mesh Chromosorb W column yielded material, $n^{20}D$ 1.4584 (lit.[24] $n^{20}D$ 1.4588).

1-Methylcyclohexyl chloride (X) was prepared by the method of Russell[25] from 1-methylcyclohexanol and thionyl chloride. Purification was effected by distillation to yield material, $n^{17}D$ 1.4580 (lit.[25] $n^{17}D$ 1.4580).

Registry No.—I, 185-94-4; II, 286-08-8; HCl 7647-01-0.

[25] G. Russell, *J. Amer. Chem. Soc.*, **74**, 3882 (1952).

Reactive Intermediates in the Bicyclo[3.1.0]hexyl and Bicyclo[3.1.0]hexylidene Systems. VI.[1] The Free-Radical Addition of Methanethiol and Methanethiol-*d* to Bicyclo[3.1.0]hexene-2

PETER K. FREEMAN,*[2] MARVIN F. GROSTIC,[3] AND FLOYD A. RAYMOND

Department of Chemistry, University of Idaho, Moscow, Idaho 83843

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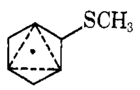
Free-radical addition of methanethiol to bicyclo[3.1.0]hexene-2 results in a mixture of *cis*-3-methylthiobicyclo[3.1.0]hexane, *trans*-2-methylthiobicyclo[3.1.0]hexane, *trans*-3-methylthiobicyclo[3.1.0]hexane, and *cis*- and *trans*-3-methyl-5-methylthiocyclopentene. The dependence of product composition upon concentration of methanethiol suggests that an equilibrium of substituted 2-bicyclo[3.1.0]hexyl and Δ^2-cyclopentylmethyl radicals are involved rather than the related delocalized intermediate. The stereochemistry of the radical addition of methanethiol-*d* leading to 3-deuterio-*trans*-2-methylthiobicyclo[3.1.0]hexane was investigated and found to be predominantly trans (81–91%).

Our interests in carbonium ion[4] and carbene[5] intermediates in the bicyclo[3.1.0]hexyl and bicyclo[3.1.0]hexylidene systems provided the impetus to investigate the nature of analogous free-radical intermediates. We have recently discussed free-radical abstraction reactions of bicyclo[3.1.0]hexane,[6] and now report on a complementary study of radical addition of methanethiol to bicyclo[3.1.0]hexene-2 (**1**). In terms of orientation, there are two possible reaction pathways. Addition of the methylthio radical to C-2 might generate a delocalized radical (**2**) analogous to the trishomocyclopropenyl carbonium ion[7] (or a related set of equilibrating classical radicals), while addition at C-3 might produce a delocalized radical analogous to either the bicyclobutonium ion[8] (**3**) or the closely related symmetrical bisected cyclopropylcarbinyl carbonium ion[9] (or, alternatively, a related set of equilibrating classical radicals).


1



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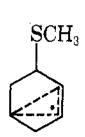

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Radical addition of methanethiol to bicyclo[3.1.0]hexene-2 proceeded smoothly upon irradiation to give an 85–95% yield of 1:1 addition products. Vapor phase chromatography on a Carbowax 1500 column showed that four components were present in a 1.5:33:59:6.5 composition. The 6.5% component was isolated by vapor phase chromatography and infrared analysis suggested a bicyclic structure (CH absorption at 3060, 3040, and 3000 cm^{-1}, no C=C absorption, and cyclopropane at 1020 cm^{-1}). In particular, the 3040-cm^{-1} CH absorption was enhanced, which indicates a cis isomer.[4] Consistent with this picture, the 6.5% component was identified as *cis*-3-methylthiobicyclo[3.1.0]hexane (**4**) by comparison of its infrared spectrum with that of an authentic standard. The 59% component was isolated by vapor phase chromatography and its infrared spectra also suggested a [3.1.0] ring system (CH at 3070, 3040, and 3005 cm^{-1}, no C=C absorption, and cyclopropane absorption at 1020 cm^{-1}). The nmr spectrum exhibited two *S*-methyl peaks at τ 7.94 and 8.02 with a relative ratio of 80:20. With this accurate lead, the composition of the 59% component was determined to be a mixture of *trans*-2-methylthiobicyclo[3.1.0]hexane (**5**) and *trans*-3-methylthiobicyclo[3.1.0]hexane (**6**), with the *trans*-2 thio ether present as the major component, by preparation of authentic standards and infrared spectral comparison.

Infrared analysis of the 33% component, isolated by vapor phase chromatography, gives a clear indication of a cyclopentene ring (3050, 3045, 1600, and 750 cm^{-1}) with a *C*-methyl group (1375 cm^{-1}). The nmr spectrum exhibits absorption for olefinic protons at τ 4.30–4.58 (2 H), hydrogen α to *S*-methyl at 6.08–6.48, hydrogen α to *C*-methyl at 6.90–7.50, *S*-methyl at 8.02 and 8.07 (two singlets, 3 H), methylene hydrogens at 7.58–8.80 (2 H), and *C*-methyl at 8.90 and 8.97 (two doublets in a 20:80 ratio). That the hydrogens α to *S*-methyl and α to *C*-methyl are allylic is indicated by comparison with the analogous hydrogens in 3-methylthiocyclopentene, τ 6.08–6.46, and 3-methylcyclopentene, 7.02–7.48. Confirmation of the methylcyclopentene ring structure was achieved by the desulfurization of the methylthiomethylcyclopentenes with deactivated Raney nickel catalyst in 3-pentanone, which produced a mixture of 1-methyl-, 3-methyl-, and 4-methylcyclo-

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[1] Part V: P. K. Freeman, F. A. Raymond, and J. N. Blazevich, *J. Org. Chem.*, **34**, 1175 (1969).

