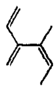
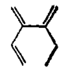
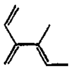
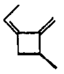
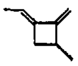
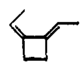
Table I. Vapor Phase Photolysis of *trans*- and *cis*-3,4-Dimethyl-1,2-dimethylenecyclobutanes,[a] **5** and **6**, at 254 nm in Quartz Vessels

Compd	Total pressure, Torr[b]/ time, min[f]	 [c]	 5		 6						
5	2/2	0.475	88.5	1.18	4.0	1.28	1.28	2.13	0.12	0.66	0.475
5	45[d]/2	0.37	94.6	0.34	2.29	0.1	0.78	1.23	0.024	0.092	0.114
5	304[e]/30	0	93	0	1.2	0	1.2	4.6	0	~0.1	~0.05
6	2/2	0.35	1.17	1.17	91.2	1.87	1.17	2.1	0.12	0.7	0.23
6	45[d]/2	0.04	7.2	0.04	89.9	0.042	1.27	1.27	0.017	0.085	0.04
6	315[e]/15	0	4.16	0	87.5	0	4.16	4.16	0	Trace	0

[a] For the structural and stereochemical assignments of these materials and the photolysis products, see ref 1c. [b] The partial pressure of **5** or **6** in each experiment was 2 Torr. [c] This material which was not previously reported in the thermal rearrangement (ref 1c) had appropriate spectroscopic properties. [d] Pentane was the added gas. [e] Nitrogen was the added gas. [f] All photolyses were conducted in the same flask with the same uv source.

generate thermal rearrangement is 46.8 kcal/mol[1e] while 254-nm radiation corresponds to an energy of 114 kcal/mol.

In order to determine the stereochemistry of the rearrangement, the *trans*- and *cis*-3,4-dimethyl-1,2-dimethylenecyclobutanes, **5** and **6**,[1c] were also photolyzed at 254 nm in the vapor phase, and again the relative quantum yields for rearrangement were inversely proportional to pressure. Moreover, the product distribution depended on inert gas pressure with hydrogen-shifted materials being major products at low pressure (Table I). At higher pressures hydrogen shifts were suppressed, and the products consisted of all of the other isomeric nongeminal dimethylenecyclobutanes derivable from 1,1′-dimethyl-**4**.[2] These were formed with some but not complete stereospecificity under conditions where the products were stable indicating a slight preference for conrotatory ring opening;[1c] however, this should be contrasted with the thermal process where conrotatory ring opening is highly favored.[1c] It should also be noted that recovery of material was very high in these photolyses indicating that cleavage to methylallene is not a favorable competing process.

Remarkably, the photolytic rearrangement of **5** and **6** in cyclohexane solution could not be detected, and after extended photolyses the starting material disappeared and no isomeric species could be detected even in solutions whose concentrations of **5** and **6** were equivalent to that in the vapor-phase experiments. This can be rationalized on the basis of a lower rate of spontaneous rearrangement of vibrationally excited **5** or **6** relative to **2** due to extra vibrational modes in the former cases. Thus, collisional deactivation competes more favorably with rearrangement in the former cases,[8] resulting in an inexorably slow rate of rearrangement of **5** and **6** in solution.

We do not regard it as critical that vibrationally excited intermediates produced upon photolysis give exactly the same product distribution as in the thermal process, particularly regarding stereochemistry as is the case here. Indeed, hydrogen shifts which are relatively high energy paths in the degenerate thermal rearrangements of **5** and **6** are the major pathways upon photolysis of **5** and **6** at low pressure. This observation is not unlike that of Srinivasan with photolysis of 1,3-butadiene where vibrationally excited species were also invoked.[7a] However, the nature of the relationship between photolysis and thermolysis either here or in other systems[7a] has yet to be delineated.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (2754-A1,4), for partial support of this work.

Joseph J. Gajewski, Chung Nan Shih
Contribution No. 1813, Department of Chemistry
Indiana University, Bloomington, Indiana 47401
Received April 21, 1970

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[8] For a discussion of this point, see S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, Chapter 9.

Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XVIII. The Conformation of Cycloheptanesemidione[1]

Sir:

Relatively few conformational studies have been performed for cycloheptene derivatives. It has been reported that 1,2-benzocyclohepten-5-one exists mainly in the chair form[2] but it has been calculated that the boat form of cycloheptene is more stable than the chair form.[3]

Nmr studies of substituted cycloheptenes and benzocycloheptenes have shown that in some cases only one conformation is populated,[4] while in other instances more than one conformation is populated at room temperature.[5]

We have previously demonstrated that cyclohexane semidione and cyclohexene have similar conformations with similar energy barriers for ring inversion.[6] We have thus examined by esr spectroscopy cycloheptanesemidione, a paramagnetic analog of cycloheptene. It

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[1] Semidiones. XIII. This work was supported by grants from the National Science Foundation and National Institutes of Health.

[2] N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 722 (1962).

[3] N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, **90**, 5773 (1968).

[4] S. Kabuss, H. Friebolin, and H. Schmid, *Tetrahedron Lett.*, 469 (1965); R. Knorr, C. Ganter, and J. D. Roberts, *Angew. Chem., Int. Ed. Engl.*, **6**, 556 (1967).

[5] S. Kabuss, A. Luttringhaus, H. Friebolin, H. G. Schmid, and R. Mecke, *Tetrahedron Lett.*, 719 (1966); H. Hart and J. L. Corbin, *J. Amer. Chem. Soc.*, **87**, 3135 (1965); E. Grunwald and E. Price, *ibid.*, **87**, 3139 (1965).

[6] G. A. Russell, G. Underwood, and D. C. Lini, *ibid.*, **89**, 6636 (1967).

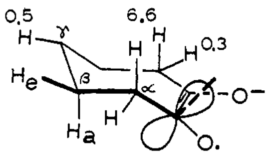
Table I. Hyperfine Splitting Constants[a] and Assignments for Substituted Cycloheptanesemidiones at 25° in DMSO

Substituent	$H_{\alpha,\alpha'}$	$H_{\beta,\beta'}$	H_{γ}
None	6.60 (2), 0.28 (2)	2.05 (2), 0.28 (2)	0.54 (1)
γ-Methyl	6.62 (2), 0.29 (2)	1.88 (2), 0.29 (2)	
γ,γ-Dimethyl	6.90 (2), 0.29 (2)	1.85 (2), 0.29 (2)	
β-Methyl	6.60 (2), 0.32 (2)	2.15 (1), 0.28 (2)	0.40 (1)
cis-β,β′-Dimethyl	6.50 (2), 0.32 (2)	0.32 (2)	0.32 (1)
trans-β,β′-Dimethyl	6.81 (1),[b] 0.33 (2) 7.25 (1)[b]	0.66 (1), 0.33 (1)	0.33 (1)

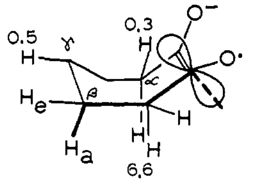
[a] Gauss. [b] The nonequivalence is caused by the loss of symmetry due to the methyl groups.

is our conclusion that only (>95%) the chair conformation is populated at temperatures up to 70°.

The α-hydrogen atoms of cycloheptanesemidione exist as two pairs of hydrogen atoms (axial and equatorial) with grossly different hyperfine splitting constants (hfsc) of 6.6 and 0.3 G which are exchanged in DMSO-d_6. This magnetic nonequivalence demands a single populated conformation. The nonequivalence of the γ-hydrogen atoms eliminates the twist-boat conformation from further consideration. The magnitude of the α-hyperfine interaction is consistent with either a chair (**1a**) or a boat (**1b**) conformation. Our assignment of the chair conformation is based on the hfsc observed for the hydrogen atoms β to the spin label. The observed hfsc for cycloheptanesemidione and several methyl derivatives are listed in Table I. Since only a single conformation was populated for each of the methyl derivatives the assignments of α and γ hfsc must be either those shown for **1a** or **1b**.



