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LONG-RANGE HYPERFINE SPLITTING IN BICYCLIC SEMIDIONES

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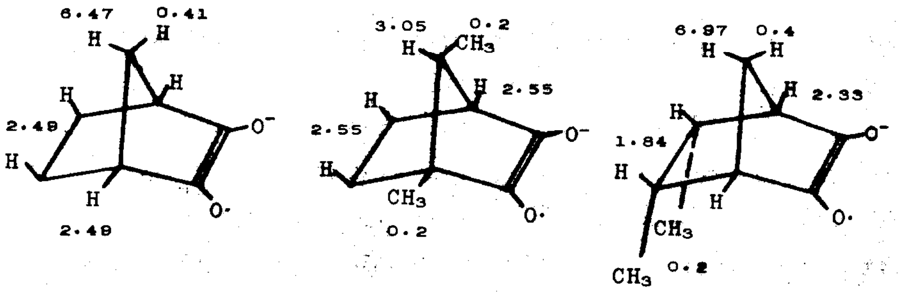
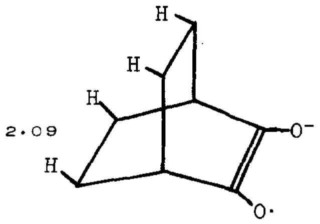
Long range hyperfine splitting, fitting the W-plan, has been previously reported for semidiones in the bicyclo[3.1.0]hexane, bicyclo-[3.1.1] and [2.2.1]heptane, bicyclo[2.2.2]- and [3.2.1]octane and bicyclo[3.2.2] and [3.3.1]nonane systems (1,2). We now report some unusual effects of alkyl substitution on the magnitude of such effects in bicyclo[2.2.1]heptane and bicyclo[2.2.2]octane systems.

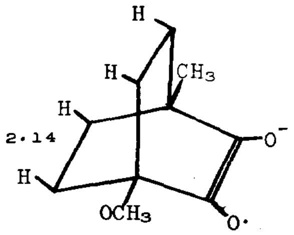
Methyl substitution at the syn C-7 position or the endo C-5,6 positions greatly reduces the magnitude of the long range hfs in the bicyclo[2.2.1]heptane system (1). There is little effect of a bridgehead methyl substituent on the magnitude of the hfsc.

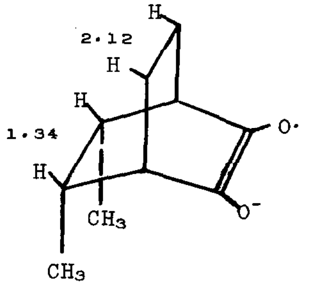


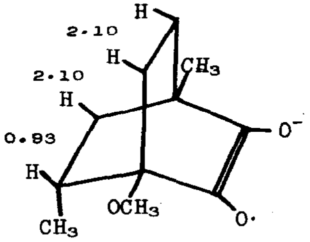
Hyperfine splitting constants in gauss

The same effect of alkyl substitution is apparent in the bicyclo[2.2.2]octane-2,3-semidiones (1).

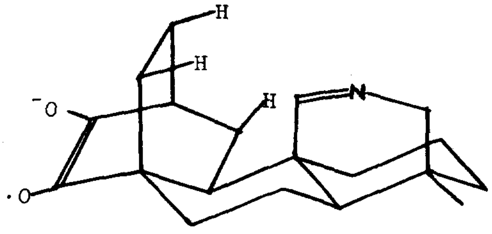




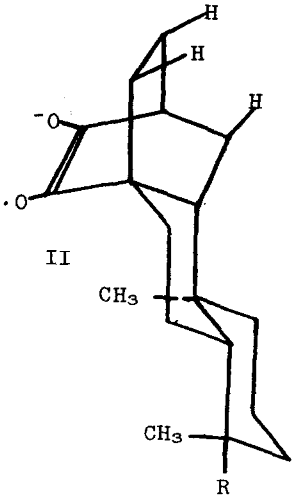




The quartet splitting observed for semidione I was of course expected in view of our previous results (1). However, the fact that II gives a similar quartet splitting is surprising.



I



II

I, $\underline{a}^H$ (1:3:3:1 quartet) = 2.2

II, $\underline{a}^H$ (1:3:3:1 quartet) = 2.3

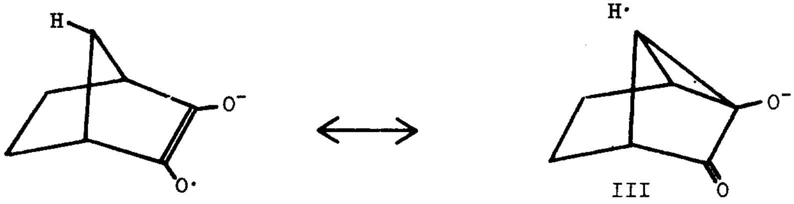
R = $-CH_3$, $-CO_2CH_3$

R

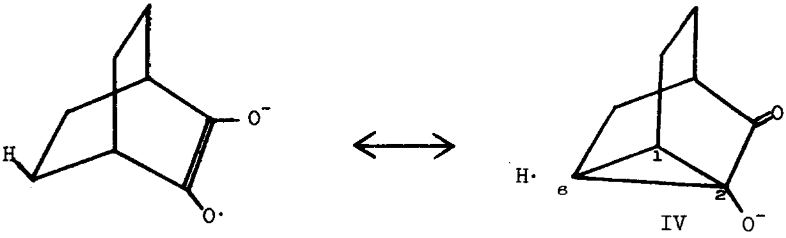
Substituents at the syn C-6 position in the bicyclo[2.2.2]octane-2,3-semidione greatly reduce the hfs by the anti C-6 hydrogen. This effect is enhanced by the presence of a C-1 substituent and no long-range hfs is observed when methylene substituents at C-1 and syn C-6 are part of a cyclohexane ring.

