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DIENE STUDIES. IV. PREPARATION AND PROTONATION OF PENTADIENYLLITHIUMS

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Pentadienyl carbanions have long been postulated as intermediates in base-catalyzed isomerizations of 1,3- and 1,4-dienes, in Birch reductions of aromatics, and in nucleophilic aromatic substitutions,[1] and they have recently been the subject of molecular orbital calculations.[2] There is indirect evidence[1] (with theoretical support[2a]) that due to an electronic factor the U shape is thermodynamically favored over the other two planar shapes, and that U-shaped pentadienyl carbanions protonate fastest at the central position[3] (simple Hückel MO calculations predicted equal electron density at carbons 1, 3, and 5, but the introduction of electron repulsion terms suggested a higher electron density at 3[2b]). To obtain direct evidence on these points and to take full advantage of these reactive substances as synthetic intermediates, it is necessary to have a method for preparing them in high concentration. We wish to report such a method, and, in addition, what we have found regarding their chemical behavior (this letter) and n.m.r. spectral properties (following letter).

After many unsuccessful attempts with a variety of strong bases to generate a pentadienyl carbanion by proton abstraction from a 1,3- or 1,4-diene, the following general procedure, used to prepare the anions I-VI in essentially quantitative yield, was found.[*]

A mixture of the appropriate 1,4-diene,[**] n-butyllithium in hexane (5% molar excess over diene), and tetrahydrofuran (half the volume of the butyllithium solution) is prepared at -78° and allowed to warm to room temperature. At about -30°, an exothermic reaction occurs, an orange-yellow color develops, and two layers form. The upper layer, containing hexane, butane, and some tetrahydrofuran, is discarded. The lower layer contains the pentadienyllithium in tetrahydrofuran, with some hexane and butane remaining.

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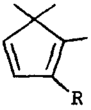
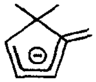
[*] We are indebted to H. H. Freedman for informing us prior to publication of this procedure for generating unstable carbanions. In the absence of tetrahydrofuran, there is no reaction; we believe that pentadienyllithiums are ionic (see the following communication) and that the function of the tetrahydrofuran is to solvate lithium ions.

We have verified the report by Alder and Windemuth[4] that salts of β-camphylic acid (i) decarboxylate to ii on heating, a reaction we believe proceeds *via* the pentadienyl carbanion iii. To explore a decarboxylation route to pentadienyllithiums, we heated the dry lithium salt of i to 280° under nitrogen. Although some gas evolution occurred and a red color developed, the n.m.r. spectrum of the residual solid in tetrahydrofuran showed none of the characteristic peaks expected for the anion iii.

i R=COOH

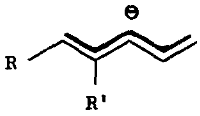
ii R=H





iii

[**] The 1,4-dienes for the preparation of I-III are commercially available. The diene for IV was prepared from 1,3-cyclohexanedione by dimethylation, lithium aluminum hydride reduction, acetylation, and pyrolysis (in our hands, the method described by Walling and Zavitsas[5] for the preparation of a mixture of 5,5-dimethyl-1,3-cyclohexadiene and 3,3-dimethyl-1,4-cyclohexadiene gave only dienes in which methyl migration had occurred; thus we suspect that their alkyl shifts had occurred *before* the copper-catalyzed reactions they were studying and not during them). The dienes for V and VI were made by lithium aluminum hydride reduction, acetylation, and pyrolysis of 4-cyclohexene-1-carboxaldehyde and cyclohexane-1,3-dicarboxylic acid, respectively.

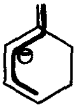


I R=R'=H

II R=n-Pr, R'=H

III R=H, R'=Me

IV



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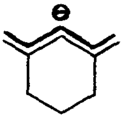

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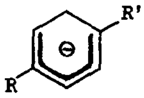


