Long-Range Proton Electron Spin Resonance Splittings in Anion Radicals of Bicyclo[2.2.1]hept-5-ene-2,3-diones[1]

Ronald L. Blankespoor* and Douglas Gollehon

Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 27109

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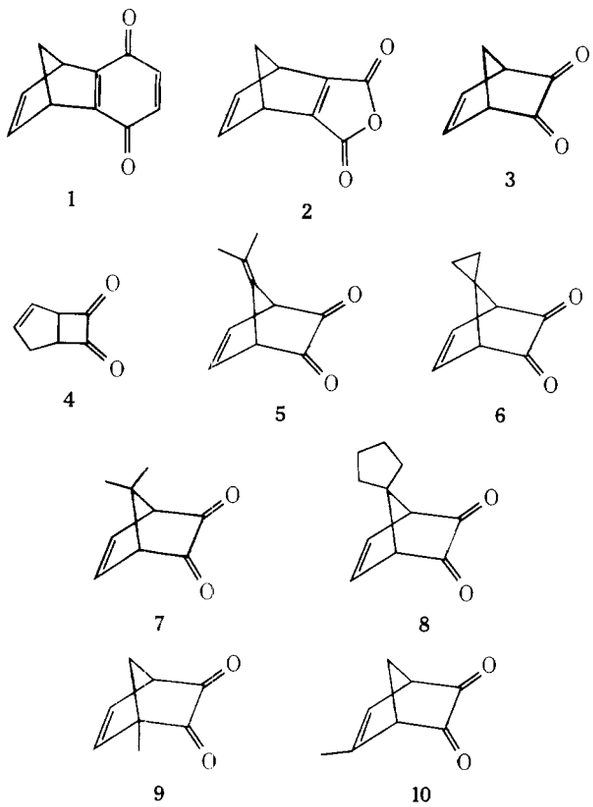
A variety of bicyclo[2.2.1]hept-5-ene-2,3-diones were prepared by hydrolysis of their cyclopentadiene–dichlorovinylene carbonate Diels–Alder adducts. Electrolytic reduction of these diketones in Me_2SO with tetra-*n*-butylammonium perchlorate as supporting electrolyte produced their anion radicals, which were examined with electron spin resonance spectroscopy. Long-range hyperfine splittings are reported and mechanisms for these interactions are discussed.

Many examples of long-range ESR splittings by nuclei separated by three or more bonds from the center containing the unpaired electron have been reported in the literature. An excellent review has been recently published which describes these splittings in semidiones, semiquinones, semifuraquinones, nitroxides, iminoxy radicals, and aliphatic radicals.[2] Some of the larger splittings have been observed in anion radicals with rigid bicyclic structures.[2] In the bicyclo[2.2.1]-heptene skeleton both the semiquinone ($1\cdot^-$)[3] and semifuraquinone ($2\cdot^-$)[4] have been examined. Although an earlier attempt to prepare the semidione ($3\cdot^-$) was unsuccessful,[5] later work revealed that a mixture of $3\cdot^-$ and $4\cdot^-$ could be obtained

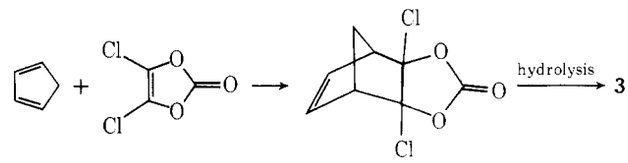


1 2 3 4 5 6 7 8 9 10

by reacting esters or silyl ethers of *endo*-3-hydroxy-2-norbornenone with base and Me_2SO.[6] We reported in a preliminary communication[1] about the same time that $3\cdot^-$ could be prepared in the absence of $4\cdot^-$ by electrolytic reduction of the diketone **3**. In this paper we report in detail long-range splittings in $3\cdot^-$ and its derivatives, $5\cdot^-$–$10\cdot^-$.