Our results may reflect a change of geometry in these systems upon alkyl substitution. However, the hfsc for the other hydrogen in the ethano-bridge gives little indication of such an effect.

We prefer to consider these interactions as homohyperconjugation, viz:



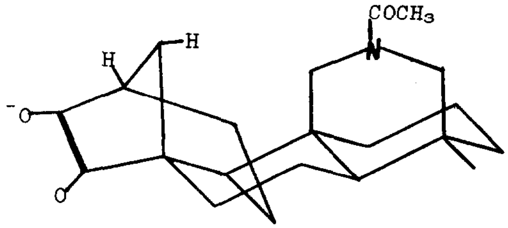
III



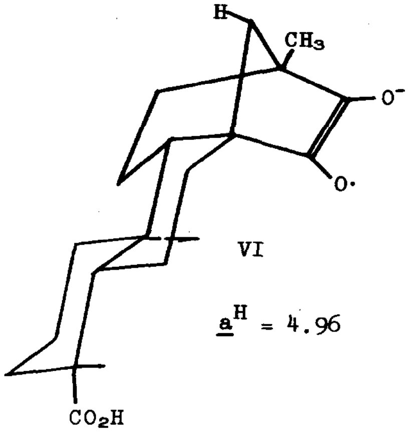
IV

Structure III contributes 1.3% (100 x 6.47/508) to the total resonance hybrid while the four equivalent structures of type IV contribute 1.6% (100 x 4 x 2.09/508). Apparently carbon-carbon bonds at C-1 and syn at C-6 in IV destabilize the resonance structure with bonding between C-2 and C-6 to such an extent that it contributes to the resonance hydrid to an extent less than 0.4% ($\underline{a}_{anti}^{H} < 0.2$ gauss).

Long range hfs is not pronounced for the exo-2-hydrogen of the bicyclo[3.2.1]octane-6,7-semidione. The hfsc observed for V and VI allow the major hfsc (2) for the parent system (VII) to be assigned as shown.

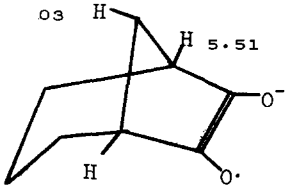


V, $\underline{a}^H$ 5.14, 3.83



VI

$\underline{a}^H = 4.96$



VII

A typical first derivative esr spectrum, observed for VII is shown in the figure. Semidione I was prepared from the α-hydroxy ketone (3), II by oxidation of the 13-ketone with R = methyl or carbomethoxy (4), V from the α-hydroxy ketone (5), VI by reduction of the diketone (6) by the enolate anion of propiophenone (7), and VII by oxidation of the ketone (8). All semidiones were prepared in dimethyl sulfoxide solution containing excess potassium t-butoxide and were stable for hours at 25°.

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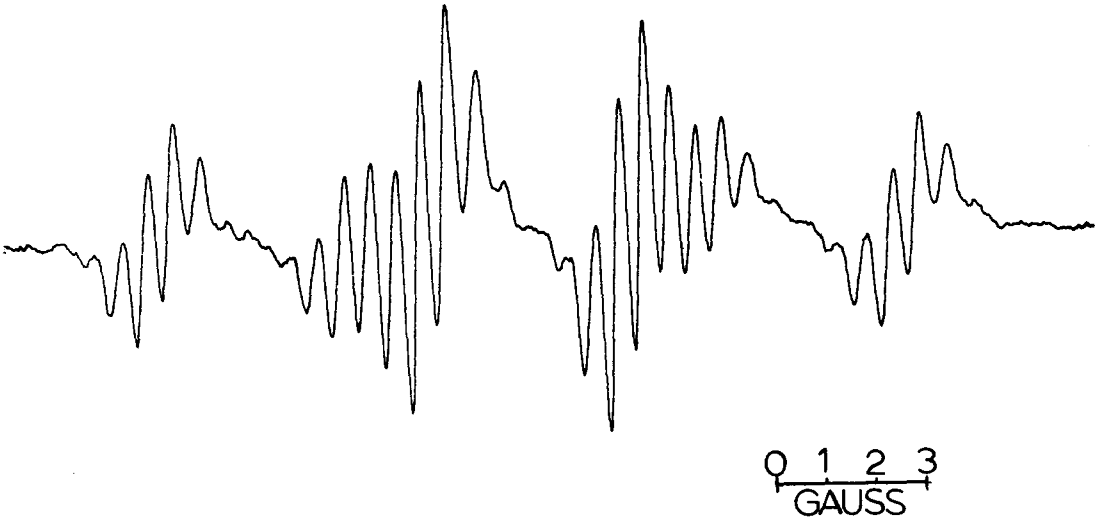

FIG. 1

First derivative esr spectrum of semidione VII prepared by oxidation of bicyclo[3.2.1]octan-6-one in dimethyl sulfoxide solution in the presence of potassium *t*-butoxide. The spectrum requires hyperfine splitting by eight protons, a^H = 5.51 (2), 4.03, 0.53 (5).

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