[2] Address all correspondence to this author at the Department of Chemistry, Oregon State University, Corvallis, Ore. 97331.

[3] NDEA Fellow, University of Idaho, 1961–1964.

[4] (a) P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, **32**, 24 (1967); (b) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *ibid.*, **30**, 771 (1965).

[5] P. K. Freeman and D. G. Kuper, *ibid.*, **30**, 1047 (1965).

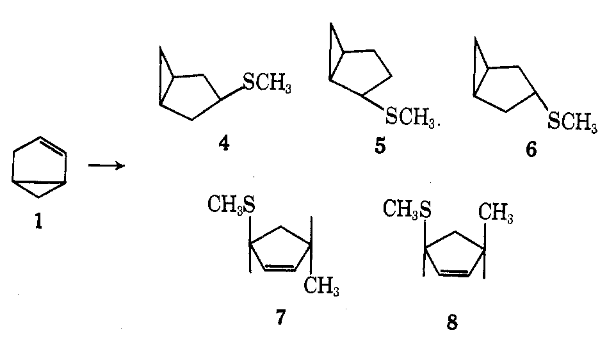
[6] P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *ibid.*, **33**, 1448 (1968).

[7] (a) S. Winstein, E. C. Friedrich, R. Baker, and Y.-I Lin, *Tetrahedron*, 621 (1966). (b) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3235 (1961); **83**, 3244 (1961); S. Winstein, *ibid.*, **81**, 6524 (1959); S. Winstein, J. Sonnenberg, and L. de Vries, *ibid.*, **81**, 6523 (1959).

[8] M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *ibid.*, **83**, 3671 (1961).

[9] P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

pentene. Since an experiment demonstrated that 3-methylcyclopentene isomerized to 1-methyl- and 4-methylcyclopentene under the reaction conditions, the desulfurization served only to establish the ring skeleton. Thus the 33% component is most reasonably identified as an 80:20 mixture of *trans*- and *cis*-3-methyl-5-methylthiocyclopentene (**7** and **8**). Since the cyclopropane methylene sterically shields electrophilic addition to the cis face of the bicyclo[3.1.0]hexene double bond,[4] hydride transfer to 2- and 3-bicyclo-[3.1.0]hexanone,[7b,10] and capture of the 2-bicyclo-[3.1.0]hexyl radical and carbonium ion,[6,10] and since bicyclic *trans*-3 thio ether predominates over bicyclic *cis*-3 thio ether, the major isomer in the 33% vpc component is assigned as the trans compound. The 1.5% component was isolated and gave a satisfactory analysis for a $C_7H_{12}S$ isomer but was not characterized further due to its low product concentration.



The cis-trans pairs of 2- and 3-methylthiobicyclo[3.1.0]hexane epimers necessary for standards were synthesized by SN2 displacement of the appropriate chlorides by thiomethoxide. Starting with a mixture of 27% *trans*- and 73% *cis*-3-chlorobicyclo[3.1.0]hexane,[4a] treatment with the potassium salt of methanethiol gave a 55% yield of *trans*-3 and *cis*-3 thio ethers (**6** and **4**) in a ratio of 72:28. The cis-trans nature of the epimers was established by infrared and nmr analyses. The infrared spectrum of the *trans*-3 thio ether exhibits absorption at 3070, 3040, 3000, and 1025 cm^{-1}, while the analogous bands for the *cis*-3 thio ether appear at 3070, 3035, 3000, and 1020 cm^{-1}. The 3035-cm^{-1} band is enhanced in the cis structure relative to the trans, as we have found to be typical for *cis*- and *trans*-3- and -2-bicyclo[3.1.0]hexane epimers.[4b] The assignment is reinforced by a consideration of the nmr spectra, since the absorption for the cyclopropane methylene protons of the *trans*-3 thio ether appears at τ 9.47–9.94, while the analogous region for the *cis*-3 thio ether is shifted downfield to τ 9.30–9.75, in accord with data on the cyclopropane region in related [3.1.0] substrates.[4b] Treatment of a mixture of 30% *trans*- and 70% *cis*-2-chlorobicyclo[3.1.0]hexane with the potassium salt of methanethiol gave a 65% yield of a mixture of thio ethers which was 77% *trans*-2 and 23% *cis*-2. The infrared spectrum of the *trans*-2 thio ether exhibits characteristic [3.1.0] absorption at 3070, 3040, 3000, and 1020 cm^{-1}, while the analogous bands for the *cis*-2 epimer appear at 3070, 3035, 3000, and 1020 cm^{-1}, with the expected enhancement of the 3035-cm^{-1} band. The nmr data is in accord with this assignment with the cyclopropane methylene absorption appearing at τ 9.38–9.97 for the *trans*-2 thio ether, while the upfield proton is shifted downfield in the *cis*-2 thio ether (τ 9.50–9.80).

At first glance the reaction pathways followed as a consequence of addition of methylthio radical to bicyclo[3.1.0]hexene-2 would appear to involve either an equilibrium of radicals (**9** and **10**) or a delocalized radical **11** for which **9** and **10** are the resonance structures. A decision between these two alternatives is possible using the method, introduced by Seubold[11] and extended by Cristol and others,[12] of increasing the, concentration of the chain transfer agent in order to attempt to trap the initially formed intermediate. Thus, in the present case, in radical addition to the trans face of the double bond, an increase of methanethiol concentration might increase the ratio of **6**:**7** if an equilibrium, **9** $\rightleftharpoons$ **10** obtains, whereas the ratio of **6**:**7** will remain uneffected if delocalized **11** is the sole product determining intermediate. A similar analysis can be applied to the intermediate(s) generated by addition of methylthio radical to the cis face of the double bond. The results of the application of this test to determine the nature of the radical intermediate(s) using varying ratios of bicyclo[3.1.0]hexene-2:methanethiol are recorded in Table I.

