7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dione and Its Radical Anion. An Experimental and Theoretical Study

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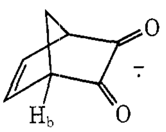
The synthesis of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dione (**2a**) and its 1-methyl derivative is described. Electrolytic reduction of **2a** gives its radical anion which has a large bridgehead hydrogen coupling of 2.48 G. Using the INDO method with a MINDO/2′ optimized geometry, spin densities for **2a**·⁻ are calculated and partitioned into their spin polarization and spin delocalization components. Mechanisms for the interaction of the vinyl and bridgehead hydrogens in **2a**·⁻ with the unpaired electron are discussed based on the spin partitioning calculation.

There has been considerable interest in studying the delocalization of the unpaired electron in rigid, strained systems using semidione,[2] semifuraquinone,[3] and semiquinone[4] radical anions as spin labels. Recently, we reported long-range coupling in the radical anion of bicyclo[2.2.1]hept-5-ene-2,3-dione (**1**) and two of its derivatives.[5] Since the hyperfine splitting constants (hfsc's) of the bridgehead (H_b) and vinyl hydrogens of these radical anions appeared to be somewhat sensitive to changes in geometry, we decided to examine what effect the introduction of a heteroatom at the 7 position would have on these couplings. We now report the synthesis of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dione (**2a**) and its radical anion.



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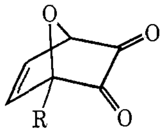

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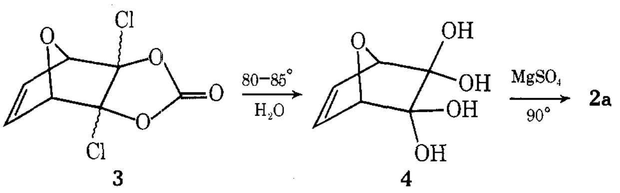
a, R = H
b, R = CH_3

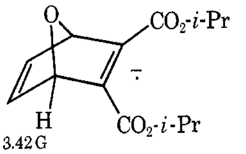
Results and Discussion

Synthesis of 2a·⁻ and 2b·⁻. Our method of preparing **2a** was based on a recent report that hydrolysis of dichlorovinylene carbonate adducts produces α-diketones.[6] Thus, a 4:1 mole ratio of dichlorovinylene carbonate to furan was heated at 120° in a sealed glass tube for 20 hr to give a 57% yield of the endo and exo furan adducts (**3**). Hydrolysis of these adducts in 50% aqueous *p*-dioxane gave the dihydrate **4**, which is surprisingly stable at room temperature. Upon heating **4** in *p*-dioxane at 90° in the presence of $MgSO_4$, the diketone **2a** was obtained. When exposed to moist air, **2a** immediately formed a mixture of its monohydrate with a small amount of **4**. An attempt to prepare the sulfur and nitrogen analogs of **2a** by the same route was unsuccessful. Both thiophene and pyrrole failed to give Diels–Alder adducts with dichlorovinylene carbonate.



Electrolytic reduction of **2a** or **3** (in DMSO with *n*-Bu_4NClO_4 as supporting electrolyte) produced an ESR spectrum consisting of a triplet of triplets with a^H = 2.48 (2 H) and 0.81 G (2 H). No signal could be detected 30 sec after the current was terminated. Treatment of **2a** with a DMSO solution of the enolate anion of propiophenone[7a] under flow conditions[7b] or with a hexamethylphosphoramide solution of sodium failed to give an ESR spectrum of **2a**·⁻. Methyl labeling was used to assign the splittings in **2a**·⁻. Electrolytic reduction of **2b** produced an ESR spectrum with a^H = 2.43 (1 H), 0.75 (2 H), and 0.16 G (3 H), which is consistent with the 2.48-G splitting in **2a**·⁻ arising from the bridgehead hydrogens.

The bridgehead coupling of 2.48 G in **2a**·⁻ is considerably larger than the 1.04-G coupling observed for the bridgehead hydrogen in **1**.[5] A similar trend has also been reported by Nelsen and coworkers for the bridgehead hydrogens in **5** and **6** where splittings of 3.42 and 0.40 G were found, respectively.[3] These authors suggested that the enhanced bridgehead splitting in **5** is not simply the result of geometrical changes but that significant spin density is present at the oxygen.



