# The Stereochemistry of the Free-Radical Addition of Thiolacetic Acid to 1-Hexyne
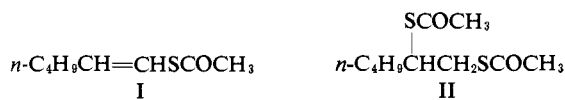
## J. A. Kampmeier and Gwendyline Chen

*Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. Received January 22, 1965*

The free-radical addition of thiolacetic acid to 1-hexyne gives a mixture of cis- and trans-1-hexenyl thiolacetates (cis- and trans-I). The cis and trans isomers have been isolated and characterized and the stereochemistry of the addition studied. When the hexyne/thiolacetic acid ratio is large, the products are configurationally stable under the reaction conditions and are formed in a trans/cis addition ratio of 82/18. This isomer ratio is not affected by a 78-fold change in the thiolacetic acid concentration. When the hexyne/thiolacetic acid ratio is small, the isomer ratio changes in the direction of the equilibrium mixture. The cis/trans-1-hexenyl thiolacetate equilibrium mixture is approximately 50/50.

## Introduction and Results

The free-radical addition of thiolacetic acid to alkyl acetylenes was first reported in 1949.[1,2] The general radical nature of the reaction and the gross chemical structure of the products were established at that time. In particular, the mono- and diadducts (I and II) of

$$n\text{-}C_4H_9CH{=}CHSCOCH_3 \qquad n\text{-}C_4H_9CHCH_2SCOCH_3$$

$$\text{I} \qquad\qquad\qquad \overset{\displaystyle SCOCH_3}{|}$$

$$\text{II}$$

thiolacetic acid to 1-hexyne were described. The stereochemistry of the monoaddition reaction was not investigated. Other workers have described the addition of thiolacetic acid to functionally substituted acetylenes.[3-5] cis and trans monoadducts were isolated and characterized in several cases, but the isomer ratios were not investigated. Recently, the *stereoselective*, but not stereospecific, formation of cis monoadducts in the addition of thiols to phenylacetylene was reported.[6] The addition of thiolacetic acid gave an 80/20 cis/trans monoadduct ratio. Although *trans* addition (giving cis adduct) is clearly preferred, Oswald and co-workers were not able to define the exact stereochemical course of the addition because of ambiguities due to isomerization of the monoadducts under the reaction conditions. Because of this isomerization, the observed adduct ratios are, at least in part, the result of thermodynamic rather than kinetic control.

This paper reports a study of the stereochemistry of the addition of thiolacetic acid to 1-hexyne. Particular emphasis is placed on the determination of the kinetically controlled isomer ratio. As reported by previous investigators,[1,2] thiolacetic acid and 1-hexyne

react rapidly on mixing to give the mono- and diadducts I and II. Deliberate initiation is not necessary. In this work, mixing 1-hexyne and thiolacetic acid at 0° in a 2/1 mole ratio and work-up by distillation gave a 55% yield of pure cis- and trans-1-hexenyl thiolacetate (I). The same procedure, employing a hexyne/thiolacetic acid mole ratio of 1/3, gave pure hexane-1,2-dithiol diacetate (II) in 33% yield. The diadduct II had physical properties in accord with those previously reported.[1,2] The 1,2-dithiol diacetate structure was established by Behringer[1] by synthesis.

The monoadduct product, cis- and trans-I, had physical properties in accord with those reported by Bader, et al.,[2] and was readily shown to be a mixture of two compounds (ca. 73/27) by v.p.c. The major component of the mixture had the lower retention time. No other materials could be detected. The n.m.r. spectrum of the monoadduct was in accord with a mixture of cis- and trans-I (ca. 75/25) and showed no extraneous absorptions. The gross anti-Markownikoff structure of the monoadduct mixture was confirmed by reaction of the mixture with 2,4-dinitrophenylhydrazine in ethanol containing sulfuric acid. This procedure, previously described by Bader, et al.,[2] gave an 85% crude yield of the 2,4-dinitrophenylhydrazone of hexanal.

**Table I.** Physical Data for *cis*- and *trans*-1-Hexenyl Thiolacetate



| | *cis* | *trans* |
|---|---|---|
| V.p.c. retention time min. | 23.5 | 25.5 |
| N.m.r.[a] | | |
| $J_{AB}$ | 9.6 | 15.9 |
| $J_{BX}$ | 7.1 | 6.4 |
| $J_{AX}$ | 1.3 | 1.1 |
| $\tau_A$ | 3.52 | 3.65 |
| $\tau_B$ | 4.28 | 4.24 |
| $\tau_{SCOCH_3}$ | 7.68 | 7.72 |
| Infrared,[b] cm.⁻¹ | | |
| C=C stretch | 1620 | Absent |
| *cis*-CH=CH out-of-plane deformation | 700 | Absent |

[a] The vinyl regions for both isomers show 12-line $ABX_2$ patterns. Coupling constants were measured directly from the line separations. Chemical shifts were calculated as the centers of gravity of the AB portions of the spectra: L. M. Jackman, "Application of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959. Coupling constants are in c.p.s. Chemical shifts are in p.p.m. relative to tetramethylsilane on the $\tau$-scale: G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958). [b] Liquid film.

