February, 1989] © *1989 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **62**, 621—623 (1989) 621

Reactivities of Stable Rotamers. XXVI. Some Bimolecular Elimination Reactions of 9-(2-Substituted 1-naphthyl)fluorene Rotamers[1)]

Yoriko Sonoda, Jiro Tsukahara, Nobuo Nakamura, and Michinori Ōki*,†
Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113

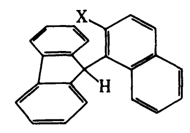
(Received August 15, 1988)

Synopsis. Various elimination reactions which are believed to proceed with E_2-type mechanisms have been examined on 9-[2-(1,2-dibromoethyl)-1-naphthyl]fluorene and 9-[2-(1-hydroxy-2-trimethylsilylethyl)-1-naphthyl]fluorene rotamers. Generally, the reaction of the *sp* rotamers was faster than that of the *ap* by a factor of 2—9. The results are attributed to the steric effects that are operative in the *ap* form.

In the course of comparative study of the reactivities of rotational isomers of 9-arylfluorene series (**1**), we have noticed that S_N2 type reactions that occur over the fluorene ring (namely in *ap*-**1**) is much slower than the same type of reactions that occur in the other rotamer (*sp*-**1**) which does not suffer from steric hindrance at the reaction site.[2)] The same was true for chromium(VI) oxide oxidation of alcohols and an aldehyde[3)] due to the fact that the rate-limiting step in these reactions is the formation of bulky transition states.[4)] Summarizing these results, we have concluded that a reaction that occurs over the fluorene ring (*ap*) with the space-demanding transition state is much slower than the counterpart (*sp*) in which the formation of the same transition state is less energy-requiring.

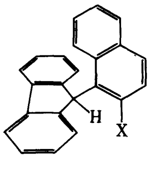
In contrast to these findings, addition reactions to a carbon-to-carbon[5)] and a carbon-to-oxygen[3)] double bonds did not show large differences in reactivities of the rotamers and we have explained the results by assuming that the least space-demanding hydrogen atom in the formyl or the vinyl group directs toward the fluorene ring in the transition states of the reactions.[5)]

The transition state of the E_2-type elimination is assumed to be synchronous elongation, with assistance of a nucleophile and an electrophile, of the two bonds which connect the leaving groups to the two carbon frame, as well as the shortening of the carbon-to-carbon bond.[6)] Thus the E_2-type eliminations will be candidates of demonstrating of a larger differences in the reactivities of rotamers than a mere addition reaction, because either a nucleophile or an electrophile must approach the group to be eliminated which is located over the fluorene ring in the *ap*-isomer whereas the steric effect will be small in the *sp*-isomer. Thus we have explored some E_2-type elimination reactions of the rotamers of the 9-arylfluorene series and wish to report the results in this paper.



ap-**1**

(if X precedes C_{8a} of naphthalene)

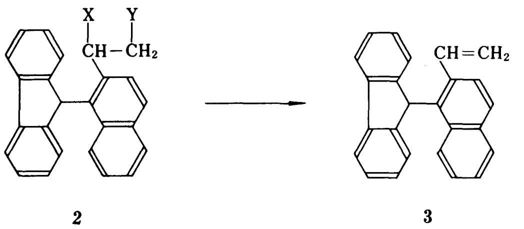


sp-**1**

There are varieties of elimination reactions reported in a paper which gives rise to *cis*-stilbene from *dl*-1,2-dibromo-1,2-diphenylethane with high stereospecificity.[7)] These reactions may be assumed to proceed with the E_2 reaction mechanisms. We have examined these reactions, namely debromination from *ap*- and *sp*-rotamers (**2**) of 9-[2-(1,2-dibromoethyl)-1-naphthyl]fluorene and compared the relative rates, k_{sp}/k_{ap}, with that in the reaction of which mechanism is thought to be different. The results are given in Table 1.

Debromination of **2** with zinc dust[8)] proceeded smoothly at room temperature but the selectivity was very low as was expected from the behavior in the elimination from *dl*-1,2-dibromo-1,2-diphenylethane. The reaction must proceed via electron transfer from the metal as was discussed in the literature and is different from the bimolecular elimination.[7)] Although sodium iodide is often used for debromination from 1,2-dibromoethane derivatives,[9)] the reaction did not occur for the compounds in question below 50 °C, the temperature which is low enough to assure nonexistence of internal rotation of the compound.

