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REACTIVITIES OF STABLE ROTAMERS. I. REACTION OF 9-(2-METHOXY-1-NAPHTHYL)FLUORENE WITH BUTYLLITHIUM

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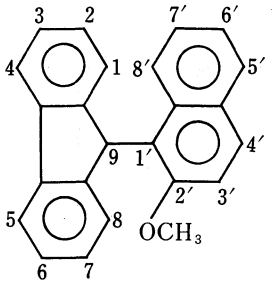
Two rotamers, sp and ap forms, of 9-(2-methoxy-1-naphthyl)-fluorene are isolated and are found to exhibit at least 10^3 fold difference in reactivities with butyllithium.

Although abundant data on the reactivities of organic compounds have been accumlated, they are usually the mean values of reactivities and populations of rotational isomers unless the compound in question reacts at the site where no rotamers are possible. Studies of the solvent effect on some reactions may also be affected by the shift in relative populations. We have been able to isolate some stable rotamers at room temperature[1,2] and have felt that these compounds should produce data which are not affected by the population. They may even exhibit a large difference in reactivities among rotamers. This paper is the first on such investigations and reports a finding of a remarkable difference in reactivities of rotamers of 9-(2-methoxy-1-naphthyl)fluorene (1) with butyllithium.



Compound 1 was prepared by the standard method from 9-fluorenone and 2-methoxy-1-naphthylmagnesium bromide followed by reduction with hydriodic acid. PMR spectrum (see Fig. 1) of 1 in $CDCl_3$ showed two methoxy signals at δ 3.13 and 4.10 which are assigned to ap and sp forms, respectively, by consideration of the magnetic anisotropy of the fluorene ring. The ap and the sp forms were separated by thin layer chromatography and melted at 121.0-122.0°C and 125.0-126.0°C, respectively.

The barriers to rotation about the C_9-$C_{1'}$ bond were obtained by measuring the growing and decreasing rates of the methoxy signals and the equilibrium constants in the temperature range of 34-56°C. The free energy difference between 1sp and 1ap was 0.8 kcal/mol at 30°C in favor of the sp form. The kinetic parameters for the rotation are summarized in Table 1.

