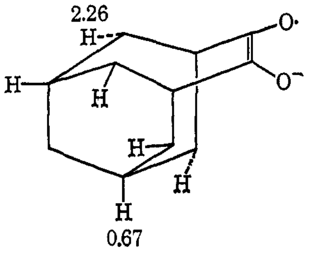
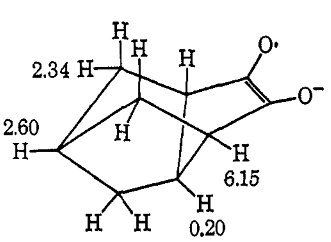
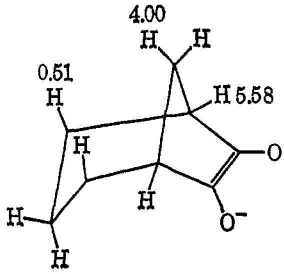


4



5

unassigned: $a^H = 0.40, 0.40, 0.25, 0.25$ G



6

unassigned: $a^H = 0.20, 0.51, 1.09$ G

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

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

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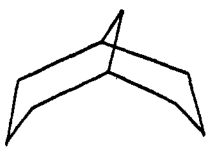
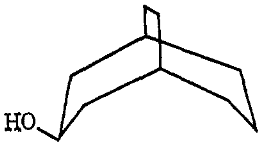
Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XIX. The Conformations of Bicyclo[3.3.2]decane-9,10-semidione and Bicyclo[3.2.2]nonane-6,7-semidione[1]

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 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**).

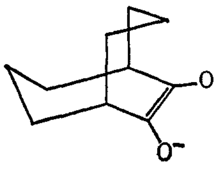


1

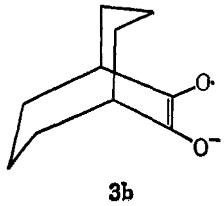


2

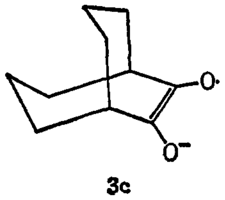
The bicyclo[3.3.2]decane system is interesting in that three conformations are possible. The esr spectra of semidiones in these conformations would be quite distinctive. The β-hydrogens which have a *trans*-coplanar arrangement of bonds to the carbon p_z orbital of the π system have large hyperfine splittings, 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



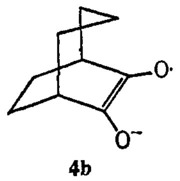
3b



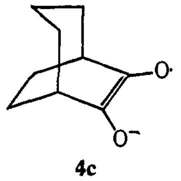
3c

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.

(2) W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 57 (1964); W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965); M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); I. Laszlo, *Recl. Trav. Chim. Pays-Bas*, **84**, 251 (1965); N. C. Webb and M. R. Becker, *J. Chem. Soc. B*, 1317, (1967); E. N. Marvel and R. S. Knutson, *J. Org. Chem.*, **35**, 388 (1970).

(3) M. P. Doyle and W. Parker, *Chem. Commun.*, 319 (1969).

(4) G. A. Russell and R. G. Keske, *J. Amer. Chem. Soc.*, **92**, 4458 (1970).

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

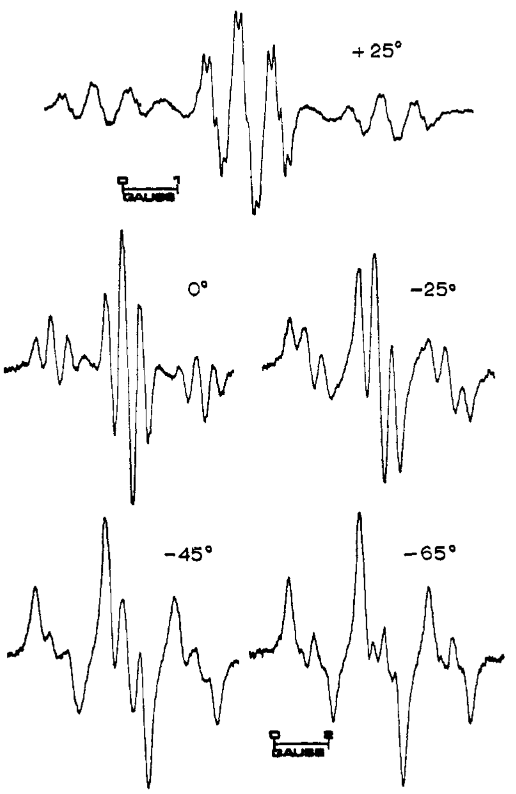

Figure 1. Esr first-derivative spectra of bicyclo[3.3.2]decane-9,10-semidione in DMSO solution at 25° and in a 4:1 DMF–DMSO mixture at lower temperature.

between −75 and 100°. At high temperature the two forms are rapidly interconverting[6] and the hfsc are population averaged, with $a^{\rm H}$ (2 H) 1.95, $a^{\rm H}$ (2 H) 1.55, $a^{\rm H}$ (2 H) 1.40, and $a^{\rm H}$ (1 H) 0.80 G. As the temperature is lowered, the large triplet, from the flexible portion of the molecule, coalesces, and at −65°, when ring inversion has been slowed, increases to 2.75 G. The magnitude of this splitting indicates[4] that the spectrum is due to **4c** where the seven-membered ring with the semidione group is in the chair form.

