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Bromine Addition to Rotameric 1-(9-Fluorenyl)-2-(1-methylvinyl)naphthalene. Fate of Intermediate Cations Produced by Bromine Cation Attack[1)]

Michinori ŌKI,* Katsumi SHIONOIRI, Katsumasa OTAKE, Masaru ONO, and Shinji TOYOTA
Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700

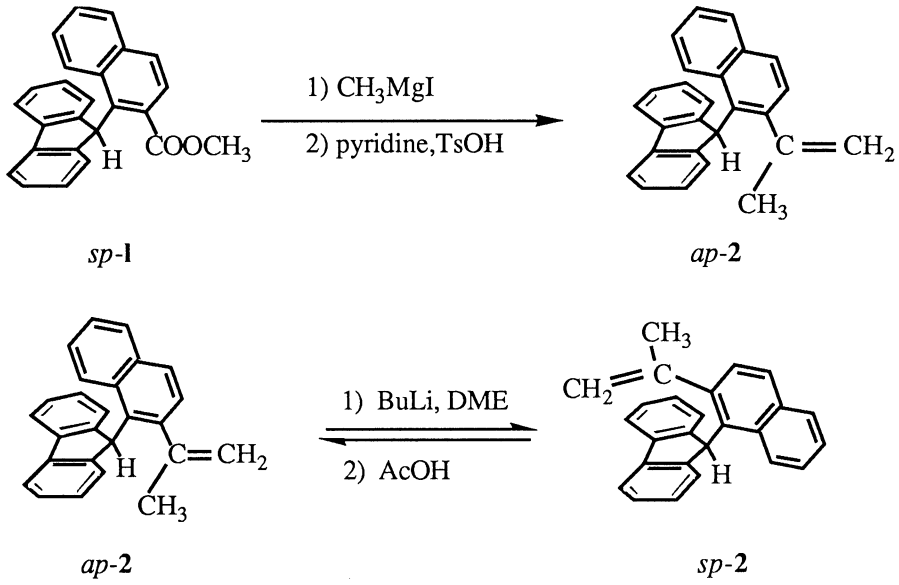
Treatment of the rotamers of the title compound with bromine afforded a normal addition compound in the case of *ap*, whereas the *sp* rotamer did bromo-olefins and a cyclic compound only. The results are discussed on the basis of the steric effects and π-participation of the fluorene ring in the case of *sp* that is not possible in the case of *ap*. Cation was produced from the bromine adduct of the *sp* form and the fate of the cation is disucssed by comparing with that of the *ap*.

We have reported the differences of the reactivities of 1-(9-fluorenyl)-2-vinylnaphthalene in various addition reactions.[2)] Generally the differences were small, the maximum difference being a factor of ca. 2 in the reaction rates. This small difference is attributed to the planar structure of the vinyl group in both rotamers which renders the access of the adding reagents rather facile even in the *sp*-isomer.

If one considers the molecules of *ap* and *sp* rotamers of 1-(9-fluorenyl)-2-(1-methylvinyl)naphthalene, one expects different situations. Namely, in these molecules, the 1-methylvinyl group should not be coplanar with the naphthalene ring to which it is attached. In addition, if an electrophilic addition such as bromination to the olefinic bond of the *sp* rotamer takes place, the back side of the intermediate should be blocked by the fluorene ring. This causes difficulty in forming the addition product. This difficulty of addition to the double bond in the *sp* isomer is expected from the fact that the addition of anionic species to the carbonyl group in a similar situation did not take place to a measurable extent.[3)]

Thus it should be interesting to investigate the fate of the carbocation which is formed by addition of a bromine cation to the olefinic bond. We wish to report the results of such investigations, to compare the products formed from the rotational isomers, *ap* and *sp*, and to discuss the probable origin of the differences.