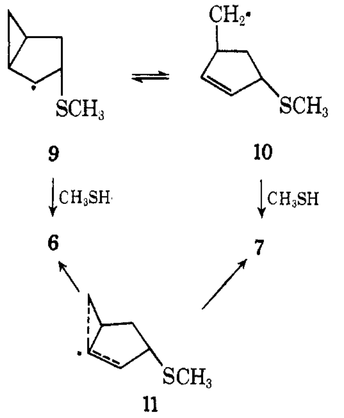


TABLE I

METHANETHIOL ADDITION TO BICYCLO[3.1.0]HEXENE-2[a]

Run	Thiol, mol	Reaction composition, %				
		7	**8**	**6**	**4**	**5**
1[b]	0.010	44.9	11.2	8.1	3.5	32.3
2[c]	0.015	43.1	10.8	8.3	4.8	33.2
3[b]	0.020	16.2	4.0	17.4	7.5	54.9
4[c]	0.020	16.9	4.2	16.8	8.8	53.3
5[b]	0.040	7.4	1.9	24.3	9.5	56.7
6[c]	0.040	6.4	1.6	25.2	8.0	58.8

[a] Bicyclo[3.1.0]hexene (0.010 mol) was used in each run. [b] Vapor phase chromatographic analysis on a 25-ft Carbowax 1500 column gave three peaks corresponding to **7** and **8**, **5** and **6**, and **4**. The ratio of **7**:**8** was determined by isolation and nmr determination of the ratio of the two *C*-methyl doublets at τ 8.97 and 8.90, while the ratio of **6**:**5** was determined by nmr measurement of the ratio of the two *S*-methyl absorptions at τ 7.94 and 8.02. [c] The ratios of **7**:**8** and **6**:**5** are assumed to be the same as the repeat or closest run.

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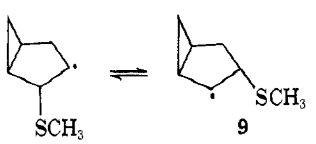
(10) E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, **85**, 1782 (1963).

(11) F. H. Seubold, *ibid.*, **75**, 2532 (1953).

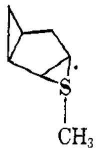
(12) S. J. Cristol and R. V. Barbour, *ibid.*, **90**, 2832 (1968); S. J. Cristol and R. V. Barbour, *ibid.*, **88**, 4262 (1966); C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966); M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965); S. J. Cristol, T. W. Russell, and D. I. Davies, *J. Org. Chem.*, **30**, 207 (1965); S. J. Cristol and D. I. Davies, *ibid.*, **29**, 1282 (1964); E. E. Huyser and J. D. Taliaferro, *ibid.*, **28**, 3442 (1963); S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Amer. Chem. Soc.*, **80**, 635 (1958).

Discussion

As the concentration of methanethiol was increased the first formed radical intermediates were trapped and the ratio of **6**:**7** as well as that of **4**:**8** increased. The results of Table I clearly favor equilibria such as **9** ⇌ **10**, rather than a single delocalized radical such as **11** for the addition of thiyl radical to both faces of the bicyclo[3.1.0]hexene double bond. It is interesting to note, however, that as the concentration of methanethiol is increased the ratio of (**6** + **7**):**5** is not constant but decreases. It appears that the radical precursor(s) for both *trans*-2-methylthio- and *trans*-3-methylthiobicyclo[3.1.0]hexane (**5** and **6**) rearranges to **10**. This suggests that a rapid equilibrium of *trans*-methylthio radicals **12** and **9** or alternatively a single bridged thiyl radical[13] (**13**) may be the product determining intermediates or intermediate.



12 **9**

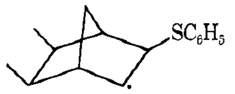


13

In order to provide further evidence bearing on these alternatives, a study of the addition of methanethiol-*d* to bicyclo[3.1.0]hexene-2 was carried out. Radical addition of methanethiol-*d* gave the expected vpc components: *cis*- and *trans*-3-methyl-5-methylthiocyclopentene, *trans*-2 and *trans*-3 thio ether, and *cis*-3 thio ether. Nmr analysis of the deuterated 3-methyl-5-methylthiocyclopentenes gave an integration of two protons for the *C*-methyl region at τ 8.97 and 8.90, which is consistent with the cyclopropylcarbinyl–allylcarbinyl β fission process (**9** ⇌ **10**) drawn above.

The nmr spectrum of undeuterated standard, *trans*-2-methylthiobicyclo[3.1.0]hexane, exhibits a doublet of doublets for the proton α to methylthio (J = 5, 2 Hz) centered at τ 6.96. The stronger J = 5 Hz coupling is due to coupling with the *cis*-3 proton[4] and the weaker J = 2 Hz is apparently due to coupling with the bridgehead proton, since, as noted below, the doublet of doublets pattern persists in the addition product resulting from the cis addition of CH_3SD to the trans face of the double bond. The nmr spectrum of the vpc fraction containing the mixture of deuterated *trans*-2 and *trans*-3 thio ethers provided evidence for a stereoselective, but not a stereospecific radical addition process. The proton α to methylthio in the *trans*-2 thio ether is resolved from the analogous *trans*-3 thio ether proton, and the normal doublet of doublet of absorption for the cis-2 proton is replaced with a broad singlet ($W_{1/2}$ = 3 Hz) with two small shoulders corresponding to the outside peaks of the doublet of doublets. Analysis of this pattern reveals that the *trans*-2 thio ether component is 81–91% *cis*-3-deuterio- and 9–19% *trans*-3-deuterio-*trans*-2-methylthiobicyclo[3.1.0]hexane. Thus the elements of CH_3SD are added 81–91% in the trans manner.