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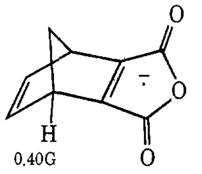

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The Optimized Geometry of 2a·⁻. Since there is no experimental structural data available for **2a**·⁻, the choice of geometry for this radical anion is significant in the evaluation of the sign and magnitude of the spin polarization (SP) and spin delocalization (SD) contributions to the resultant spin density. MINDO/2′ [8] (half-electron method[9]) has been quite reliable in predicting the heat of formation and equilibrium geometry of hydrocarbons. We performed the Simplex[10] optimization to locate the energy-minimized equilibrium geometry with respect to the heat of formation (see Experimental Section for details). The optimized geometry of **2a**·⁻ is shown in Figure 1.

Owing to the high cost of computer time, we did not optimize the geometry of the neutral diketone **2a**. It is reasonable to assume that the major geometrical differences between **2a** and **2a**·⁻ are in the C_2–O_{12} (C_3–O_{13}) and C_2–C_3 bond lengths.[11] A comparison between the HOMO Ψ_2 of **2a** with the HOMO Ψ_3 of **2a**·⁻ leads one to conclude that in **2a**·⁻ the C_2–O_{12}(C_3–O_{13}) bond length would be longer and the C_2–C_3 bond length would be shorter.

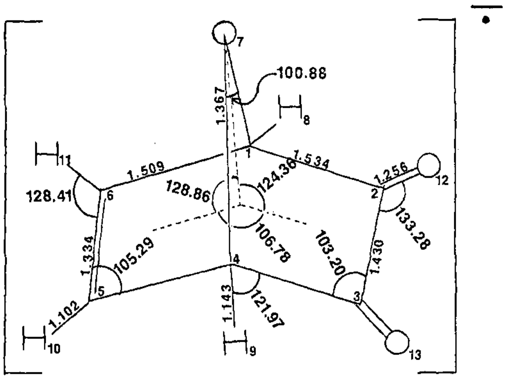
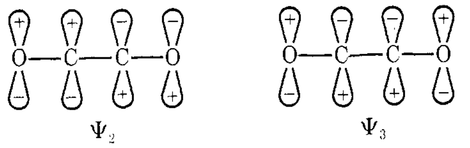


Figure 1. MINDO/2′ optimized geometry of **2a**·⁻. Nonbonded distance 1–4 = 2.130 Å. Dihedral angle (8,1,2,12) is 18.46°.



Although MINDO/2′ (half-electron method) tends to underestimate the C_1–O_7 (C_4–O_7) bond length by ~0.05 Å and the C_2–O_{12} (C_3–O_{13}) bond length by ~0.02 Å,[13] it does indicate that the interaction between the ethylenic and semidione π systems in **2a**·⁻ is slightly greater than the interaction between the two ethylenic π systems in norbornadiene (the bond angle θ^{12} in the optimized geometry of **2a**·⁻ is 106.78° compared to 115.00° for the same angle in norbornadiene[14]). The C_1–C_4 nonbonded distance in **2a**·⁻ (Table I) is ~0.1 Å shorter than its hydrocarbon analog **1**.[15]

Table I
Bond Lengths (Å) of 2a·⁻ and Norbornadiene

Bond	2a·⁻ Standard	2a·⁻ Optimized	Norbornadiene[b]
C_2–C_3	1.460	1.430	
C_2–C_{12}(C_3–O_{13})	1.220	1.256	
C_1–C_2(C_3–C_4)	1.515	1.534	1.538
C_1–C_6(C_4–C_5)	1.515	1.509	1.538
C_1–O_7(C_4–O_7)	1.430	1.367	
C_5–C_6	1.340	1.334	1.339
C_1–C_4[c]		2.130	
C_4–H_9(C_1–H_8)	1.090	1.143	1.100
C_6–H_{11}(C_5–H_{10})	1.080	1.102	1.098

[a] Reference 16. [b] Reference 14. [c] Nonbonded distance.

