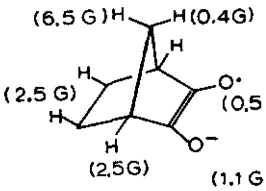
LONG RANGE INTERACTIONS IN BICYCLIC SEMIDIONES CONTAINING HETERO ATOMS[1]

Glen A. Russell,* Lourdes L. Herold, and K.-Y. Chang
Department of Chemistry, Iowa State University, Ames, Iowa
50011, U.S.A.

Abstract -- Long range hyperfine splittings are observed for anti hydrogen atoms in the semidiones 4, 8, 9, 11, and 12, but a corresponding spin delocalization by the lone pair of electrons of a nitrogen or phosphorous bridge in 8, 9, 10, 11, 12, or 13 cannot be observed.

We have previously reported long range interactions in semidiones such as 1 - 3 where the assignments of hyperfine splitting constants (hfsc) are based on the effects of alkyl or deuterium substitution on the ESR spectra.[2-4]



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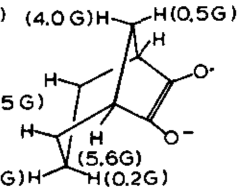

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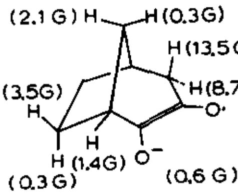
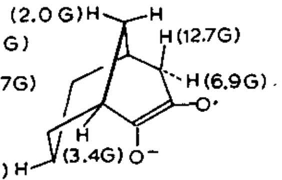
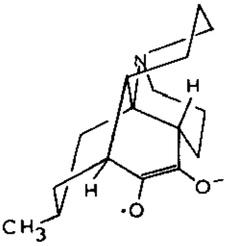


3[4]



4[4]

The assignment of hfsc for 4 is based on the fact that oxidation of exo-7-methylbicyclo[3.3.1]nonan-2-one[5] in Me_2SO/Me_3COK gave the exo-7-methyl derivative with a^H = 12.8, 8.0, 3.4 and 1.6 G while treatment of 6-hydroxylycopodine[6] with base in Me_2SO formed 5 with a^H = 14.1 and 3.7 G.



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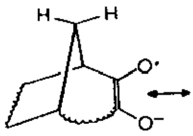
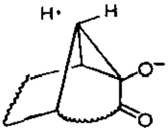
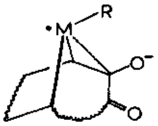


6a



6b

The long range hfs of the anti hydrogen atoms of the methylene bridge in 1 - 4 has been interpreted as resulting from homohyperconjugation as illustrated in 6a ↔ 6b.[2,7] Consistent with the homohyperconjugation structure 6b, syn alkyl substitution at a methylene bridge greatly reduces the magnitude of the hfsc by an anti hydrogen atom as in 5.[2] Replacement of the methylene bridge in 6a by a hetero atom allows the possibility of a homoconjugative interaction as depicted in 7. However, with the heterocyclic semidiones investigated we have found no evidence for this interaction. Thus, treatment of 2-benzoyloxytropinone with Me_3COK in Me_2SO gave two species (a^H = 15, 7.5, 3.5 G and 11, 7.9, 3.5 G) whose relative concentrations did not change appreciably between -60 and 90°C, and which we assign to the syn and anti isomers 8 and 9. There was no evidence of time averaging of 8 and 9 on the ESR timescale. Since structure 7 involves an expansion of the valence shell of atom M to a penta-coordinated state, the possibility of such an interaction should be better with a phosphorous bridge. However, attempts to prepare the corresponding phosphorous and sulfur bridged semidiones by oxygenation in Me_2SO/Me_3COK of 8-phenyl-8-phosphabicyclo[3.2.1]octane-3-one or 8-thiabicyclo[3.2.1]octan-3-one failed to produce ESR signals attributable to a semidione. Heterocyclic derivatives of 4 are more easily prepared by oxygenation of the enolate anions. Thus, pseudopelletierine[8] and 9-phenyl-9-phosphabicyclo-[3.3.1]nonan-3-one[9] gave 10 and 11. There was no detectable a^N in 10 (<1G) while



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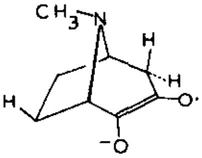

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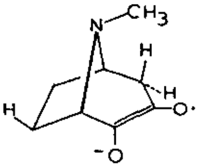

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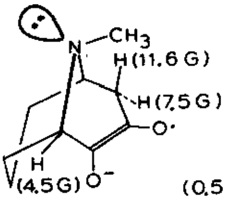