As noted above, the concave side of bicyclo[3.1.0]hexane is sterically shielded by the cyclopropane methylene. One might expect, in fact, that the ratio of trans:cis attack in the chain transfer step for the 3-bicyclo[3.1.0]hexyl radical might be similar to the ratio of exo:endo attack in the chain transfer reactions of the 2-norbornyl radical, based on the similar stereoselectivities exhibited in lithium aluminum hydride reduction (3-bicyclo[3.1.0]hexanone,[7b] trans:cis attack = 89:11; 2-norbornanone,[14] exo:endo attack = 89:11) and epoxidation (bicyclo[3.1.0]hexene,[7b] trans:cis attack ≥ 100:1, norbornene,[15] exo:endo attack = 200). However in the case of *trans*-2-methylthio radical **12**, the most accessible convex side of the bicyclohexane skeleton is blocked by the methylthio substituent. One might, therefore, consider for purposes of comparison the steric course of chain transfer for *exo*-3-phenylthio-2-norbornyl radical and the analogous aldrinyl radical, since in these radicals (**14**), the most accessible exo side is similarly blocked by a thiyl substituent. As the radical additions of *S*-deuteriothiophenol to both aldrin[16] and norbornene[17] proceed to form predominantly cis–exo addition products, one might argue that the trans addition of the elements of methanethiol leading to **5** suggests a 1,2-bridged thiyl radical **13** or a trans-substituted trishomocyclopropenyl radical **2**.



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Neither bridged thiyl radical **13** nor trans-substituted **2** can be the sole product determining intermediate leading to **5**, since the reaction is not completely stereospecific, and the necessity for involving either intermediate as part of an equilibrium with classical radicals **12** and **9** is reduced by the possibility that steric access to the concave side of bicyclo[3.1.0]hexane may be greater than to the endo side of norbornane. We see some evidence of this in this work in the ratios of thio ethers **6**, **4**, and **5** formed in the addition of methanethiol to **1**, while, in contrast, in analogous radical additions of *p*-thiocresol (no endo attack observed)[18] and thiophenol (99.5% exo attack)[15] to norbornene, steric control appears to be more severe.[19] Similarly, electrophilic addition of DCl to bicyclo[3.1.0]hexene-2 proceeds by a route involving cis addition of the elements of DCl to the double bond, but with attack at both the trans and cis faces of the double bond in a ratio of 66:31,[4a] while similar additions of DCl to norbornene[20] or HCl to 2,3-dideuterionorbornene[21] pro-

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[13] See, for example, P. D. Readio and P. S. Skell, *J. Org. Chem.*, **31**, 759 (1966). The role of analogous bromine bridged radical intermediates is a matter of divergent opinions: D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Amer. Chem. Soc.*, **91**, 7398 (1969); J. G. Traynham and W. G. Hines, *ibid.*, **90**, 5208 (1968); P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964); P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963); W. Thaler, *ibid.*, **85**, 2607 (1963).

[14] H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6381 (1967).

[15] H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201 (1970).

[16] S. J. Cristol and T. W. Russell, quoted by D. I. Davies and S. J. Cristol, *Advan. Free Radical Chem.*, **1**, 162 (1965).

[17] D. I. Davies and J. A. Claisse, quoted by S. J. Cristol and D. I. Davies, *ibid.*, **1**, 162 (1965).

[18] S. J. Cristol and G. D. Brindell, *J. Amer. Chem. Soc.*, **76**, 5699 (1954).

[19] Some endo attack of thiyl radicals upon norbornadiene has recently been uncovered [T. V. Van Auken and E. A. Rick, *Tetrahedron Lett.*, 2709 (1968)], which reinforces the cautionary comment on assuming complete exo attack of thiyl radicals on norbornene derivatives voiced by D. I. Davies and S. J. Cristol, *Advan. Free Radical Chem.*, **1**, 155 (1965).

[20] H. C. Brown and K-T. Lin, *J. Amer. Chem. Soc.*, **89**, 3900 (1967).

[21] J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, **88**, 4922 (1966).

ceed *via* cis–exo stereochemistry for that portion of reaction leading to unrearranged product.

Thus, it appears most reasonable to represent the radical addition of methanethiol to bicyclo[3.1.0]hexene-2 in terms of attack at the trans face of the double bond, which generates an equilibrium of **12** and **9**, with **9** rearranging to **10** by a cyclopropylcarbinyl–allylcarbinyl β fission process, while attack at the cis face produces an equilibrium of radicals analogous to $\mathbf{12} \rightleftharpoons \mathbf{9}$, although one cannot rule out a role for bridged radical intermediates analogous to **13** and **2**.

Experimental Section

Methanethiol Addition to Bicyclo[3.1.0]hexene-2.—Into a 50-ml reaction flask was placed 0.80 g (0.010 mol) of bicyclo[3.1.0]-hexene-2 and the flask placed on a vacuum line. The flask was cooled in a Dry Ice–isopropyl alcohol bath and the system evacuated. Methanethiol (0.020 mol, measured as a gas) was introduced into the system and condensed in the reaction flask. The Dry Ice trap was removed and the reaction mixture irradiated for about 2 min with a General Electric sun lamp and then immersed in the cold trap. These 2-min irradiations followed by cooling were continued for a total of about 2 hr of irradiation time. Following the completion of the reaction time, the reaction flask was removed from the vacuum line and the product mixture allowed to warm to room temperature leaving 1.1 g of (0.0094 mol, 94%) product.