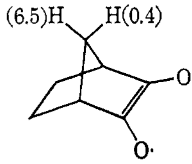
1a



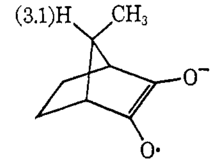
1b

It has been demonstrated in numerous systems that the hfsc of a methylene hydrogen atom with a *trans* (zig-zag) coplanar arrangement of bonds and an unpaired electron in a carbon p_z orbital is much larger than the hfsc of the other methylene hydrogen atom.[7] For **1a** the β-equatorial hydrogen atom has the desired *trans* arrangement of bonds while for **1b** the β-axial hydrogen possesses the proper geometry. Experimentally, the β-hydrogens with the *trans* arrangement have a hfsc of 2.05 G while the other β-hydrogens have a hfsc of only 0.28 G. Introduction of a β-methyl and *cis*-β,β′-dimethyl substituents into cycloheptanesemidione gave single populated conformations in which, respectively, one and two of the 2.05-G hfsc were lost by methyl substitution. Since one or two of the β-methyl groups would occupy an equatorial position in either **1a** or **1b** it follows that the β-hydrogen atoms with the 2.05 G hfsc are equatorial hydrogen atoms and that the conformation of cycloheptanesemidione is most likely **1a**, the chair structure. A possibility exists that equatorial β-methyl substituents in **1b** might greatly reduce the magnitude of the β-hfsc of axial hydrogen atoms from ~2 G to ~0.3 G. The *trans*-β,β′-dimethyl semidione completely eliminates this possibility unless it is also postulated that an axial-β-methyl substituent increases the equatorial β-hydrogen hfsc from ~0.3 to 0.66 G.

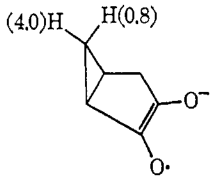
On the other hand the result observed for the *trans*-β,β′-dimethyl semidione is perfectly in agreement with a prediction based on structure **1a**. The equatorial methyl would remove one of the ~2-G hfsc of the parent semidione while the axial methyl would reduce the magnitude of the hfsc of other equatorial hydrogen atoms by about two–threefold using **2**[8] and **3**[9] as models.



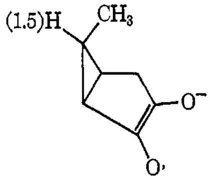
2a



2b



3a



3b

The substituted cycloheptanesemidiones were prepared from commercial glutaric acids *via* conversion to the dimethyl pimelates by the Arndt–Eistert reaction. Acyloin condensation in the presence of trimethylchlorosilane[10] gave the bis(trimethylsiloxy)alkenes which could be converted to the semidiones by treatment with potassium *t*-butoxide in deoxygenated DMSO solution.[11]

The assignment of hfsc in the chair conformation of cycloheptanesemidione is in excellent agreement with the hfsc assigned in **4**[12] and **5**[13] where the cycloheptene ring(s) must be held in a chair conformation. On the other hand, the hfsc observed for bicyclo[3.2.1]octane-5,6-semidione, **6**,[13,14] wherein the cycloheptene ring would be expected to assume a boat conformation, presents quite a different pattern.

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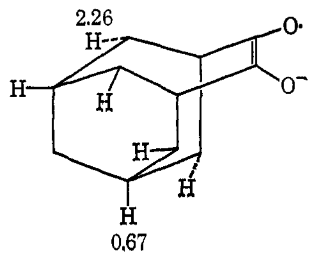
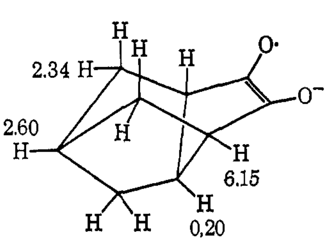
(12) Prepared by Dr. R. S. Givens.

(13) Originally prepared by Dr. K.-Y. Chang.

(14) G. A. Russell, G. Holland, K.-Y. Chang, and L. H. Zalkow, *Tetrahedron Lett.*, 1955 (1967).

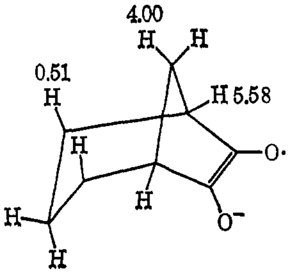


4



5

unassigned: $a^{\mathrm{H}} = 0.40, 0.40, 0.25, 0.25$ G



6

unassigned: $a^{\mathrm{H}} = 0.20, 0.51, 1.09$ G

(15) National Science Predoctoral Fellow, 1967–1970.