INDO Calculation of Spin Densities for 2a·⁻. The INDO (UHF)[17] s-orbital spin density was partitioned into spin polarization[18] and spin delocalization[19] components to elucidate the mechanism of hyperfine interaction in the open shell system. Previous work in UHF spin partitioning has been published by Kato and coworkers.[20] The isotropic hfsc's were calculated using the equation

$$a^n \cong A^n \rho_n \qquad (1)$$

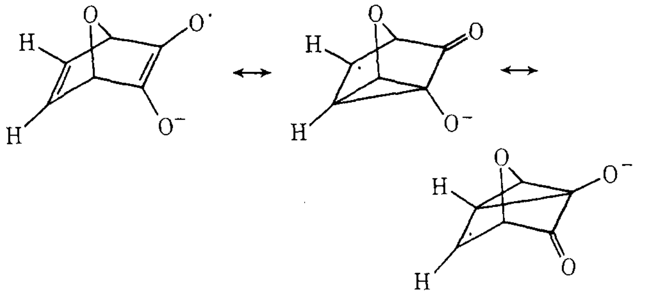
where A^n was evaluated by the direct parametization scheme, proposed recently,[21] and ρ_n is the INDO s-orbital spin density. Based on the MINDO/2′ optimized geometry (with a slight modification of the C–O and C=O bond lengths[13]), we obtained the values given in Table II.

It is apparent that spin density is transferred to C_5 and C_6 by overlap of the semidione and ethylenic π systems. This 1,3-π orbital overlap (homohyperconjugation) has been previously postulated in unsaturated bicyclic systems.[5b,22] The interaction places spin density on C_5 and C_6 which can then be transmitted to H_{10} and H_{11} by spin polarization. Our spin partitioning calculation fully supports this mechanism (+6.895 G contribution); however, spin polarization to C_5 and C_6 from C_3 and C_2, respectively, cannot be neglected (−4.024 G contribution).

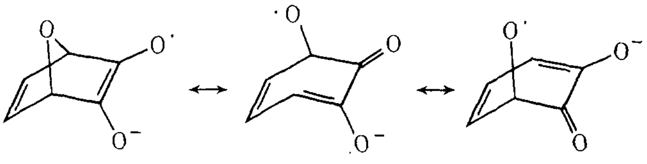
Table II
INDO Calculation of Hfsc's for 2a·⁻

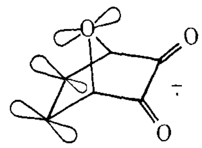
Atom no.	Element	Spin density	SP, G	SD, G	Hfsc, G[a]
1, 4	^{13}C	−0.0021	−2.346	+0.005	−2.341
2, 3	^{13}C	−0.0011	−1.417	+0.218	−1.199
12,13	^{17}O	+0.0094	−15.537	−0.002	−15.539[b]
7	^{17}O	+0.0026	−0.818	−3.415	−4.233
5, 6	^{13}C	+0.0026	−4.024	+6.895	+2.871
8, 9	^{1}H	+0.0034	−0.767	+3.781	+3.014
10, 11	^{1}H	−0.0016	−1.558	+0.126	−1.432

[a] SP + SD. [b] Note that A^n for ^{17}O in eq 1 is negative.

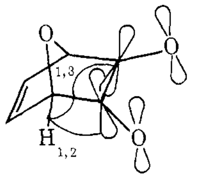


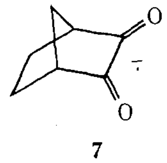
Although positive spin density is transmitted to O_7 by *both* spin polarization and spin delocalization, the latter predominates through a homohyperconjugation interaction.[22a,23] One cannot exclude the possibility of overlap of the back lobe of an oxygen sp^3 orbital with the ethylenic π system which would be facilitated by the size of the oxygen and its proximity to the ethylenic π orbitals as is found in **2a**·⁻.





