.85	82.0–75.0	0.2	1.5054
6	1.15	Residue		

TABLE II

RATES OF SOLVOLYSIS OF CHLORO SULFIDES

Compd	Infrared absorptions, μ	Isomeric purity, %	Found, %[a] C	Found, %[a] H	Temp, °C	k^t, sec^{-1} $\times 10^6$ [b]
	11.48, 14.52	100	59.96	9.80	100	0.54
	12.90, 14.27	~70	60.04[c]	10.12[c]	100	6
	13.63				25.2	48
						Probably same as VII
	14.72	>87	59.99	9.54	24.9	730

[a] *Anal.* Calcd for $C_{11}H_{21}ClS$: C, 59.83; H, 9.59. [b] Ethanol–water (80:20). [c] Recrystallization residue.

was obtained. *trans*-3-Methylmercapto-*trans*-4-chloro-*t*-butylcyclohexane (II) was the predominant product in all fractions as indicated by infrared analysis (characteristic absorption at 14.52 μ). The absorption at 14.72 μ due to VII (*trans*-3-chloro-*cis*-4-methylmercapto-*t*-butylcyclohexane) was prominent in the spectra of the first three fractions, decreasing in intensity in going from fraction 1 to 3; the 14.72-μ band was not present before distillation. Fractions 4 and 5 appeared to be relatively pure adduct II, the spectrum of fraction 5 showing a small absorption band at 14.3 μ attributed to adduct III.

Recrystallization from pentane at −70° separated pure II, mp 35–36°, concentrating the other isomers in the mother liquors. The lower-boiling fractions were richest in VII, the higher-boiling fractions in III. Maximum purities, compositions, etc. are listed in Table II.

Recrystallization of a crude reaction mixture prior to distillation yielded a concentrate of III (12.90 and 14.27 μ) and IV (13.63 μ), uncontaminated by VII (14.72 μ). Extended vacuum distillation or heating in a sealed ampoule (130–140°, 4 hr) resulted in nearly complete conversion of III to VII as evidenced by changes in the infrared spectrum and an increase in the rate of solvolysis of the rapid-solvolyzing component.

Pure II was oxidized with 30% hydrogen peroxide in glacial acetic acid to the sulfone, mp 141–142.5°.

Anal. Calcd for $C_{11}H_{21}ClO_2S$: C, 52.26; H, 8.37. Found: C, 52.19; H, 8.36.

7-Azabenzonorbornadiene[1]

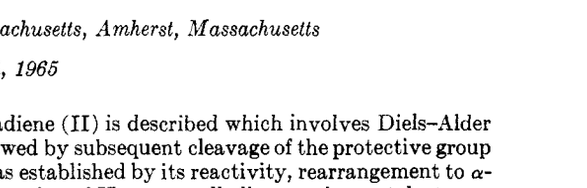
LOUIS A. CARPINO AND DONALD E. BARR

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

Received October 4, 1965

A practical method for the synthesis of 7-azabenzonorbornadiene (II) is described which involves Diels–Alder addition of benzyne to *t*-butyl pyrrole-1-carboxylate (IX) followed by subsequent cleavage of the protective group by hydrogen chloride in nitromethane. The structure of II was established by its reactivity, rearrangement to α-naphthylamine, and spectral examination. Catalytic hydrogenation of II over a palladium–carbon catalyst gave the dihydro derivative XII. Both II and XII yielded N-nitroso derivatives, although that obtained from II was unusual in undergoing facile decomposition to naphthalene.

Because of their unique structural features 7-substituted 7-azanorbornadienes such as the 7-halo, 7-hydroxy, and 7-amino derivatives are of considerable theoretical interest.[2] Since nitrogen-unsubstituted 7-azanorbornadienes could probably be converted to such compounds by means of ordinary techniques, we have begun an investigation of the synthesis of 7-azanorbornadiene (I) and its mono- (II) and dibenzo



I II III

(III) derivatives. The present paper describes a practical route to the middle member (II) of the series.

The first authentic derivative of the 7-azanorbornadiene system was reported by Mandell and Blanchard,[3] who showed that the 7-benzyl-2,3-dicarboxylic acid

(1) Abstracted from a portion of the thesis submitted by D. E. Barr in partial fulfillment of the requirements for the Ph.D. degree, 1965. Supported in part by the National Science Foundation under Grants NSF G-19506 and GP-4283.

(2) For a review of the interesting effects observable in the corresponding carbon compounds, see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 192–205.

(3) L. Mandell and W. A. Blanchard, *J. Am. Chem. Soc.*, **79**, 6198 (1957).