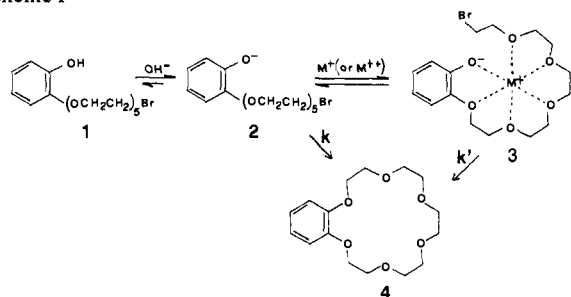


**Figure 1.** Cation concentration–rate profiles for the base-promoted cyclization of **1–4** in the presence of added cations. The cyclization rate constant in the presence of 0.022 M  $\text{Et}_4\text{N}^+\text{OH}^-$  was taken as the reference in the calculation of  $k_{\text{rel}}$  values.

**Scheme I**



trophotometrically by monitoring the disappearance of the phenoxide ion absorption at 291 nm. Clean first-order behavior was observed in all cases. The kinetic results<sup>7</sup> are shown graphically in Figure 1. The most striking finding is a marked  $\text{Ba}^{2+}$ - and  $\text{Sr}^{2+}$ -induced increase in the cyclization rate, which strongly suggests that a template effect is involved in the process according to Scheme I, where the rate constant  $k'$  for the conversion of the complexed form (**3**) of the open-chain precursor (**2**) is much greater than the rate constant  $k$  for the uncatalyzed path. The observed effect occurs at reasonably low cation concentration (0.1 M or less), so that the operation of significant medium effects on the reaction rates is unlikely. In contrast, with the monovalent alkali metal and the quaternary ammonium ions, rate effects are observed at significantly higher concentrations. Since in the case of  $\text{Et}_4\text{N}^+$  the formation of a complexed form having structure **3** is most unlikely, the observed reactivity pattern may be attributed to a medium effect, the bulky organic cation being probably responsible for the marked deviation from dilute solution behavior. Although the interpretation of the results obtained with the alkali metal cations is made difficult by the high concentrations required for the rate-enhancing effect to be significant, the following points are worth noting. The behavior of both  $\text{K}^+$  and  $\text{Na}^+$  is markedly different from that of  $\text{Li}^+$ , where a negligible effect is observed, as well as from that of  $\text{Et}_4\text{N}^+$ , whose curve intersects those of both  $\text{K}^+$  and  $\text{Na}^+$ . Notably, in the concentration range  $\sim 0.1$ – $1$  M, the rate-enhancing effect of the latter cations

is appreciably larger than that of  $\text{Et}_4\text{N}^+$ , and, therefore, seems far too large to be attributed to a general medium effect. Moreover, the curves of the different metal cations are displaced to higher concentrations by roughly the same extent as the logarithms of the related association constants with dibenzo-18-crown-6 in water at 25 °C,<sup>8</sup> which are reported in parentheses:  $\text{Ba}^{2+}$  (3.6) >  $\text{Sr}^{2+}$  (3.2)  $\gg$   $\text{K}^+$  (2.2) >  $\text{Na}^+$  (1.7)  $\gg$   $\text{Li}^+$  (0.6). The fact that the complexing ability of different cations with polyoxa compounds appears to follow the same order with either ring compounds or their open-chain analogues<sup>9</sup> strongly indicates that the above close correspondence between catalytic effect as observed in the present study and stability constants with dibenzo-18-crown-6 is hardly fortuitous. Consequently, the operation of a template effect is also suggested in the case of  $\text{K}^+$  and  $\text{Na}^+$ , for which relatively high concentrations are required because of their unfavorable binding constants as compared with those of the divalent metal ions. A medium effect is possibly superimposed into the template effect in the case of  $\text{K}^+$  and  $\text{Na}^+$ , particularly at the highest concentrations used. The present data do not allow to estimate the relative importance of these effects.