Two mechanisms also appear to be operative in the hfs of H_8 and H_9. Spin polarization induced by the negative spin densities at C_1 and C_4 seems to be less important than 1,2-hyperconjugation and 1,3-homohyperconjugation[5b] of the spin label with the C–H bond. A comparison of our spin-partitioning calculation for **2a**·⁻ with an equivalent calculation for **1** and **7**[5b,24] reveals that the spin polarization contribution to the hfs's of the bridgehead hydrogens in these radical anions varies little. Since negative spin polarization contributions indicate a direct through space interaction





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mechanism, it is apparent that the spin polarization contribution from O_7 to H_8 and H_9 is not very significant. Interestingly, the hfs's of the bridgehead hydrogens of **1** and **7** are 1.04 and 2.49 G, respectively, which shows that an enhancement of coupling at this position is possible with a change in geometry alone. We conclude, therefore, that the large hfs of the bridgehead hydrogens in **2a**$\cdot^-$ relative to **1** results primarily from changes in geometry rather than an electronic effect of O_7. It seems likely that this is also true for **5**, although the symmetry plane which bisects the HOMO of the spin label is different in **5** than in **2a**$\cdot^-$.[2]

Experimental Section

ESR Spectra. The spectra were recorded in dimethyl sulfoxide (distilled from CaH_2) using a Varian Associates V-4502 spectrometer.

Computational Method. The MO calculation is based on the following steps. (A) After inputting the initial geometrical parameters, the MINDO/2′ [25] wave function is built from monoelectronic MO's obtained by linear combination of a basis set of AO's (LCAO). (B) For n geometrical parameters to be optimized, $n + 1$ vertices are constructed and wave functions at each of the $n + 1$ vertices are solved for self-consistency (i.e., for the best possible LCAO with respect to the total energy). (C) Inherent in the standard direct search Simplex[10] method[26] is the procedure of reflection, expansion, and contraction (REC) of the initial vertices with respect to the centroid (center of gravity) of the remaining vertices. (D) The procedure of REC is repeated iteratively until tests (mean square deviation of geometrical parameters and the heat of atomization) show that the calculation converges to the point which represents the true equilibrium geometry. (E) From the set of optimized geometrical parameters, spin properties of the molecule in question are computed by the INDO method.

Preparation of 3. A sealed tube containing a solution of 35 g of dichlorovinylene carbonate[6] and 4.0 g of freshly distilled furan was heated at 120° for 20 hr. The resulting solution was cooled and the excess carbonate was removed by distillation [60–61° (30 mm)] giving a thick paste. Chromatography of this material on silica gel followed by elution with benzene–ethyl acetate (95:5) gave a light yellow solution of the endo and exo isomers which was decolorized with Norit. Removal of solvent in a rotatory evaporator gave 5.72 g of a white solid (57% yield of the combined isomers).

Separation of the endo and exo adducts could be achieved by recrystallization from ether. The adduct formed in smaller amounts (38%) recrystallized first: mp 177–179°; ir (KBr) 1870 cm^{-1} (C=O); NMR (acetone-d_6) δ 5.53 (t, 1, J = 2.3 Hz) and 6.87 (t, 1, J = 2.3 Hz); mass spectrum (70 eV) m/e 222 (parent), 154, 68 (base).

Anal. Calcd for $C_7H_4Cl_2O_4$: C, 37.70; H, 1.81. Found: C, 37.81; H, 1.73.

The adduct formed in larger amounts (62%) recrystallized next: mp 112–114°; ir (KBr) 1874 cm^{-1} (C=O); NMR (acetone-d_6) δ 5.47 (t, 1, J = 2.3 Hz) and 6.70 (t, 1, J = 2.3 Hz); mass spectrum (70 eV) m/e 222 (parent), 154, 68 (base).

Anal. Calcd for $C_7H_4Cl_2O_4$: C, 37.70; H, 1.81. Found: C, 37.78; H, 1.84.