(1) H. Behringer, *Ann.*, **564**, 219 (1949).
(2) H. Bader, L. C. Cross, I. Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 619 (1949).
(3) L. N. Owen and M. U. S. Sultanbawa, *ibid.*, 3109 (1949).
(4) L. W. C. Miles and L. N. Owen, *ibid.*, 817 (1952).
(5) H. Bader, *ibid.*, 116 (1956).
(6) A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *J. Am. Chem. Soc.*, **86**, 2877 (1964).

**Table II.** cis Isomer[a] (%) and Yield of Monoadducts[b] (%) in the Addition of Thiolacetic Acid to 1-Hexyne

| Run | Mole ratio[c] of H/TA/PC | Reaction time, min. | | | | | |
|-----|--------------------------|------|------|------|------|------|------|
| | | 0.5 | 1 | 5 | 30 | 120 | ∞[d] |
| 1 | 1.01/1.00/0.37 | 78 (35) | 76 (45) | 76 (45) | 74 (46) | 74 (45) | 73 (45) |
| 2 | 1.71/1.00/0.34 | 81 (33) | 80 (46) | 79 (52) | 79 (55) | 79 (53) | ... |
| 3 | 2.01/1.00/0.45 | 82 (23) | 81 (38) | 81 (51) | 80 (57) | 80 (58) | 79 (59) |
| 4 | 5.45/1.00/0.61[e] | ... | 83 (33) | 81 (54) | 82 (63) | 82 (66) | 81 (65) |
| 5 | 14.7/1.00/0.27 | ... | 83 (37) | 82 (57) | 82 (72) | 83 (75) | 82 (72) |
| 6 | 63.3/1.00/0.40 | ... | 83 (28) | 82 (48) | 83 (59) | 83 (64) | 82 (60) |
| 7 | 131/1.00/0.65 | ... | 83 (19) | 83 (30) | 83 (40) | 83 (44) | 82 (45) |
| 8 | 530/1.00/0.18[f] | ... | ... | 84 (5) | 82 (12) | 84 (17) | 83 (17) |

[a] $\% \, cis = \dfrac{cis}{cis + trans} \times 10^2$.  [b] Based on thiolacetic acid. Values are per cent cis isomer; values in parentheses are per cent yield.
[c] H = 1-hexyne; TA = thiolacetic acid; PC = phenylcyclohexane.  [d] Final measurements were made at varying times. The minimum time for the final measurement was 2.5 days, the maximum time was 15 days.  [e] $[CH_3COSH] = 1.28 \, M$.  [f] $[CH_3COSH] = 0.0165 \, M$.

Pure samples of the components of the monoadduct mixture were isolated by preparative-scale v.p.c. The n.m.r. spectra allowed definite structural assignments. Relevant data are shown in Table I. Similar data for the cis and trans adducts of thiols and phenylacetylene have been reported by Oswald and co-workers.[6] Most compelling are the olefinic coupling constants, $J_{AB \, cis}$ and $J_{AB \, trans}$. It is clear from previous work that the larger of these coupling constants is to be associated with the trans isomer.[7-10] The qualitative agreement between the v.p.c. and n.m.r. peak areas for the cis and trans monoadduct mixture suggested that the adducts were not isomerized by v.p.c. This was quantitatively confirmed by preparing mixtures of known weight proportions from the pure cis and trans isomers. A plot of weight ratio vs. v.p.c. peak area ratio was linear with a slope of 1.

The stereochemistry of the monoaddition reaction was quantitatively determined in the following manner. Mixtures of known weights of 1-hexyne, thiolacetic acid, and phenylcyclohexane (an inert, internal standard for v.p.c. analysis) were prepared rapidly at 0° and samples were withdrawn at various intervals. The samples were added immediately to dilute aqueous sodium hydroxide at 0° to quench the reaction.[6] The cis/trans monoadduct ratio and the per cent yield of the monoadducts were determined for each sample by v.p.c. analysis. Examination of the isomer ratio as a function of per cent reaction allowed a determination of the importance of isomerization of the monoadducts under the reaction conditions. The isomer ratio and per cent conversion were also studied as a function of the concentration of thiolacetic acid. Extensive control studies (see Experimental) established the validity of the analytical procedure. The results of the quantitative studies are shown in Table II.