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## References and Notes

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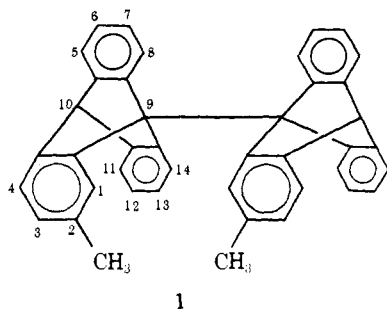
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## 2,2'-Dimethyl-9,9'-bitriptycyl. A Case of an Enormous Rotational Barrier between $\text{sp}^3$ -Hybridized Carbon Atoms<sup>1</sup>

Sir:

Highly hindered compounds capable of exhibiting appreciable rotation barriers between  $\text{sp}^3$ -hybridized carbon atoms have been the subject of considerable interest and numerous reports in recent years.<sup>2</sup> The largest rotational barrier of this kind that has been reported is 37.7 kcal mol<sup>-1</sup> for 9,10-bis(1-

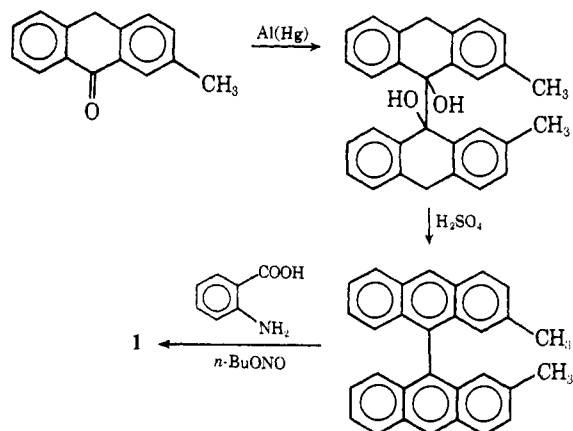
cyano-1-methylethyl)triptycene.<sup>3</sup> Previously, we reported the synthesis of 9,9'-bitriptycyl.<sup>4</sup> We report herein on 2,2'-dimethyl-9,9'-bitriptycyl (**1**), which exhibits an enormous rotational barrier between the central 9 and 9' sp<sup>3</sup>-hybridized carbon atoms, in excess of 54 kcal mol<sup>-1</sup>.



The synthesis of **1** is outlined in Scheme I.<sup>5</sup> The NMR spectrum, in CDCl<sub>3</sub>, of the initially isolated material from column chromatography exhibited two closely spaced singlets at  $\delta$  1.83 and 1.81 (ArCH<sub>3</sub>). In repetitive experiments, the higher field singlet was ~50–80% the height of the lower field singlet. The rest of the spectrum consisted of a singlet at  $\delta$  5.55 (H<sub>10</sub> and H<sub>10'</sub>) and a complex multiplet at 7.6–6.4 (ArH). IR, UV, and mass spectra were consistent with structure **1**. This material was separated into two samples, **1a** (mp 473–478 °C dec, more soluble) and **1b** (mp 505 °C dec, less soluble) by repeated crystallization from chloroform-acetone and combination of appropriate fractions. **1a** and **1b** exhibited virtually identical TLC, IR, UV, and mass spectral behavior, both to one another, as well as to the initially isolated material. Their NMR spectra differed from each other and from the initially isolated material only in the methyl region. Both showed  $\delta$  1.83 and 1.81 peaks. However, the  $\delta$  1.83/1.81 peak height ratios differed,  $2.10 \pm 0.04$  for **1a** and  $0.44 \pm 0.02$  for **1b**. We conclude, from these results, that **1a** and **1b** are both mixtures of differing amounts of noninterconverting skew and anti conformers of **1**. The  $\delta$  1.83 peak corresponds to one of the conformers and the  $\delta$  1.81 peak to the other.<sup>6</sup> On the basis of higher melting point and lower solubility, the  $\delta$  1.81 peak is, tentatively, assigned to the more symmetrical anti conformer.

