Conformational Interconversion in the 1,1,4,4-Tetramethyltetralin-2-ketyl Radical Anion by Electron Spin Resonance

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A moderately stable ketyl free radical containing two protons bonded to the carbon atom in the α-position of the carbonyl group has been prepared by alkali metal reduction of 1,1,4,4-tetramethyl-2-tetralone. The e.s.r. spectrum shows a line broadening effect which is explained on the basis of the conformational interconversion of the radical anion between two equivalent conformations. The thermodynamic parameters of the process are obtained and their dependence on the counter ion is discussed.

KETYLS with two aromatic substituents are very stable species which can be obtained in high concentration by alkali metal reduction of the corresponding ketones.[1] When one or both substituents are alkyl groups the ketyls are stable only if no hydrogen atoms are bonded to the α-carbon atom.[2] An exception to this observation is provided by the relative stability of isopropyl t-butyl ketyl and of cyclopropyl phenyl ketyl which has been ascribed to a preferred conformation of the radical with the α-hydrogen in the nodal plane of the π system.[3] A few e.s.r. spectra attributed to stable ketyl radicals with hydrogens at the α-carbon atom were later shown to be due to semidione radical anions produced by an oxidation process.[4]

By alkali metal reduction of 1,1,4,4-tetramethyl-2-tetralone in ethereal solvents we have produced a radical species whose stability is sufficient to record the e.s.r. spectra at room temperature. The spectra indicate that the species is an alkali metal–ketyl radical ion pair and this is the first observation of a relative stable alkyl ketyl with two α-hydrogen atoms.

In this paper we discuss the e.s.r. results and the line-width effects displayed by the spectra, caused by intramolecular motion, as well as the dependence on the counter ion.

EXPERIMENTAL

1,1,4,4-Tetramethyl-2-tetralone (Tetralone) was prepared by the method of Bruson *et al.*[5] by addition of powdered aluminium chloride to a benzene solution of 2,2,5,5-tetramethyltetrahydrofuranone. The latter was synthesized from 2,5-dihydroxy-2,5-dimethylhex-3-yne.

Tetralone–alkali metal ion pairs were prepared by treating tetralone with a metal mirror, or small pieces of lithium under vacuum. Standard vacuum techniques were

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used. Solvent methyltetrahydrofuran (MTHF) was purified by distillation over calcium hydride and stored under vacuum over potassium anthracenide.

The e.s.r. spectra were recorded with a JEOL PE 3X spectrometer operating in the X band and equipped with variable temperature accessories.

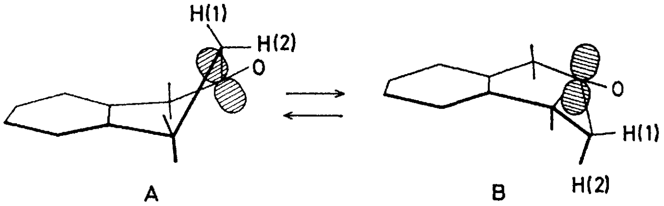
RESULTS AND DISCUSSION

The low temperature (−85°) e.s.r. spectrum of tetralone reduced with potassium consists of a doublet of doublets with hyperfine separations a_H^1 32.67 and a_H^2 5.06 G. This spectrum is consistent with a ketyl structure with two non-equivalent β-protons interacting with the unpaired electron. A possible semidione structure with two β-protons, produced by insertion of a CO group in the ring, as suggested for the reaction product of 2,2,4,4-tetramethylcyclobutanone,[6] is ruled out by the high values of the hyperfine couplings. In fact the β-proton couplings are known to be given by relationship (1).[7] For *cis*-semidiones $B\rho_c^\pi$, as obtained

$$a_H^\beta = B\rho_c^\pi \cos^2 \theta \qquad (1)$$

from the methyl proton hyperfine splitting of dimethyl semidione, is 14 G and this is the maximum value expected for β-protons of semidiones. In our case $B\rho_c^\pi$ was obtained by substituting a_H^1 and a_H^2 into equation (1) and taking into account the fact that the angles θ_1 and θ_2 for the two protons are related ($\theta_2 = \theta_1 \pm 120°$). We found $B\rho_c^\pi = 33$ G which is the typical value for ketyls radicals[3] while the values of θ_1 and θ_2 are 8 and 112° respectively; thus the tetralone anion has a conformation with one of the two protons close to the nodal plane of the unpaired electron $2p$ orbital.

On increasing the temperature the two inner lines of the spectrum broaden until they become undetectable and finally coalesce in a broad central line at close to room temperature. This behaviour reveals the occurrence of internal motion with exchange of the two proton couplings.* The ion pairs with Li and Na behave in a similar way. Here the room temperature spectrum clearly reveals the alkali ion splitting. We attribute these spectral features to an interconversion between the two equivalent conformations A and B in the Figure. It is worth noting that both protons spend half their time in a position close to the nodal plane of the p orbital and this may be a cause of the relative stability of the radical. Although in this system the exchange process could be investigated at the fast exchange limit (coalesced lines) accurate measurements could be performed only in the slow exchange region because of the instability of the radical species at high temperatures.



Molecular structures of the tetralone radical anion. Interconversion of the two equivalent conformations A and B leads to exchange of the positions of protons H(1) and H(2)

The e.s.r. spectra were computer simulated with a program in which the exchange between the equivalent sites was taken into account, employing the density matrix formalism.[8]

Calculations were performed for different values of the exchange rate in order to fit the experimental spectrum. The exchange frequencies thus obtained for each temperature were used to obtain the thermodynamic parameters (Table) which show a dependence on the cation in the ion pair.

Cation	ΔE/ kcal mol^{-1}	A/MHz	$\Delta H^\ddagger$/ kcal mol^{-1}	$\Delta S^\ddagger$/ cal mol^{-1} K^{-1}
Li	5.5	9.2×10^5	4.9	−6.0
Na	4.0	6.5×10^4	3.3	−11.8
K	6.2	2.6×10^7	6.6	+5.7

Thermodynamic parameters for tetralone in MTHF. ΔE and A were obtained by the Arrhenius relation $\ln \tau^{-1} = -\Delta E/RT + \ln A$ with τ^{-1} the exchange rate. For the evaluation of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ the relation $\ln\delta = \Delta H^\ddagger/R^{-1/T} - \Delta S^\ddagger/R$ was used where $\delta = RT/Nh$.

Thus by contrast with other cases,[9,10] in the case of tetralone there is a striking effect of the counter ion on the interconversion rate, which indicates that the latter is strongly involved in the process.

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* At temperatures >0 °C each line is further split into a complex structure due to the hyperfine interaction with methyl protons and possibly by the cation nucleus.

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