RESTRICTED ROTATION INVOLVING THE TETRAHEDRAL CARBON. IX

ISOLATION OF ISOMERS DUE TO RESTRICTED ROTATION ABOUT AN

sp^3-sp^2 CARBON BOND.[1]

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Barriers to rotation about carbon-carbon single bonds are, in general, so small[2] that isomers due to restricted rotation cannot be isolated at room temperature.[3] An exception is the classical work by Christie and Kenner[4] who succeeded in resolving an enantiomeric mixture of a biphenyl derivative which represents restricted rotation about a $C_{sp}{}^2$-$C_{sp}{}^2$ bond. Another classical work by Lüttringhaus and Gralheer[5] may be cited which is the resolution of a cyclophane derivative, restricted rotation about sp^3-sp^2 bonds being involved. These findings drew attention of many investigators to produce ample examples of these sorts.

Since we have been able to isolate rotational isomers involving an sp^3-sp^3 carbon bond,[1,6] we are naturally interested in isolation of isomers due to restricted rotation about an sp^3-sp^2 carbon bond. Except the cyclophane derivatives which are rather special in a sense that rotation about two sp^3-sp^2 bonds is involved, there are not many examples which clearly suggest the presence of stable rotational isomers. Only report which has dealt with this problem is that by Siddall et al.[7] who claim isolation of one of the isomers of 9-(2-methyl-1-naphthyl)fluorene with better than 90% purity. An analogous case, the restricted rotation about a $C_{sp}{}^3$-$N_{sp}{}^2$ bond, has been reported.[8]

Barrier to rotation about C_s-C_{ar} bond of 9-(2,6-dimethyphenyl)fluorene (1) was reported to be higher than 25 kcal/mol from the PMR results.[9] Since this barrier is high enough for isolation of isomers, if one of the methyl groups in this compound is substituted, we should be able to obtain stable

isomers at room temperature. The purpose of this paper is to report reallization of such an expectation.

Bromination of compound 1 with N-bromosuccinimide, using benzoyl peroxide as a catalyst in refluxing benzene, gave a mixture of two bromides, 2 (sp form) and 3 (ap form), the ratio being 2.2 : 1 as judged from the integrated intensities of PMR spectrum. Assignment of the structure is straight forward. One of the isomers shows a methyl signal at a very high field and a methylene signal at a low field which should be attributed to the magnetic anisotropy of the benzene rings. Another isomer, on the contrary, shows a methyl signal at a low field and a methylene signal at a high field.

(1)   (2)   (3)
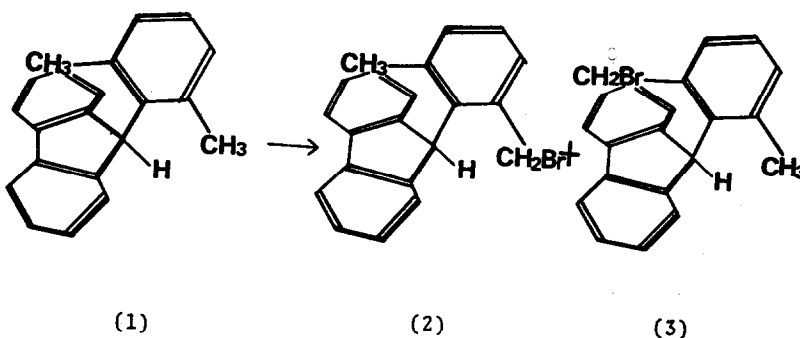
The reaction mixture was chromatographed on silica gel and eluted with hexane. 2 was obtained as an easily eluted fraction. Recrystallization gave pure 2, mp 115.0-115.5°C, and 3, mp 125-126°C. The PMR spectra of these isolated compounds are given in the figure.

Equilibration between these isomers could be reached by heating hexa-chlorobutadiene solution at 121°C for a few hours, both isomers giving an identical composition. The ratio at equilibrium was 3.6 ± 0.2 in favor of 2 and was independent of temperature in the range of 80-121°C. Thus k_1/k_{-1} in the following reaction is 0.28 ± 0.02 in this temperature range.
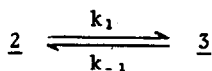
$$2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 3$$

Table 1 Rates of Isomerization

temperature (°C)	$k_1 \times 10^5$ (sec^{-1})	$k_{-1} \times 10^5$ (sec^{-1})
80	1.0	0.36
100	6.4	2.3
111	19	6.9
121	57	21