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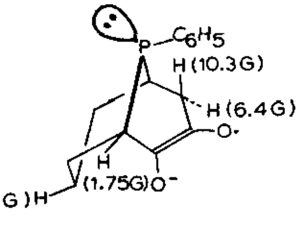
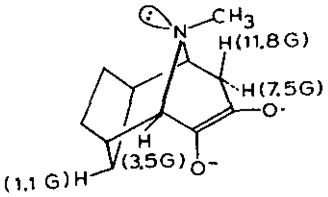


11

for 11 there is an additional unassigned doublet splitting of 0.5 G which may possibly be a result of ^{31}P hfs or possibly a result of hfs by the *exo*-hydrogen at C-8 or the *endo*-hydrogen at C-7. 9-Thiabicyclo[3.3.1]nonan-3-one,[10] upon oxidation in basic solution gave a species with $\underline{a}^H$ = 7.9, 5.6, 2.25, 0.63, and 0.06 Gauss, which may be the sulfur analog to 10 and 11. However, the observed hfsc can also be rationalized with the product of β-elimination of the thia bridge to give an 8-substituted $\Delta^{3,4}$-cyclooctane-1,2-semidione.

A homohyperconjugative long range interaction (such as 7) should depend on the orientation of the orbital containing the lone pair relative to the semidione spin probe. In both 12 and 13 the lone pair is favorably oriented (anti) to the spin probe for this long range interaction. Oxidation of 6,9-*endo*-methylenepseudopelletieriene[11] in Me_2SO/Me_3COR yielded a spectrum consistant with 12 but without a detectable $\underline{a}^N$. Oxygenation of the appropriate symmetrical tricyclic ketone[12,13] yielded 13 which again did not display a nitrogen coupling, although the nitrogen lone pair forms an excellent W-plan arrangement with the p-orbital of the semidione spin probe.



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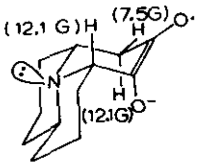

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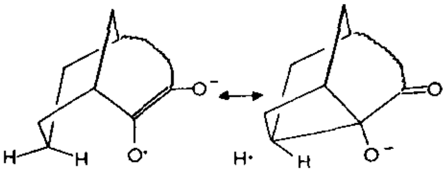
We conclude that delocalization of the unpaired electron by structures such as 7 (M = N or P) which require valence shell expansion is less favorable than homohyperconjugation by a suitably oriented *anti* C-H bond such as in 6 or 14.



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Although the presence of the *syn* alkyl or aryl groups in 9 - 12 may be a contributing factor, the complete absence of long range interactions involving lone pairs is surprising.

ACKNOWLEDGMENT

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REFERENCES

1. Aliphatic Semidiones. Part 41.
2. G. A. Russell, G. W. Holland, K.-Y. Chang, R. G. Keske, J. Mattox, C. S. C. Chung, K. Stanley, K. Schmitt, R. Blankespoor, and Y. Kosugi, *J. Am. Chem. Soc.*, 1974, **96**, 7237.
3. G. A. Russell, R. G. Keske, G. Holland, J. Mattox, R. S. Givens, and K. Stanley, *J. Am. Chem. Soc.*, 1975, **97**, 1892.
4. G. A. Russell, K.-Y. Chang, and C. W. Jefford, *J. Am. Chem. Soc.*, 1965, **87**, 4383.
5. See R. A. Appleton and S. H. Graham, *Chem. Comm.*, 1965, 297.
6. W. A. Ayer, J. A. Berezowsky, and D. A. Law, *Can. J. Chem.*, 1963, **41**, 649.
7. G. A. Russell and K.-Y. Chang, *J. Am. Chem. Soc.*, 1965, **87**, 4381.
8. A. C. Cope, H. L. Dryden, Jr., and C. F. Howell, *Org. Syn. Coll. Vol. IV.*, 1962, 816.
9. Y. Kashman and E. Benary, *Tetrahedron*, 1972, **28**, 4091.
10. T. Sasaki, S. Equchi, and T. Hioki, *J. Org. Chem.*, 1978, **43**, 3808.
11. L. A. Paquette and J. W. Heimaster, *J. Am. Chem. Soc.*, 1966, **88**, 763.
12. W. A. Ayer and K. Furuichi, *Can. J. Chem.*, 1976, **54**, 1494.
13. R. V. Stevens and A. W. M. Lee, *J. Am. Chem. Soc.*, 1979, **101**, 7032.

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