

DIENE STUDIES. V. STRUCTURES OF AND ROTATION BARRIERS IN PENTADIENYL LITHIUMS

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The preparation of some pentadienyllithiums in tetrahydrofuran-hexane solution was described in the previous letter, with evidence from deuteration studies supporting the view that pentadienyllithiums had really been obtained. In this communication we would like to describe and discuss the n.m.r. spectra of these substances and their bearing on the following questions regarding them: (1) whether they are ionic or covalent, (2) the distribution of charge density, (3) coupling constants as a function of geometry and bond order, (4) the preferred shape for carbanions of unfixed geometry, and (5) rotational barriers about the carbon-carbon bonds. The probe temperature n.m.r. spectra of carbanions I (fixed in the U shape), II (fixed in the sickle shape), and IV (free to assume any shape) are shown in Fig. 1, and pertinent spectral parameters for carbanions I-V at various temperatures are in Fig. 2.

(1) In no case was there spectral evidence for any unchanged starting material or more than traces of any products other than butane and pentadienyl carbanions. The probe temperature (ca. 35°) spectra of each of the carbanions consisted of reasonably sharp peaks with one notable exception, shown in Fig. 1: The probe temperature spectrum of IV shows a greatly broadened absorption at τ , integrating for 4 protons, evidently the protons attached to carbons 1 and 5. This broadening might

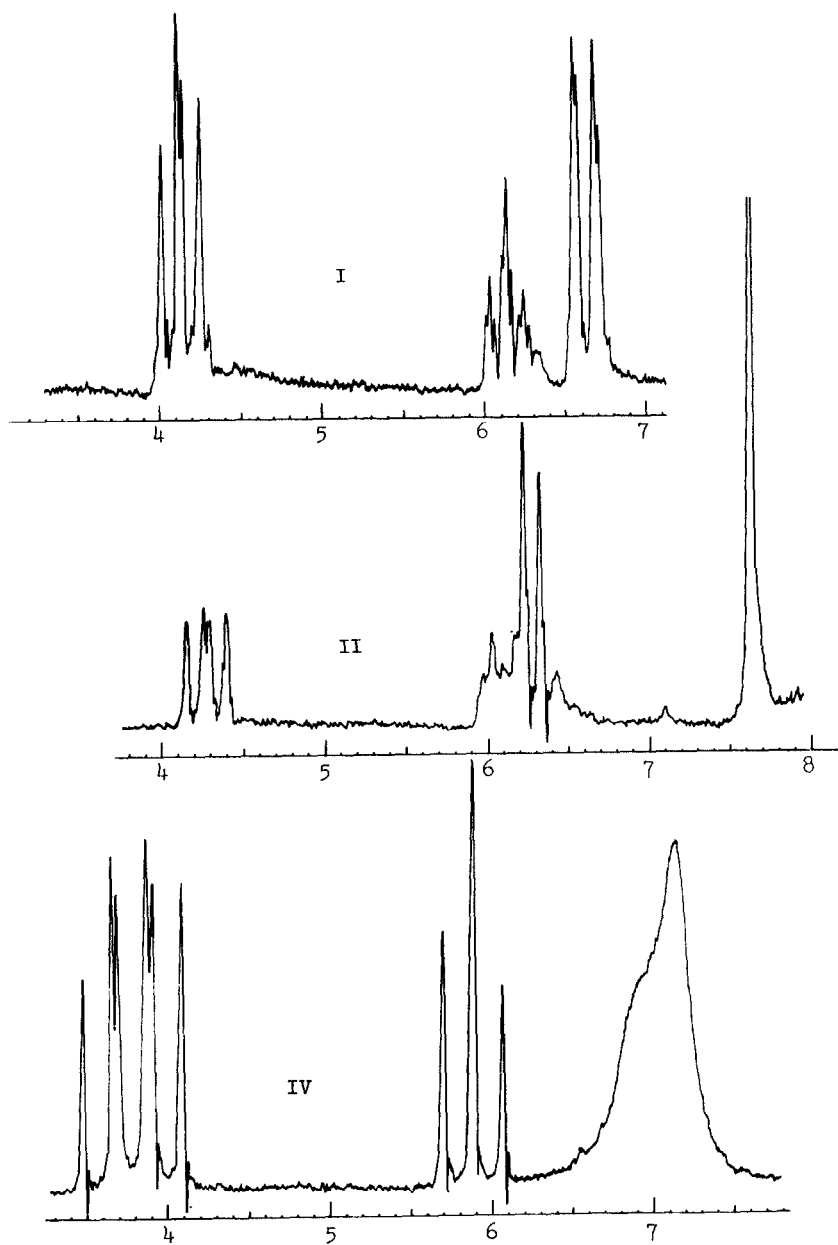


Fig. 1

Probe temperature n.m.r. spectra of I, II, and IV,
ca. 20% in perdeuterotetrahydrofuran at 60 Mc.).

have been due to lithium-hydrogen coupling, but this possibility was ruled out when warming to 40° gave 2 sharp peaks in this region and cooling to 15° gave 4 peaks, arranged as indicated in Fig. 2. Clearly the broadening at probe temperature was due to an exchange process which makes the two protons in a terminal methylene group equivalent slightly above probe temperature. An important fact emerges at this point: While the high temperature spectra might be interpreted in terms of rapidly equilibrating forms with covalent carbon-lithium bonds, the low temperature spectra cannot, and