Synthesis of Bicyclo[2.2.1]hept-5-ene-2,3-diones and Their Anion Radicals. The method for synthesizing compounds **5–10** was based on a report in the literature[7] for the synthesis of **3** which is given in Scheme I. The conditions required to prepare the Diels–Alder adducts did vary somewhat. Dimethylfulvene and spiro[4.2]hepta-2,4-diene were heated with an excess of dichlorovinylene carbonate at 115 °C for 1 h resulting in a mixture of endo and exo adducts from each diene. Reaction of spiro[4.4]nona-2,4-diene and 5,5-dimethylcyclopenta-1,3-diene with the carbonate required a reaction period of ~21 h at 130–145 °C and only one isomer in significant yield (presumably the endo one) was formed from each diene. In the preparation of **9** and **10**, a solution of methylcyclopentadiene dimer and the carbonate was simply heated to reflux for 1 h. The reaction mixture consisted of the exo and endo adducts of 1-methylcyclopenta-1,3-diene and 2-methylcyclopenta-1,3-diene. Unfortunately, there was no evidence for the formation of the exo and endo adducts from 5-methylcyclopenta-1,3-diene.

Scheme I



The diketones **5–10** were prepared from their corresponding Diels–Alder adducts by hydrolysis under acid or base conditions. Acid hydrolysis was accomplished by heating the adduct in 50% aqueous dioxane at 85–90 °C for a period of at least 1 h, whereas base hydrolysis was effected by reaction with alcoholic KOH at room temperature.

The anion radicals of **3** and **5–10** were obtained by electrolytic reduction of their diketones or carbonate precursors in Me_2SO or DMF at room temperature using tetra-*n*-butylammonium perchlorate as supporting electrolyte. The ESR spectrum for each of these anion radicals gives no evidence for a second radical specie. Thus, rearrangements to the bicyclo[3.2.0]heptene skeleton (e.g., $3\cdot^- \rightarrow 4\cdot^-$) do not occur under these conditions. Substitution at the syn and anti C-7 positions enhances the stability of these anion radicals considerably. When the current was terminated, $3\cdot^-$ and $5\cdot^-$ were undetectable by ESR spectroscopy after several minutes whereas $7\cdot^-$ and $8\cdot^-$ decayed with half-lives of 15–30 min.

Assignment of Hfsc's to Anion Radicals of Bicyclo[2.2.1]hept-5-ene-2,3-diones. Electrolytic reduction of **3** and **5–10** in the cavity of an ESR spectrometer produced ESR spectra for their anion radicals. All of the anion radicals except $7\cdot^-$ gave well-resolved spectra which were simulated giving the hfsc's in Table I. Generation of $7\cdot^-$ from **7** or its carbonate precursor at room temperature or below gave a ten-line multiplet with a line width of 0.40 G. Presumably the broadening is caused by a small methyl splitting which is below the resolution limit of our spectrometer (<0.10 G).

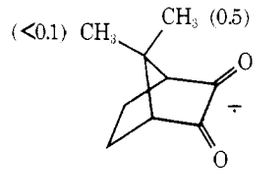
The assignment of the 1.04 and 0.70 G coupling in $3\cdot^-$ to the bridgehead and vinyl positions, respectively, follows from an

Table I. Hyperfine Splitting Constants for Anion Radicals of Bicyclo[2.2.1]hept-5-ene-2,3-diones in Me_2SO at 25 °C

		a^H, G				
Registry no.	Anion radical	C-1,4	C-5,6	C-7s	C-7a	Other
53602-58-7	**3**·⁻	1.04	0.70	2.14	8.08	
53602-59-8	**5**·⁻	0.89	0.56			1.63 (2 CH_3)
53531-36-5	**6**·⁻	0.95	0.68			0.20 (CH_2)
60526-36-5	**7**·⁻	0.96	0.72			0.78 (CH_3)
60526-37-6	**8**·⁻	0.96	0.70			0.21 (CH_2), 0.41 (CH_2)
55689-06-0	**9**·⁻	1.01 (1)	0.66, 0.74	2.07	7.69	0.16 (CH_3)
55689-07-1	**10**·⁻	0.97	0.85 (1)	1.81	7.86	0.59 (CH_3)

examination of the hfsc's for **9**·⁻ and **10**·⁻. The very large 8.08 coupling is assigned to the anti-7 position based on the large W-plan couplings that have been observed in bicyclic semidiones[6,8] and from an INDO calculation for **3**·⁻.[6] A long-range interaction of one methyl group (0.78 G) is observed in **7**·⁻.