VII R=R'=H

VIII R=Me, R'=i-Pr

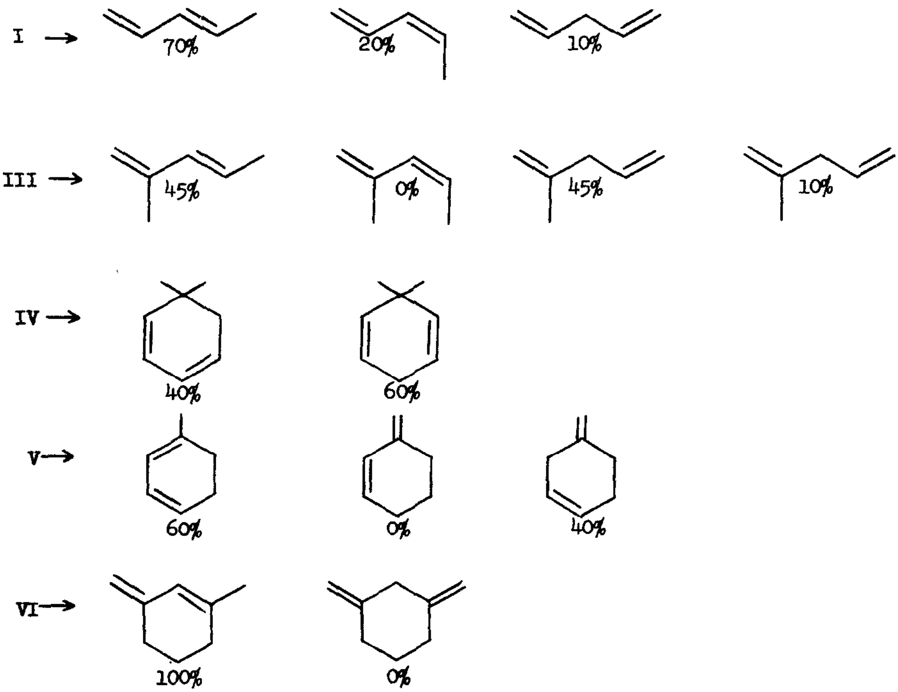
or R=i-Pr, R'=Me

In accordance with the finding of Paul and Tchelitcheff[6] regarding the rapid decomposition of cyclohexadienylsodium (VII with $Na^{\oplus}$) into benzene and sodium hydride, we have found that the butyllithium treatment described above quantitatively and rapidly converts 1,4-cyclohexadiene into benzene and γ-terpinene into p-cymene. Presumably VII and VIII are intermediates, although neither of these carbanions built up sufficient concentration to permit observation of its n.m.r. spectrum.

In contrast to the behavior noted above for 1,4-dienes on mixing with butyllithium and tetrahydrofuran, 1,3-dienes do not give pentadienyllithiums under these conditions. We have not established whether this is due to polymerization or simply to lesser reactivity. The latter can be rationalized as being largely due to the greater thermodynamic stability of some conjugated dienes (e.g., 1,3-pentadiene, the conjugated diene we tried most often, is more stable than 1,4-pentadiene by more than 5 kcal./mole[7]). Thus, the reactivity order for butyllithium may be 1,4-dienes > tetrahydrofuran > 1,3-dienes.

The evidence that the pentadienyllithiums described above have the assigned structures rests largely on their n.m.r. spectra (described in the following communication) and in their behavior on the addition of D_2O, which gives monodeuterated dienes with the deuterium in the expected position (e.g., I gives 5-deutero-1,3-pentadiene (cis and trans) and 3-deutero-1,4-pentadiene).

With the pentadienyl carbanions I-VI in hand, it was possible to directly determine the position of protonation not only of a U-shaped anion (IV), but of anions with the other planar shapes as well. The results obtained were as follows:*



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* Percentages of dienes in the diene mixture were determined by n.m.r. and vapor phase chromatography for the protonation products of the anions except II, which gave a very complex mixture of dienes.

Thus, *the direct rate-controlled protonation of a U-shaped pentadienyl carbanion (IV) is faster by a factor of 3 at the central carbon than at each end carbon*. This is in qualitative agreement with results obtained indirectly on other U-shaped pentadienyl carbanions under different protonation conditions.[3]

The other cases, which involve sickle- and W-shaped anions, show that the 1,4-diene is not always the predominant product; unlike the case of IV, however, they are complicated by the primary nature of at least one of the terminal carbons (n.m.r. evidence is presented in the following communication that the electron density is greater at the primary than at the secondary carbons in these systems, and this should favor protonation at the primary sites). Still, the yield of unconjugated diene (protonation at a secondary site) from V is not much lower than that of the major product (primary site) and is much larger than that of the third product (secondary site), and it seems reasonable to conclude that if one corrects for this difference in alkyl substitution, *protonation of a sickle-shaped pentadienyl carbanion is also favored at the central carbon*.*

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