A 2-Azapentadienyl Carbanion: a Nonstereospecific Electrocyclization

D. H. HUNTER AND R. P. STEINER
Department of Chemistry, University of Western Ontario, London, Ontario N6A 3K7
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D. H. HUNTER and R. P. STEINER. Can. J. Chem. **53**: 355 (1975).

Treatment of 1,3,5-triphenyl-4-aza-1,3-pentadiene under selected basic conditions leads to either isomerization among the azapentadienes or to cyclization. Analysis of the products from reaction under aprotic conditions (LiTMP in THF) suggested that the open-chain delocalized carbanion exists in both the W and sickle forms. The open-chain anions were observed to electrocyclize in a nonstereospecific manner to produce a 1:1 mixture of *cis*- and *trans*-2,4,5-triphenyl-1-pyrrolines. Reaction in protic media (methanol and *tert*-butyl alcohol) produced a 1,5-proton transfer as well as cyclization. The details of the 1,5-proton transfer reaction were elucidated using methanol-*O*-*d* and the collapse preferences and intramolecularity in this medium were determined.

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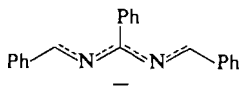
Le traitement du triphényl-1,3,5 aza-4 pentadiène-1,3, dans des conditions basiques choisies, conduit soit à une isomérisation entre les azapentadiènes soit à une cyclisation. L'analyse des produits formés par la réaction dans des conditions aprotiques (LiTMP dans THF) suggère qu'un carbanion délocalisé sur une chaîne ouverte existe dans la forme W et dans la falsiforme. On a observé que les anions en chaîne ouverte s'électrolisent d'une façon non-stéréospécifique pour conduire à un mélange 50:50 des triphényl-2,4,5 pyrrolines-1 *cis* et *trans*. La réaction dans des milieux protiques (méthanol ou *tert*-butanol) conduit à un transfert-1,5 de proton de même qu'à une cyclisation. On a élucidé les détails de la réaction de transfert-1,5 de proton en faisant appel à du méthanol-*O*-*d*; on a déterminé la nature des effondrements préférentiels et la nature intramoléculaire de la réaction dans ce milieu. [Traduit par le journal]

Introduction

We have previously reported (1) the remarkably rapid and stereoselective electrocyclization of a 2,4-diazapentadienyl anion. This stands in contrast to the lack of reactivity of the pentadienyl anion (2). We have now studied a 2-azapentadienyl anion since its propensity for cyclization might be expected to lie between the other two systems. This in fact was the case and as a consequence information has been obtained about open-chain anion stabilities and geometries. A striking effect of aza-substitution on the electrocyclization rate and stereochemistry has been observed.

In order to make a direct comparison with our earlier work on the 1,3,5-triphenyl-2,4-diazapentadienyl anion **5**, the particular system chosen for study was the 1,3,5-triphenyl-2-azapentadienyl anion **4**.



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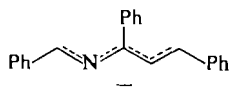

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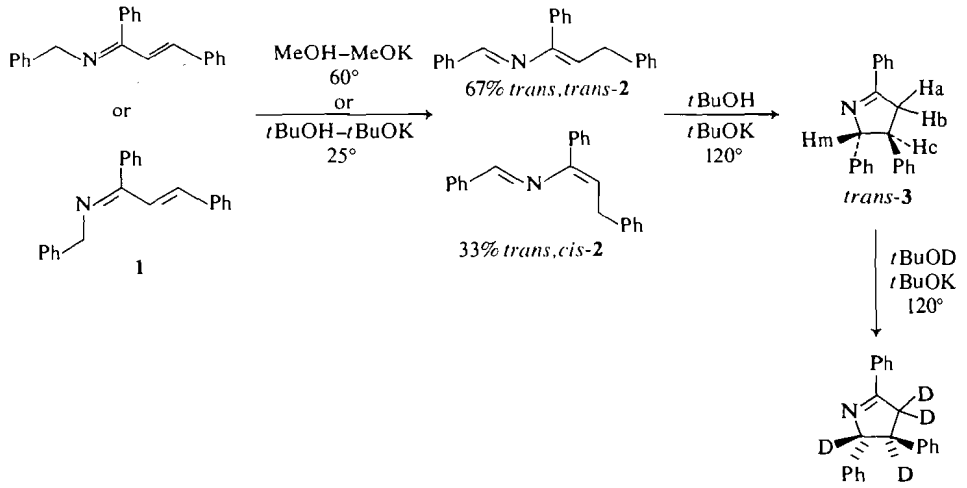
Results

Preparation and Characterization of Substrates

1,3,5-Triphenyl-4-aza-1,3-pentadiene

From a synthetic viewpoint, of the three carbon acid precursors to the 1,3,5-triphenyl-2-azapentadienyl anions, 1,3,5-triphenyl-4-aza-1,3-pentadiene **1** appeared to be the most attractive substrate. Synthesis of **1** was accomplished by condensation of chalcone and benzylamine yielding a 3:1 mixture of geometrical isomers of **1**. On the basis of the magnitude of the proton–proton coupling constant between the vinyl protons ($J \approx 17$ Hz), the carbon–carbon double bond in **1** was assigned the *trans*-geometry in both isomers. Thus apparently the two isomers of **1** differ by being *syn* or *anti* at the carbon–nitrogen double bond. The major equilibrium isomer was obtained in a pure state by recrystallization. However, it is not known whether this isolated isomer of **1** corresponds to the *syn* or *anti* possibility. The *syn–anti* interconversion rates of **1** are sufficiently slow to permit characterization but are accelerated by base.