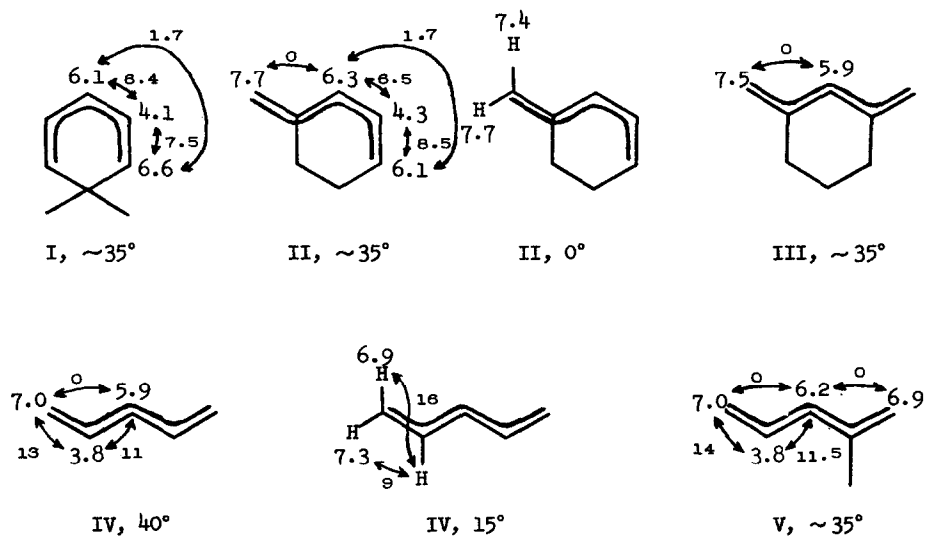


Fig. 2

Chemical shifts in τ units and coupling constants in cps (smaller numbers) for pentadienyl carbanions at various temperatures.

these compounds must be >90% ionic.*

(2) The chemical shifts of the protons attached to the 5 sp^2 carbons give some clue concerning the charge distribution in the anions. It is striking that the chemical shifts for the 2- and 4-protons are in the 3.8-4.3 τ range, whereas the protons on carbons 1, 3, and 5 absorb from 5.7-7.9 τ , abnormally high for protons attached to sp^2 carbon. This is consistent with greater charge density on the odd-numbered carbons, as predicted by MO theory.⁴ The protons attached to carbons 1 and 5 absorb from 6.1-6.6 when these carbons are secondary as compared to 6.9-7.9 when they are primary, and the protons attached to carbon 3 (secondary in all cases) absorb from 5.7-6.3. Unfortunately, anisotropic effects make it dangerous to conclude anything from these shifts regarding the charge on carbon 3 relative to 1 and 5.

(3) The coupling constants in these anions are of interest since the bond orders are unusual: 1.33 for the inner two carbon-carbon bonds and 1.67 for the outer two bonds. The observed values are in narrow non-overlapping ranges and should thus be of some diagnostic value: (a) Inner bonds, cis, 6.4-6.5 cps; (b) Inner bonds, trans, ~12 cps;^{**} (c) Outer bonds, cis, 7.5-9 cps; (d) Outer bonds, trans, 16 cps. The couplings across 4 bonds are very small except, as expected,⁵ when the geometry is most favorable they are 1.7 cps (in I and II).

* This would tend to support the view of Grovenstein *et al.*¹ that allyl-lithium is at least under some conditions ionic; in spite of the early interpretations of Nordlander and Roberts² and Johnson, Weiner, Waugh and Seyferth³ to the contrary, there seems to be no evidence that allyllithiums, -sodiums, -potassiums, and Grignards are not primarily ionic under all conditions.

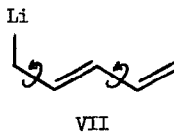
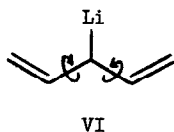
** This value is estimated from IV and V, in which these protons are largely trans (see below).

(4) The preferred shape for the simplest acyclic pentadienyl carbanion, IV, cannot be U or sickle since the coupling constants are so different from those in I and II, and it is thus apparently W. The coupling constants observed at 15° are in very good agreement with those expected for such a shape. Models show considerable steric hindrance for the U shape of this anion. We believe V to be a mixture of approximately equal amounts of W and the less sterically hindered of the two possible sickles, for reasons given below.

(5) As noted above, the terminal methylene protons in IV are equivalent above 40° and non-equivalent below 15°. From the chemical shift difference for this change, one can calculate⁶ that rotation about the outside carbon-carbon bonds in this acyclic pentadienyl carbanion occurs 60 times a second at 30° (the coalescence temperature). A very similar value was obtained for II and V. In the interest of determining the barrier to rotation about the inner carbon-carbon bonds, we cooled IV to -20°, but no appreciable change occurred below 15° other than considerable line broadening. When V was cooled, however, considerable broadening occurred for the peaks between 6 and 7 τ in the +10 to -20° range, and we feel that this must be due to the freezing out of rotation about the inner bonds, observable in this case because of the small difference in energy between the W and one of the sickles; at -20°, the spectra of W and sickle are superimposed. Due to the broadness of all of the lines at this temperature, we were not able to determine the relative amounts of these two species. Nevertheless, it was possible to calculate that in this case rotation about the inside carbon-carbon bonds occurs 130 times a second at -5°.

The simplest mechanism for these exchange processes is collision between a carbanion and a lithium ion with formation of a covalent bond for

a time sufficiently long to permit rotation about the resulting single bonds.*
 Since a bond between lithium and carbon 3 to give VI allows rotation about inner bonds only, whereas a bond to carbon 1, giving VII, allows rotation about both inner and outer bonds, the barrier to rotation about the inner bonds would be expected to be lower, as observed.**



* Such a mechanism was invoked by Grovenstein *et al.* (Ref. 1) for the allyl carbanion case.

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