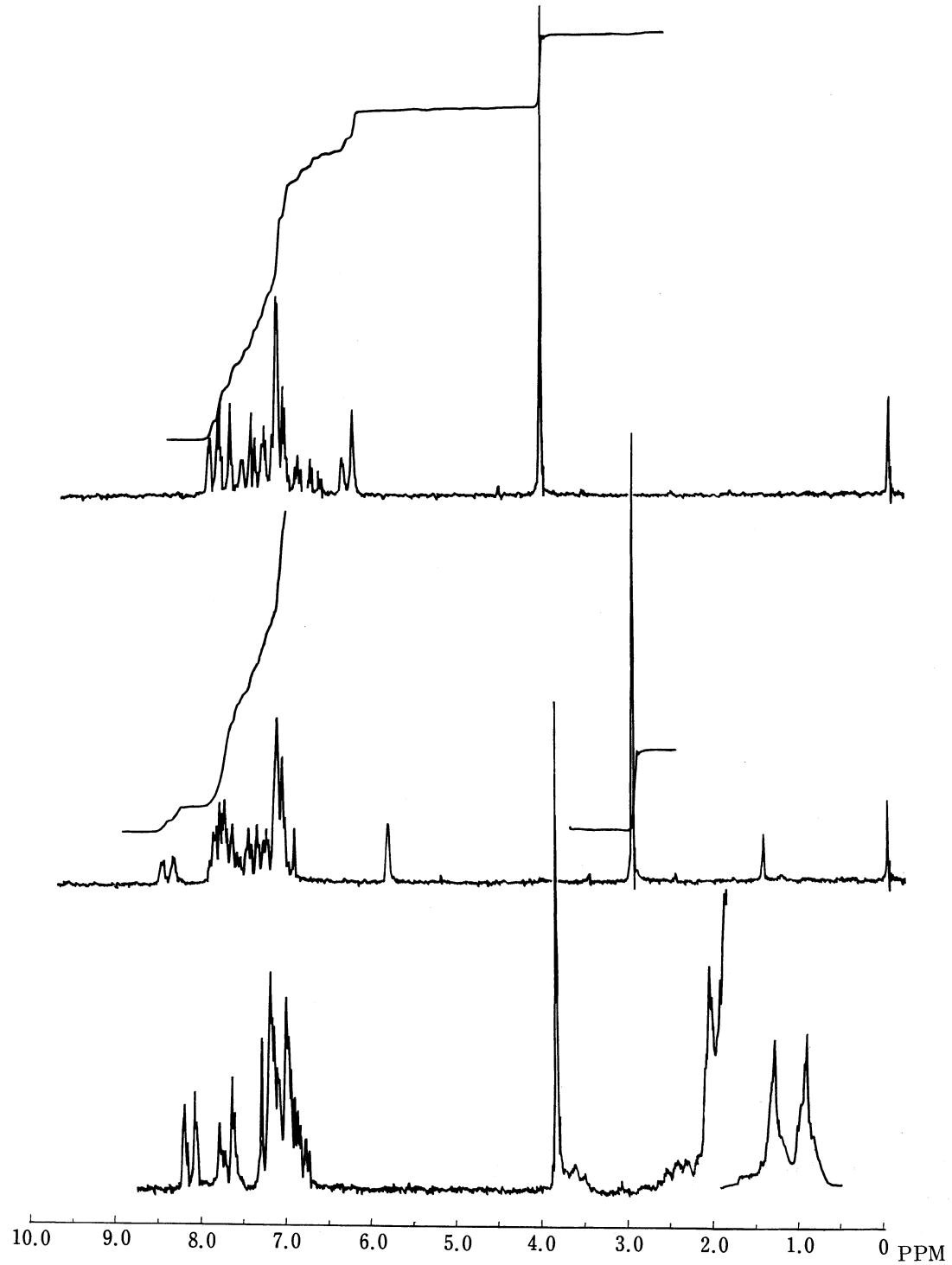
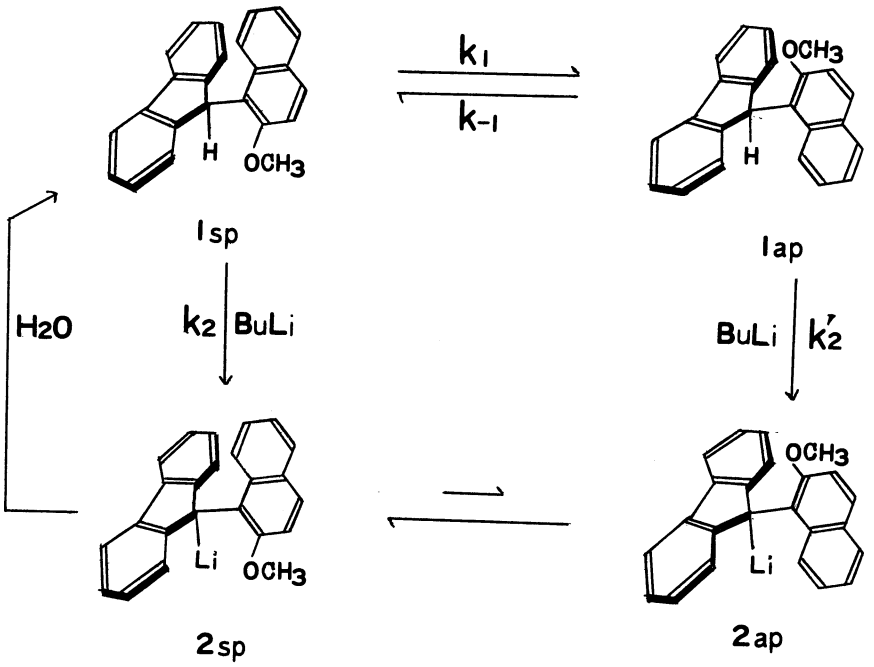


Fig. 1 PMR spectra of sp (top) and ap (middle) forms of 9-(2-methoxy-1-naphthyl)fluorene in $CDCl_3$ and lithium 9-(2-methoxy-1-naphthyl)-fluorenide (bottom) in hexane at room temperature.

