the fact that no methane is obtained in the reaction of VII.

It is also significant that only trace amounts (<1%) of benzene were formed in the thermal decomposition of IX. The ylide triphenylbenzylidenephosphorane, presumably an intermediate in the borohydride reaction, has been reported[11c] to give benzyldiphenylphosphine on reduction with lithium aluminum hydride. It appears that complex formation between the ylide and generated borane, with subsequent rearrangement, competes more successfully with an alternate cleavage process in the borohydride than in the lithium aluminum hydride reaction.

[13] National Science Foundation Senior Postdoctoral Fellow, 1966–1967.

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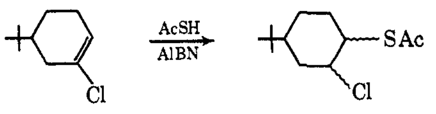
The Stereochemistry of the Free-Radical Addition of Thiolacetic Acid to 2-Chloro-4-*t*-butylcyclohexene

Sir:

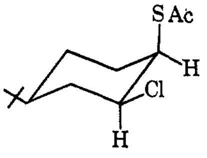
Contemporary studies of radical-chain additions to cyclohexenes[1] have been directed toward determination of both the *trans/cis* addition stereoselectivity and the conformational preference imparted to both the addition and the displacement steps by use of "conformationally fixed" cyclohexenes.[2–5] Although the additions of thiols are not stereospecific in contrast to those of hydrogen bromide,[2,6] *trans* stereoselectivity with a predominance of *trans*-diaxial addition has been observed.[2–4] In at least one case, the results have been attributed to the intervention of an unsymmetrically bridged thiyl radical which was said to account for ~88% of the reaction pathway.[3] The reported dependence of isomeric adduct (*trans/cis*) composition from 1-halocyclohexenes[7] on the ratio of thiol addenda to olefin was not verified with the 4-substituted cyclohexenes.[3–5]

We wish to report a study of the AIBN-initiated addition of thiolacetic acid to 2-chloro-4-*t*-butylcyclohexene (**1**). The *four* possible diastereomeric products were detected and characterized, and reproducible temperature and concentration effects were observed.[8] The results provide significant new data for a more detailed description of the stereochemical course of free-radical additions to cyclohexenes.

Typical runs afforded the following product distributions: 53.2% **2**, 5.7% **3**, 28.3% **4**, and 12.8% **5** in hexane at 63°; 78.7% **2**, 1.6% **3**, 12.8% **4**, and 6.9% **5** in hexane at −78°. A summary of pertinent stereochemical data is given in Table I. The products were separated by gas chromatography and characterized independently; in addition, **2** and **3** were compared with authentic samples. Proton nmr and infrared spectra completely supported the structural assignments.



1 **2-5**



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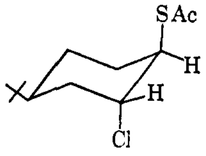

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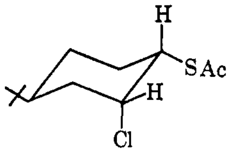

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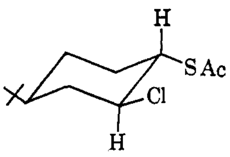

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Table I

Run	Molar ratio^a	Solvent (temp, °C)^b	(**2** + **3**)/(**4** + **5**)	**2**/**3**	**4**/**5**
1	1:10	Hexane (63)	1.2	6.3	1.9
2	1:1	Hexane (−78)^c	4.1	49.2	1.8
3		Pentane (37)	2.2	12.4	2.4
4		Hexane (63)	1.4	9.3	2.2
5		Heptane (86)	1.2	7.5	2.5
6		Heptane (106)	1.2	6.6	2.6
7		Methanol (64)	1.3	6.9	1.8
8	10:1	None (67)	2.4	11.4	2.0
9		Pentane (40)	3.1	15.5	2.4
10		Hexane (63)	2.5	10.0	2.2
11		Heptane (86)	1.8	8.2	2.2
12		Methanol (63)	1.9	7.7	1.8
13	30:1	None (63)	3.0	10.5	2.1
14		Methanol (66)	2.2	8.2	2.0

^{a} AcSH:olefin. Most solutions were made by adding AcSH to 3 ml of a 1 *M* solution of **1** in the solvent. ^{b} Reactions were generally run for 1 hr to 40–60% completion with 5 mole % AIBN. Analyses were by gc; deviations in normalized percentages were ±1.0% for **2** and **4**, and ±0.5% for **3** and **5**. ^{c} Ultraviolet initiated.

