Tetrahedron Letters No. 27, pp 2421 - 2424, 1978.   0040-4039/78/0701-2421$02.00/0

AN ELECTRON SPIN RESONANCE STUDY
OF
THE 8-METHYL-ENDO-TRICYCLO[3.2.1.0^{2,4}]OCTAN-8-YL RADICAL

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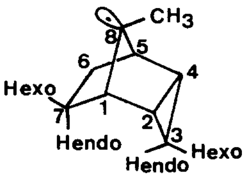
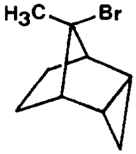
(Received in Japan 5 April 1978; received in UK for publication 8 May 1978)

Large interaction between the cyclopropane ring and the methano bridge carbon atom in the skelton of endo-tricyclo[3.2.1.0^{2,4}]octane has been proposed to account for the highly regioselective hydrogen atom abstraction from the methano bridge of endo-tricyclo[3.2.1.0^{2,4}]octane by t-butoxy radical and stereoselective chlorine atom transfer from t-butyl hypochlorite to the endo-tricyclo[3.2.1.0^{2,4}]octan-8-yl radical.$^{1)}$ In this communication we report the esr spectrum of the 8-methyl-endo-tricyclo[3.2.1.0^{2,4}]octan-8-yl radical (I) and its stable structure, which suggests the existence of homoconjugation between the cyclopropane ring and the tervalent carbon atom.



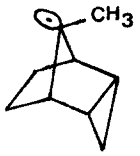
I



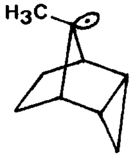
II

Figure 1 illustrates esr spectra of I observed at various temperatures during photolysis of cyclopropane or ethane solution of a mixture of bromide II,$^{2)}$ triethylsilane, and t-butyl peroxide. The spectrum in Figure 1b observed at -87°C was analyzed as a quartet (21.60 G) split into doublets (6.59 G) and two sets of triplets (1.88 G and 0.94 G). The g factor was 2.00240. Figure 1a shows the simulated spectrum obtained from this analysis. The quartet splitting is due to the methyl protons and the hyperfine splitting constant (hfsc) is smaller than the methyl proton hfsc (26.9 G)[3)] of ethyl radical with a planar tervalent carbon atom and that of t-butyl radical (22.7 G)[3)] with a somewhat pyramidal[4)] tervalent carbon atom, showing that the tervalent carbon atom of I is pyramidal.[5)]

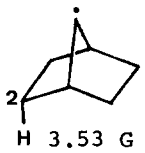
Two structures,Ia and Is, are possible for the stable geometry of I. On the



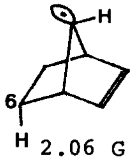
Ia



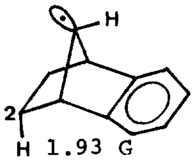
Is



III



IV



V

basis of hfsc's of endo protons of ethano bridges of III,[6)]IV,[6)]and V,[7)]the hfsc of 7-endo proton of Ia is expected to be less than 3.5 G, whereas that of Is to be 3-8 G.[7)] The largest triplet splitting of I is 1.88 G, which is smaller than 3.5 G, implying Ia to be the stable structure of I.

The doublet of 6.59 G is due to one of exo-3 and endo-3 protons and the other proton has a hfsc less than the linewidth, 0.3 G, showing the long-lange interaction is highly stereoselective. We prefer the assignment of $a(H_{3exo})=6.59$ G because the C_3-H_{3exo} bond is arranged appropriate for the interaction with the odd electron orbital via the double "through-three-bond" mechanism[8)] in the stable geometry of Ia. We would like to point out that to our knowledge the hfsc of exo-3 proton is the largest δ proton hfsc ever observed for the alkyl radicals

A comparison of spectra in Figure 1 reveals that the rotation of the methyl group is hindered at temperatures below -100°C but not "frozen" even at -152°C in the esr time-scale. The rate of the rotation at -152°C is estimated to be around 6×10^7 sec^{-1}.