Vapor phase chromatographic analysis on a 25-ft Carbowax 1500 column showed four peaks in the ratio of 1.5:33:59:6.5. The 33% peak was collected by vpc and the infrared and nmr spectra were recorded. The nmr spectrum contained two olefinic protons (τ 4.30–4.58), one hydrogen α to *S*-methyl (6.08–6.48), one hydrogen α to *C*-methyl (6.90–7.50), two types of *S*-methyl absorption (8.02 and 8.07), methylene hydrogens (7.58–8.80, 2 H, part of this region falling under the *S*-methyl absorption), and two types of *C*-methyl absorption (doublet at 8.90 and a doublet at 8.97, J = 7 Hz). The relative ratio of the two types of *C*-methyl absorption was 80:20. The infrared spectra showed olefinic CH absorption at 3050 and 3045 cm^{-1}, C=C absorption at 1600 cm^{-1}, cis hydrogens on a double bond at 750 cm^{-1}, and absorption at 1375 cm^{-1} assignable to a *C*-methyl group. An analytical sample was isolated by vpc.

Anal. Calcd for $C_7H_{12}S$: C, 65.56; H, 9.44. Found: C, 65.36; H, 9.33.

The infrared spectra of the 59% component had absorption indicating that the bicyclo[3.1.0]hexane ring structure was present (CH at 3070, 3040, and 3005 cm^{-1}, no C=C absorption, and cyclopropane at 1020 cm^{-1}).[4] The nmr spectrum of this component contained one tertiary proton (doublet of doublets at τ 6.82–6.96), two types of *S*-methyl absorption at 7.94 and 8.02, four methylene protons and two tertiary protons (8.17–8.75 region), and two methylene protons on a cyclopropane ring (τ 9.33–9.87). The two *S*-methyl absorptions were in the ratio of 80:20. An analytical sample was isolated by vpc.

Anal. Calcd for $C_7H_{12}S$: C, 65.56; H, 9.44. Found: C, 65.56; H, 9.56.

The infrared spectra of the 6.5% component (containing about 10% of the 59% component) had absorption supporting the bicyclo[3.1.0]hexane ring structure (CH at 3060, 3040, and 3000 cm^{-1}, no C=C absorption, and cyclopropane at 1020 cm^{-1}). An enhancement of the band at 3040 cm^{-1} indicated that this component was the cis isomer. Spectral comparisons with the 2- and 3-methylthiobicyclo[3.1.0]hexanes described below established the 6.5% component as the *cis*-3-methylthiobicyclo[3.1.0]-hexane isomer. An analytical sample free of the 59% component was isolated by vpc.

Anal. Calcd for $C_7H_{12}S$: C, 65.56; H, 9.44. Found: C, 65.46; H, 9.37.

The 1.5% component was not completely characterized due to its low concentration in the product fraction. An analytical sample was isolated by vpc.

Anal. Calcd for $C_7H_{12}S$: C, 65.56; H, 9.44. Found: C, 65.43; H, 9.53.

Other addition reactions were run in a similar manner and using the various concentrations of methanethiol (Table I). The cyclopentenyl products were isolated by vpc from three of these runs (1, 3, and 5, Table I) and the ratios of the trans to cis isomers analyzed by nmr using the ratio of the two *C*-methyl doublets at τ 8.90 and 8.97. This ratio was found to be 80:20 for all three runs studied.

The peak corresponding to the *trans*-2 and *trans*-3 thio ether mixture was isolated by vpc and analyzed by nmr using the ratio of the *S*-methyl peaks at τ 7.94 and 8.02. The ratio of *trans*-2 to *trans*-3 thio ether was found to be 80:20 at 0.01 mol of methanethiol (run 1), 76:24 at 0.02 mol of methanethiol (run 3), and 70:30 at 0.04 mol of methanethiol (run 5).

Desulfurization of 3-Methylthiocyclopentene.—Raney nickel catalyst was deactivated by a modification of the method described by Spero, McIntosh, and Levin.[22] The catalyst (9 g) was washed five times with 20–30-ml portions of 3-pentanone to remove the ethyl alcohol. The catalyst was transfered to a 100-ml flask with approximately 60 ml of 3-pentanone. The catalyst was deactivated by refluxing the mixture for a period of 2 hr. To the mixture of deactivated catalyst in 3-pentanone was added 1.0 g of 3-methylthiocyclopentene, and the mixture was heated at reflux for a period of 4–5 hr.

After refluxing, the reaction was arranged for simple distillation and 3 ml of distillate was collected in a graduate cyclinder immersed in an ice bath. The distillate showed two peaks corresponding to cyclopentane and cyclopentene in the ratio of 3:1 when analyzed by vpc on a 30-ft Carbowax 1500 column.

Desulfurization of *cis*- and *trans*-3-Methyl-5-methylthiocyclopentene.—Raney nickel catalyst (6 g) was washed five times with 20–30 ml-portions of 3-pentanone and then transferred with approximately 50 ml of 3-pentanone to a 100-ml round-bottom flask equipped with a magnetic stirrer. The catalyst was deactivated by refluxing for 1 hr and 0.5 ml of methylthiomethylcyclopentenes (collected by vpc from the methanethiol–bicyclo-[3.1.0]hexene-2 reaction mixture) was added at reflux temperature. The mixture was allowed to cool to 70° at which temperature it was heated for 9 hr. After the heating period was completed, the flask was cooled and arranged for simple distillation. A total of 2.5 ml of distillate was collected in a graduate cylinder immersed in an ice bath.