The preparation of the rotational isomers of *ap* and *sp*-1-(9-fluorenyl)-2-(1-methylvinyl)naphthalene (**2**) was carried out in the following ways. *sp*-1-(9-Fluorenyl)-2-naphthoic acid[4)] was converted to the methyl ester (**1**), which was then treated with methylmagnesium iodide to give the corresponding tertiary alcohol



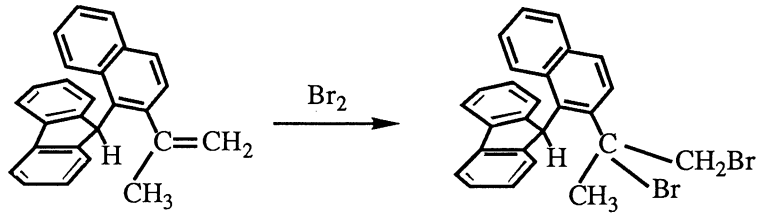
sp-**1** *ap*-**2** *ap*-**2** *sp*-**2**

that was then dehydrated in the presence of pyridine *p*-toluenesulfonate. This treatment afforded the *ap*-rotamer of the olefin (*ap*-**2**). The *ap*-olefin was treated with butyllithium in 1,2-dimethoxyethane and, after heating the solution for 2 h, the mixture was acidified to yield a ca. 1:1 mixture of *ap* and *sp*-olefins (*ap*-**2** and *sp*-**2**, respectively), which were separated by column chromatography. The barrier to isomerization of these olefins was determined to be 27.5 kcal/mol at 80 °C for the *sp* → *ap* process. Thus we can assure that we see the reactivities of each rotamer if we carry out reactions at room temperature or lower than that.

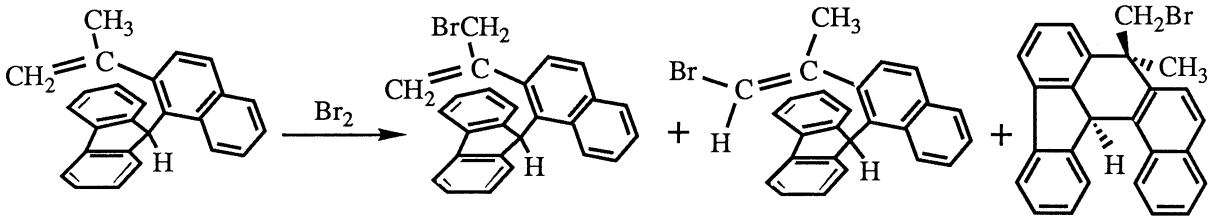
The bromination of these olefins was carried out in carbon tetrachloride at room temperature. The features of the reactions are instantaneous observation of hydrogen bromide in the case of *sp* and rather slow fading of the color of bromine and absence of observable hydrogen bromide in the case of *ap*.

Treatment of the reaction mixture afforded a single compound which was identified as the correspodning dibromide (**3**) in the case of *ap*. On the other hand, the *sp*-isomer afforded three products, which were identified as 1-(9-fluorenyl)-2-(1-bromomethylvinyl)naphthalene (**4**), 1-(9-fluorenyl)-2-[(*E*)-2-bromo-1-methylvinyl]-naphthalene (**5**), and 8-bromomethyl-8-methyl-8,14c-dihydrodibenz[*a,l*]acean-thrylene (**6**). The stereochemistry of compound **6** is tentatively assigned as shown by comparison of the chemical shift of the 8-methyl-protons with that of a similar compound.[5] The stereochemistry of compound **5** is assigned on the grounds that, in a similar reaction, a product of the similar stereochemistry is formed in major quantity[6] and the nuclear Overhauser enhancement is not observed between the methyl and the olefinic protons in **5**. No bromine-addition product was detected from the *sp*.