In the saturated semidione **11**, a splitting for only one methyl group is also observed (0.53 G) and has been experi-



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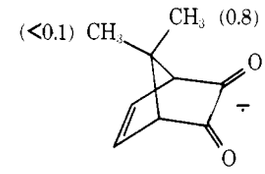
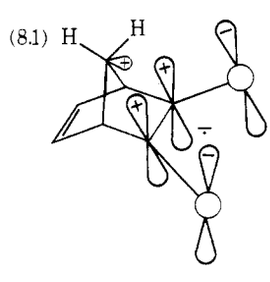


7·⁻

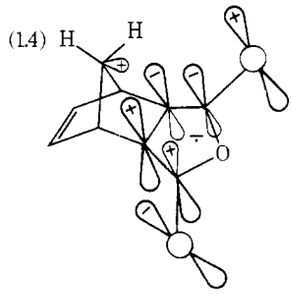
mentally determined to be the *syn*-methyl.[6] If a through space interaction is occurring between the *syn*-methyl group and the spin label as has been previously suggested,[6] it seems reasonable to assign the 0.78 G splitting in **7**·⁻ to the *syn*-methyl in view of its proximity to the spin label. A similar argument could also be used, although with less certainty, to assign the 0.20 and 0.41 G splittings in **6**·⁻ and **8**·⁻, respectively, to the *syn*-methylene groups.

Mechanisms for Long-Range Couplings in Anion Radicals of Bicyclo[2.2.1]hept-5-ene-2,3-diones. One approach to studying long-range interactions is to consider the spin label and interacting σ or π moieties as localized molecular orbitals.[2,9] If the highest occupied π molecular orbital (HOMO) of the spin label is symmetric with respect to a plane perpendicular to the spin label and bisecting the σ or π moiety, the interaction between the hydrogen(s) in the σ or π moiety with the unpaired electron in the spin label will be significantly greater than for spin labels whose HOMO is antisymmetric. The semidione and semifuraquinone spin labels can be used to study this effect since their HOMO's are symmetric and antisymmetric, with respect to this plane, respectively, and both spin labels have similar spin densities at C_{α}.[10]

The a_{7a}^H splitting in semidione **3**·⁻ (8.1 G) is considerably greater than in semifuraquinone **12** (1.4 G). This large dif-

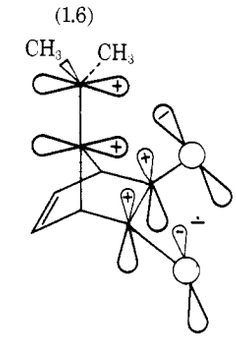


3·⁻

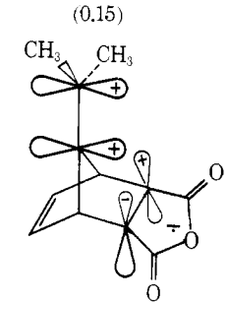


12

ference arises because a spin delocalization interaction (homohyperconjugation) in **3**·⁻ between the C–H moiety and spin label is possible a as result of their HOMO's having the same symmetry. This interaction is not possible in **12** since the HOMO's of the C–H moiety and semifuraquinone spin label have opposite symmetries. A striking illustration of this effect can also be seen in comparison between **5**·⁻ and **13** where



5·⁻



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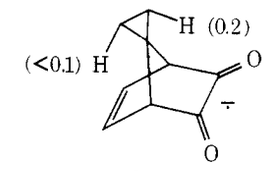
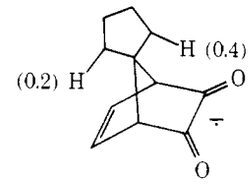
methyl splittings of 1.63 and 0.15 G are obtained, respectively. The HOMO's of the ethylenic moiety and the spin label in **5**·⁻ are symmetric with respect to the plane bisecting the spin label but are of opposite symmetry in **13**. The proximity of the ethylenic and semidione orbitals in **5**·⁻ promotes spin delocalization through a homohyperconjugative mechanism.

Although spin delocalization to the 7-anti hydrogen (H-7a) in **3**·⁻ appears to be the predominant interaction, spin polarization contributions to both H-7a and H-7s cannot be neglected as has previously been discussed.[6] This is evident in **12** where the hydrogens of the methylene bridge lie in the nodal plane but have significant splittings of 1.4 (H-7a) and 0.8 G (H-7s).

