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THE BARRIER TO ROTATION IN α,β-SUBSTITUTED STYRENES.
A DNMR INVESTIGATION

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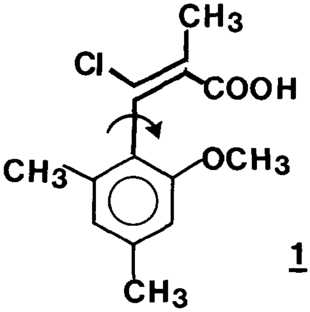
Abstract: The effect of α- and β-substituents on the barrier to rotation in styrenes is deduced from a dynamic nmr study of β-naphthylethylenes, 3,4-disubstituted styrenes.

α-Substituted and cis-β-substituted styrenes are markedly different from their parent in one important respect. While styrene is a planar molecule with a barrier of 3 kcal/mol to rotation about the phenyl to olefin bond[1], the substituted compounds have the two parts skewed[2], and the rotational barrier is to passage through the planar conformation.

Almost forty years ago[5] Adams and his co-workers prepared substituted styrenes, optically active due to hindered rotation of the olefin part with respect to the aromatic ring, and by observing the racemisation on one enantiomer of 1, for example, determined the barrier to rotation to be 24.1 kcal/mol. That investigation was a sequel to earlier studies of piphenyls with ortho-substituents--2 for example, is clearly similar to 1-- and the barrier is no doubt due to steric interactions in a coplanar transition state while rotating between two stable conformations with olefin and aromatic ring more or less orthogonal.



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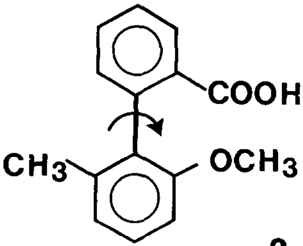

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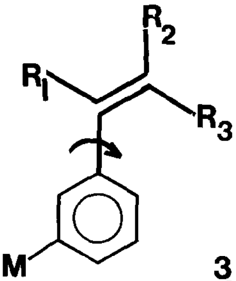

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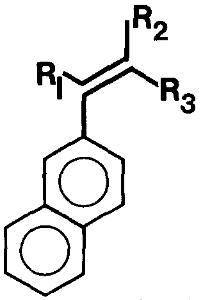
The dynamic nmr method which applies for barriers between about 4 and 25 kcal/mol should be suitable for investigating styrenes less highly substituted than 1, and we now want to report results for simple α,β-substituted styrenes



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of the general type 3, without ortho-substituents. A phenyl group attached to an sp^2-hybridised carbon is a common molecular situation about whose conformations little is known.

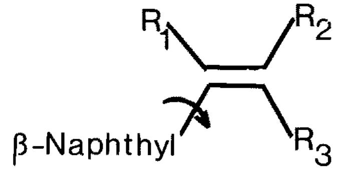
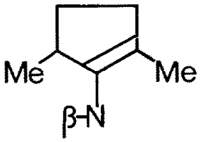
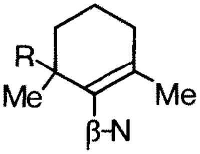
The dynamic nmr method requires that the phenyl group be asymmetric due to a meta-substituent M, and that at least one of the substituents R_1-R_3 or M contain enantiotopic groups which become diastereotopic when rotation of the unsymmetrical phenyl group becomes slow on the nmr timescale[6]. For this reason the compounds we investigated are of type 4. We believe that the steric environment in the β-naphthyl series is similar to that in the phenyl series[7].

All the compounds studied had nmr spectra indicating that rotation is fast on the nmr timescale at about room temperature, but some showed changes at lower temperature which allowed the measurement of barriers to rotation[8] as shown in Table 1. As an example, the isopropyl doublet of 5a (δ=0.92, J-6.8 Hz) broadens and splits below about -27° to two equal doublets (δ=0.87, 0.96) while all other signals are essentially unchanged. The barrier to rotation can be calculated therefrom to be 12.9 kcal/mol.

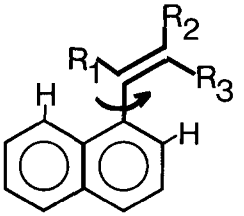
These results give an indication of how hindered rotation is in simple substituted styrenes. Larger substituents in the α-position and the cis-β-position raise the barrier, as one might expect.

It is remarkable how the replacement of a hydrogen on R_1 or R_3 by a methyl group produces a considerable change in the barrier 5b → 5a or 5d →5a. α and β substituents thus have uncommonly large effects on conformation. A single one changes the ground state conformation, as stated in the opening paragraph while additional branching with only one extra methyl group can double the barrier to rotation.

Another striking result is the effect of a trans β-substituent when there is already an α-substituent, seen by comparing 5c and 5a where introduction of the remote trans-β-methyl group raises the barrier from 5.2 to 12.9 kcal/mol. This is an extreme example of a buttressing effect, the trans-methyl presumably forcing the isopropyl methyl groups in the α-substituent towards the ortho hydrogens of the benzene ring, precisely the interaction which in the transition state, produces the barrier to rotation.

	R_1	R_2	R_3	Coalescence Temperature T_c, °C	Barrier to Rotation at T_c/mol kcal/mol	Barrier to Rotation of Corresponding α-naphthyl compound 6 kcal/mol Ref 9,10.
5a	*i*-Pr	Me	Me	-27°	**12.9**	>25
5b	*i*-Pr	Me	H	<-150°	**<6.0**	16.1
5c	*i*-Pr	H	Me	~-165°	**5.2**	21.1
5d	Et	CH_3	CH_3	-135°	**6.6**	25.8
 5e				<-157°	**<5.8**	14.5
 5f	R = H			-117°	**7.9**	>25
5g	R = Me			31°	**15.5**	>25

It is interesting to compare the present results with those for α-naphthylethylenes 6[9 10], shown in the last column of the Table. Here the interactions in the planar transition state are even more marked, as the peri-hydrogen is much nearer the substituent R_1 in 6 than the corresponding hydrogen in 4. The relationship between the two series is not direct, but is regular enough to suggest that the one might serve as a model for the other when results fall outside the range of the dynamic nmr method.



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2. Evidence from both U V spectroscopy[3] and photoelectron spectroscopy[4] both support a conformation change when styrene is substituted in the side chain.

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   b. T Kobayashi, T Arai, H Sakuragi, K Tokumaru, and C Utsanomiya, *Bull. Chem. Soc., Japan*, 54, 1658 (1981).

5. R Adams and J W Mecorney, *J. Amer. Chem. Soc.*, 67, 798 (1945) and earlier papers cited therein. Their result for 1 was a half-life of 74 minutes at 440° for one enantiomer whence we have calculated the barriers.

6. An alternative is to use a chiral olefin.

7. We have found that the barrier to rotation in the analogue of 5a with the β-naphthyl group replaced by a 3-phenylphenyl group has a barrier only 0.2 kcal/mol less than in 5a, the same within experimental error.

8. Barriers to rotation are free energies of activation at the coalescence temperature shown. Where an upper limit is quoted, nmr spectra were unchanged even at very low temperatures.

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