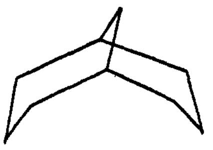
Glen A. Russell, R. G. Keske[15]
Department of Chemistry, Iowa State University
Ames, Iowa 50010

Received April 21, 1970

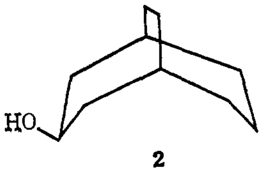
Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XIX. The Conformations of Bicyclo[3.3.2]decane-9,10-semidione and Bicyclo[3.2.2]nonane-6,7-semidione[1]

Sir:

It has been shown that bicyclo[3.3.1]nonane exists in the conformation (**1**) where both six-membered rings are in the chair form.[2] On the basis of chemical-shift data in a recent nmr study, Doyle and Parker have assigned an analogous conformation (**2**) to bicyclo[3.3.2]-nonan-3-ol.[3] We wish to report our findings on



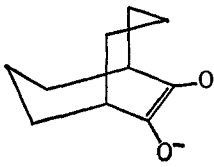
1



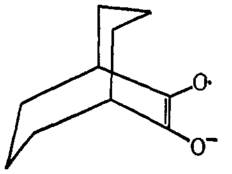
2

bicyclo[3.3.2]decane-9,10-semidione (**3**) and bicyclo-[3.2.2]nonane-6,7-semidione (**4**), which suggest that the conformation of bicyclo[3.3.2]decane and bicyclo-[3.3.2]dec-9-ene would have one seven-membered ring in the chair form and the other seven-membered ring in the boat form (**3a**).

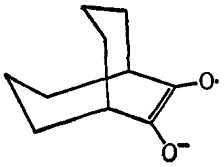
The bicyclo[3.3.2]decane system is interesting in that three conformations are possible. The esr spectra of semidiones in these conformations would be quite distinctive. The β-hydrogens which have a *trans*-coplanar arrangement of bonds to the carbon p_z orbital of the π system have large hyperfine splittings, 1.8–2.8 G, when the seven-membered ring is in the chair form,[4] whereas when the seven-membered ring is a boat, the splittings are about 0.5 G.[5] Thus **3a** would have two splittings of ~2 G, **3b** would not show any large hyperfine splitting constants (hfsc), and **3c** would have four large hfsc. In addition, **3a** would be the only form which could have hydrogens which are different from all the others in the molecule, and hence be the only one with doublet splittings.



3a



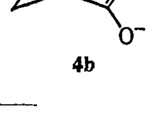
3b



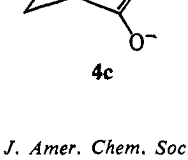
3c

The room-temperature and low-temperature spectra of **3** are shown in Figure 1. The room-temperature spectrum gave the following analysis: a^{H} (2 H) 2.36 G, a^{H} (2 H) 0.54 G, and a^{H} (3 or 5 H) 0.1 G. At low temperature the smaller triplet was split into a doublet of doublets, a^{H} 0.42 and 0.77 G. Thus conformation **3a** is required both from the doublet splittings and from the number of β-hydrogen atoms with a *trans*-coplanar arrangement of bonds leading to a^{H} ~2 G.

In relating the conformation of bicyclo[3.3.2]decane-9,10-semidione to the conformation of the parent-saturated hydrocarbon, it was considered worthwhile to determine the relative preferences of the saturated and unsaturated seven-membered rings for the chair form. If the seven-membered ring with a semidione group did not have as great a preference for the chair as the saturated ring, it would be quite possible for **3** to be in conformation **3a** while the conformation of the saturated hydrocarbon is **3c**. This question would appear to be answered by the determination of the conformation of **4**, where two possibilities exist, **4b** and **4c**. The temperature-dependent spectra of **4** was determined



4b



4c

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(1) Aliphatic Semidiones. XIV. This work was supported by grants from the National Science Foundation and the National Institutes of Health.

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(5) G. A. Russell, G. Holland, K.-Y. Chang, and L. H. Zalkow, *Tetrahedron Lett.*, 1955 (1967).