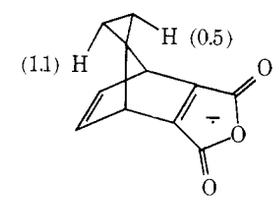
If the assignments for the methyl and methylene splittings in semidiones **6**·⁻–**8**·⁻ are correct, it is likely that the larger



6·⁻



8·⁻



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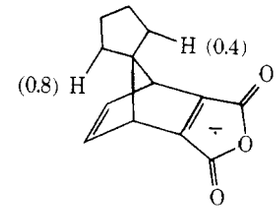

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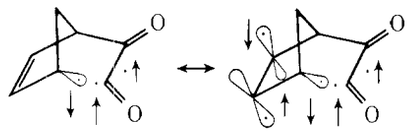
splittings for the syn hydrogens result from a through space interaction. This is apparently not the case for semifuraquinones **14** and **15**, where the larger splittings occur for the anti hydrogens.[10] Irregardless of how the assignments are made for **6**·⁻ and **8**·⁻, it is clear that the hfsc's for the bridging hy-

drogens are larger in the semifuraquinones than in the corresponding semidiones. This could be the result of spin polarization and delocalization contributions that are opposite in sign giving partial cancellation in the semidiones.

INDO calculations by Russell and co-workers[6] have been made on $2\cdot^-$ and $3\cdot^-$ and vinyl hydrogen (H_v) splittings of +1.56 and −0.52 G, respectively, were obtained. These values compare with experimental splittings of 0.8 and 0.7 G where the signs of the couplings constants have not been determined. These authors concluded that the −0.5 G coupling (calculated) in $3\cdot^-$ is the net effect of a −2.0 G spin delocalization contribution (e.g., 1,3-π overlap) and a +1.5 G spin polarization contribution (e.g., structures **16** and **17**). If the major contribution of spin density to the vinyl carbon by spin polarization occurs via **16** and **17**, a vinyl methyl coupling similar in magnitude to the H_v coupling but opposite in sign would be expected. Interestingly, the methyl splitting in $10\cdot^-$ (0.60 G) is about the same as the H_v splitting (0.85 G).



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Experimental Section

ESR Spectra. Spectra were recorded on a Varian Associates V-4502 spectrometer. Electroreductions were carried out at the surface of a mercury pool in Me_2SO or DMF (both distilled from CaH_2) using a standard electrolytic cel.

Bicyclo[2.2.1]hept-5-ene-2,3-dione (3) was prepared by the method of Scharf and co-workers, mp 42–43 °C (lit.[11] mp 43 °C).

7-(1-Methylethylidene)bicyclo[2.2.1]hept-5-ene-2,3-dione (5). Dichlorovinylene carbonate[7] (10 g) was introduced into a three-neck round-bottomed flask fitted with a septum for N_2 inlet, a condensor, and a dropping funnel. After the system was purged with N_2 for 15 min, the flask was immersed into a mineral oil bath at 115 °C. With stirring dimethylfulvene (1.1 g) was added to the carbonate over 5 min and the resulting solution was heated at 115 °C for an additional 1 h. Removal of excess carbonate gave a solid which was dissolved in ether and partially decolorized with charcoal. Filtration and removal of solvent gave 1.38 g of an off-white solid consisting of the endo and exo Diels–Alder adducts. Without further purification these adducts were dissolved in 50 ml of H_2O–dioxane (1:1) and heated to 85 °C for 2 h. The aqueous solution was extracted with CH_2Cl_2 until colorless and the combined extracts were washed with H_2O and dried over $MgSO_4$. Removal of the methylene chloride gave a red solid which was sublimed (60–70 °C, 0.1 mm) and recrystallized from ligroin (bp 63–73 °C) to give 0.41 g of **5** (26% from dimethylfulvene) as red crystals: mp 101–102 °C; ^1H NMR ($CDCl_3$) δ 6.61 (t, 1, J = 2.0 Hz), 3.88 (t, 1, J = 2.0 Hz), 1.77 (s, 3).

***exo*- and *endo*-7-Spirocyclopropane-2,3-dichlorobicyclo[2.2.1]hept-5-ene-2,3-diol Carbonate. Precursors to 6.** A solution of spiro[4.2]hepta-2,4-diene (2.0 g) and dichlorovinylene carbonate (15.0 g) was heated in a sealed tube at 115 °C for 1 h. Removal of excess carbonate under reduced pressure gave a deeply colored residue which was chromatographed on silica gel and eluted with benzene. The light yellow benzene solution was decolorized with charcoal. Removal of the benzene gave a colorless solid which was recrystallized from ligroin giving initially 1.25 g of a colorless single isomer: mp 137–140 °C; ir (KBr) 1825 cm^{-1}; ^1H NMR (CCl_4) δ 6.47 (t, 2, J = 2.0 Hz), 2.98 (t, 2, J = 2.0 Hz), 1.18–0.40 (A_2B_2, 4).