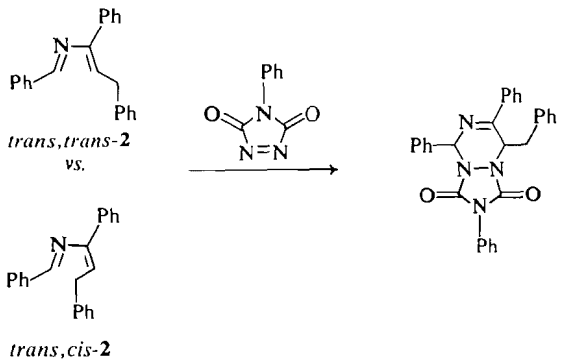
1,3,5-Triphenyl-2-aza-1,3-pentadiene

The 1,3,5-triphenyl-2-aza-1,3-pentadienes **2** were prepared by base-catalyzed isomerization of **1** and the appropriate data are gathered in Table 1. As indicated in runs 4 and 5, when **1** was reacted in 0.22 *M* potassium methoxide – methanol at 60° the fastest reaction was equilibration of the *syn* and *anti* forms of **1** to provide a 3.2:1 mixture of unassigned geometry. More slowly a mixture of geometrical isomers of **2** was produced in a time-dependent ratio. At low percentages of conversion (run 4) *trans,cis*-**2** was preferred by about 3:1, whereas at apparent equilibrium (run 5) *trans,trans*-**2** was favored by 2:1 and no **1** was observed.

The major isomer from run 5 (assigned the *trans,trans* geometry as described below) was isolated by t.l.c., purified, and characterized by n.m.r., i.r., and mass spectrometry. The minor isomer could not be isolated due to hydrolysis on silica gel.[1] Instead, its structure was assigned on the basis of its n.m.r. spectrum in the mixture of the two isomers of **2**.

The geometries of the isomers of **2** were assigned on two counts. First, the geometry of the carbon–nitrogen double bond was assumed to be *trans*(*syn*) since geometrical isomerization around this bond ought to be rapid at ambient temperature (3) and thermodynamics should certainly favor the *syn*-isomer. Second, the geometry at the carbon–carbon double bond was assigned on the basis of relative reactivity of the two isomers of **2** with 4-phenyl-1,2,4-triazoline-3,5-dione to form a Diels–Alder type product. The relative reactivity was assessed by n.m.r. monitoring of the changes in the ratio of the two isomers of **2** in a mixture upon successive addition of aliquots of the triazolinedione. The major isomer of run 5 reacted at least five times faster than the minor isomer. This reactivity ratio is a minimum because the increasing signals of the product partially overlapped those of **2**.

The more reactive isomer (the major isomer of run 5) was assigned the *trans,trans*-**2** structure since it is anticipated that it will more readily adopt the *S-cis* conformation necessary for Diels–Alder reactivity. The product of the reaction of *trans,trans*-**2** with the triazolinedione was isolated by t.l.c. and characterized by n.m.r., i.r., and mass spectrometry. These data were consistent with the product of a Diels–Alder reaction.



[1]The major isomer also underwent some hydrolysis during t.l.c. yielding β-phenylpropiophenone.

TABLE 1. Results of base-catalyzed isomerization of **1** to **2**

Run	Base-solvent[b]	T,°C	Time, min	Products[a] % **1**[c]	% *trans,trans*-**2**	% *trans,cis*-**2**
1	$KOC(CH_3)$–$HOC(CH_3)_3$	25	20	0	67	33
2	$KOC(CH_3)_3$–$HOC(CH_3)_3$	25	120	0	67	33
3	$LiOC(CH_3)_3$–$HOC(CH_3)_3$	60	60	60	10	30
4	$KOCH_3$–$HOCH_3$	60	60	60	10	30
5	$KOCH_3$–$HOCH_3$	60	4300	0	67	33
6	$KOCH_3$–$DOCH_3$[d]	60	7	60[e]	10[f]	30[f]
7	$KOCH_3$–$DOCH_3$[d]	40	20	80[g]	≤5	15[h]
8	$KOCH_3$–$DOCH_3$[d]	40	60	65[i]	10	25
9	LiTMP–THF	−78	300	25	50	25
10	LiTMP–THF	−10 to −20	180	25	50	25

[a]Yields are based upon n.m.r. integration; 0% means not detected by n.m.r. or t.l.c.
[b]See Experimental for concentrations and procedures.
[c]Recovered **1** was a 3.2:1 mixture of *syn* and *anti* isomers.
[d]Contains 10 vol. % THF.
[e]0.8 atoms D/molecule by n.m.r.
[f]Analysis of hydrolyzed material yielded d_0, 10.5%, d_1, 78%, d_2, 12% by mass spectrum.
[g]0.35 atoms D/molecule by n.m.r.
[h]d_0, 10.5%, d_1, 85%, d_2, 4.5% by mass spectral analysis of hydrolysis product.
[i]0.7 atoms D/molecule by n.m.r.

TABLE 2. Results of base-catalyzed cylization and exchange of **1** and **3**

Run	Substrate: Nature	Concn., *M*	Base-solvent[a]	T,°C	Time, min	Products: % **2**[b]	% *cis*-**3**[c]	% *trans*-**3**
11	**1**	0.5	$KOC(CH_3)_3$–$HOC(CH_3)_3$	120	30	12	0	70
12	*cis*-**3**	0.5	$KOC(CH_3)_3$–$HOC(CH_3)_3$	120	30	0	0	88
13	*trans*-**3**	0.25	$KOC(CH_3)_3$–$DOC(CH_3)_3$	120	30	0	0	[d]
14	**1**	0.07	LiTMP–THF	0–5	30	15	35	29[e]
15	**1**	0.07	LiTMP–THF	25	180	0	21	26[f]

[a]See Experimental for concentrations.
[b]Based upon recovered β-phenylpropiophenone from hydrolysis of 2.
[c]Yields are based upon isolated purified materials. 0% means not detected by n.m.r. or t.l.c.
[d]Four atoms D/molecule in the pyrroline ring.
[e]5% of 2,3,5-triphenylpyrrole.
[f]11% of 2,3,5-triphenylpyrrole.

trans-2,4,5-Triphenyl-1-pyrroline (trans-3)

Treatment of **1** under more basic conditions, *tert*-butyl alcohol – potassium *tert*-butoxide, first at 25° led to isomerization to **2** (runs 1 and 2 of Table 1) and then at 120° to *trans*-**3** (run 11 of Table 2) as the only observed product in good yield. This product was shown to be isomeric with **1** and **2** by mass spectrometry but unlike **1** and *trans,trans*-**2**, *trans*-**3** yielded the five-membered ring oxidation product, 2,3,5-triphenylpyrrole, upon oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).

