

serial product $U_1^{(n)}$ of statistical weight matrices U_i (see eq 1), and

$$\mathcal{Y}_i = (U_i \otimes E_i) \|\mathbf{Y}_i\|, \quad 1 < i < n \quad (\text{A8})$$

$\|\mathbf{Y}_i\|$ is the diagonal array of the generator matrices \mathbf{Y}_i for the several rotational states for bond i , and E_i is the unit matrix of the same order t as \mathbf{Y}_i . The terminal matrices in eq A7 are given by^{19,20}

$$\begin{aligned} \mathcal{Y}_{[1]} &= U_1 \otimes \mathbf{Y}_{[1]} \\ \mathcal{Y}_{[n]} &= U_n \otimes \mathbf{Y}_{[n]} \end{aligned} \quad (\text{A9})$$

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- (23) The RIS scheme applicable to longer sequences breaks down for cyclization of the tetramer owing to the fact that coalescence of the terminal Si atoms, and appended groups, in the hypothetical process of cyclization (see Figure 1) eliminates the second-order interaction responsible for $\omega = 0$ in eq 1. The same circumstance occurs in the closure of the six-membered polymethylene sequence. This qualification of the treatment, which does not apply to larger rings, has been noted and taken into account by Semlyen and Wright⁵ and by M. Sisido, *Macromolecules*, **4**, 737 (1971). Calculations in the text for $x = 4$ are for illustration only and are not applicable to actual tetrameric rings.
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- (26) NOTE ADDED IN PROOF. L. E. Scales and J. A. Semlyen, *Polymer*, **17**, 601 (1976), attribute the minimum and maximum in K_x for $x = 10$ –13 to peculiarities of the PDMS conformations arising from the inequality of the bond angles at O and Si. By enumeration of all conformations, they find that, within this range of x , the probability $W(\mathbf{0})$ depends critically on the precise value assigned to the bond angle at O. The locations of the extrema in K_x are considered therefore to be related to this structural feature of the PDMS chain.

Macrocyclization Equilibria. 3. Poly(6-aminocaproamide)

M. Mutter, U. W. Suter, and P. J. Flory*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received March 3, 1976

Abstract: The probability density function $W(\mathbf{0})$ at $r = \mathbf{0}$ and the directional correlation factors $2\Gamma_0(1)$ for homologous poly(6-aminocaproamide) sequences with $x = 2$ to 7 units (14–49 bonds) are evaluated and the influences of these factors on the cyclization equilibria constants K_x are determined through application of the theory presented in the first paper of this series. For $x = 3$ –6, the departure of $W(\mathbf{0})$ from its value for the Gaussian distribution accounts for ca. 60% of the discrepancies between experimental results and calculations according to the theory of Jacobson and Stockmayer. The inclusion of the factor for orientational correlations between terminal bonds further depresses K_x by ca. 60% for $x = 3$, 30% for $x = 4$, and 20–25% for $x = 5$ and 6. Agreement of theory with published experimental results for $x = 3$ –6 is within limits set by uncertainties in the calculations combined with the experimental errors, i.e., within about 15%.

Poly(6-aminocaproamide), (PACA), normally synthesized by polymerization of ϵ -caprolactam, contains cyclic species $[\text{NH}(\text{CH}_2)_5\text{CO}]_x$ in the amount of ca. 12% in the melt at 500 to 550 K at equilibrium with the linear polymer.^{1,2} Of this, ca. 3–4% comprises cyclic oligomers for which $x \geq 2$. The cyclization constants K_x for x -meric rings with $x = 1$ –6 have been determined by Semlyen and co-workers¹ and earlier by Zahn, Rothe, and their co-workers.² Gas-liquid chromatography was used in these experiments for determination of the concentrations of cyclic monomer and dimer; gel permeation chromatography was employed for $x = 3$ –6, and it was applied as an alternative method for $x = 1$ and 2. Inasmuch as the repeat unit comprises seven members, successive oligomers are more easily separated than members of the PDMS series³ discussed in the preceding paper,⁴ designated 2. Hence, the results for PACA should be less subject to errors of analysis.