Anal. Calcd for $C_{10}H_8Cl_2O_3$: C, 48.61; H, 3.26. Found: C, 48.73; H, 3.19.

A second crop of crystals (0.30 g) consisted of a mixture of the exo and endo isomers.

7-Spirocyclopropanebicyclo[2.2.1]hept-5-ene-2,3-dione (6). A solution of the carbonate precursors to **6** (0.5 g) in 50 ml of 50% aqueous dioxane was heated at 80–85 °C for 2 h. The solution was extracted with CH_2Cl_2 (4 × 10 ml) and the extracts were combined, washed with H_2O, and dried over $MgSO_4$. Removal of the methylene chloride gave a yellow oil that solidified on standing. Recrystallization from ligroin gave 0.23 g (77%) of yellow crystals: mp 67–68 °C; ir (melt) 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.54 (t, 2, J = 2.0 Hz), 2.82 (t, 2, J = 2.0 Hz), 0.80 (s, 4).

Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.90; H, 5.32.

7,7-Dimethyl-2,3-dichlorobicyclo[2.2.1]hept-5-ene-2,3-diol Carbonate. Precursor to 7. A solution of 5,5-dimethyl-1,3-cyclopentadiene (1.25 g) and dichlorovinylene carbonate (10.30 g) was heated in a sealed tube at 145 °C for 20 h. Removal of carbonate and unreacted diene gave a colored residue which was chromatographed several times on silica gel and eluted with benzene–cyclohexane (3:1) to give light yellow crystals of only one isomer, presumably the endo one. Recrystallization from ligroin gave colorless crystals in poor yield (<10%): mp 112–113 °C; ir (Nujol) 1830 cm^{-1}; ^1H NMR (CCl_4) δ 6.28 (t, 2, J = 2.0 Hz), 3.1 (t, 2, J = 2.0 Hz), 1.46 (s, 3), 1.12 (s, 3).

Anal. Calcd for $C_{10}H_{10}Cl_2O_3$: C, 48.24; H, 4.02. Found: C, 48.38; H, 4.11.

7,7-Dimethylbicyclo[2.2.1]hept-5-ene-2,3-dione (7). To a solution of the carbonate precursor (0.20 g) in 10 ml of 95% ethanol at 25 °C was slowly added 14.04 ml of a 0.23 M alcoholic NaOH solution with stirring. The resulting yellow solution was diluted with 50 ml of water and extracted with CH_2Cl_2 until the aqueous layer was colorless (5 × 15 ml). The CH_2Cl_2 extracts were combined and dried over $MgSO_4$. Removal of the methylene chloride gave a yellow solid that was recrystallized from ligroin to give 0.115 g (95%) of yellow crystals: mp 124–126 °C; ir (Nujol) 1760 cm^{-1}; ^1H NMR (CCl_4) δ 6.41 (t, 2, J = 2.0 Hz), 2.91 (t, 2, J = 2.0 Hz), 1.28 (s, 3), 1.17 (s, 3).

Anal. Calcd for $C_9H_{10}O_2$: C, 72.03; H, 6.66. Found: C, 72.16; H, 6.67.

7-Spirocyclopentane-2,3-dichlorobicyclo[2.2.1]-hept-5-ene-2,3-diol Carbonate. Precursor to 8. A solution of spiro[4.4]nona-2,4-diene[12] (1.1 g) and dichlorovinylene carbonate (7.35 g) was heated in a sealed tube at 130 °C for 21 h. Removal of excess carbonate, chromatography of the residue on silica gel, and elution with benzene–ligroin (1:1) gave 0.6 g of a light yellow solid consisting of only one isomer. Recrystallization from hexane after decolorization with charcoal gave 0.45 g (18%) of colorless crystals: mp 110–111 °C; ir (Nujol) 1840 cm^{-1}; ^1H NMR (CCl_4) δ 6.7 (t, 2, J = 2.0 Hz), 3.23 (t, 2, J = 2.0 Hz), 2.25–1.43 (m, 8).