The results in Table II (runs 4–8) show that at hexyne/thiolacetic acid ratios ≳6, the isomeric composition of the monoadduct mixture is independent of the extent of the reaction. The cis/trans ratio is constant at 82/18 while the per cent yield of monoadducts approximately doubles. Since the reaction is clearly proceeding, the

constant isomer ratio indicates that either (1) product isomerization is not important under these conditions, or (2) the cis/trans equilibrium mixture has an 82/18 composition. Table III shows that the composition of the equilibrium mixture is approximately 50/50. It is clear, therefore, that the true cis/trans adduct ratio is 82/18 and that this is the kinetically controlled ratio. The addition of thiolacetic acid to 1-hexyne, therefore, is preferentially trans, but not stereospecific.

**Table III.** Equilibration of cis- and trans-1-Hexenyl Thiolacetate

| Procedure | Initial % cis isomer | Final % cis isomer |
|-----------|----------------------|--------------------|
| a | 77 | 50 |
| | 17 | 50 |
| b | 74 | 53 |
| | 20 | 52 |

[a] Samples heated at 90° under nitrogen for 11–12 days.  [b] Samples irradiated with a sunlamp in Pyrex at 21–25° in the presence of ca. 1 mole % thiophenol for 2–3 days.

At hexyne/thiolacetic acid ratios ≲6, the composition of the monoadduct mixture is a function of the extent of reaction and is also sensitive to the hexyne/thiolacetic acid ratio. The changes in the isomer ratio are in the direction of the equilibrium mixture. This variation is logically attributed to the interconversion of the isomeric monoadducts by thiolacetic acid. A change in the isomer composition of the monoadduct mixture would also result if the cis and trans monoadducts were converted to diadduct (II) at different rates. We have not studied diadduct formation directly, but it may account for some of the deviation from the kinetically controlled isomer ratio at hexyne/thiolacetic acid ratios ≲6. Diadduct formation is an unfortunate attribute of the hexyne/thiolacetic acid system, since it complicates a study of the monoaddition reaction in the presence of high concentrations of thiolacetic acid.

**Discussion**

These results on the stereochemistry of the addition of thiolacetic acid to 1-hexyne may be compared with data involving other acetylenes and addenda. Skell and Allen[11,12] have studied the free-radical addition of

(7) L. M. Jackman, Table I, footnote a.
(8) N. S. Bhacca and D. H. Williams, "Applications of N.M.R. Spectra in Organic Chemistry," Holden-Day, Inc., San Francisco Calif., 1964.
(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 238 ff.
(10) M. Karplus, J. Chem. Phys., 33, 1842 (1960).

(11) P. S. Skell and R. G. Allen, J. Am. Chem. Soc., 80, 5997 (1958).
(12) P. S. Skell and R. G. Allen, ibid., 86, 1559 (1964).

hydrogen bromide to propyne in solution and in the gas phase. The reaction is stereospecific and *trans* in both cases under conditions where the products are configurationally stable. Skell suggested that other radical additions to acetylenes might also be stereospecific. Benkeser found that the radical addition of trichlorosilane to 1-heptyne gives a 75/25 *cis/trans* adduct ratio.[13,14] The *cis/trans* ratio was reported to be "essentially constant" after reaction times of 4, 10, and 20 hr. Since it was not established that the reaction is still in progress after 4 hr., it is not permissible to equate the 75/25 adduct ratio with the kinetically controlled adduct ratio. In several other cases of radical additions to acetylenes, the available data also do not allow a definitive assignment of the stereochemistry of the reaction.[15]

The over-all addition reaction presumably involves a vinyl radical intermediate. A description of the reaction is shown in Chart I. In the most general case, the composition of the product mixture will depend on

Chart I
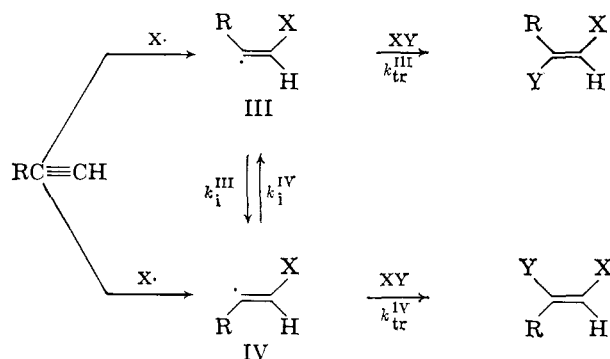


the stereochemistry of the initial radical addition step (giving III and/or IV) and on the relative rates of interconversion ($k_i^{III}$ and $k_i^{IV}$) and chain transfer ($k_{tr}^{III}$ and $k_{tr}^{IV}$) of the intermediate radicals. Two limiting cases of this "general case" are possible.

A. $k_i \ll k_{tr} [XY]$. The product composition is determined by the stereochemistry of the initial addition step.

B. $k_i \gg k_{tr} [XY]$. The product composition is determined by the difference in free energies of the transition states for the conversion of III and IV to product. The stereochemistry of the initial addition step is irrelevant.[16]

It is difficult to give a detailed description of these radical additions because of a lack of information about the individual steps. Unfortunately, there is no compelling, independent evidence concerning the stereochemistry of the initial addition step.[17] E.s.r. studies

(13) R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958).