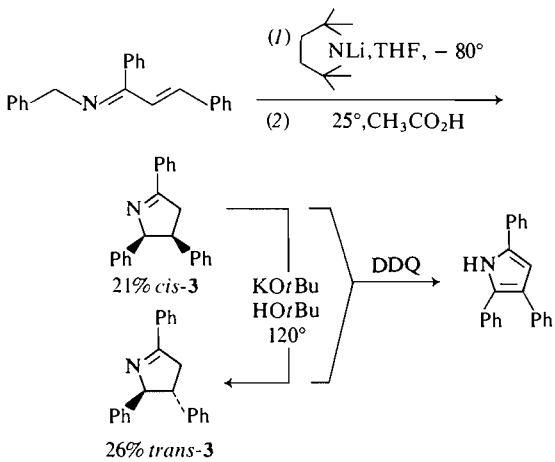
The presence of a carbon–nitrogen double bond in *trans*-**3** was verified by i.r. with observation of a band due to C=N and absence of an N—H bond. The analysis of the 100 MHz proton n.m.r. spectrum as an ABCM pattern, with assistance of the LAOCOON III program, was consistent with placement of the carbon–nitrogen double bond as in *trans*-**3** and is inconsistent with the other possibility. The proton–proton coupling constant for the 4 and 5 hydrogens, $J = 6.7$ Hz, was consistent with but did not require a *trans* configuration.

The *trans* configuration was assigned by establishing that this material had the thermodynamically preferred configuration at positions 4 and 5. This was done in two ways. First, treatment of *trans*-**3** with potassium *tert*-butyl alcohol-*O*-*d* at 120° (run 13) which is the condition required for its formation from **1** (run 11) yielded *trans*-**3** back again but having incorporated **4** atoms D/molecule in the pyrroline ring. This indicates that the conditions of run 11 are more than sufficient to ensure formation of the thermodynamically more stable isomer or *trans* phenyl groups. More convincingly when *cis*-**3**, whose preparation is discussed below, was treated un-

der the same conditions (run 12), *trans*-**3** was observed as the only reaction product and in good yield.

cis-2,4,5-Triphenyl-1-pyrroline (cis-3)

When **1** was treated with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in tetrahydrofuran (THF) and the resultant blue solutions were quenched with acetic acid, a new product distribution was observed. As indicated in runs 9 and 10 of Table 1, if the temperature was kept below $-10°$ only **1** and **2** were obtained. However upon warming the solutions to 0° and above (runs 14 and 15) cyclized materials became the major products. In contrast to *tert*-butoxide in *tert*-butyl alcohol (run 11), both *cis*-**3** and *trans*-**3** were produced and in similar amounts. The two cyclized products could be separated by t.l.c. The structure assignment for *cis*-**3** was analogous to that for *trans*-**3**.



Mass spectrometry confirmed its isomeric nature to **1**, **2**, and *trans*-**3**, and oxidation with DDQ yielded 2,3,5-triphenylpyrrole. The presence of C=N was shown by i.r., and n.m.r. was consistent with the structure indicated. As mentioned above, evidence for the *cis* assignment lies in its conversion to *trans*-**3** upon treatment with potassium *tert*-butoxide in *tert*-butyl alcohol at 120° (run 12).

Discussion

As described in the Results section, the reaction of **1** under selected basic conditions can lead to specific types of isomerization. Under mildly basic conditions interconversion between open-chain isomers can be observed both in protic media (potassium methoxide in methanol or lithium *tert*-butoxide in *tert*-butyl alcohol at 60° and potassium *tert*-butoxide in *tert*-butyl alcohol at 25°) and aprotic media (LiTMP in THF below $-10°$). Under more vigorous basic conditions conversion to cyclic isomers occurs also in protic media (potassium *tert*-butoxide in *tert*-butyl alcohol at 120°) and aprotic media (LiTMP in THF above 0°). This differing reactivity between open-chain isomerization and cyclization has made it possible to obtain information on the role of the 1,3,5-triphenyl-2-aza-pentadienyl anion **4** in both processes.

The discussion of the properties of the 1,3,5-triphenyl-2-azapentadienyl anion **4** will first center on the geometries of the open-chain anion, then its electrocyclization reaction, both rate and stereochemistry, and then on its behavior as a short-lived species in protic solvent with emphasis on stability, collapse ratio, and intramolecularity.

Anion Geometries

In an attempt to ascertain the geometry that anion **4** prefers to adopt, quenching of the lithium salt of **4** in THF with acetic acid was investigated. When pure **1** was treated with a slight excess of LiTMP in THF at $-78°$, a deep blue color resulted. As indicated in runs 9 and 10 of Table 1, addition to this of an equivalent of acetic acid at either $-78°$ or $-15°$ led to the same mixture of four open-chain isomers. That these isomers had arisen from quenching of **4** was established using CH_3CO_2D. The n.m.r. spectrum of the reaction mixture was qualitatively consistent with incorporation of 1 atom D/molecule. In spite of the sensitivity of **1** to geometrical isomerization a control experiment verified that the isolated isomer of **1** survived the work-up conditions unchanged. The 3:1 geometrical isomer ratio for **1** is then both the kinetic and thermodynamic mixture.

The observation of four geometrical isomers of **1** and **2** requires that anion **4** exist in more than one geometry. The interconversion between anion geometries must be reasonably facile since equilibration occurs within 300 min at $-78°$ (run 9). Rapid interconversion rates are not unexpected since allyl and pentadienyllithiums show coalescence phenomena in their proton n.m.r. spectra consistent with fairly rapid geometrical interconversions (4).