In an attempt to measure the rotational barrier between the conformers, **1a** and **1b** were heated in a variety of solvents. However, we were unable to bring about a significant change in the ratio of the  $\delta$  1.83 and 1.81 peaks. Our most severe conditions involved heating in naphthalene solution, under a nitrogen atmosphere in a sealed glass vial, for 171 h at 300  $\pm$  5 °C. Sublimation of the naphthalene resulted in quantitative recoveries of **1a** and **1b** with  $\delta$  1.83/1.81 ratios of  $2.06 \pm 0.05$

Scheme I



and  $0.42 \pm 0.02$ , respectively. Assuming an Arrhenius preexponential factor of  $10^{13.7}$  and an error of 2.5% in the measurement of the  $\delta$  1.83/1.81 ratio, a minimum rotation barrier of 54 kcal mol<sup>-1</sup> is calculated.<sup>8</sup> By comparison with the large rotation barriers previously observed for 9-alkyl substituted triptycenes,<sup>2b,3</sup> the enormity of the barrier in the 9,9'-bitriptycyl system is reasonable.

## References and Notes

- (1) Partial support from the National Science Foundation, the Research Corporation, and the General Faculty Research Committee of the City College of New York is gratefully acknowledged.
- (2) For leading references, see (a) J. E. Anderson, C. W. Doeke and D. I. Rawson, *Tetrahedron Lett.* 3531 (1975); (b) M. Oki, *Angew. Chem., Int. Ed. Engl.*, **15**, 87 (1976).
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- (5) All new compounds gave satisfactory elemental analyses and exhibited spectral properties (IR, NMR, mass, UV) consistent with their structures.
- (6) To eliminate the possibility that a major contaminant was present which caused one of the peaks in the  $\delta$  1.8 region, we synthesized, for comparison, a variety of compounds which could either be contaminants or would serve as models for possible contaminants. These included<sup>5</sup> 2-methylantracene; 2,3-benzotriptycene; 2,2'-, 3,3'-, and 4,4'-dimethyl-9,9'-bianthryl; 1-, 2-, and 9-methyltriptycene; and 3,3'- and 4,4'-dimethyl-9,9'-bitriptycyl. The spectral properties of these compounds led to the conclusion that they could not be present to any significant degree in our sample of **1**.
- (7) For leading references, see ref 2b.
- (8) A change of one order of magnitude in the estimated Arrhenius preexponential factor results in a change of ~2.6 kcal mol<sup>-1</sup>. If the error in measurement of the  $\delta$  1.83/1.81 ratio is taken to be  $\pm 5\%$ , the calculated minimum rotational barrier is 53 kcal mol<sup>-1</sup>.

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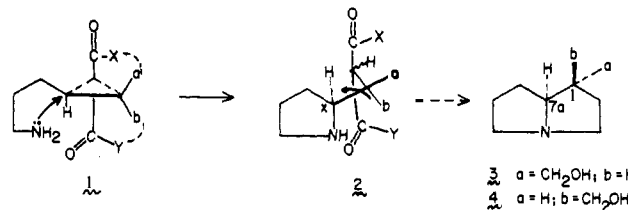
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## Stereospecific Total Synthesis of *dl*-Hastanecine and *dl*-Dihydroxyheliotridane

Sir:

Recently<sup>1</sup> we described a new method for achieving stereospecific control in the synthesis of the simple necine bases<sup>2</sup> trachelanthamidine (**3**) and isoretronecanol (**4**). The approach drew heavily on the notion of ring mutations<sup>3,4</sup> of activated cyclopropanes bearing intramolecular nucleophiles. At a crucial stage, systems such as **1**, of defined chirality, are unmasked. Ring mutation, through the spiro mode,<sup>3</sup> with *inversion of configuration*, leads to system **2** and thence to the final products.



Below we describe the extension of this strategy to the synthesis of the more complex necine bases, bearing oxygen at C<sub>7</sub>. Nature provides us with one representative enantiomer from each of the four diastereomeric families of these bases.<sup>2</sup> These are shown in formula **5–8**. Aside from the intellectual interest in learning how to systematically solve the stereochemical issues posed by these structures, the diverse,<sup>5,7</sup> and potentially useful,<sup>8</sup> biological properties of the senecio alkaloids (various acylated versions of the necine bases) provide additional synthetic incentives. In this paper, we report the stereospecific total synthesis of *dl*-hastanecine (**5**)<sup>9</sup> and *dl*-dihydroxyheliotridane (**6**).<sup>10</sup>