In keeping with observations on most of the other series of cyclic homologues that have been investigated,^{3,5–7} the ex-

perimental cyclization constants for PACA^{1,2} in the intermediate range $x = 2$ –6 are substantially smaller than values calculated according to the theory of Jacobson and Stockmayer⁸ under the assumption that the density of chain vectors \mathbf{r} at $r = \mathbf{0}$ is given by the spherical Gaussian distribution; see eq 12 of the first paper⁹ of this series, hereafter designated as 1. The rotational isomeric state analysis of the configurational statistics of linear PACA chains carried out by Williams and one of the present authors¹⁰ provides the basis for calculation of the second moment $\langle r_x^2 \rangle$ required for evaluation of the Gaussian density. The values of K_x for PACA show even greater departures from theory (eq 1–12) based on the Gaussian density than has been observed in other systems. Thus, the ratios of observed values of K_2 , K_3 , K_4 , K_5 , and K_6 to those calculated in this manner are 0.17, 0.26, 0.48, 0.53, and 0.45, respectively.

In this paper we apply the treatment set forth in 1⁹ and applied to PDMS in 2⁴ to the PACA chain having a repeat unit that embraces a greater variety of skeletal bonds, including the

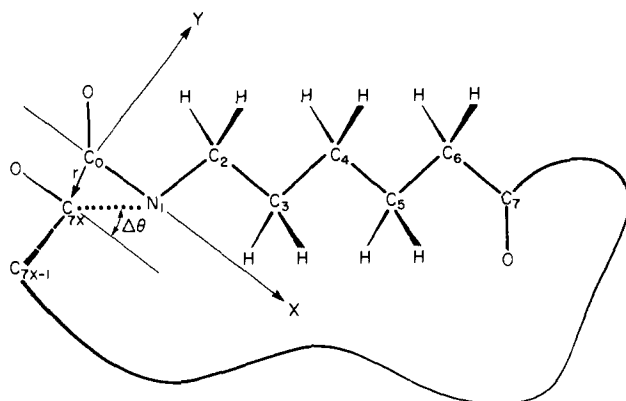


Figure 1. Poly(6-aminocaproamide) in the reference frame of the first amide bond. $\Delta\theta$ denotes the angle between the direction of the hypothetical $(7x + 1)$ th bond and the first bond.

planar, trans amide linkage. We first treat the density $W(\mathbf{0})$ in higher approximation, and then turn to the angle correlation function $2\Gamma_0(1)$.

Basis for the Computations

The repeat unit of PACA in the all-trans conformation is depicted in Figure 1. The arbitrary numbering of the skeletal atoms is indicated. The coordinate system of reference is attached to bond 1 (connecting atoms 0 and 1), i.e., its X axis lies along the C-N bond of the amide group. Other axes are specified according to convention.⁴

Our procedure is to generate $7x + 1$ bonds on the basis of the rotational isomeric state scheme used previously for the analysis of the PACA chain.^{10,11} In order to form a ring, the atom numbered $7x$ must coincide with atom 0, and the hypothetical bond $7x + 1$, shown dotted in Figure 1, must be parallel to bond 1; i.e., $\Delta\theta$ must vanish.

Geometrical parameters assigned to the PACA unit are as follows: bond angle supplements $\theta_1 = 57^\circ$, $\theta_2 = \theta_3 = \theta_4 = \theta_5 = \theta_6 = 68^\circ$, $\theta_7 = 66^\circ$ and bond lengths $l_1 = 1.33 \text{ \AA}$, $l_2 = 1.46 \text{ \AA}$, $l_3 = l_4 = l_5 = l_6 = 1.53 \text{ \AA}$, $l_7 = 1.51 \text{ \AA}$. Rotational isomeric states for bond 2 to 7 were chosen at $\varphi = 0$ and $\pm 120^\circ$. The amide group (bond 1) is assumed to be fixed in the trans configuration ($\varphi = 0^\circ$). Statistical weights at the temperature, 525 K, of the equilibration experiments were calculated from the conformational energies estimated by Flory and Williams,¹⁰ the statistical weights being expressed by Boltzmann exponentials with pre-exponential factors of unity. The statistical weight matrices thus evaluated at 525 K are:

$$U_1 = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$$

$$U_2 = [1 \ 1 \ 1]$$

$$U_3 = U_6 = U_7 = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0.27 \\ 1 & 0.27 & 1 \end{bmatrix}$$

$$U_4 = U_5 = \begin{bmatrix} 1 & 0.62 & 0.62 \\ 1 & 0.62 & 0.09 \\ 1 & 0.09 & 0.62 \end{bmatrix}$$

with states indexed in the order t, g^+ , and g^- .