The 2-azapentadienyl anion can, in principle, adopt four different geometries; a W shape, two

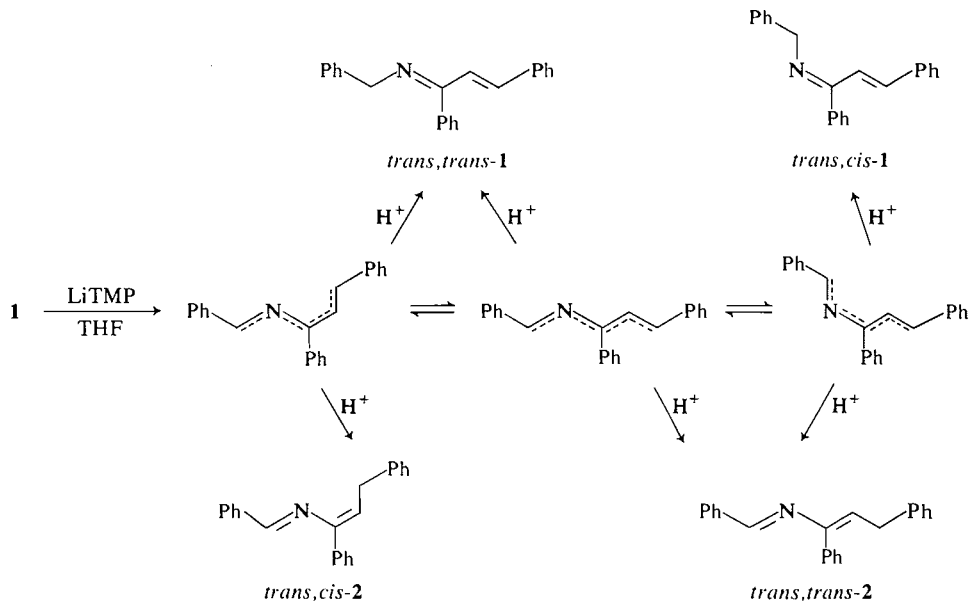


FIG. 1. Geometries anticipated for **4** and products of quenching.

sickle shapes, and a U shape. Of these, the U shape should be the least favored and n.m.r. results for pentadienyllithiums (2) support this contention. If phenyl rings are placed at the 1,3, and 5 positions of the W and two sickle shapes so as to minimize nonbonded interactions (5), the anions shown in Fig. 1 are obtained. Figure 1 also indicates the four products that could arise upon quenching of these anions. Since all four products are observed and occur in similar amounts, it would appear that the three geometries of anions do exist and in similar amounts. A direct calculation of anion populations from product distribution was not achieved since all three anions can form two products.

However, it can be concluded that anion **4** exists in a W shape and in two sickle shapes. These shapes can interconvert fairly rapidly and at equilibrium they exist in similar amounts.

The Electrocyclization Reaction

As mentioned above, under more vigorous conditions cyclization was observed in both protic and aprotic media and information was gathered on both the rates and stereochemistry of the cyclization reaction.

Rate of Cyclization

Information on the propensity of anion **4** for electrocyclization has been obtained in both protic and aprotic media and can be compared with the earlier results (1) for the 1,3,5-triphenyl-2,4-diazapentadienyl anion **5**. As is indicated in runs 9, 10 and 14, 15, while anion **4** may be generated at $-78°$ in THF, electrocyclization is not observed until above 0°. This is in contrast with **5** which electrocyclizes competitively with its formation at $-78°$ in THF.

This same phenomenon is illustrated for protic solvents in runs 1–5 and 11. Both potassium methoxide in methanol and lithium *tert*-butoxide in *tert*-butyl alcohol at 60° are sufficiently basic to convert **1** to **2**, presumably through the short-lived anion **4**. However, potassium *tert*-butoxide in *tert*-butyl alcohol, a kinetically much stronger base, at 120° must be used to produce electrocyclization. A rate ratio of at least 10^6 between the rate of anion formation and the rate of electrocyclization can be deduced.[2]

The results in both protic and aprotic media correspond to a reaction profile where a more rapidly formed open-chain anion **4** slowly electrocyclizes in the rate-determining step. This should be contrasted with the results obtained

[2]Potassium *tert*-butoxide in *tert*-butyl alcohol is a kinetically stronger (6) base than potassium methoxide in methanol by about 10^6. The 60° temperature difference (120° *vs.* 60°) should correspond to an additional rate ratio depending upon the activation energy (an unknown).

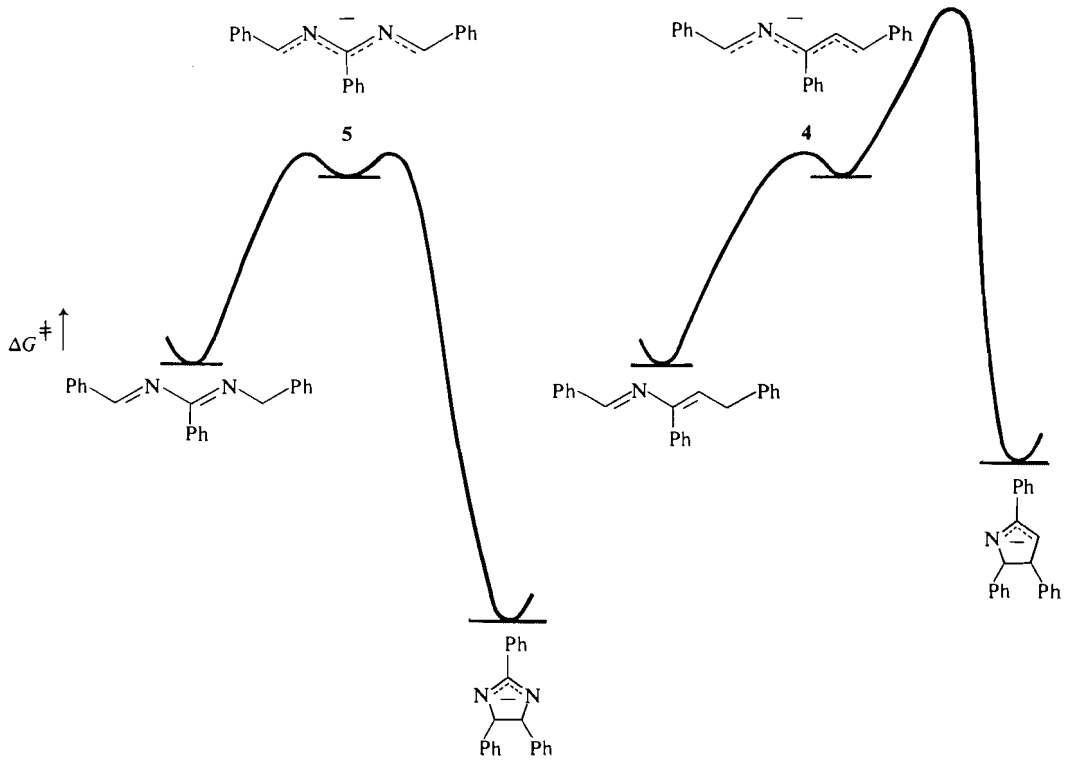


FIG. 2. Free energy profiles for formation and electrocyclization of anions **4** and **5**.