Anal. Calcd for $C_{12}H_{12}Cl_2O_3$: C, 52.42; H, 4.36. Found: C, 52.60; H, 4.44.

7-Spirocyclopentanebicyclo[2.2.1]hept-5-ene-2,3-dione (8). A solution of the carbonate precursor (0.285 g) in 30 ml of 95% ethanol was titrated with 15.94 ml of 0.26 M NaOH in 95% ethanol. The reaction mixture was poured into a separatory funnel containing 200 ml of H_2O and 200 ml of $CHCl_3$. After shaking, the $CHCl_3$ layer was separated and dried over $MgSO_4$. Removal of $CHCl_3$ gave 0.165 g (90%) of a viscous yellow liquid that was purified by GLC (30% SE-30/Chromosorb P column, 180 °C) to give a yellow solid: mp 37 °C; ir (melt) 1755 cm^{-1}; ^1H NMR (CCl_4) δ 6.42 (t, 2, J = 2.0 Hz), 3.03 (t, 2, J = 2.0 Hz), 1.97–1.50 (m, 8).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.95; H, 6.78.

1-Methylbicyclo[2.2.1]hept-5-ene-2,3-dione (9) and 5-Methylbicyclo[2.2.1]hept-5-ene-2,3-dione (10). A solution of methylcyclopentadiene dimer (4.0 g) and dichlorovinylene carbonate (2.5 g) was heated to reflux for 30 min. After removal of unreacted carbonate and excess dimer, the residue was chromatographed on silica gel and eluted with ethyl acetate–ligroin (1:49) giving partial separation of the four Diels–Alder adducts, the exo and endo carbonate precursors to **9** and **10**. The last fraction was rechromatographed giving a carbonate precursor to **9** essentially pure: mp 111–113 °C; ir (Nujol) 1830 cm^{-1}; ^1H NMR (CCl_4) δ 6.43 (q, 1, J = 3.3 and 5.8 Hz), 6.16 (q, 1, J = 1.3 and 5.8 Hz), 3.54 (m, 1), 1.98 (d, 2, J = 1.7 Hz), 1.58 (s, 3). It was unnecessary, however, to separate the above adducts since titration with alcoholic NaOH (4 equiv) and workup (see preparation for **8**) gave a mixture of **9** and **10** which could be separated by GLC (30% SE-30/Chromosorb P column, 180 °C). Compound **10** was obtained as a viscous yellow liquid in 95% purity: ir (neat) 1741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.13 (m, 1), 3.35–2.80 (m, 3), 2.46 (broad d, 1, J = 10.5 Hz), 1.98 (d, 3, J = 1.5 Hz). Compound **9** was obtained analytically pure as a yellow solid: mp 46–47 °C; ir (melt) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.57 (q, 1, J = 3.5 and 5.0 Hz), 6.27 (broad d, 1, J = 5.0 Hz), 3.36 (m, 1), 2.92 (q, 1, J = 2.1 and 11.0 Hz), 2.32 (broad d, 1, J = 11.0 Hz), 1.38 (s, 3).

Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.69; H, 5.66.

Acknowledgment. We gratefully acknowledge financial support of this work by the Research Corporation.

Registry No.—**5**, 60526-38-7; **5** *endo*-carbonate precursor, 60526-39-8; **5** *exo*-carbonate precursor, 60562-31-4; **6**, 60526-40-1; **6** *exo*-carbonate precursor, 60526-41-2; **6** *endo*-carbonate precursor, 60562-32-5; **7**, 0526-42-3; **7** *endo*-carbonate precursor, 60526-43-4; **8**, 60526-44-5; **8** carbonate precursor, 60526-45-6; **9**, 60526-46-7; **9** *exo*-carbonate precursor, 60526-47-8; **9** *endo*-carbonate precursor, 60562-33-6; **10**, 60526-48-9; **10** *exo*-carbonate precursor, 60526-49-0; **10** *endo*-carbonate precursor, 60562-34-7; dichlorovinylene carbonate, 17994-23-9; dimethylfulvene, 2175-91-9; spiro[4.2]hepta-2,4-diene, 765-46-8; 5,5-dimethyl-1,3-cyclopentadiene, 4125-18-2; spiro[4.4]-nona-2,4-diene, 766-29-0; methylcyclopentadiene dimer, 26472-00-4.