(14) R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *ibid.*, **83**, 4385 (1961).

(15) (a) *Cf.* references quoted by Oswald, *et al.*[6]; (b) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962); (c) N. O. Brace, *J. Org. Chem.*, **27**, 4492 (1962); K. Leedham and R. N. Haszeldine, *J. Chem. Soc.*, 1634 (1954); (d) L. D. Bergelson, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1235 (1960).

(16) D. Y. Curtin, *Record Chem. Prog.* (Kresge-Hooker Sci. Lib.), **15**, 111 (1954).

(17) Adrain, Cochran, and Bowers observed the formation of only

the *trans* vinyl radical, $\begin{smallmatrix} D \\ {}_{\diagup}=<{} \\ D \quad\; H \end{smallmatrix}$ , in the addition of a hydrogen atom to deuterioacetylene in a matrix at 4°K.[18] They pointed out, however, the difficulties in interpreting this observation.

of the vinyl radical, $CH_2\text{==}CH$, show that there is only an $\sim 2$-kcal./mole barrier to inversion at the radical center.[18,19] The 1-methylvinyl radical,[19] which is similar to III and IV, shows two distinct $\beta$-couplings[20] at $-172°$; the line widths indicate that the barrier to inversion is greater than *ca.* 2.7 kcal./mole.[21] The radical was not studied at higher temperatures and so the actual barrier is not known. The lifetime of the vinyl radical, but not the 1-methylvinyl radical, is probably determined by tunneling.[19] The difference in mass between hydrogen and methyl also suggests that the 1-methylvinyl radical should have a greater configurational stability than the unsubstituted vinyl radical. Although one can do little more than guess at the barrier at the present time, these factors are probably small and the isomerization of the 1-methylvinyl radical (or III and IV) is probably a very rapid process.[22] Chain transfer ($k_{tr}$) in these systems is also a rapid, low activation energy process. Sivertz[24] has measured the absolute rates of the individual steps in the addition of *n*-butylmercaptan to 1-pentene. Although *n*-butyl mercaptan/1-pentene is not a particularly good model for the thiolacetic acid/1-hexyne system, Sivertz's data suggest that chain transfer might compete with an isomerization step having a small activation energy. It should be clear, therefore, that there is no independent basis for choosing between case A, case B, or "the general case" as an appropriate description of a radical addition to an acetylene.

Skell[12] has proposed that case A adequately describes the addition of hydrogen bromide to propyne. This interpretation requires that the initial addition step be stereospecific, giving III only. Case A, however, can accomodate the data in this paper only if the initial addition of the thiyl radical to 1-hexyne gives an 82/18 mixture of III and IV. It seems unlikely that the addition of a bromine atom and a thiyl radical would be stereochemically different. Case B is obviously in accord with the nonstereospecific addition of thiolacetic acid to 1-hexyne, but is incompatible with the stereospecificity of the hydrogen bromide addition. If case B correctly describes the addition of thiolacetic acid to 1-hexyne, then the 82/18 *cis/trans* adduct ratio is a reflection of the difference in free energies of the transition states leading to *cis* and *trans* adducts. The energy difference involved is quite small (<1 kcal./mole).

The "general case," involving similar rates of interconversion and chain transfer, cannot accommodate either the stereospecificity of the hydrogen bromide

(18) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).

(19) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

(20) The two distinct $\beta$-couplings demonstrate that vinyl radicals are not linear at the radical center and that it is reasonable to consider isomeric vinyl radicals such as III and IV.[19]

(21) Private communication from R. W. Fessenden.

(22) Skell[12] has concluded that the activation energy for the isomerization of $\begin{smallmatrix} CH_3 \quad\;\; Br \\ {}^{\diagdown}=<{} \\ \quad\quad H \end{smallmatrix}$ is $\geq 17$ kcal./mole. This number has been incorrectly calculated from the data. The difference in isomerization frequencies and wagging frequencies discussed by Skell corresponds to an activation energy of *ca.* 10 kcal./mole at room temperature rather than 17 kcal./mole. In addition, the great difference in the e.s.r. spectra of the vinyl[19] and formyl[23] radicals suggests that they are not comparable species.

(23) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962).

(24) C. Sivertz, *J. Phys. Chem.*, **63**, 34 (1959), and earlier papers.

reaction or the data in Table I. The "general case" predicts that the composition of the product mixture will be a function of the concentration of the chain transfer agent. Table I, however, shows that a 78-fold change in the thiolacetic acid concentration (runs 4 and 8) has no effect on the isomeric product ratio.

There are two reasonable interpretations of the available data. The rate constants shown in Chart I might be considerably different for the two reactions in question. Thus, it is possible that the hydrogen bromide addition is best described by limiting case A, as suggested by Skell, but that the thiolacetic acid addition is best described by limiting case B. Other conditions and chain transfer agents may be discovered for which the "general case" does obtain. Alternatively, the scheme outlined in Chart I may not apply to hydrogen bromide additions. These reactions may constitute a "special case" in which the stereochemistry of the reaction is determined by a bridged radical intermediate.[25,26] Recent e.s.r. data[27] support the concept of a bridged radical intermediate in the acetylene-hydrogen bromide reaction.