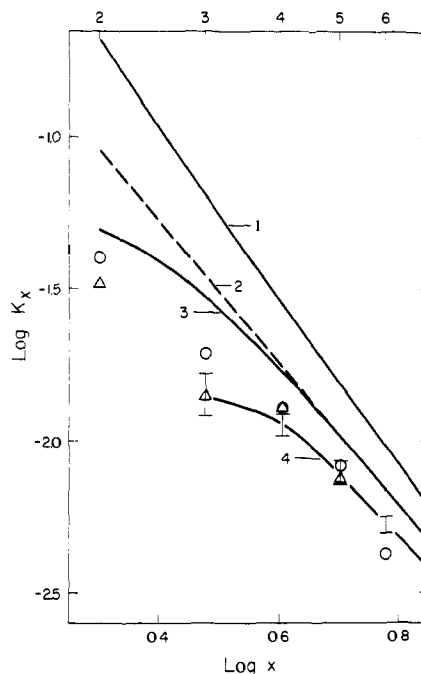


Figure 2. Cyclization equilibrium constants K_x plotted on log scales against the degree of polymerization x . Curves 1, 2, and 3 correspond to different approximations (see text) for $W(\mathbf{0})$, with neglect of orientational correlations between terminal bonds. Curve 4 is calculated according to eq 1-14, including both departures from the Gaussian distribution and angular correlations; see text. Experimental points at 525 K: (O) Andrews, Jones, and Semlyen;¹ (Δ) Spoor, Rothe, Zahn, and co-workers.²

Cyclization Constants Calculated From $W(\mathbf{0})$

Curve 1 in Figure 2 is drawn through values of K_x calculated according to eq 1-12, in which $W(\mathbf{0})$ is represented in the spherical Gaussian approximation. Curves 2 and 3 were calculated from eq 1-11 using higher approximations for $W(\mathbf{0})$. Procedures described in detail in 2 were followed.

Curve 2 rests on the Hermite series truncated at g_4 (see eq 1-25 and 1-26) for the estimation of $W(\mathbf{0})$. The required moments $\langle r^2 \rangle$ and $\langle r^4 \rangle$ were evaluated by matrix generation.

The density $W(\mathbf{0})$ was also estimated for $x = 2-7$ from Monte Carlo calculations (see 2), 30 000 chains being generated for each value of x using conditional probabilities calculated for each bond from the statistical weight matrices given above. In order to achieve equitable sampling, δr was set equal to $0.3 \langle r^2 \rangle^{1/2}$. Choice of the larger radius $\delta r = 0.5 \langle r^2 \rangle^{1/2}$ used in 2 affected the values of $W_x(\mathbf{0})$ by less than 5%. Equilibrium constants K_x calculated from these densities according to eq 1-11 are represented by the line labeled 3 in Figure 2.

Curves 2 and 3 differ significantly for $x = 2$ but are in close agreement for all larger rings. As in the case of PDMS, the departures from the Gaussian density lower K_x significantly.

Experimental values taken from various sources^{1,2} are included in Figure 2. Although curve 2 is consistently higher than the experimental points, it is much closer to them than curve 1 representing the Gaussian approximation for $W(\mathbf{0})$. Thus, for the comparison of the experimental points with curves 2 and 3 we are led to conclude that the non-Gaussian character of the distribution accounts for about 60% of the difference between the experimental value of K_x and the Jacobson-Stockmayer approximation (curve 1) for $x = 3-6$. The points fall consistently below these curves, and the discrepancies remaining to be explained are substantial. Curve 4 in this figure is discussed in the following section.