Failure of the *sp*-rotamer in giving the corresponding dibromide can be attributed to the steric crowding around the vinyl group in this rotamer. UV spectra of these compounds suggest that in both rotational isomers the vinyl group is not planar with

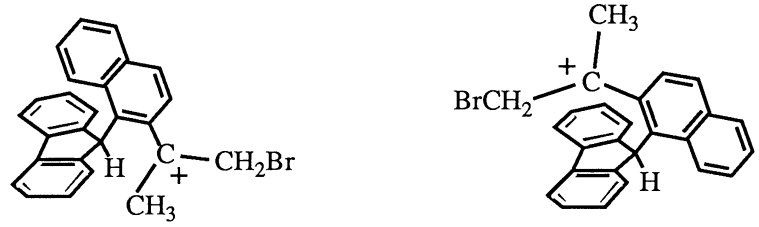


ap-**2** *sp*-**3**



sp-**2** *ap*-**4** *ap*-**5** **6**

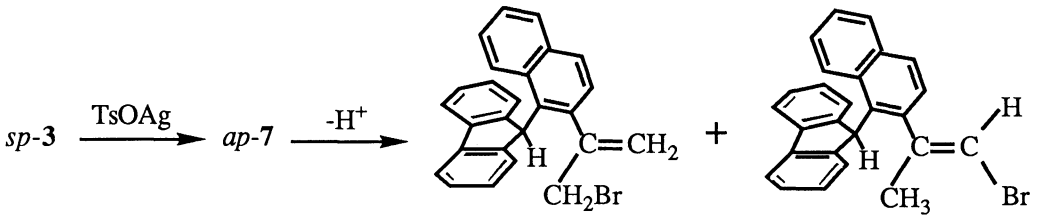
the naphthalene ring[7] to which it is attached. In the *sp*-isomer, after the attack of a bromine cation to the olefinic bond, the second attack by a bromide ion is impossible due to the steric effect, thus occurring at a proton on the methyl or the bromomethyl group in the cation (*sp*-**7**).



ap-**7** *sp*-**7**

At any rate, the reaction with an anion at the methyl proton of *sp*-**7** gives **4**, that with an anion at the bromomethyl proton **5**, and that with the π-system of the fluorene ring **6**. It becomes then interesting to see the fate of the corresponding *ap*-cation (**7**). Thus compound *sp*-**3** was treated with silver *p*-toluenesulfonate. This silver salt was used because the proton affinity of *p*-toluenesulfonate anion is known to be close to that of the bromide anion[8] and its nucleophilicity is low. The reaction was carried out in dichloromethane because of the difficulty in carbon tetrachloride.

The product analysis indicates that only olefins, *sp*-1-(9-fluorenyl)-2-(1-bromomethylvinyl)naphthalene (**4**) and *sp*-1-(9-fluorenyl)-2-(2-bromo-1-methylvinyl)naphtalene (**5**), are formed: no cyclized product was obtained in this reaction, as expected from other experiences.[9] Heating these olefins (*sp*-**4** and *sp*-**5**) gave identical mixtures of rotamers which were obtained by heating *ap*-**4** and *ap*-**5**, respectively, to prove that these **4** and **5** isomers are really rotational isomers with each other.



sp-**4** *sp*-**5**

Interesting is the difference in the formation ratio of **4** to **5**. Whereas the *ap*-cation in dichloromethane afforded 9:1 **4** and **5**, the *sp*-cation produced in the same solvent did a mixture of 2.5:6.0:1.5 **4**, **5**, and **6**. Thus the formation of the bromomethyl compound is more favored in *ap*-**7** than in *sp*-**7**. Due to the π-participation of the fluorene ring in the *sp* form, the cation must be more open than the *ap* counterpart. Although bromine participation is known to be weak in addition reactions of bromine to styrene derivatives[10] and in ^{13}C NMR spectroscopy,[11] this π-participation also reduces the bromonium ion (3-membered ring) character. This difference together with the steric effects and the π-participation should be responsible for the observed difference in product ratios. The details will be discussed in a full paper.

References

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7) The longest wavelengths of absorption are 315 and 322 nm with log ε of 2.5 and 2.6, respectively, for *ap*-**2** and *sp*-**2** in hexane. In comparison, those for 1-(9-fluorenyl)-2-vinylnaphthalene are ca. 345 nm with log ε of ca. 1.75.[2]

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