## Experimental

*Materials.* Thiolacetic acid obtained from Distillation Products Industries was distilled at least twice under nitrogen at room temperature and water-pump pressure; a Dry Ice trap was used to exclude moisture. A center cut about one third of the weight of the charge was collected as a very pale yellow liquid, $n^{23}$D 1.4564 (lit.[28] $n^{20}$D 1.4636). V.p.c. analysis indicated a very minor impurity near the air peak.[29] 1-Hexyne obtained from Chemicals Procurement Laboratories was slurried with alumina and distilled twice at atmospheric pressure, b.p. 71° (lit.[30] b.p. 71–72°), $n^{23}$D 1.395 (lit.[30] $n^{19}$D 1.402). Phenylcyclohexane from Distillation Products Industries was purified by preparative scale v.p.c. using a 30 ft. × 0.25 in. Carbowax 20M column at 170° and a helium flow of 90 cc./min.; retention time was 100 min.[31] The collected material showed no impurities on reinjection.

*cis- and trans-1-Hexenyl Thiolacetate.*[2] To 24.72 g. (0.30 mole) of 1-hexyne cooled to 0° in an ice bath and stirred well, 11.53 g. (0.15 mole) of thiolacetic acid at room temperature was added slowly (within a period of a few minutes). The mixture was stirred and kept at 0° for 1.5 hr., then at room temperature for 5 hr. more. After being stored for 2 days in a refrigerator (at about 5°), the mixture was distilled under reduced pressure. After low-boiling starting materials were removed, 16.31 g. (69%) of 1-hexenyl thiolacetate was collected at ~90°. The product was redistilled. The center cut of the distillate, b.p. 83° at 22 mm. (lit.[2] b.p. 83° at 20 mm.), weighed 13.03 g. (55%) and had $n^{23}$D

1.4865 (lit.[2] $n^{20}$D 1.4899). The product had an absorption maximum in ethanol at 254 m$\mu$[32] (lit.[2] 254 m$\mu$ ($\epsilon$ 8500)). A v.p.c. analysis[33] showed only two peaks with retention times 23.5 and 25.5 min.; the component with the shorter retention time represented about 73% of the total area. The infrared spectrum of cis- and trans-1-hexenyl thiolacetate (liquid film) had strong absorption bands at 2800–3000, 1706, 1400–1480, 1356, 1125, and 950 cm.$^{-1}$ and weak absorption bands at 3050, 1623, and 700 cm.$^{-1}$.[35] The n.m.r. spectrum[36] showed two complex groups of absorptions in the vinyl region from $\tau$ 3.3 to 4.5, two singlets at 7.68 and 7.72 (-SCOC$H_3$), and three, broad, complex absorptions between 7.8 and 9.4 (allylic -CH$_2$-, saturated -CH$_2$-, terminal -CH$_3$). The thioacetyl absorption areas were approximately 75/25. A sample of cis- and trans-1-hexenyl thiolacetate was collected by preparative scale v.p.c. for analysis. *Anal.*[37] Calcd. for $C_8H_{14}OS$: C, 60.7; H, 8.9; S, 20.3. Found: C, 60.8; H, 8.8; S, 20.2. A mixture of the mono-adduct mixture containing 73.5% cis isomer was kept at 5°. After 1 month, the cis isomer content was 73.4%.

*Preparation of the 2,4-Dinitrophenylhydrazone.*[2] The reagent was prepared by adding 1.218 g. of 2,4-dinitrophenylhydrazine to 20 ml. of 95% ethanol containing 0.807 g. of concentrated sulfuric acid. To this mixture, 0.510 g. of cis- and trans-1-hexenyl thiolacetate was added and the whole mixture was refluxed for 5 hr. The mixture was then cooled to room temperature; a yellow crystalline product was present. After being collected and dried, the product weighed 0.767 g. (85.0% yield), yellow needles with m.p. 98–99°. The crude product was recrystallized four times from 95% ethanol (activated charcoal). The pure product was very light yellow and melted at 106–106.5° (lit.[2] 104°), 0.497 g. (55.0%). Mixture melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of hexanal showed no depression, and the infrared spectra of the two hydrazones (KBr) were identical.

