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RESTRICTED ROTATION IN SUBSTITUTED PROPANE EPOXIDES

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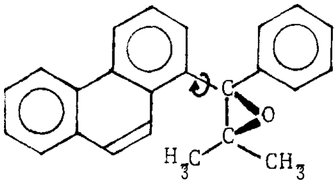
Abstract: Dynamic nmr spectroscopy is used to show that 1,1-diaryl-2-methyl-1,2-epoxypropanes display restricted rotation.

Dynamic nmr spectroscopy has been used to study restricted rotation about single bonds in a variety of organic compounds.[1] Of particular relevance to the present studies are the use of this nmr technique to study barriers to rotation in substituted styrenes[2] and other olefins[3].

In connection with our studies of carbonyl oxides as monooxygenase enzyme models we have ozonized 1-(1-phenanthryl)-1-phenyl-2-methyl-1-propene, 1, and observed an intramolecular 0 atom transfer from an intermediate carbonyl oxide[4]. Included among the other ozonolysis products of 1 was 1-(1-phenanthryl)-1-phenyl-2-methyl-1,2-epoxypropane, 2.[5] The formation of 2 as an ozonolysis product is not entirely unexpected inasmuch as sterically hindered olefins are known[6] to give epoxides as ozonolysis products in some cases. We present evidence that the barrier to rotation in 2 and 3 is high enough to permit observation of the conformer mixture at room temperature. To the best of our knowledge this is the first example of this phenomenon in epoxides.



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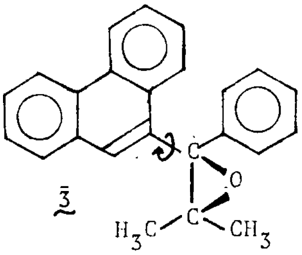

3

The room temperature nmr spectrum of 2 has four sharp singlets for the methyl protons indicating a high barrier to rotation about the C-C single bond bearing the 1-phenanthryl group. The diastereotopic methyl groups are seen as arising from conformations of 2 in whichtheremote part (carbons 5 through 10) of the phenanthrene ring system is cis or trans to the epoxy oxygen. As the temperature is raised the four singlets in the nmr (270 MHz) spectrum begin to broaden until a one pair coalescence is observed at 142°C, a full coalescence at 147°C, and finally two singlets are observed at 167°C. There are six possible ways for the methyl absorptions to be involved in a pairwise exchange process. We have used simulated nmr spectra to show that only two of these are compatible with the observed variable temperature spectra. The methyl absorptions in the extreme conformations are either 1.354 plus 1.240 exchanging with 1.099 plus 1.059

or 1.354 plus 1.059 exchanging with 1.099 plus 1.240. Such assignments indicate that the conformers are present in approximately equal amount. We have also synthesized epoxide **2** using the *m*-chloroperbenzoic acid and the N-bromoacetamide methods. All three methods give the same distribution of conformers of **2** as indicated by their respective nmr spectra.

An approximate equation (1)[7] has been used to calculate the free energy barrier at the coalescence temperature for **2**.

$$\Delta G^{\ddagger} = 19.14\, T_c\, (9.97 + \log T_c/\delta\nu)\ (\mathrm{J\ mol^{-1}}) \qquad (1)$$

When this equation is applied to the coalescence at 147°C and $\delta\nu$ determined from the exchanging methyl pair at 1.354 and 1.099 then $\Delta G^{\ddagger}$ is calculated to be 20.67 kcal/mole.[8]

The nmr spectrum[9] of the isomeric 1-(9-phenanthryl)-1-phenyl-2-methyl-1,2-epoxypropane, **3**, also indicates a high barrier to rotation as indicated by the presence of four separate absorptions for the methyl protons.

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3. a) D. Nasipuri and P.R. Mukherjee, J. Chem. Soc. Perkin II, 464 (1975), b) D. Nasipuri, P.K. Bhattacharya, and G.T. Furst, J. Chem. Soc. Perkin II, 356 (1977).
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5. Compound 2 was obtained as colorless crystals, m.p. 107-109°C; ^{1}H NMR ($CDCl_3$): 8.6-7.0 (m, 14H), [1.354 (s), 1.240 (s), 1.099 (s), 1.059 (s)] (6H), ^{13}C NMR (DMSO), ^{1}H decoupled: 139.8-122.25 (m), 70.3 (s), 68.99 (s), 65.57 (s), 64.02 (s), 23.71 (s), 22.20 (s), 20.15 (s), 20.05 (s); MS: 324 (23), 308 (10), 293 (5), 281 (9), 266 (75), 158 (95), 156 (100), 141 (85), 111 (80), 77 (45), 75 (39), IR (CCl_4): 3075, 2990, 2950, 1500, 1460, 1400, 1180, 1040, 900 cm^{-1}. Anal. Calc'd. for $C_{24}H_{20}O$: C, 88.85; H, 6.23; O, 4.93. Found: C, 88.56, H, 6.33, O, 4.91. All attempts to separate the diastereomers were unsuccessful. Methods used were: fractional crystallization, fractional sublimation, column chromatography, thin layer chromatography, HPLC and GLPC.
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8. If the same T_c is used for the other exchanging pair then $\Delta G^{\ddagger}$ is calculated to be 20.95 kcal/mole. If instead the earlier T_c (142°C) is assigned to this pair then $\Delta G^{\ddagger} = 20.69$ kcal/mole. It appears that one pair does indeed coalesce before the other.
9. Compound 3 has ^{1}H NMR (60 MHz, $CDCl_3$); 8.6-8.4 (m, 2H), 8.00-7.00 (m, 12H), [1.46 (s), 1.25 (s), 1.20 (s)], (6H); 100 MHz ^{1}H NMR (DMSO): the absorption at 1.46 (60 MHz) observed as 2 singlets 1.497, 1.460 (3H); MS: 324 (30), 308 (10), 282 (10), 266 (100), 177 (8), 134 (30), 105 (8), 77 (14).

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