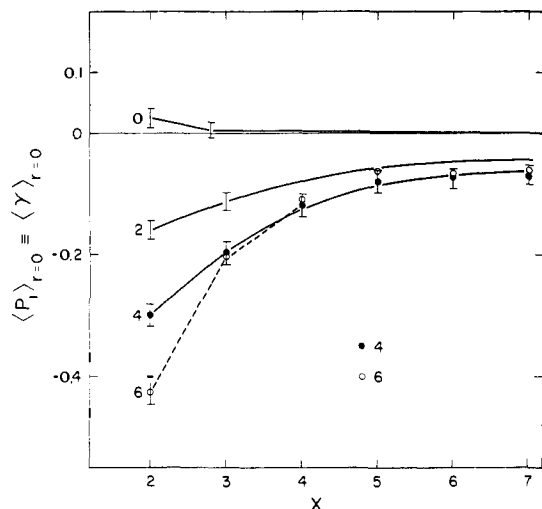


Figure 3. Averaged Legendre polynomial of first-order $\langle P_1 \rangle_{r=0}$ calculated with truncation of the series expansion in eq 1-27 at the term $f_{1,2s}$ of the indicated rank $2s$. Error bars denote $2\sigma_m$ limits.

Directional Correlation Factors

The angular correlation factor $2\Gamma_0(1)$ was evaluated according to eq 1-19. The averaged Legendre polynomials $\langle P_k \rangle_{r=0}$ of $\gamma \equiv \cos \Delta\theta$ at $\mathbf{r} = \mathbf{0}$ were obtained according to eq 1-27 by Monte Carlo generation of the required polynomials $f_{k,2s}$, as set forth in detail in 1 and 2. For this purpose 30 000 chains of each length were generated using conditional probabilities. The Hermite polynomial $\mathcal{H}(0)$ required in eq 1-27 was calculated according to eq 1-25 truncated at g_4 . In Figure 3, we show $\langle P_1 \rangle_{r=0} \equiv \langle \gamma \rangle_{r=0}$ calculated with truncation of eq 1-27 at the terms $f_{1,2s}$ of the indicated rank $2s$ plotted against x . The first term of eq 1-27, i.e., $f_{1,0}$, is positive for $x = 2$; it converges rapidly to zero for $x > 3$. By including the second term, $f_{1,2}$, in eq 1-27, $\langle P_1 \rangle_{r=0}$ is rendered negative for all $x \geq 2$. Inclusion of $f_{1,4}$ decreases $\langle P_1 \rangle_{r=0}$ further, but its influence on $\langle P_1 \rangle_{r=0}$ vanishes beyond $x = 2$. The next term, $f_{1,6}$, contributes appreciably to $\langle P_1 \rangle_{r=0}$ only for $x = 3$ and virtually vanishes for $x \geq 3$ within the limits of error in the Monte Carlo calculations. Hence, terms up to and including $f_{1,4}$ suffice to determine $\langle P_1 \rangle_{r=0}$ for $x > 2$. These observations are in harmony with those for PDMS,⁴ for which termination of eq 1-27 at $f_{1,4}$ is permissible for $n \geq 20$.

The Legendre polynomials of second order, $\langle P_2 \rangle_{r=0}$, calculated similarly from 30 000 Monte Carlo chains, are shown in Figure 4. Equation 1-27 was truncated at the term $f_{2,2s}$ of the rank $2s$ indicated with each line. Again, for $x > 2$, terms beyond $f_{2,2}$ are inconsequential, and the contribution of $\langle P_2 \rangle_{r=0}$ to $2\Gamma_0(1)$ is negligible within the error limit $2\sigma_m$. Inclusion of $f_{2,2}$ has a significant influence on $\langle P_2 \rangle_{r=0}$ only for $x = 2$.

Averaged Legendre polynomials $\langle P_k \rangle_{r=0}$ of higher orders up to $k = 5$ also have been computed. For $x > 2$, none of them departs significantly from zero. Hence, $2\Gamma_0(1)$ is adequately represented by

$$2\Gamma_0(1) = 1 + 3\langle P_1 \rangle_{r=0} \quad (1)$$

The values for $\langle P_1 \rangle_{r=0}$, obtained from eq 1-27 truncated at $f_{1,4}$ (curve 4 in Figure 3), yield $2\Gamma_0(1) = 0.406, 0.625, 0.745, 0.796,$ and 0.814 for $x = 3, 4, 5, 6,$ and 7 , respectively, with $2\sigma_m$ error limits of ca. ± 0.018 throughout. Although for $x = 2$ the series in eq 1-27 does not converge satisfactorily even at $f_{1,8}$, the value of $\langle P_1 \rangle_{r=0}$ is assured to be negative; hence $2\Gamma_0(1) < 1$.