The results unequivocally demonstrate that the relative proportions of adducts vary significantly with changes in the molar ratio of starting materials and with temperature. These variations persisted in solvents of widely different polarity. The ratio of adducts resulting from axial relative to equatorial attachment of the thiyl group in the addition step [(**2** + **3**)/(**4** + **5**)] increases with lower reaction temperatures (runs 2–6, 8–11) and with higher molar ratios of thiol (runs 1, 4, 10; 5, 11; 7, 12, 14; 8, 13).

It is reasonable to attribute these *primary* concentration and temperature effects to reversibility of the addition step. Stereoelectronic control leads to preferential axial attack by the thiyl radical, affording intermediate **6**, whereas **7** would result from less-favored "equatorial attack."[9] This initial preference is at least 4:1 (run 2) and is probably much higher. Elevated temperatures and low thiol concentration favor reversal and

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[1] The stereochemistry of free-radical additions to olefins has been reviewed: B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962).

[2] N. A. LeBel, R. F. Czaja, and A. DeBoer, to be published.

[3] P. D. Readio and P. S. Skell, *J. Org. Chem.*, **31**, 759 (1966).

[4] F. G. Bordwell and G. S. Whitney, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, p 64Q; F. G. Bordwell, P. S. Landis, and G. S Whitney, *J. Org. Chem.*, **30**, 3764 (1965).

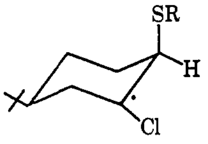
[5] *Cf.* also E. S. Huyser and J. R. Jeffrey, *Tetrahedron*, **21**, 3083 (1965); E. S. Huyser, H. Benson, and H. J. Sinnige, *J. Org. Chem.*, **32**, 622 (1967).

[6] See P. D. Readio and P. S. Skell, *ibid.*, **31**, 753 (1966).

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

[8] The synthesis of **1** and the results of other additions to **1** will be reported in the full article. Satisfactory elemental analyses have been obtained for most new compounds reported herein.

accumulation of products from the more stable[9] intermediate **7**. On the other hand, low temperature and high thiol concentration promote rapid displacement from the kinetically favored **6**. Radical-chain additions of HX species to 4-*t*-butylcyclohexenes, examined under similar reaction conditions, lead to decreasing amounts of products with axial-X groups in the following order: HBr > RSH > ArSH > AcSH > HSH. Reversibility is less important for the former three addenda, as a consequence of the lower stability of alkanethiyl radicals and the high transfer rate with ArSH, and especially with HBr.



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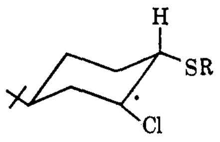

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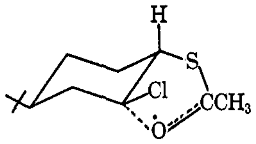

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The displacement reactions with intermediates **6** and **7** lead to over-all *trans* stereoselectivity, but that from **6** is considerably higher and is enhanced at low temperatures and high thiol concentrations. One tempting explanation for preferential *trans*-diaxial addition (to produce **2**) involves an *unsymmetrically* bridged thiyl radical as previously utilized.[3] However, if a bridged intermediate is dominant in promoting the high **2**/**3** adduct ratio, a significant variation in the magnitude of this ratio would be anticipated as the thiol addendum is altered. Although additional accurate data are required, it appears that the proportions of adducts **2** to adducts **3** are very similar for most thiols under identical conditions. Furthermore, even *symmetrically* bridged sulfur radicals, if such are intermediates, cannot maintain configurational integrity in additions to acyclic olefins.[1]

On the other hand, preferential axial chain transfer has been established for the 4-*t*-butyl-[10] and 1-thiolacetylmethyl-4-*t*-butylcyclohexyl[4] radicals. The vicinal, axial 1-thiyl substituent of **6** should direct displacement at C-2 even more toward the axial position, and a bridged thiyl radical is not required.