Table 1. Kinetic Parameters for Rotation about the C_9-$C_{1'}$ Bond.

	sp ap	ap sp
Ea (kcal/mol)	25.3	24.1
$\Delta H^{\ddagger}$ (kcal/mol)	24.7	23.4
$\Delta S^{\ddagger}$ (eu)	-4.1	-5.6
$\Delta G^{\ddagger}$ (kcal/mol)	25.9	25.1

Treatment of a mixture of 1sp and 1ap with excess butyllithium in hexane erased the signal of 9-proton (δ 6.3) of the sp form almost instantaneously, whereas that (δ 5.9) of the ap form decreases slowly in its intensity. The intensity of the 9-H signal of 1ap becomes one third after 3 hours and it is after 10 hours that the signal becomes unobservable. Both forms of 1 gave an identical anion which is thought to be 2sp because the anion is rapidly formed from 1sp, 2sp can be stabilized relative to 2ap due to participation of the methoxy group, and quenching of the anion with water gives 1sp. The anion shows signals at δ 3.8 (OCH_3) and 8.1 (4- and 5-H's) among others (see Fig. 1), if the methyl signal of hexane is assumed to be at δ 0.9. The feature of the spectrum is the paramagnetic shift of the 7'- and 8'-protons of which signals are hidden in the aromatic region, whereas they are observable at δ 6.7 and 6.4, respectively, in 1sp. The results may be taken as an indication that the anion has a near-planar structure. The presence of signals due to 4- and 5-H's at the lower fields also supports the near-planar structure. The shift must at least be 0.4 ppm since these signals of 1sp were hidden in the aromatic region. Plausible explanation for the paramagnetic shift of 4- and 5-H's is the aromatic character of the 5-membered ring induced by formation of the anion. The shift of 7'- and 8'-H's to the lower field can also be attributed to the ring current effect of the fluorenide anion because these protons come closely to the plane of the ring in the near-planar structure.



As paths for the transformation of 1ap to 2sp, two possibilities may be considered. One is a path in which 1ap slowly converts to 1sp which reacts very rapidly to form 2sp. The other is a path in which the 9-H of 1ap is directly abstracted as a proton to form 2ap which rapidly converts to 2sp. An alternative pathway to the latter may be postulated: the 9-proton is directly abstracted with butyllithium spanning between the methoxy group and the proton. However, this mechanism may tentatively be neglected because of the unfavorable distance for spanning. The internal rotation of 2ap to 2sp is considered to be slow when the molecule is planar, because these are the analogs of optically active biphenyls. Nonetheless, it is possible to convert 2ap to 2sp rapidly by exchange of the lithium ion.

To distinguish roles of the pathways, the kinetic study was undertaken. The rotameric mixture of 1 (sp/ap = 1.65) was treated with large excess of butyllithium in hexane at 40°C. The rates were measured by the decrease in signal intensity due to the methoxy group in 1ap. The pseudo-first-order rate law was obeyed and the rate constant was obtained as 13×10^{-5} sec^{-1}. Putting the isomerization rate of 1ap and the concentrations of the substrate and butyllithium, we obtain k_2', which is the direct conversion rate of 1ap, as 7×10^{-5} $l \cdot mol^{-1} \cdot sec^{-1}$. The rates of reactions of 1sp were too fast to follow with the conventional method. Assuming that 90% of 1sp reacts with butyllithium within a minute under the conditions, we obtain the rate constant k_2 for the transformation of 1sp to 2sp as 3×10^{-2} $l \cdot mol^{-1} \cdot sec^{-1}$. Since the rate constant k_2 is the minimum, the rate ratio k_2/k_2' must be larger than 10^3. Although there are some approximations, this is a significant difference in the reactivities.

The large difference in reactivities between 1sp and 1ap may in part be derived by the stability of 2sp. If one assumes that the structure of the transition state for abstracting the 9-proton is close to that of the anion, the reactivity is easily explained. Lithiation of anisole is known to produce o-lithioanisole[3] and other related phenomena are known.[4] The methoxy group in the sp form, being close to the site of the reaction, must play an important role in stabilizing the transition state.

References

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