Vpc analysis of the distillate on a 30-ft aluminum column of 25% Carbowax 1500 on Chromosorb P (30–60 mesh) revealed two peaks which corresponded to methylcyclopentenes and indicated an overall yield of 10–15%. The largest peak of the methylcyclopentenes had a retention time of 11.5 min, and it corresponded in retention time to 3-methylcyclopentene and 4-methylcyclopentene. The second peak had a retention time of 13.7 min corresponding to that of 1-methylcyclopentene. The two peaks were collected and analyzed on a 1-m silver nitrate column. The 11.5-min peak showed two peaks in a 1:1 ratio corresponding in retention times to those of 3-methylcyclopentene and 4-methylcyclopentene. The 13.7-min peak had a retention time corresponding to that of 1-methylcyclopentene.

Stability of 3-Methylcyclopentene to Desulfurization Conditions.—To 6 g of deactivated Raney nickel catalyst in 50 ml of 3-pentanone was added 0.4 ml of 3-methylcyclopentene, and the mixture was heated at 70° for 9.5 hr. After the heating period was completed, the apparatus was arranged for simple distillation and a total of 4 ml of distillate was collected in a graduate cylinder immersed in an ice bath. Analysis of the distillate by vpc using a 30-ft Carbowax 1500 column showed two products peaks in the ratio of 40:60. The two peaks corresponded to methylcyclopentane, with a shoulder for 3- and 4-methylcyclopentene, and 1-methylcyclopentene. The two peaks were collected and the infrared spectra of the 60% component showed it to be 1-methylcyclopentene by comparison with the infrared of an authentic sample. The 40% components were analyzed by vpc using a 1-m silver nitrate column. The analysis showed it to be mostly methylcyclopentane with small amounts of 3- and 4-methylcyclopentene in the ratio of 2:1.

Preparation of the Potassium Salt of Methanethiol.—Metallic potassium (0.78 g, 0.02 g-atom) was added to 50 ml of anhydrous ether in a three-necked reaction flask equipped with a gas bubbler, stirrer, and Dry Ice condenser. The reaction flask was cooled with a Dry Ice–isopropyl alcohol bath and methanethiol (about 0.03 mol) bubbled into this solution over a 2-hr period. The flask was allowed to warm slowly to room temperature and the solution stirred overnight. The ether was removed by distillation leaving 1.4 g (0.018 mol, 93%) of product.

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[22] G. B. Spero, A. V. McIntosh, and R. H. Levin, *J. Amer. Chem. Soc.*, **70**, 1907 (1948).

cis- **and** *trans*-**3-Methylthiobicyclo[3.1.0]hexane.**—A solution of 2.0 g (0.017 mol) of a mixture of 27% *trans*- and 73% *cis*-3-chlorobicyclo[3.1.0]hexane[4a] in 10 ml of acetone was added dropwise with stirring to a slurry of 1.72 g (0.02 mol) of the potassium salt of methanethiol in 40 ml of acetone. The mixture was stirred at room temperature for 12 hr and then heated at reflux temperature for 2 hr. The solution was filtered and the residue thoroughly washed with ether. The solvent was removed from the combined washings and filtrate, and the residue was distilled under vacuum to give 1.0 g (0.009 mol, 55%) of the thio ether product. The vpc analysis of this product on a 25-ft Carbowax 1500 column showed it to be a mixture of 72% trans and 28% cis. The infrared spectrum of the *trans*-3 methylthio substrate shows CH stretching absorptions at 3070, 3040 and 3000 cm^{-1} and an absorption at 1025 cm^{-1} for cyclopropane, while the analogous absorptions for the *cis*-3 methylthio substrate appear at 3070, 3035, 3000, and 1020, with the absorption at 3035 enhanced relative to the trans epimer as is typical for 3-substituted epimers on the bicyclo[3.1.0]hexane skeleton.[4] A comparison of the infrared spectrum of *trans*-3-methylthiobicyclo[3.1.0]hexane with that of the 59% component from the thiol addition reaction showed that the minor component was the *trans*-3 thio ether, while the spectrum of *cis*-3-methylthiobicyclo[3.1.0]hexane was identical with that of the 6.5% component from the thiol addition reaction.

The nmr spectrum of the *trans*-3-methylthiobicyclo[3.1.0]-hexane shows high-field cyclopropane methylene absorption (τ 9.47–9.94), which is typical for a trans-3 epimer,[4b] an *S*-methyl peak at τ 8.02, a complex splitting pattern in the region τ 7.10–7.90 for the proton α to the thiol group, and a complex splitting pattern from τ 7.90 to 8.90 for six protons. Since the *trans*-2 and *trans*-3 thio ethers could not be separated by vpc, one could still analyze for the proton α to the thiyl group in the *trans*-2 thio ether without any interference from the complex absorption for the analogous proton in the *trans*-3 thio ether.

The nmr spectrum of the *cis*-3-thiomethoxybicyclo[3.1.0]-hexane shows high-field cyclopropane methylene absorption (τ 9.30–9.75) which is typical for a cis-3 epimer,[4] an *S*-methyl peak at τ 8.00, a complex splitting pattern for the proton α to the thiyl group in the region τ 6.67–7.17, and a complex splitting pattern for six protons in the region τ 7.40–8.90.

cis- **and** *trans*-**2-Methylthiobicyclo[3.1.0]hexane.**—A solution of 2.0 g (0.017 mol) of a mixture of 30% *trans*- and 70% *cis*-2-chlorobicyclo[3.1.0]hexane[4a] in 10 ml of acetone was added dropwise with stirring to a slurry of 1.72 g (0.02 mol) of the potassium salt of methanethiol in 40 ml of acetone. The mixture was stirred at room temperature for 12 hr and then heated at reflux temperature for 2 hr. The solution was filtered and the residue thoroughly washed with ether. The solvent was removed from the combined washings and filtrate, and the product was distilled under vacuum to give 1.24 g (0.011 mol, 65%) of the thio ether product. The vpc analysis of this product using a 25-ft Carbowax 1500 column showed it to be a mixture of 77% trans and 23% cis. The infrared spectrum of the *trans*-2-methylthio epimer exhibits CH stretching absorptions at 3070, 3040, 3000 cm^{-1} and cyclopropane absorption at 1020 cm^{-1}, while the *cis*-2-methylthio epimer shows absorptions at 3070, 3035, 3000, and 1020 cm^{-1}, with the 3035 absorption enhanced relative to the trans epimer.