*Hexane-1,2-dithiol Diacetate.*[1,2] To 41.30 g. of thiolacetic acid (0.542 mole) cooled to 0°, 14.39 g. of 1-hexyne (0.176 mole) was added slowly with stirring. The mixture was kept at 0° for 2 hr. and then the low-boiling starting materials were removed under reduced pressure at room temperature. The product was then distilled through a spinning-band column at 0.03 mm. to give 2.66 g. of monoadduct, b.p. 50° at 0.03 mm., and 26.22 g. (63.9% yield) of pale yellow hexane-1,2-dithiol diacetate, b.p. 77–84° at 0.03 mm. When this diadduct was redistilled, the center cut weighed 13.61 g. (33%), was colorless, and had b.p. 74.5–75° at 0.034 mm. (lit.[2] 85° at 0.05 mm.), $n^{20.4}$D 1.5066 (lit.[2] $n^{21}$D 1.5070), $\lambda_{max}^{EtOH}$ 232 m$\mu$ ($\epsilon$ 9800) (lit.[2] $\lambda_{max}^{EtOH}$ 231

(25) Skell has also suggested this possibility: ref. 12, footnote 5.
(26) The radical addition of hydrogen bromide to olefins is stereospecifically *trans*. All other addenda give nonstereospecific reactions. A bridged radical intermediate has been frequently postulated to explain the unique behavior of hydrogen bromide. The stereochemistry of radical additions to olefins has been reviewed recently.[15b]
(27) P. I. Abell and L. H. Piette, *J. Am. Chem. Soc.*, 84, 916 (1962).
(28) W. W. Crouch, *ibid.*, 74, 2926 (1952).
(29) Analytical v.p.c. work was carried out with an Aerograph A-90-P-2 instrument equipped with a thermal conductivity detector; helium was used as a carrier gas.
(30) V. Grignard, L. Lapayer, and T. Faki, *Compt. rend.*, 187, 519 (1928).
(31) Preparative scale v.p.c. work was carried out with an Aerograph Autoprep A-700 instrument with a thermal conductivity detector.

(32) Determined on a Cary Model MS 11 recording spectrophotometer.
(33) A 17 ft. × 0.25 in. 15% QF-1 on 60–80 mesh treated Chromosorb-W column gave the best separation of cis- and trans-1-hexenyl thiolacetate. The solid support, Chromosorb-W, was treated with hexamethyldisilazane and polyethylene glycol 400 to decrease tailing.[34] The v.p.c. conditions were: column 92°, injector 230°, helium flow 100 cc./min. Peak areas were calculated by triangulation.
(34) J. Bohemen, S. H. Langer, R. H. Perrett, and J. H. Purnell, *J. Chem. Soc.*, 2444 (1960).
(35) A Perkin-Elmer Model 421 grating spectrophotometer was used.
(36) Varian A-60 and V-4300 B, 60-Mc. instruments were used. Samples were run neat or in carbon tetrachloride by Mr. S. Unger, Miss S. Didenko, and Dr. L. D. Colebrook.
(37) Analyses by Micro-Tech Laboratory, Skokie, Ill.

Table IV

| $\left(\dfrac{cis}{cis + trans}\right)_M$, % | $\left(\dfrac{M}{PC}\right)_{wt}$ | $\left(\dfrac{cis}{cis + trans}\right)_{peak\ area}$, % | $\left(\dfrac{M}{PC}\right)_{peak\ area}$ | $\left(\dfrac{M}{PC}\right)_{wt} \Big/ \left(\dfrac{M}{PC}\right)_{peak\ area}$ |
|---|---|---|---|---|
| 73.5 | 3.963 | 73.3 | 3.95 | 1.004 |
| | | 74.3 | 4.19 | 0.946 |
| 73.5 | 1.840 | 74.2 | 1.90 | 0.966 |
| 73.5 | 1.126 | 73.7 | 1.14 | 0.990 |
| 73.5 | 0.7852 | 74.1 | 0.810 | 0.969 |
| 73.5 | 0.2736 | 73.8 | 0.290 | 0.944 |
| Average | | 73.9 | | 0.970 |
| Average deviation | | ±0.3 | | ±0.020 |

$m\mu$ ($\epsilon$ 9500)). The infrared spectrum of this diadduct had strong absorption bands at 2840–2990, 1695, 1125, and 950 cm.$^{-1}$ and medium absorptions at 1400–1480 and 1355 cm.$^{-1}$. A weak absorption band at 3375 cm.$^{-1}$ was attributed to an impurity. The n.m.r. spectrum had a broad absorption centered at $\tau$ 6.6 (five lines), two doublets centered at 6.9, two singlets centered at 7.7, and two broad absorptions between 7.9 and 9.5. The areas were approximately 1:2:6:9, respectively. The two thioacetyl absorptions near $\tau$ 7.7 confirm the 1,2-dithiol diacetate structure. *Anal.*[37] Calcd. for $C_{10}H_{18}O_2S_2$: C, 51.2; H, 7.7; S, 27.4. Found: C, 51.1; H, 7.7; S, 27.6.