Hydrolysis of 3. A mixture of the endo and exo adducts (2.5 g) was added to a solution of 50 ml of H_2O and 50 ml of *p*-dioxane. The mixture was heated to 80–85° for 1 hr, during which time the solid completely dissolved, giving a light yellow solution. Upon cooling in ice-water, the solution became colorless and the pH of the solution was then adjusted to ~4.5 with the careful addition of $NaHCO_3$. Removal of the solvent under reduced pressure in a rotatory evaporator gave a white solid consisting of **4** and NaCl which was used directly to prepare **2a**. Small amounts of pure **4**, however, could be obtained by adding the mixture of **4** and NaCl to boiling acetone, filtering, and cooling to −10°. Colorless crystals of **4** were formed: mp 94–95° (crystals turned yellow at ~90°); ir (KBr) 3235 (OH) and 1084 cm^{-1} (C-O); NMR (DMSO-d_6) δ 6.30 (t, 1, J = 2.0 Hz), 4.42 (t, 1, J = 2.0 Hz), and 4.6–5.9 (broad s, 2); mass spectrum (20 eV) m/e 142 (P − H_2O), 141, 124 (P − $2H_2O$), 123 (base), 68.

Anal. Calcd for $C_6H_8O_5$: C, 45.00; H, 5.04. Found: C, 45.25; H, 5.10.

Preparation of 7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dione (2a). The above mixture of NaCl and **4** was introduced into a Schlenck tube containing 50 ml of *p*-dioxane (distilled from CaH_2) and 3 g of $MgSO_4$. While stirring the mixture was heated at 80–90° for 1 hr, resulting in the formation of a deeply orange solution. The mixture was transferred to a second Schlenk tube (fitted with a filter) attached to a simple distillation apparatus which had been evacuated and filled with nitrogen several times. The orange solution was then filtered into the distillation apparatus and the *p*-dioxane was removed under reduced pressure, giving a red liquid. The pressure was further reduced to ~1 mm and **2a** distilled at ~70°, giving 1.15 g of red crystals (82% yield from **3**); mp 64–66°; ir ($CDCl_3$) 1780 cm^{-1} (C=O); NMR ($CDCl_3$) δ 4.94 (t, 2, J = 1.0 Hz) and 6.83 (t, 2, J = 1.0 Hz).

Anal. Calcd for $C_6H_4O_3$: C, 58.07; H, 3.25. Found: C, 58.36; H, 3.68.

It was necessary to keep **2a** under a dry atmosphere since exposure to moist air resulted in the rapid formation of a white solid consisting of its monohydrate and **4**.

1-Methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dione (2b) was prepared by the method described for **2a**. Reaction of 2-methylfuran with dichlorovinylene carbonate gave a 58% yield of endo and exo adducts. Only one of these adducts, the one that recrystallized first from ether, could be obtained pure: mp 94–96°; ir 1845 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.72 (s, 3), 5.14 (d, 1, J = 2.0 Hz), 6.36 (d, 1, J = 6.0 Hz), and 6.53 (q, 1, J = 2.0 and 6.0 Hz).

Anal. Calcd for $C_8H_6Cl_2O_4$: C, 40.54; H, 2.55. Found: C, 40.66; H, 2.80.

Hydrolysis of 3.0 g of a mixture of these adducts in aqueous *p*-dioxane followed by dehydration in *p*-dioxane and $MgSO_4$ gave **2b** as red crystals: mp 30–33°; ir ($CDCl_3$) 1770 cm^{-1}; NMR ($CDCl_3$) δ 1.58 (s, 3), 4.93 (d, 1, J = 2.0 Hz), 6.57 (d, 1, J = 5.5 Hz), and 6.87 (q, 1, J = 2.0 and 5.5 Hz).

Anal. Calcd for $C_7H_6O_3$: C, 60.87; H, 4.38. Found: C, 61.32; H, 4.70.

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Registry No.—**2a**, 55058-68-9; **2a** radical ion, 55058-69-0; **2b**, 55058-70-3; **2b** radical ion, 55058-71-4; **2b** endo adduct, 55058-72-5; **2b** exo adduct, 55102-63-1; *endo*-**3**, 55058-73-6; *exo*-**3**, 55102-64-2; **4**, 55058-74-7; dichlorovinylene carbonate, 17994-23-9; furan, 110-00-9; 2-methylfuran, 534-22-5.