As in the case of PDMS,⁴ the directional correlations between bond 1 and $n + 1$ are unfavorable for the formation of

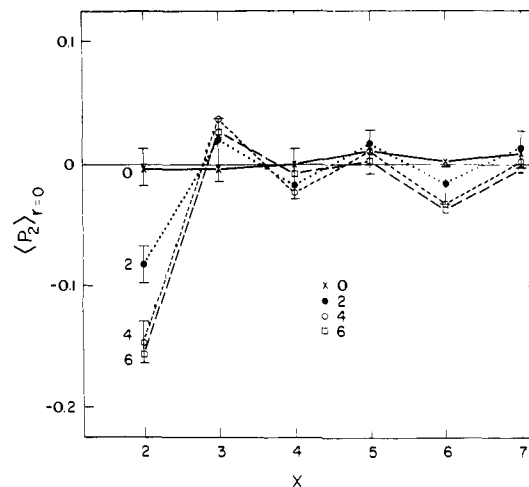


Figure 4. Averaged Legendre polynomials of second-order $\langle P_2 \rangle_{r=0}$ calculated according to eq 1-27 truncated at terms in $f_{2,2s}$ of the rank $2s$ indicated.

rings with $x > 1$, according to the calculations. Although the angle correlation factor $2\Gamma_0(1)$ approaches unity with increase in chain length, it is only ca. 0.85 even at $x = 7$ ($n = 49$ bonds).

Cyclization Equilibrium Constants

The constants K_x were evaluated according to eq 1-14. The scalar Hermite series approximation, truncated at g_4 (see above), was used for $W(\mathbf{0})$. The angle correlation factors $2\Gamma_0(1)$ were calculated according to eq 1. The symmetry number σ_{cx} equals x . Results of these calculations in the range $3 \leq x \leq 7$ are shown by curve 4 in Figure 2.

The theoretical values for K_4 and K_5 are in close agreement with experimental data from different sources. The value calculated for K_3 agrees with the experimental result of Spoor and Zahn² but is somewhat below that found by Andrews, Jones, and Semlyen.¹ The calculated value for K_6 exceeds the result of Andrews et al.¹ by about 15%. Resolution of the peak in the gel permeation chromatogram for this large ring, present in small quantity, is inferior to the resolutions of peaks for the members with $x < 6$. Hence, K_6 may be presumed to be subject to a greater experimental error, and this may account for the discrepancy between observation and the lower limit of the calculated value.

It is noteworthy that the experimental results for K_2 indicate an unfavorable angle correlation, i.e., $2\Gamma_0(1) < 1$. This is consistent with the indications of calculations presented above, which, as we have pointed out, fail to yield a quantitative result at $x = 2$.

We conclude that the theoretical calculations are generally in good agreement with experiment. Differences in the range $3 \leq x \leq 6$ appear to be within the combined limits of error in the calculations and the experimental measurements. Unfavorable angle correlations are a major factor in lowering K_x for rings of intermediate size.

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- 185 (1973), are exceptions to this rule. Their cyclization constants are considerably larger than values calculated from Gaussian densities at $r = 0$.
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The Conformational Analysis of Saturated Heterocycles. 77.¹ Rationalization of the Equilibria of Tetraalkylhexahydro-1,2,4,5-tetrazines

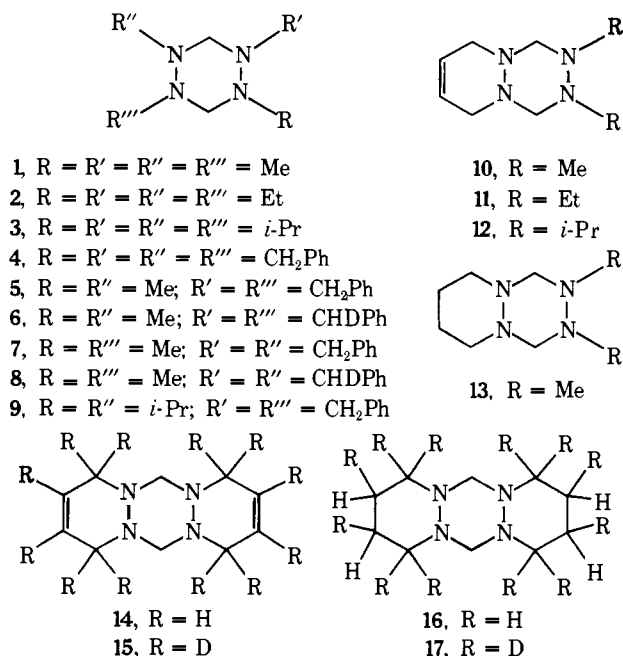
Victor J. Baker, Alan R. Katritzky,* Jean-Pierre Majoral, Arnold R. Martin,
 and John M. Sullivan