*Separation of cis- and trans-1-Hexenyl Thiolacetate.* Pure *cis-* and *trans-*1-hexenyl thiolacetate were obtained by preparative scale v.p.c.[38] The *cis* and *trans* assignments were made on the basis of physical data. In addition to the data reported in Table I, the following observations are relevant. The infrared spectra of the two isomers are very similar, the only differences being in 1620- and 700-cm.$^{-1}$ absorptions for the *cis* which are absent in the *trans*. Both isomers show absorption at 950 cm.$^{-1}$ (*trans* strong, *cis* medium) which might have been assigned as *trans*, out-of-plane olefinic hydrogen deformation.[6] The diadduct II, however, also showed strong 950-cm.$^{-1}$ absorption. Both isomers had $\lambda_{max}^{EtOH}$ 245 $m\mu$ ($\epsilon$ 7500–8000). The exact extinction coefficients were not recorded because of the small amounts of sample available.

*Quantitative Product Studies.* A mixture of known weights of 1-hexyne and phenylcyclohexane was cooled to 0° and stirred vigorously. A known weight of thiolacetic acid was added rapidly from a dropping funnel. Time zero was taken as the beginning of the introduction of thiolacetic acid; ~5 sec. was required to add the thiolacetic acid. Samples of 1-ml. size were withdrawn from the reaction flask at specified reaction times and immediately added to 4% aqueous NaOH solution precooled to 0°. The mixture was shaken thoroughly and stored in an ice bath or refrigerator at *ca.* 5° for a period of a few minutes to several hours and then the organic layer was analyzed by v.p.c. The volume of sodium hydroxide solution was twice that required to neutralize the thiolacetic acid. If $P_c$, $P_t$, and $P_i$ represent the peak areas of *cis-* and *trans-* 1-hexenyl thiolacetate and phenylcyclohexane (internal standard), respectively, the per cent *cis* isomer was measured as $P_c/(P_c + P_t) \times 100$. The weight of monoadducts was calculated as $[(P_c + P_t)/P_i] \times 0.970 \times$ the

(38) A 30 ft. × 0.25 in. 20% QF-1 on 30–60 mesh Chromosorb P column was used; column 102°, injector 222°, helium flow 100 cc./min.

weight of phenylcyclohexane; the per cent yield of monoadducts relative to the quantity of thiolacetic acid could consequently be calculated. The *cis* isomer proportion and per cent yields of monoadducts at specified reaction times are listed in Table II.

The weight–peak area relationship between the monoadducts and phenylcyclohexane and the precision of the measurements were determined as follows. Five mixtures of known weights of *cis-* and *trans-*1-hexenyl thiolacetate, containing 73.5% *cis* isomer, and phenylcyclohexane were prepared. V.p.c. analysis indicated that the weight ratio of the monoadducts/phenylcyclohexane equaled the ratio of the corresponding peak areas × 0.970. This experiment also indicated the precision in measuring the *cis/trans* isomer ratio and the proportionality constant. The data are given in Table IV where M represents the monoadduct mixture and PC represents phenylcyclohexane.

*Control Experiments. A.* The stability of *cis-* and *trans-*1-hexenyl thiolacetate to the v.p.c. conditions was indicated by the following experiment. Five mixtures of known weights of pure *cis-* and *trans-*1-hexenyl thiolacetate were prepared. The peak areas of each isomer in the corresponding five v.p.c. spectra were measured. The isomeric weight ratios and the peak area ratios were found to be in good agreement (see Table V).

Table V

| Sample | $\left(\dfrac{cis}{cis + trans}\right)_{wt}$, % | $\left(\dfrac{cis}{cis + trans}\right)_{peak\ area}$, % |
|---|---|---|
| 1 | 93.4 | 93.5 |
| 2 | 79.9 | 82.1 |
| 3 | 69.7 | 71.2 |
| 4 | 50.2 | 50.1 |
| 5 | 42.1 | 42.1 |

*B.* The stability of phenylcyclohexane (PC) to thiolacetic acid was shown as follows. Phenylcyclohexane was dissolved in benzene, thiolacetic acid, and 1-hexyne to make three solutions of known concentration. After 30 hr. at room temperature, 9 $\mu$l. of each solution was analyzed by v.p.c. The relative peak areas of phenylcyclohexane for the three solutions were found to be identical with the known relative concentrations of the three solutions (see Table VI).

*C.* The monoadduct mixture was shown to be stable to the quenching conditions. A mixture of 0.1669 g. of phenylcyclohexane, 0.4629 g. of 1-hexyne,

Table VI

| Solvent | Relative [PC]$_{wt.}$ | Relative [PC]$_{peak\ area}$ |
|---|---|---|
| Benzene | 1.057 | 1.057 |
| Thiolacetic acid | 1.013 | 1.034 |
| 1-Hexyne | 1.000 | 1.000 |

and 0.4542 g. of monoadducts (73.8% cis isomer) was added to 10 ml. of 4% aqueous sodium hydroxide solution containing 0.4888 g. of thiolacetic acid. This mixture was shaken well at room temperature and then stored in a refrigerator at ~5°. After 4 days, the organic layer was analyzed by v.p.c.; the mixture contained 73.4% cis isomer and the measured peak area of the monoadducts relative to phenylcyclohexane was 2.89, while the calculated unchanged value was 2.81.