References and Notes

(1) Supported in part by grants from the Research Corporation while at Wake Forest University and the Duncan Research Fund while at the University of Wisconsin—Oshkosh.

(2) G. A. Russell, K. D. Schmitt, and J. Mattox, *J. Am. Chem. Soc.*, **97**, 1882 (1975), and references cited therein.

(3) S. F. Nelsen and E. T. Travecedo, *Tetrahedron Lett.*, 2685 (1969); S. F. Nelsen, E. F. Travecedo, and E. D. Seppanen, *J. Am. Chem. Soc.*, **93**, 2913 (1971).

(4) D. Kosman and L. M. Stock, *J. Am. Chem. Soc.*, **91**, 2011 (1969), and references cited therein.

(5) (a) R. L. Blankespoor, *J. Am. Chem. Soc.*, **96**, 6196 (1974); (b) G. A. Russell, G. W. Holland, K.-Y. Chang, R. G. Keske, J. Mattox, C. S. C. Chung, K. Stanley, K. Schmitt, R. L. Blankespoor, and Y. Kosugi, *ibid.*, **96**, 7237 (1974).

(6) H.-D. Scharf, W. Droste, and R. Liebig, *Angew. Chem., Int. Ed. Engl.*, **7**, 215 (1968).

(7) (a) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964); (b) G. A. Russell and R. L. Blankespoor, *Tetrahedron Lett.*, 4573 (1971).

(8) QCPE No. 228, Indiana University, Bloomington, Ind.

(9) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Am. Chem. Soc.*, **90**, 1953 (1968).

(10) A simplex is an n-dimensional analog of a triangle or of a tetrahedron. The only properties of simplices required for this optimization procedure are that any n-dimensional simplex has $n + 1$ vertices and $n + 1$ $(n - 1)$-dimensional hyperfaces, and that any m-dimensional hyperface is itself a m-dimensional simplex. In addition, there are two other properties of simplex. First, every simplex has $\frac{1}{2}n(n + 1)$ edges (There are $n + 1$ vertices, each of which can pair up with one of n others. This counts each edge twice, hence the factor of $\frac{1}{2}$). Second, given any vertex as origin, the set of vectors, $\mathbf{Q}_i - \mathbf{Q}_o$ (where $\mathbf{Q}_i$ and $\mathbf{Q}_o$ are vectors corresponding to the vertix i and the origin, respectively) form a basis for the n-dimensional space in which the simplex lies.

(11) A change in the C_2–C_3 bond length from **2a** to **2a**$\cdot^-$ would likely affect the amount of strain present and result in a change of the angle θ.[12] The hfs's of the vinyl and bridgehead hydrogens are sensitive to changes in θ.

(12) Angle between planes C_1–C_2–C_3–C_4 and C_1–C_4–C_5–C_6.

(13) This is one of the artifacts of MINDO/2′: unpublished result of G. A. Russell and C. S. C. Chung, 1974, after thorough testing and comparison with both experimental structural data and ab initio MO calculations [with extended basis set (e.g., 4-31G)]. The optimized geometry of **2a·**$^-$ was modified accordingly.
(14) G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **87**, 805 (1968), and references cited therein.
(15) Based on the MINDO/2′ optimized geometry of **1**, unpublished results of G. A. Russell, C. S. C. Chung, and R. L. Blankespoor, 1974.
(16) J. A. Pople and D. L. Beveridge, "Approximate MO Theory", McGraw-Hill, New York, N.Y., 1970.
(17) (a) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954); (b) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, **90**, 4201 (1968); QCPE No. 141, Indiana University, Bloomington, Ind.
(18) The definition of spin polarization is the same as suggested by J. P. Copla, E. de Boer, D. Lazdins, and M. Karplus, *J. Chem. Phys.*, **47**, 3098 (1967).
(19) G. A. Russell and C. S. C. Chung, *Mol. Phys.*, in preparation.
(20) H. Nakatsuji, H. Kato, and T. Yonezawa, *J. Chem. Phys.*, **51**, 3175 (1969), and references cited therein.
(21) M. F. Chiu, B. C. Gilbert, and B. T. Sutcliffe, *J. Phys. Chem.*, **76**, 553 (1972).
(22) (a) G. A. Russell, G. W. Holland, and K.-Y. Chang, *J. Am. Chem. Soc.*, **89**, 6629 (1967); (b) S. F. Nelsen and E. D. Seppanen, *ibid.*, **89**, 5740 (1967); (c) D. Kosman and L. M. Stock, *Chem. Commun.*, 551 (1968).
(23) G. A. Russell, G. W. Holland, K.-Y. Chang, and L. H. Zalkow, *Tetrahedron Lett.*, 1955 (1967).
(24) G. A. Russell and C. S. C. Chung, to be published.
(25) A. Brown, M. J. S. Dewar, H. Metiu, P. Student, and J. Wasson, *Proc. R. Soc., London*, to be published.
(26) (a) J. A. Nelder and R. Mead, *Comput. J.*, **7**, 308 (1964); (b) R. O'Neill, *Appl. Stat.*, **20**, 338 (1971); (c) private communication with P. W. Dillon and G. R. Underwood; (d) W. Boekelheide, J. N. Murrell, and W. Schmidt, *Tetrahedron Lett.*, 575 (1972).