A surprising observation is that the ratio **4**/**5** is relatively insensitive to reaction conditions. The "open-chain" intermediate **7** appears to control product formation; however, it is intriguing to note that *trans* addition is favored over *cis* addition (**4**/**5** $\sim$ 1.8–2.6). Investigations of additions of other thiols to 1- or 2-halo-4-*t*-butylcyclohexenes have indicated that thiolacetic acid seems to be unique in providing a **4**/**5** ratio > 1.[2,3] A possible rationale for this reversal could involve the five-membered, bridged intermediate **8** in equilibrium with **7**, since this pathway is unavailable to alkyl- and arylthiols. However, a dipolar factor may be contributory, particularly in light of the results reported for 1-methyl-4-*t*-butylcyclohexene and thiolacetic acid.[4]

In the present case, the observed concentration effect does not involve chair–chair interconversions,[7] but rather comes mainly from reversibility of the addition step complemented by a secondary effect of variable chain-transfer preference with the axial thiyl radical **6**.

In the full article we shall elaborate a general scheme to accommodate all available data on the stereochemistry of radical additions of thiols to cyclohexenes. The present report serves to clarify certain existing ambiguities and also emphasizes the need for complete product identification.

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(9) It has been suggested that intermediates of type 7 arise by rapid and irreversible conformational reorganization of an initial twist-boat radical.[4,5]

(10) F. D. Greene, C. Chu, and J. Walia, *J. Am. Chem. Soc.*, **84**, 2463 (1962); *J. Org. Chem.*, **29**, 1285 (1964).

Coordination-Catalyzed Skeletal Rearrangement of 1,4-Dienes

Sir:

Our forthcoming publication[1] describes the addition of α-olefins to conjugated dienes, to produce high yields of 1,4-dienes. A homogeneous catalyst, prepared *in situ* from the reaction of a bis(tertiary phosphine)nickel(II) salt and an alkylaluminum compound, is employed. In an extension of this work we have investigated the behavior of the 1,4-diene products in the presence of the catalyst species.

3-Methyl-1,4-pentadiene (I, 0.012 mole), bis(tri-*n*-butylphosphine)nickel dichloride (0.001 mole), and diisobutylaluminum chloride (0.004 mole) were mixed in 100 ml of dry deoxygenated toluene. During 90 min at 24°, *ca.* 53% of I was converted to a mixture of products which included components with vpc retention times corresponding to a 35% yield of 1,4-hexadiene (*trans*:*cis* ratio = 11), a 4% yield of *trans*-2-methyl-1,-3-pentadiene, 8% *cis*-3-methyl-1,3-pentadiene, a 15% combined yield of *trans*-3-methyl-1,3-pentadiene and *trans,trans*-2,4-hexadiene, and 3% *trans,cis*-2,4-hexadiene. Two components, *ca.* 9 and 7%, have not been resolved and identified. The remainder was nonvolatile material, presumably oligomers of conjugated C-6 products.

It is apparent that the 3-methyl-1,3-pentadienes are derived from the double bond positional isomerization of I. However, the remaining products arise from skeletal rearrangements. A strong indication that the remaining C-6 conjugated products are derived from 1,4-hexadiene, as the primary rearrangement product, was found when *trans*-[2] and *cis*-1,4-hexadienes[3] were treated separately with the catalyst under the above conditions. During 120 min, 34% of the *trans* isomer was converted to *trans,trans*- and *trans,cis*-2,4-hexadiene (*trans,trans*:*trans,cis* ratio = 2.7) in 87% yield.

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(1) R. G. Miller, T. J. Kealy, and A. L. Barney, submitted for publication.

(2) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **87**, 5638 (1965).

(3) G. Hata, *ibid.*, **86**, 3903 (1964).