The rates of isomerization were measured at various temperatures and were found to follow the first order kinetics. The results are shown in Table 1. Arrhenius plot of these data yielded the activation energy of 27.₁ kcal/mol and
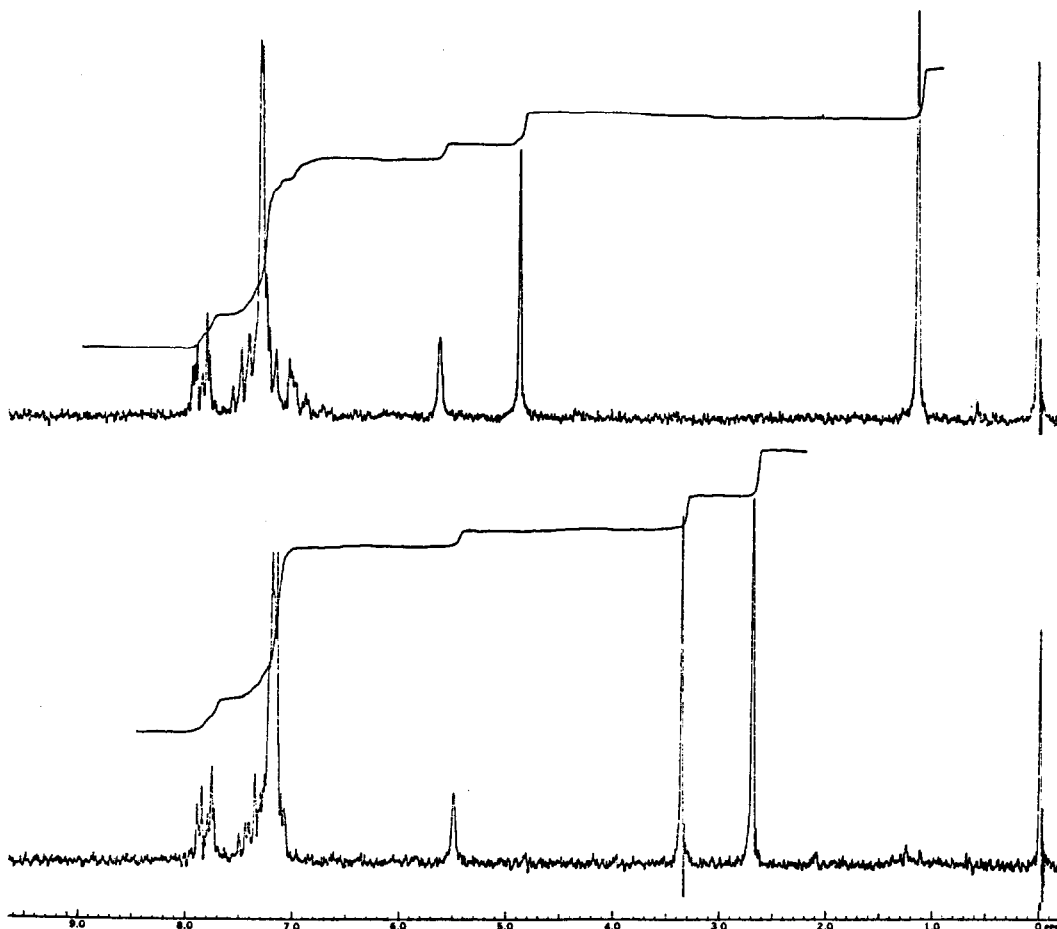

Fig. PMR spectra of isomeric 9-(2-bromomethyl-6-methylphenyl)fluorenes:
    2 above; 3 below.

log A of 10.₈ for the process of 2 —→3. Those for the process of 3 —→2 were obtained as 27.₁ kcal/mol and 11.₄, respectively.

Thus both equilibrium 2 ⇌ 3 and rate processes of isomerization ᵃre controlled by the entropy factor. The bromomethyl group will be able to take any conformation possible in the sp form 2, whereas bromine-inside conformation is highly unfavorable from the steric grounds in the ap form 3. Solvation difference together with this conformational aspect will be the main factors controlling the equilibrium and the isomerization processes.

The rate constant of isomerization at 80°C is so small that isomerization of 2 or 3 under the reaction conditions may be negligibly small. Thus the ratio of 2.2 : 1 can be taken as a result of kinetic control. Rationale for the favored attack on the outside methyl group must again be the steric effect of the fluorene portion.

References

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