Thus, the seven-membered ring containing the semidione group prefers the chair conformation to a slightly greater extent than does the saturated seven-membered ring, at least at −65°. Relating this to **3**, it would seem that **3** would have a greater preference for conformation **3c** than would the parent hydrocarbon. Since **3** does not assume the conformation **3c** it would be unlikely for the saturated parent system to do so. The instability of **3c** must then be due to the (unfavorable) "saddle" conformation of the eight-membered ring.[8]

The semidiones were generated from known compounds, *i.e.*, **3** from the diester,[9] and **4** also from the diester prepared by oxidation of bicyclo[3.2.2]non-6-ene obtained by the bisdecarboxylation[10] of the hydrogenated Diels–Alder adduct of cycloheptadiene and maleic anhydride,[11] using methods which have previously been discussed.[12]

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[6] Thus this system possesses a small energy of activation for interconversion as does the bicyclo[3.2.2]nona-6,8-diene system.[7]

[7] A. J. Baker, A. M. Chalmers, W. W. Flood, D. D. MacNicol, A. B. Penrose, and R. A. Raphael, *Chem. Commun.*, 166 (1970).

[8] This is contrary to the suggestion of J. Dale, I. Laszlo, and W. Ruland, *Proc. Chem. Soc.*, 190 (1964).

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[11] E. P. Kohler, M. Tischler, H. Potter, and H. T. Thompson, *ibid.*, **61**, 1057 (1939).

[12] G. A. Russell and P. R. Whittle, *ibid.*, **89**, 6781 (1967).

[13] National Science Foundation Predoctoral Fellow, 1967–1970.

G. A. Russell, R. G. Keske[13]
Department of Chemistry, Iowa State University
Ames, Iowa 50010

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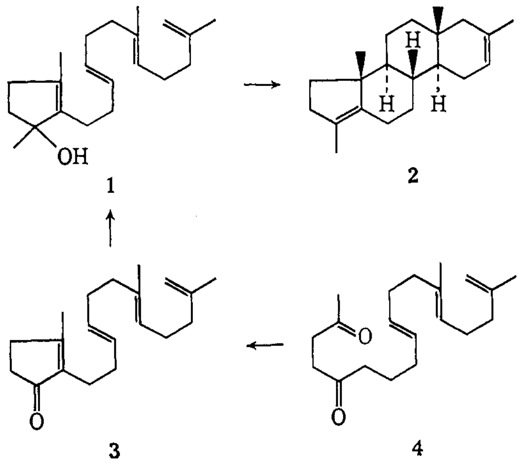
Further Developments in the Nonenzymic Biogenetic-like Steroid Synthesis

Sir:

We have previously shown that the tetraenol **1**, on acid-catalyzed cyclization, is transformed stereospecifically into the crystalline tetracyclic diene **2** which, on oxidative cleavage followed by a double intramolecular aldol cyclodehydration, affords *dl*-16,17-dehydroprogesterone.[1] The substrate **1** is readily produced from the dione **4** by cyclodehydration (to give **3**), followed by treatment with methyllithium. The dione **4** was previously produced by a multistep linear synthesis.[1] We now report a much improved synthesis of **4**, which is *convergent* and depends upon the use of the S$_{\rm N}$i′ reaction of thionyl chloride with an allylic alcohol for the stereospecific production of the *trans*-trisubstituted olefinic bond.[2]



The olefinic aldehyde **5**, which is easily produced by Claisen rearrangement of the vinyl ether of methallyl alcohol, afforded the dienol **6** (mass spectrum m/e 140, M$^+$) on treatment with isopropenyllithium. The dienol, on treatment in anhydrous ether for 1 hr at 25° with 1.3–1.9 equiv of thionyl chloride, gave the *trans* diene chloride **7** contaminated with about 9% of the secondary chloride arising from direct substitution and 3–7% of an unidentified impurity. Fortu-

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[1] W. S. Johnson, M. F. Semmelhack, M. U. S. Sultanbawa, and L. A. Dolak, *J. Amer. Chem. Soc.*, **90**, 2994 (1968).

[2] This reaction was shown by F. F. Caserio, G. E. Dennis, R. H. DeWolfe, and W. G. Young, *ibid.*, **77**, 4182 (1955), to be stereospecific for the production of *trans*-disubstituted olefinic bonds, *e.g.*, CH_3CH-$OHCH{=}CH_2 \rightarrow CH_3CH{=}CHCH_2Cl$ (100% *trans*). In addition to the present case, we have found that the method is applicable to the stereospecific production of *trans*-trisubstituted olefins in two other instances.