*Equilibration of cis- and trans-1-Hexenyl Thiolacetate.* *A.* Two samples of the monoadduct mixture containing 77 and 17% cis isomer, respectively, were heated under nitrogen on a steam bath (ca. 90°) for several days. The mixtures were analyzed periodically by v.p.c. Both samples were converted to the same mixture after 11–12 days as shown in Table III. Further heating had no effect. Neither iodine nor *t*-butylthiol accelerated the isomerization.

*B.* Approximately 1 mole % of thiophenol was added to two samples of monoadduct containing 73 and 20% cis isomer, respectively. The samples were irradiated in Pyrex tubes with a General Electric sunlamp at 21–25° and analyzed periodically. Both samples gave the same mixture after 2–3 days as shown in Table III. The addition of more thiophenol and further irradiation had no effect.

*C.* Approximately 5 mole % of thiolacetic acid was added to a sample of monoadduct containing 74% cis isomer. After 4 days at 5°, the mixture contained 71% cis isomer and the thiolacetic acid could not be detected by v.p.c.

# Photochemistry of 1,3-Cyclobutanediones.
# Decomposition Modes and Chemical Intermediates[1]

Nicholas J. Turro,[2] Peter A. Leermakers, H. R. Wilson,
D. C. Neckers, G. W. Byers, and G. F. Vesley

*Contribution from the Departments of Chemistry, Wesleyan University, Middletown, Connecticut, Harvard University, Cambridge, Massachusetts, and Columbia University, New York, New York. Received February 13, 1965*

*Several tetrasubstituted 1,3-cyclobutanediones have been photolyzed, with remarkably high quantum yield, in inert solvents (in the presence and absence of oxygen), in hydroxylic solvents, and in the vapor phase. Chemical evidence, supported by a recent report of spectroscopic evidence, indicates that in solution one of the primary intermediates, formed by monodecarbonylation, is the corresponding cyclopropanone. The latter reacts with alcohols (to form hemiketals which subsequently may react thermally), with dienes, and with oxygen. In the absence of the above scavengers, further decarbonylation occurs to give a tetraalkyl olefin in good yield. The vapor phase photolysis of tetramethyl-1,3-cyclobutanedione involves complex radical processes but one of the primary photolytic paths is apparently cleavage to yield 2 moles of dimethylketene which is subsequently photolyzed to carbon monoxide, propylene, and methane. Some tetramethylethylene is also formed. It is proposed that the chemically active excited state of the diones may be an n–π\* singlet.*

## Introduction

Cyclopropanone and its derivatives are believed to be intermediates in the Favorskii reaction.[3] A 2,3-diazocyclopropanone was recently prepared[4] and possesses remarkable thermal stability and low reactivity toward nucleophiles. In contrast, no example of the unambiguous isolation and characterization of a cyclopropanone has been reported.[5,6] The photochemistry of tetraalkyl-1,3-cyclobutanediones was undertaken to determine if tetraalkylcyclopropanones are produced by monodecarbonylation and whether they exist as short-lived intermediates (perhaps capable of

(1) Preliminary accounts of part of this work have appeared previously: (a) N. J. Turro, G. W. Byers, and P. A. Leermakers, *J. Am. Chem. Soc.*, **86**, 955 (1964); (b) P. A. Leermakers, G. F. Vesley, N. J. Turro, and D. C. Neckers, *ibid.*, **86**, 4213 (1964).

(2) Visiting scientist, summer, 1964, Dow Chemical Co., Eastern Research Laboratory, Framingham, Mass.; National Science Foundation Postdoctoral Fellow, Harvard University, 1963–1964.

(3) See, for example, A. S. Kende, *Org. Reactions*, **11**, 261 (1960); A. W. Fort, *J. Am. Chem. Soc.*, **84**, 2620, 2625 (1962); **82**, 4979 (1960); R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.*, 129 (1963).

(4) F. D. Green and J. C. Stowell, *J. Am. Chem. Soc.*, **86**, 3569 (1964).

(5) Although a number of cyclopropanones are claimed to have been prepared and isolated, none of these cases have been substantiated. See, for example, J. F. Cogdell, *Dissertation Abstr.*, **19**, 2751 (1959); H. K. Ingold, *et al.*, *J. Chem. Soc.*, **119**, 305 (1921); **121**, 1177 (1922); F. B. LaForge and F. Acree, *J. Org. Chem.*, **5**, 430 (1940); **6**, 208 (1941).

(6) The elegant attempts of Lipp and co-workers to prepare cyclopropanone indicate the difficulties to be encountered in isolation of this compound and its relatives: P. Lipp, J. Buchkremer, and H. Seeles, *Ann.*, **499**, 1 (1933); P. Lipp and R. Köster, *Ber.*, **64**, 2823 (1931); P. Lipp and H. Seeles, *ibid.*, **62**, 2456 (1929). See also: D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 3221 (1956).