Contribution from the School of Chemical Sciences, University of East Anglia,
 Norwich, NR4 7TJ, England. Received November 21, 1975

Abstract: Seven monocyclic, four bicyclic, and two tricyclic hexahydro-*s*-tetrazines, including specifically deuterated derivatives, have been studied by ¹H NMR, ¹³C NMR, and other physical techniques. The conformational equilibria are elucidated in terms of four types of conformer (tetraequatorial, triequatorial-monoaxial, and two alternative diequatorial-diaxial), which form three sets equilibrating rapidly at medium temperatures. Conformational preferences are explained in terms of steric, electronic, and entropy effects, and a rational picture of the conformational equilibria in the series is presented.

In an earlier paper² we clarified the conformational equilibria of tetramethyl- and tetraethylhexahydro-tetrazines (**1**, **2**) together with those of one bicyclic (**10**) and three tricyclic analogues (**14-16**). At that time it was not possible to rationalize the equilibria. We have now studied a considerable number of further compounds (cf. Scheme I), which allows

Scheme I. Compounds Studied in Ref 2 and This Paper

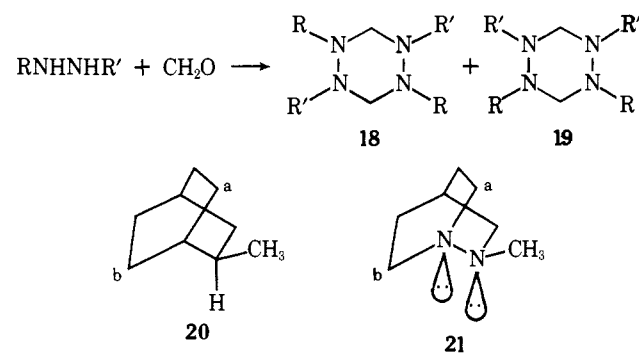


firmer conclusions regarding the factors determining conformational preferences in hexahydro-tetrazines. We have also applied ¹³C NMR to the compounds previously studied. Our earlier paper² summarized the previous work up to 1973. Since then the full x-ray structure of hexahydro-1,4-dimethyl-*s*-tetrazine has been published:³ it exists as the di-Me-equatorial

di-H-axial form, but there is evidence for the occurrence of nonsymmetrical isomers in solution.⁴

Preparation of Compounds. 1,2,4,5-Tetrasubstituted hexahydro-1,2,4,5-tetrazines in which all the substituents are identical are easily prepared from the appropriate 1,2-disubstituted hydrazine with formaldehyde;⁵⁻⁷ difficulties in the procedure have been discussed in terms of the mechanism.^{8,9} By this method we prepared the new tetrabenzyl compound **4**. From unsymmetrical 1,2-disubstituted hydrazines and formaldehyde, two products **18** and **19** could be formed: in the

Scheme II



methyl/benzyl series we isolated both products (**5** in pure form, **7** somewhat contaminated with **5**), in the isopropyl/benzyl series we obtained only the symmetrical product **9**. The specifically deuterated compounds **6** and **8** were prepared similarly from the deuterated hydrazine (MeNHNHCHDPh). Previously, unsymmetrical hydrazines of type PhNHNHR (R = Me, Et, *i*-Pr) have been condensed with formaldehyde^{10,11} to give presumably mixed products; isomer determination was not attempted by these workers.

We previously² reported the preparation of the bicyclic compound **10**; analogues **11**, **12**, and **13** were prepared similarly. The deuterated tricyclic compound **17** was prepared by hydrogenation of **15**.