for the 2,4-diazapentadienyl anion **5**. In this earlier study (1) it was found that while formation of **5** seemed to occur at a rate comparable to **4** in both protic and aprotic media, the rate of electrocyclization of **5** was significantly faster. Electrocyclization and anion formation occurred at competitive rates with **5**. The difference in behavior in the two systems is summarized in the energy profiles of Fig. 2. The difference in ease of electrocyclization is presumably a reflection of the difference in the stability of the cyclized forms of the anions. The negative charge should reside primarily on the termini of the three atom system coincident with the position of the nitrogen.

Stereochemistry of Electrocyclization

When a solution of the lithium salt of **4** in THF was allowed to warm to 0–5° for 30 min and then quenched with acetic acid (run 14) significant amounts of cyclization were observed and cyclization was complete at 180 min and 25° (run 15). Under these conditions both *cis*-**3** and *trans*-**3** were isolated as the major products and in similar amounts (a *cis–trans* ratio of 1.2 in run 14 and 0.8 in run 15) along with minor amounts of the oxidation product, 2,3,5-triphenyl-pyrrole. It is likely that the observed *cis*-**3**:*trans*-**3** of *ca.* 1 is close to the actual kinetic product distribution on two counts. First, base-catalyzed equilibration of *cis*-**3** (run 12) and *trans*-**3** (run 13) yields just *trans*-**3** in analogy to the diaza-system (1). Second, if there is *cis–trans* equilibrium in THF, it must be slow as shown by the slight, if real, change in the *cis*-**3**:*trans*-**3** ratio with a significant change in reaction conditions (runs 14 and 15).

In contrast to the kinetic distribution in the aprotic medium, the conditions necessary to produce electrocyclization in protic media are also sufficient to equilibrate any cyclized products. As shown in run 11, reaction of **1** in a potassium *tert*-butoxide – *tert*-butyl alcohol solution at 120° for 30 min is necessary to produce significant cyclization and only *trans*-**3** is observed. As mentioned earlier, reaction of *cis*-**3** under the same conditions (run 12) results in complete conversion to *trans*-**3**. That *trans*-**3** is probably

the thermodynamically most stable of the possible, 2,3,5-triphenylpyrrolines is shown by the base-catalyzed exchange results of run 13 with *trans*-**3**; *trans*-**3** was recovered as the only product of run 13 and had completely exchanged the pyrroline ring (4 atoms D/molecule). Thus apparently all centers within the pyrroline ring had an opportunity to epimerize and *trans*-**3** remained the sole product. Thus the results in *tert*-butyl alcohol do not also allow determination of the kinetic ratio of *cis*-**3** and *trans*-**3** from electrocyclization of **4** but provide the equilibrium product.

A comparison (Fig. 3) with the stereochemical behavior of the 2,4-diazapentadienyl anion **5** is revealing since **5** produced exclusively the cyclized material with *cis*-phenyl groups ($\geq$ 99.7%). This change in stereoselectivity corresponds to a change in the *cis–trans* product ratio of $\geq$300 on aza-substitution. This marked sensitivity of stereochemistry to aza-substitution deserves some mechanistic comment, as does the observation of a nonstereospecific electrocyclization.

One mechanistic scheme invokes the same U-shaped geometry of anion (as in Fig. 3) for electrocyclization of both the diazapentadienyl anion **5** and the monoazapentadienyl anion **4**. In this scheme the change in product distribution would reflect a change in the relative rates of the conrotatory and disrotatory modes of electrocyclization. In the symmetrical anion **5** the expected disrotatory mode (7) is exclusively involved. However, in the unsymmetrical anion **4** the conrotatory and disrotatory modes are competitive. This change in stereoselectivity could be a result of changes in orbital symmetry demands accompanying loss of molecular symmetry (8).

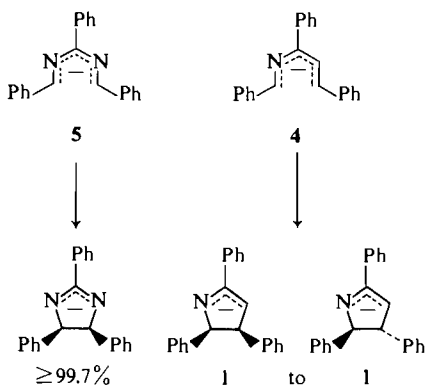


FIG. 3. Comparison of the stereochemistry of electrocyclization of anions **4** and **5**.

A second and similarly unprecedented scheme assumes the same disrotatory mode of electrocyclization for both **4** and **5**. The different product stereochemistries are then a consequence of reaction from different anion geometries. Both U and W shaped anions would lead to cyclized material with *cis*-phenyl rings and the 'sickle' shaped anion would produce *trans*-product. Such differing stereochemistries could then arise if the highly reactive diazapentadienyl anion **5** were produced initially in the W shape and electrocyclized before or while geometrical interconversions occurred.

The much less reactive azapentadienyl anion **4**, in contrast, is observed to undergo geometrical interconversions much faster than electrocyclization. Analogous mechanistic schemes in which both **4** and **5** undergo equilibration of geometries before electrocyclization suffer from the disadvantage of having to postulate either different distributions of geometries or differing geometry reactivities as a result of aza-substitution. While these remain as possibilities, they prove difficult to rationalize convincingly.

These two contrasting mechanisms correspond to cases where the changes in product stereochemistry are attributed to changes, first, in reaction pathway or second, in reactant structure (geometry). The data gathered in this study are insufficient to distinguish between these mechanistic possibilities but a more complete analysis will be reported in a subsequent paper on the all-carbon system.