References and Notes

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Determination of the Configuration and Conformation of α-, β-, and Isotripiperideine by Carbon-13 Nuclear Magnetic Resonance Spectroscopy[1]

H. Kessler,*[2a] H. Möhrle,[2b] and G. Zimmermann[2a]

Institut für Organische Chemie der Universität, D-6000 Frankfurt (Main), West Germany, and Institut für Pharmazeutische Chemie der Universität, D-4000 Düsseldorf, West Germany

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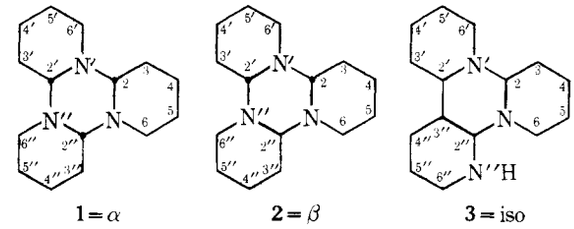
The constitution, configuration, and conformation of the three isomeric tripiperideines (α-, β-, and iso-) have been established by ^{13}C NMR spectroscopy. α-Tripiperideine (**1**) exhibits a five-line spectrum at room temperature which changes to a 15-line spectrum at low temperatures. This is due to a slowing down of the equilibration between three asymmetric topomers of conformation B, which, at room temperature, average to apparent C_3 symmetry. The conformation F of β-tripiperideine (**2**) is established by comparison of the observed ^{13}C chemical shifts with calculated ones using the approach of empirical increments. The same procedure enables one to prove the dominant configuration and conformation I of isotripiperideine (**3**). By comparison of the most stable conformations of **1**, **2**, and **3** it was possible to estimate the energetic limits of the syn-axial lone pair interaction (generalized anomeric effect) between two nitrogen atoms.

NMR spectroscopic investigations of the conformation and dynamic behavior of heterocyclic six-membered ring systems have attracted considerable interest.[3] During the last few years ^{13}C NMR investigations have provided new information about the constitution of natural products[4] and the ground state conformation[5] of a number of saturated heterocycles. In connection with our interest in dynamic ^{13}C NMR studies[6] we report here our investigation of tripiperideines. The temperature dependence of their ^{13}C NMR spectra gives information about constitution, configuration, and conformation as well as about the mechanism and the kinetics of intramolecular rate processes, in contrast to the ^1H NMR spectra of these compounds, which are complex and less informative. In this paper we present our results regarding the ground state conformation of the tripiperideines.

Constitution and Configuration. By dehydrohalogenation of *N*-chloropiperidine three isomeric trimers have been obtained.[7] The α (**1**) and β isomers (**2**) result from the normal trimerization reaction of the azomethine and differ only in the relative configuration of the three asymmetric methine carbons, whereas the iso compound is constitutionally isomeric to the α and β compounds.[8]

α- and β-tripiperideine each contain three asymmetric carbon atoms. The configurational isomers differ in their overall symmetry: one of the compounds is dissymetric (C_3 symmetry, racemic mixture of *RRR* and *SSS* chirality), the other is asymmetric (C_1 point group, also a racemic mixture in this case of *RRS* and *SSR* chirality). The assignment of the configuration of **1** and **2** is easy by ^{13}C NMR spectroscopy: at room temperature the α isomer shows five sharp signals (C_3 symmetry), the β isomer 15 (C_1 symmetry) (Figure 1).

Isotripiperideine (**3**) has only two tertiary carbon atoms (C-2 and C-2″) attached to two nitrogen atoms (signals at 80.9 and 81.8 ppm, Table I) but one tertiary carbon (C-2′) which is attached to only one nitrogen atom (64.2 ppm) and another one (C-3″) which has only carbon neighbor atoms (47.7 ppm).[9] Altogether 15 carbon signals are seen in the spectrum of **3** at room temperature. The constitution of all three isomers and



1 = α **2** = β **3** = iso

the configuration of **1** and **2** are thus directly evident from ^{13}C NMR spectroscopy.

Conformation[10] of 1. The C_3 symmetric conformation of α-tripiperideine requires axial orientation of all three lone pairs of the nitrogen atoms. In conformation A all rings are trans fused.[11] The resulting electron pair repulsion (generalized anomeric effect or "rabbit ear effect")[5a,12] destabilizes