The Chemistry of Polyunsaturated Bicyclo[4.2.2]decyl Systems

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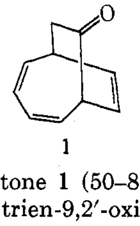
Bicyclo[4.2.2]deca-2,4,9-trien-7-one (**1**, 50–85%) and spiro[bicyclo[4.2.1]nona-2,4,7-trien-9,2′-oxirane] (**6**, 15–50%) result from reaction of bicyclo[4.2.1]nona-2,4,7-trien-9-one (**1**) and diazomethane. Bicyclo[4.2.2]deca-2,4,9-trien-7-one tosylhydrazone (**7**) is converted by methyllithium to bicyclo[4.2.2]deca-2,4,7,9-tetraene (**8**, 78%), *cis*-9,10-dihydronaphthalene (**9**, <1%), and naphthalene (5%). 7-Acetoxy- (**10**) and 7-pyrrolidinobicyclo[4.2.2]deca-2,4,7,9-tetraenes (**11**) are formed in excellent yields from acid-catalyzed reactions of **1** with isopropenyl acetate and pyrrolidine, respectively. Bases convert **1** to bicyclo[4.2.2]deca-2,4,9-trien-7-one enolate (**2**); **2** reacts with deuterium oxide to give *anti*-8-deuteriobicyclo[4.2.2]deca-2,4,9-trien-7-one (**13**), which is then converted to 8,8-dideuteriobicyclo[4.2.2]deca-2,4,9-trien-7-one (**15**) upon much longer exposure to the basic deuterating medium. Enolate **2** reacts with acetyl chloride to yield **10** (85%) and with trimethylsilyl chloride to form 7-trimethylsiloxybicyclo[4.2.2]deca-2,4,7,9-tetraene (**12**, 72%). Methylation of **2** in hexamethylphosphoramide or dimethylformamide at 0° produces 7-methoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (**16**, 92%); in glyme **16** (43%) and 8,8-dimethylbicyclo[4.2.2]deca-2,4,9-trien-7-one (**18**, 26%) are formed. Enolate **2** rearranges slowly to the β-tetralone anion and probably the anion of *cis*-9,10-dihydro-2-naphthol; secondary methylation products are 2-methoxy-3,4-dihydronaphthalene (**22**) and 2-methoxynaphthalene (**23**). Thermolysis of **16** gives naphthalene (66%) and **23** (33%). Enolate **2** reacts with isoamyl nitrite to produce bicyclo[4.2.2]deca-2,4,9-triene-7,8-dione monooxime (**32**, 63%) and with methyl formate to yield 8-formylbicyclo[4.2.2]deca-2,4,9-trien-7-one (**35**, 95%). Oxime **32** is converted to bicyclo[4.2.2]deca-2,4,9-triene-7,8-dionequinoxaline (**33**) by *o*-phenylenediamine; **35** and hydrazine give 3,4-diazatricyclo[5.4.2.0^{2,6}]trideca-2,5,8,10,12-pentaene (**36**). 8-Diazobicyclo[4.2.2]deca-2,4,9-trien-7-one (**37**, 55%) forms from **35**, tosyl azide, and triethylamine. Diazo ketone **37** photolyzes in dioxane–water to bicyclo[4.2.1]nona-2,4,7-triene-*syn*-9-carboxylic acid (**39**, 61%). Decomposition of **37** by acetic acid and by hydrogen chloride occurs with rearrangement to *exo*- and *endo*-2-acetoxybicyclo[5.2.1]deca-3,5,8-trien-10-ones (**43** and **44**), and *exo*-2-chlorobicyclo[5.2.1]deca-3,5,8-trien-10-one (**54**, 94%), respectively. Chloride **54** reacts with silver acetate yielding **43** (53%); hydrogenolysis of **54** produces bicyclo[5.2.1]decan-10-one (**56**, 61%). Hydrogenation of **43** gives *exo*-2-acetoxybicyclo[5.2.1]decan-10-one (**50**, 73%) which upon saponification and oxidation results in bicyclo[5.2.1]deca-2,10-dione (**52**, ~100%). Acetate **43** and chloride **54** rearrange to *endo*-6-(*cis*-2′-acetoxyvinyl)-*cis*-bicyclo[3.3.0]octa-3,7-dien-2-one (**58**, 93%) and *endo*-6-(*cis*-2′-chlorovinyl)-*cis*-bicyclo[3.3.0]octa-3,7-dien-2-one (**60**, 100%), respectively. Lead tetraacetate oxidizes **1** to *anti*-8-acetoxybicyclo[4.2.2]deca-2,4,9-trien-7-one (**64**, 100%). Attempted Wolff–Kishner reductions of bicyclo[4.2.2]deca-2,4,9-trien-7-one hydrazone (**66**) or the semicarbazone produce 2,3-diazatricyclo[6.3.1.0^{4,11}]dodeca-1,5,9-triene (**70**, 47–54%). 3-Methyl-2,3-diazatricyclo[6.3.1.0^{4,11}]dodeca-1,5,9-triene (**73**, 75%) is formed from **1** and methylhydrazine. Photolysis of **1** leads to tricyclo[3.3.2.0^{2,8}]deca-3,6-dien-9(10)-one (**78**, 68%), which reverts to **1** upon treatment with acid.