A comparison of the infrared spectrum of the *trans*-2 thio ether with that of the 59% component mixture from the thiol addition reaction demonstrated that *trans*-2-methylthiobicyclo[3.1.0]-hexane represents the major isomer present in the 59% peak. A comparison of the infrared spectra of the *cis*-2 thio ether with that of the components isolated from the thiol addition reaction indicated that *cis*-2-methylthiobicyclo[3.1.0]hexane was not formed to any great extent in the reaction (<3%).

The nmr spectrum for the trans isomer shows high-field cyclopropane absorption (τ 9.38–9.97), which is typical for *trans*-2-bicyclohexane epimers,[4b] an *S*-methyl peak at τ 7.94, a complex splitting pattern in the region τ 9.00–8.88 for six protons, and a doublet of doublets (J = 5 and 2 Hz) for the proton α to SCH$_3$.

The nmr spectrum of the *cis*-2 thio ether shows high-field cyclopropane methylene absorption (τ 9.50–9.80), which is typical for *cis*-2-bicyclohexane epimers, an *S*-methyl peak at τ 7.94, a complex splitting pattern for the proton α to the thiyl group in the region τ 6.58–7.03, and a complex splitting pattern for six protons in the region τ 8.00–9.30.

3-Methylthiocyclopentene.—3-Methylthiocyclopentene was prepared by the reaction of the potassium salt of methanethiol with 3-chlorocyclopentene in acetone. To 0.13 mol of the potassium salt of methanethiol in 100 ml of acetone was added dropwise with stirring 10.0 g (0.10 mol) of 3-chlorocyclopentene. After the addition was completed, the reaction mixture was stirred at room temperature for an additional 30 hr. The salts were filtered off and the acetone was evaporated under reduced pressure. The residue was distilled through a 6-in. Vigreux column yielding 4.50 g (40%) of product which had bp 49–52° (25 mm).

Anal. Calcd for C$_6$H$_{10}$S: C, 63.07; H, 8.82. Found: C, 62.72; H, 8.44.

The nmr spectrum of methylthiocyclopentene shows the *S*-methyl peak at τ 8.02, two olefinic protons with a complex splitting pattern in the region τ 4.03–4.50, an allylic proton α to the thiyl group represented by a complex splitting pattern in the region τ 6.08–6.46, and two allylic methylene and two methylene protons represented by a complex splitting pattern in the region τ 7.33–8.30. The infrared spectrum shows high energy CH absorption above 3000 cm^{-1}, a double bond absorption band at 1600 cm^{-1}, cis hydrogen out-of-plane deformation absorption bands at 740 cm^{-1}, and other strong bands at 1415, 1205, 1015, 950, and 905 cm^{-1}.

Preparation of Methanethiol-*d*.—The potassium salt of methanethiol (0.1 mol) was prepared as described above. Deuterium oxide (8 ml, 99.5%) was added dropwise to the potassium salt under a gentle flow of carbon dioxide gas. The methanethiol-*d* was collected at −80° in a cold trap, which was fitted with ground glass joints and a high vacuum stopcock. The cold trap was fitted to a vacuum system and the methanethiol-*d* was distilled into a storage flask, whereupon it was purified by several distillations in the vacuum system.

Nmr analysis of the deuterated mercaptan showed complete disappearance of the SH peak at *ca.* τ 9.0, and it was concluded that the deuteration was greater than 98%. Infrared analysis indicated complete deuteration of the mercaptan by the complete disappearance of the SH band at 3.79 μ and the appearance of the SD band at 5.24 μ.

Addition of Methanethiol-*d* to Bicyclo[3.1.0]hexene-2.—Methanethiol-*d* (12.6 mmol) was allowed to react with 0.8 g (10.0 mmol) of bicyclo[3.1.0]hexene-2 in the manner described above. After 60 min of irradiation an 80% yield of thio ethers was obtained. Analysis on a 30-ft aluminum column of 25% Carbowax 1500 at 150° showed peaks for methylthiomethylcyclopentenes, *trans*-2- and *trans*-3-thiomethoxybicyclo[3.1.0]-hexane, and *cis*-3-thiomethoxybicyclo[3.1.0]hexane. The cyclopentenes and trans bicyclic compounds were collected for nmr and infrared analysis.

The nmr spectrum of the mixture of 3-methyl-5-methylthiocyclopentenes shows it to be a 70:30 mixture of the trans and cis isomers. The spectrum exhibits a total integration equivalent to 11 protons with the region for the two methyl doublets (τ 8.92 and 8.97) integrating for an area of two protons. The other protons appeared as in the undeuterated compounds. The integration of 11 protons also gave evidence for complete deuteration of the methanethiol. The infrared spectrum shows a strong CD stretching frequency at 2180 cm^{-1} and C=C band at 1600 cm^{-1}.