Relative Stability of the Azapentadienes

The relative thermodynamic stabilities of some of the isomers of **1** and **2** can be deduced from the isomerization results of runs 1–6 of Table 1. Analysis of the reaction mixture of runs 3, 4, 6, 7, and 8 in which unreacted **1** was present revealed a facile base-catalyzed *syn–anti* isomerization which provided a 3:1 mixture of **1**. The results of equilibration of **1** (runs 1, 2, and 5) showed that only **2** is present at equilibrium between **1** and **2** and *trans,trans*-**2** predominates over *trans,cis*-**2** by a factor of 2. Although there is no direct evidence bearing on the point, by analogy with **2**, it is likely that the isolated and major equilibrium isomer of **1** also has the *trans,trans* structure. While *trans,trans*-**2** is predominant at equilibrium, it is *trans,cis*-**2** that is

the kinetically preferred product (runs 3, 4, 6, 7, and 8). This occurs whether the reaction involves ion-pairs ($LiOC(CH_3)_3$ in $HOC(CH_3)_3$; run 3) or dissociated ions ($KOCH_3$ in $HOCH_3$; run 4). If the initial product distribution reflects the intermediate anion stability, the sickle shaped anion would appear to be the most stable.

While it is not surprising that none of the 2-aza-1,4-pentadienes were present upon equilibration of **1** and **2**, the exclusive formation of **2** was unexpected. Simple Hückel molecular orbital calculations predict the reverse. Although the generality of this observation has not been demonstrated, base-catalyzed isomerization of 2-aza-2,4-pentadienes to 2-aza-1,3-pentadienes may be a satisfactory synthetic route to some examples of this unique functionality, *i.e.* vinylimines.

Intramolecularity

Since examples of base-catalyzed 1,5-proton transfer reactions are few, an attempt was made to further characterize the intermediate anion by comparing isomerization and hydrogen–deuterium exchange (runs 6, 7, and 8). The extent of involvement of an intramolecular component in the 1,5-proton shift was estimated from the percentage of d_0 material found in *trans,trans*-**2** and *trans,cis*-**2** produced from **1** after short reaction times in CH_3OD (runs 6 and 7). The geometrical isomers of **2** were not analyzed directly but the combined hydrolysis product, β-phenylpropiophenone, was analyzed by mass spectrometry and showed 0.9 atoms D/molecule. Although this 10% intramolecular component should be a lower limit, due to concurrent exchange of both **1** and **2**, model calculations indicate corrections should be minor.

Although the observed 1,5-proton shift could actually be the result of two consecutive 1,3 shifts, this is unlikely. The anion **5** produced by proton abstraction from the central carbon of the analogous 2,4-diazapentadienyl system, hydrobenzamide, was found to protonate exclusively at the terminal position. The 1,3-proton shift via **5** occurred with 14% intramolecularity in CH_3OD. The only other examples of base-catalyzed 1,5-proton shifts involves tautomers of triphenylmethane (9) (Fig. 4). Only one of these systems has been studied in methanol-*O*-*d* but comparable results are available for *tert*-butyl alcohol-O-*d* and these systems show consistently higher intramolecular components (~50%) than the open-chain systems (~10%). While the geometries differ between these two types of substrates, the difference in pK_a between substrate and solvent has also changed. The pK_a's of the aza-substituted pentadienes are estimated from kinetic acidity to be ~24 and triphenylmethane has been assigned a pK_a of 32.5 on the MSAD scale (6). It is surprising that in comparison to the large change in substrate pK_a's, the change in intramolecularity is quite small. However, the actual intramolecularity will be less than 10% if significant amounts of protium are introduced from the protons in solvent reinforced by an isotope effect on protonation.

Collapse Ratios

The exchange data of runs 6, 7, and 8 also can be used to determine the preferred positions of protonation of the intermediate anions **4**. The percentage of isotopic exchange in recovered **1** gives a measure of the acts of carbanion formation that have occurred but with deuteration at the 1-position. The percentage of **2** observed gives a measure of carbanion formation from **1** but with collapse at the 5-position. The extent of isotopic exchange in **1** does not give a true measure of collapse at the 1-position since there is a small intramolecular component (see above) but the correction is small.

The results of runs 6, 7, and 8 were simulated by numerical integration of the corresponding reaction scheme using the MIMIC language of the CDC computer. As is qualitatively evident from the isotopic exchange results and as borne out more quantitatively ($k_{-1}/k_{-5} = 1.6$), there is only a slight preference for deuteration of anion **4** at the 1-position. A comparison of these results with the quenching results of runs 9 and 10 shows that again there is a close competition between reaction at each end of anion **4** but under quenching conditions, reaction at the 5-position predominates ($k_{-1}/k_{-5} = 0.3$). Although several factors could be involved, the products do indicate that different ratios of anion geometries are present and different geometries may show different collapse ratios.

The overall picture from both these studies indicates that in spite of apparently large differences in the thermodynamic stability of the two products of anion collapse (**1** and **2**), there is only slight selectivity in the collapse ratio. The observed collapse ratio is consistent with an anion whose positional reactivity is little affected

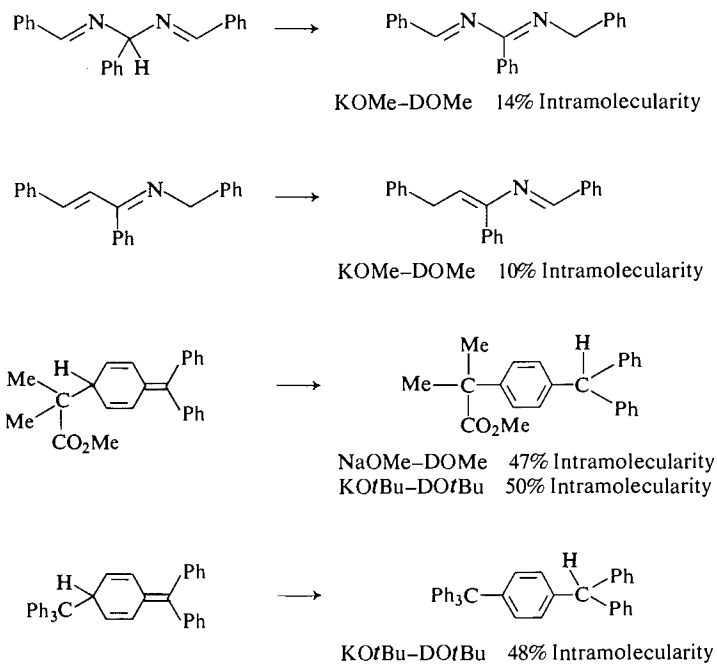
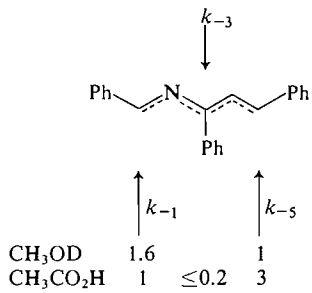