The stable geometry of Ia implies the homoconjugation between the cyclo-

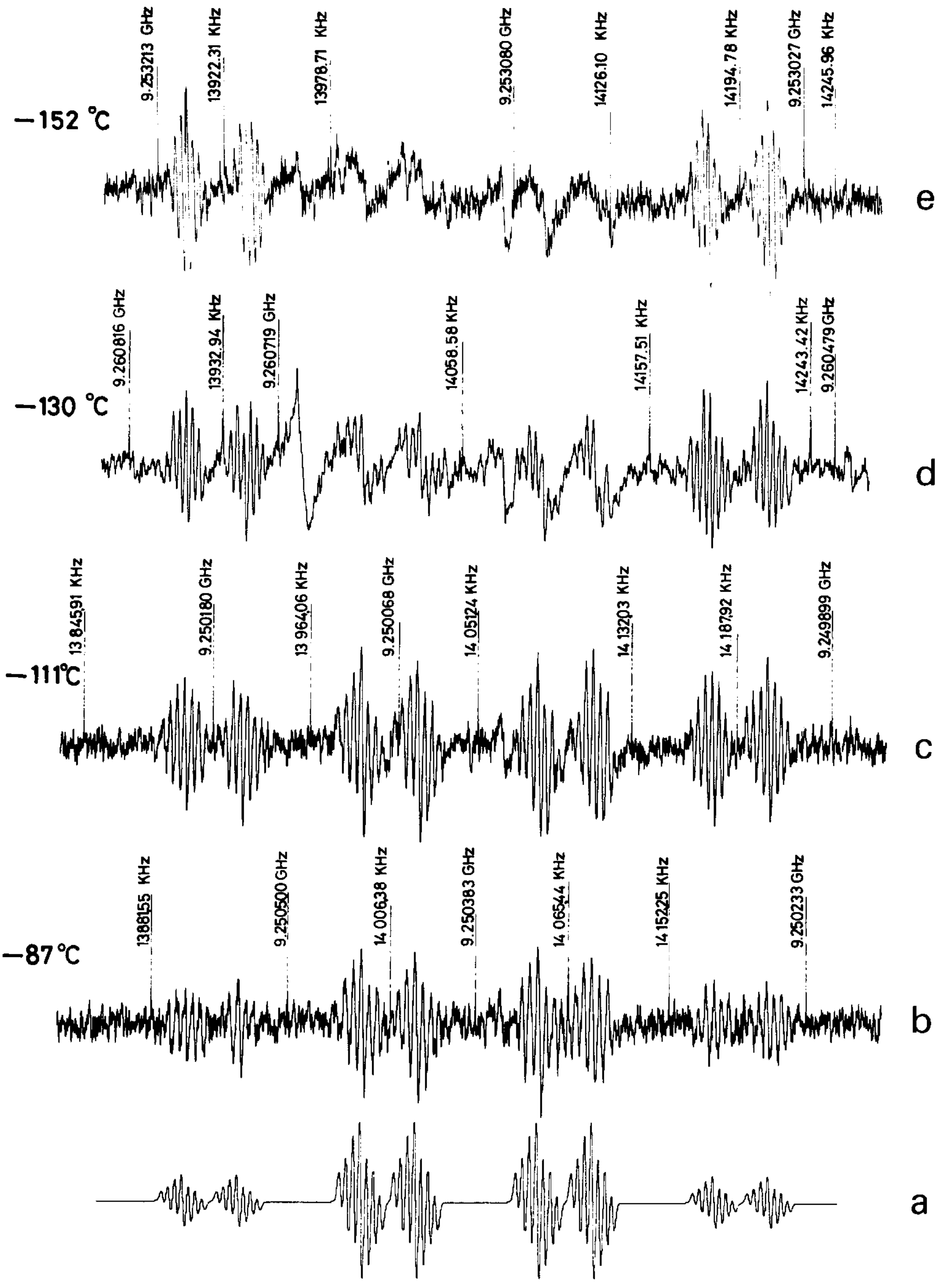


Figure 1. Esr spectra of I at various temperatures (b-e) and the simulated spectrum (a).

propane ring and the odd electron orbital. The highly stereoselective chlorine atom transfer from t-butyl hypochlorite to endo-tricyclo[3.2.1.0^{2,4}]octan-8-yl radical in the anti side relative to the cyclopropano bridge is consistent with the stable pyramidal geometry of Ia.

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