The nmr spectrum of the vpc collection for the *trans*-2- and *trans*-3-methylthiobicyclo[3.1.0]hexane showed them to be in the ratio of 72:28 as determined from the ratio of the *S*-methyl peaks at τ 7.94 and 8.02. The spectrum shows typical high-field cyclopropane methylene absorption (τ 9.40–10.00) for a *trans*-bicyclo[3.1.0]hexane isomer. The doublet of doublets in the nmr spectrum for the proton α to the thiyl group in the undeuterated *trans*-2 thio ether now is reduced to a somewhat broadened singlet ($W_{1/2}$ = 3 Hz) with two small shoulders corresponding to the outside peaks of the doublet of doublets. The singlet corresponds to trans addition of the elements of CH$_3$SD across the double bond, while the doublet of doublets represents the cis addition product. Analysis of the absorption region for hydrogen α to methylthio allows one to estimate that trans addition occurs to an extent greater than 81% and less than 91%.

Registry No.—**1,** 694-01-9; **4,** 27557-67-1; **5,** 27557-65-9; **6,** 27557-66-0; **7,** 27557-70-6; **8,** 27557-71-7; methanethiol, 74-93-1; methanethiol-*d*, 16978-68-0; 3-methylthiocyclopentene, 27557-68-2.

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Preparation and Pyrolysis of Some 2,6-Dimethyl-4-pyrone–Alkyne Photoadducts. Bicyclic Claisen Rearrangement

J. WILLIAM HANIFIN* AND ELLIOTT COHEN

Organic Chemical Research Section, Lederle Laboratories, A Division of American Cyanamid Company, Pearl River, New York 10965

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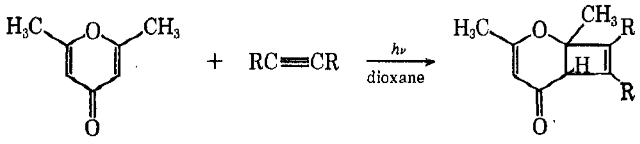
The photoaddition reaction of 2,6-dimethyl-4-pyrone with acetylenes has produced the desired 1:1 photoadducts. The pyrolysis of these cyclobutene derivatives was carried out in an attempt to convert them to the oxacyclooctatrienone ring system. However, the adducts underwent a symmetry-allowed bicyclic Claisen rearrangement followed by aromatization to substituted phenols.

Several examples of addition reactions of photochemically excited molecules to substituted acetylenes to produce cyclobutene derivatives have been reported in the literature.[1-3] The photoaddition reaction of 2-cyclopentenone with butyne-2 was the first reported example of this type reaction.[1] Recently we have shown that chromone undergoes a similar photoaddition with butyne-2.[4,5]

We would now like to report the unsensitized photoaddition reaction of 2,6-dimethyl-4-pyrone with substituted acetylenes to produce the cyclobutene derivatives. The purpose of this work was to prepare these 1:1 adducts in the hope that they would serve as useful intermediates in the preparation of medium-sized oxygen heterocycles. The results of pyrolysis experiments carried out on the photoadducts are described.

Results

A solution of 2,6-dimethyl-4-pyrone, butyne-2, and dioxane was irradiated with the 450-W mercury arc lamp. Gas–liquid chromatography indicated that only one major product was produced. The major product was isolated by liquid-liquid partition chromatography (llpc) and shown to be the desired 2,6-dimethyl-4-pyrone–butyne-2 adduct (Ia) by nmr, ir, uv, and mass spectral analysis.

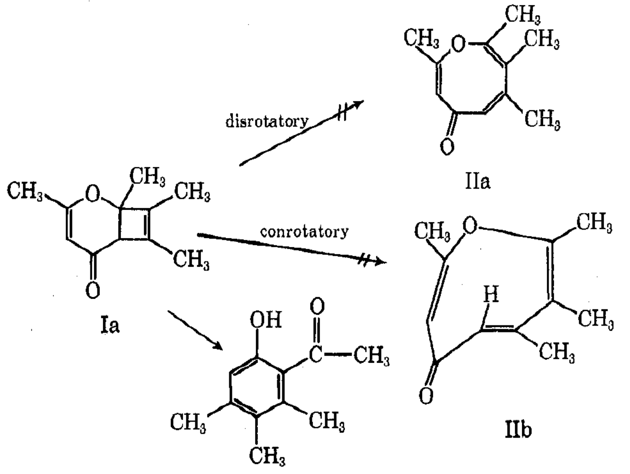


Ia, R = CH_3

b, R = CH_3

The pyrolysis of Ia was undertaken in an attempt to convert it to the *cis,cis,cis*-oxa-2,5,7-cyclooctatrien-4-one ring system, IIa. Such a ring opening would have to occur by a symmetry-forbidden disrotatory mode, or by a heterolytic or homolytic pathway, all of which are predicted to require highly energetic conditions. It was hoped that the reaction might occur under the forcing conditions of high temperature since the allowed conrotatory opening of the cyclobutene ring should be very difficult due to the formation of a trans double bond in the product, *cis,trans,cis*-oxa-2,5,7-cyclooctatrien-4-one (IIb).

The pyrolysis of adduct Ia was accomplished by refluxing in *o*-dichlorobenzene for 2 days. By glpc it was shown that one major and one very minor product were formed during the pyrolysis. The major product isolated by llpc was identified as 2-acetyl-3,4,5-trimethylphenol (III). The structure of this product was determined by nmr, ir, uv, mass spectrum, and comparison with an authentic sample prepared by an independent route.[6]



One can envision two different pathways for the pyrolysis reaction leading to the formation of III. In order to distinguish between these two different pathways, it was necessary to carry out the pyrolysis of the **2,6-dimethyl-4-pyrone–hexyne-3 adduct (Ib)**. The preparation of Ib was carried out *via* the photoaddition reaction and its structure determined by nmr, ir, uv, and mass spectrum.

Path a involves initial cleavage of the ether oxygen–C_8 bond to give the diradical intermediate IV. This is followed by bond formation between C_3 and C_8

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