FIG. 4. Examples of reactions involving 1,5-proton shifts of pentadienyl anions and the observed intramolecularity.

by product stability but may reflect similar steric demands. The absence of quenching products due to reaction in the middle (the 3-position) would also seem to support this hypothesis. The charge distribution in **4** may also be important (10) but its contribution is not readily evaluated in the present system.



Experimental

Solvent and Bases

The methanol was distilled from magnesium and the *tert*-butyl alcohol was distilled from calcium hydride. The potassium *tert*-butoxide in *tert*-butyl alcohol (0.53, 0.03 *M* in H_2O) and the potassium methoxide in methanol (0.22, 0.05 *M* in H_2O) were prepared by the reaction of the alcohol with freshly cleaned potassium and were stored under argon. The methanol-*O-d* was prepared from dimethyl carbonate (11) and the base solution was prepared as above (0.59, 0.08 *M* in D_2O). The *tert*-butyl alcohol-*O-d* (12) was similarly reacted with potassium to produce a base solution (0.53 *M*).

Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride before use. Solutions of lithium 2,2,6,6-tetramethylpiperidide in THF (1.0–2.0 *M*) were prepared by adding an equivalent of *n*-butyllithium (Alfa Inorganics) to a cooled solution (~−20°) of 2,2,6,6-tetramethylpiperidine in THF followed by stirring for 1 h from cold up to ambient temperature.

1,3,5-Triphenyl-1-4-azapenta-1,3-diene (1)

A mixture of chalcone (5.0 g, 23.3 mmol) and benzylamine (2.5 g, 23.3 mmol) in 150 ml of hexane (freshly distilled from calcium hydride) was refluxed 8 h over 50 g of 5A molecular sieves using a Barrett water trap. After filtration and solvent removal, the crude oil crystallized upon refrigeration. Recrystallization from hexane yielded 2.6 g (30%) of product, m.p. 83–85°. It is imperative that the crystals be grown slowly.

Mass spectrum: *m/e* 297, molecular ion. The n.m.r. spectrum (CCl_4) showed a 2 hydrogen singlet at δ = 4.40, and one hydrogen doublet at δ = 6.35 (*J* = 17 Hz), and a 16 hydrogen multiplet in the region δ = 6.96–7.53. The i.r. spectrum ($CHCl_3$) showed C=N at 1598 cm^{-1}.

A second geometrical isomer was present in the crude oil but was not isolated. The n.m.r. (CCl_4) of the second component in the mixture showed a 2 hydrogen singlet at δ = 4.80, a 1 hydrogen doublet at δ = 6.67 (*J* = 17 Hz), and an apparent 16 hydrogen multiplet at δ = 6.96–7.53 as obtained by difference.

1,3,5-Triphenyl-2-azapenta-1,3-diene (2)

A degassed solution of **1** (0.1 g, 0.34 mmol) in 0.64 ml of 0.53 *M* potassium *tert*-butoxide in *tert*-butoxide in

tert-butyl alcohol was stirred at ambient temperature for 0.5 h. The reaction mixture was extracted using ether and water. After the ether layer was washed once with water, once with saturated sodium chloride, and dried with magnesium sulfate, the solvent was removed under reduced pressure. An n.m.r. of the residual oil indicated a 3:1 ratio of *trans,trans*-**2** to *trans,cis*-**2**.

Thin-layer chromatography (silica gel, 10% ether-in-hexane) resulted in isolation of β-phenylpropiophenone (66% yield, m.p. 68–69°) and *trans,trans*-**2** (28%, m.p. 44–46°). Mass spectrum: *m/e* 297 for molecular ion. The n.m.r. spectrum (CCl_4) showed a 2 hydrogen doublet at $\delta = 3.72$ ($J = 7.5$ Hz), a 1 hydrogen triplet at $\delta = 5.60$ ($J = 7.5$ Hz), a 15 hydrogen multiplet in the region $\delta =$ 6.82–7.78, and a 1 hydrogen singlet at $\delta = 8.09$.

The i.r. spectrum ($CHCl_3$) showed C=N at 1630 cm^{-1}.

The geometrical isomer, *trans,cis*-**2** was not isolated but was characterized from its n.m.r. spectrum (CCl_4) in the mixture before t.l.c.; a 2 hydrogen doublet at $\delta =$ 3.36 ($J = 8$ Hz), a 1 hydrogen triplet at $\delta = 6.01$ ($J =$ 8 Hz), a 1 hydrogen singlet at $\delta = 7.86$, and a 15 hydrogen multiplet at the region $\delta =$ 6.82–7.78 as obtained by difference.