The properties and interconversions of C_{10} bicyclopolyunsaturated systems are subjects of intense interest.[2] We now describe the chemistry of bicyclo[4.2.2]deca-2,4,9-trien-7-one (**1**) and its derivatives, and the 8-ketobicyclo[4.2.2]deca-2,4,9-trien-7-yl carbanion (**2**) and carbonium ion (**3**).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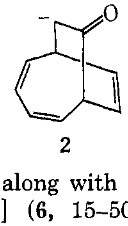
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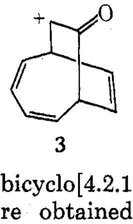
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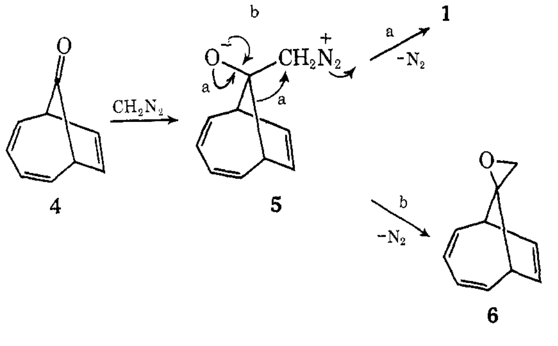
Ketone **1** (50–85%) along with spiro[bicyclo[4.2.1]nona-2,4,7-trien-9,2′-oxirane] (**6**, 15–50%) are obtained from reactions of bicyclo[4.2.1]nona-2,4,7-trien-9-one (**4**)[3a–c] with diazomethane and lithium chloride[3d] in methanol–chloroform–ether at 0°. Ketone **1** and epoxide **6** are presumably formed by nucleophilic approach of diazomethane



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