Diels–Alder Reaction of trans,trans-2 and trans,cis-2 with 4-Phenyl-1,2,4-triazoline-3,5-dione

The relative rates of reaction of a 2:1 mixture of *trans,cis*-**2** and *trans,trans*-**2** (0.1 g, 0.34 mmol in 0.5 ml CCl_4) were followed by n.m.r. monitoring of the doublets at $\delta = 3.36$ and 3.72 as aliquots (3 mg, 0.017 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione were added. The final ratio of doublets was 8:1 before the upfield doublet disappeared into the other increasing signals. After solvent removal, the crude oil was separated by t.l.c. (silica gel, chloroform) yielding the Diels–Alder adduct (45 mg, 33%) as the major product (m.p. 105–107° from hexane–benzene). Mass spectrum: $m/e = 472.7$ for molecular ion. The n.m.r. spectrum ($CDCl_3$) showed a 2 hydrogen AB part of an ABX at $\delta = 3.05$–3.65 ($\nu_a = 3.16$, $\nu_b = 3.50$ and $J_{ab} = 14$ Hz, $J_{ax} = 5$ Hz, and $J_{bx} = 6$ Hz), the 1 hydrogen X part at $\delta = 5.72$, a 1 hydrogen singlet at $\delta =$ 6.46, and a 20 hydrogen multiplet at $\delta = 6.86$–8.06. The i.r. spectrum ($CHCl_3$) showed carbonyl bands at 1780 and 1720 cm^{-1}.

trans-2,4,5-Triphenyl-1-pyrroline (trans-3)

A degassed solution of **1** (0.1 g, 0.34 mmol) in 0.68 ml of 0.53 *M* potassium *tert*-butoxide in *tert*-butyl alcohol in a sealed evacuated tube was heated for 30 min at 120°. The reaction mixture was extracted using ether, and washed with water, with saturated sodium chloride and dried with magnesium sulfate. After ether removal, the residue was separated by t.l.c. (10% ether in hexane) and the main band yielded 68 mg (68%) of material (m.p. 89.5–91, from hexane). Mass spectrum: $m/e = 297$ for molecular ion.

The n.m.r. spectrum ($CDCl_3$) showed a 2 hydrogen multiplet $\delta = 7.61$–8.02 and a 13 hydrogen multiplet $\delta = 6.94$–7.50. The remaining 4 hydrogen pattern was analyzed as an ABCM with the assistance of the LAOCOON III program: $\nu_a = 3.16$, $\nu_c = 3.40$, $\nu_b = 3.58$, $\nu_m = 5.30$ and $J_{ab} = -16.8$ Hz, $J_{ac} = 7.6$ Hz, $J_{bc} = 9.3$, $J_{am} = 2.0$ Hz, $J_{bm} = 2.2$ Hz, and $J_{cm} = 6.7$ Hz. The i.r. spectrum ($CHCl_3$) showed no N—H absorption and C=N at 1602 cm^{-1}.

cis-2,4,5-Triphenyl-1-Pyrroline (cis-3)

A solution of **1** (0.1 g, 0.34 mmol) in a minimum of THF was added by syringe to a solution of 0.5 mmol lithium 2,2,6,6-tetramethylpiperidide in 5 ml of THF held at −78° under an argon atmosphere. After stirring for 30 min at 0–6°, the dark blue solution was treated with an excess of acetic acid. The reaction mixture was treated with water and ether and the ether layer was washed twice with water, once with saturated sodium chloride solution, dried, filtered, and solvent removed. Nuclear magnetic resonance of the residual oil indicated 85% conversion to cyclic materials. Silica gel t.l.c. (10% ether in hexane) yielded 29% *trans*-**3** and 35% *cis*-**3** plus 5% of 2,3,5-triphenylpyrrole. Compound *cis*-**3** (m.p. 88–90°) depressed the m.p. of *trans*-**3** and was recovered unchanged after melting. Mass spectrum: *m/e*-297 for molecular ion. The n.m.r. spectrum (CCl_4) showed a 2 hydrogen multiplet $\delta = 7.82$–8.15, a 13 hydrogen multiplet $\delta = 6.60$–7.58, 1 hydrogen multiplet 5.43–5.64, 1 hydrogen multiplet 3.79–4.21, 2 hydrogen multiplet 3.18–3.48. The i.r. spectrum ($CHCl_3$) showed no N—H absorption and C=N at 1611 cm^{-1}.

2,3,5-Triphenylpyrrole

Both *cis*-**3** and *trans*-**3** (94 mg, 0.32 mmol) were oxidized separately in 5 ml of benzene at reflux under an argon atmosphere using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (72 mg, 0.32 mmol). After 1 h at reflux, the solution was concentrated and the product purified by t.l.c. (silica gel, 10% ether in benzene) yielded 63 mg (67%) of material (m.p. 138–140°, undepressed by admixture with an authentic sample) (13).

Isotopic Exchange of trans-3

A degassed solution of *trans*-**3** (75 mg, 0.25 mmol) in 1 ml of 0.24 *N* potassium *tert*-butoxide in *tert*-butyl alchol-*O-d* in a sealed evacuated tube was heated at 120° for 30 min. After cooling, the reaction mixture was extracted using ether and water. After drying and solvent removal, the residue was purified by t.l.c. (silica gel, 10% ether–hexane). After recrystallization from hexane, mixture m.p. with *trans*-**3** showed no depression and both the n.m.r. and mass spectra showed incorporation of 4 atoms D/molecule into the pyrroline ring.

Isomerization of cis-3

A degassed solution of *cis*-**3** (100 mg, 0.34 mmol) in 0.68 ml of 0.54 *M* potassium *tert*-butoxide in *tert*-butyl alcohol in a sealed evacuated tube was heated at 120° for 30 min. After the usual work-up, the residue recrystallized from hexane yielded 88% of material of m.p. 89–91° (undepressed by admixture with an authentic sample of *trans*-**3**).

Isomerization and Exchange of 1

To the stirred degassed potassium methoxide in methanol (methanol-*O-d*) solution held at constant temperature and under an argon atmosphere was added solid **1**. At the reported time the reaction was poured into water and ether. The ether layer was washed twice with water, once with saturated sodium chloride solution, dried over magnesium sulfate and solvent removed on a rotary evaporator. The residual oils were analyzed by n.m.r. and separated by t.l.c. (silica gel, 10% ether in hexane).

The deuterium content of **1** was determined by analyzing (mass spectroscopy) the β-phenylpropiophenone obtained by hydrolysis on silica gel.

Isomerization of 1 with Lithium 2,2,6,6-Tetramethylpiperidide

To a stirred degassed solution of LiTMP in THF under argon at the reported temperature, was added solid **1**. After stirring for the reported time, the reaction was quenched with water and extracted with ether *vs.* water. The ether layer was further extracted twice with water, once with saturated sodium chloride solution, dried over magnesium sulfate, filtered, and the solvent removed with a rotary evaporator. The residual oils were separated by silica gel t.l.c. (10% ether in hexane) and analyzed by n.m.r.

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