Among the reagents that eliminate bromine from the dibromide listed in the literature, lithium tetrahydridoaluminate is one of those which give the highest stereoselectivity in the reaction.[7)] Indeed, this reagent gave the highest k_{sp}/k_{ap} values of the reagents examined here, as are shown in Table 1. Interestingly, the selectivity was insensitive to the temperature of the reaction.



2 **3**

Table 1. The Conditions and the Relative Rates of the Elimination Reactions of **2**

X	Y	Reagent	Temp/°C	k_{sp}/k_{ap}
Br	Br	Zn	Room temp	1.4
Br	Br	$LiAlH_4$	−15	8.6
Br	Br	$LiAlH_4$	0	8.8
Br	Br	$LiAlH_4$	40	8.7
Br	Br	Na_2Te	Room temp	3.1
OH	$Si(CH_3)_3$	H_2SO_4	15	2.6
OH	$Si(CH_3)_3$	H_2SO_4	0	2.5

---

† Present address: Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700.

Recently, Suzuki and Inouye described that sodium telluride gave the high stereospecificity in the elimination reactions of 1,2-dibromides.[10] Examination of this reagent with our rotamers revealed that, though the elimination in the *sp*-dibromo compound (**2**: X=Y=Br) was indeed faster than in the *ap*, the selectivity was not so high as that observed with the tetrahydridoaluminate reagent.

Another example of stereospecific elimination is Peterson reactions,[11] of which stereoselectivity was studied by Hudrlik and Peterson.[12] It is known that, if acid is used for the elimination from *β*-hydroxyalkylsilanes, the elimination takes place in the trans-fashion and, if the base is used, the reaction is cis-elimination. Since the compounds we examine, 9-arylfluorenes, carry acidic hydrogen at the 9-position, the strong base can cause isomerization.[2,3] We therefore concentrated our effort to the acidic trans-elimination, which should be compared with the debromination described in this paper. The results in Table 1 indicate that the Peterson reaction is modestly selective.

Summarizing the results, we notice that the steric effects in the *ap*-form of the 9-arylfluorene series are operative in various elimination reactions, relative to the *sp*-series. The results will mean that a nucleophile or an electrophile, which is larger than a hydrogen atom, must approach a leaving group at the *α*-position of the substituent of the naphthalene ring, which is over the fluorene ring, to make the reaction of the *ap*-form slower than that of the *sp*. The enhancement of the selectivity, though small, relative to the addition to the olefinic bond,[5] should be attributed to the fact that the nucleophile or the electrophile is larger than the hydrogen atom which is the main cause of steric interaction with the fluorene moiety in the case of addition reactions in the olefin and the aldehyde. Yet, the selectivity in the elimination reactions studied here is inferior to that of the S_N2 type reactions. We believe this is due to the fact that, while in the S_N2 reactions two bulky groups, a leaving group and a incoming group, approach the *α*-position of the substituent over the fluorene ring in the *ap* form, there is only one bulky group, the nucleophile or the electrophile, approaching the *α*-position of the substituent over the fluorene ring in the case of E_2-type reactions. Thus the steric effects in the E_2-reactions are less demanding than the S_N2 reactions.

Experimental

9-[2-(1,2-Dibromoethyl)-1-naphthyl]fluorene rotamers (**2**: X=Y=Br) were prepared according to the method described in the literature.[5]

9-[2-(1-Hydroxy-2-trimethylsilylethyl)-1-naphthyl]fluorene (2: X=OH, Y=Si(CH$_3$)$_3$). To a solution of 100.0 mg (0.313 mmol) of *ap*-9-(2-formyl-1-naphthyl)fluorene[3] in 10.0 mL of ether, was added 0.34 mL (0.34 mmol) of 1.0 mol L^{-1} solution of trimethylsilylmagnesium chloride in ether which was available from Aldrich Chemical Co. under a nitrogen atmosphere at once. The mixture was stirred for 80 min with vigorous refluxing and then decomposed with aqueous ammomium chloride. The ether layer was washed with aqueous sodium hydrogencarbonate and dried over magnesium sulfate. After evaporation of the solvent, the product was purified by preparative TLC on silica gel with a 5:7 hexane–dichloromethane eluent and then recrystallized from hexane to give the *ap* form of the desired product in 74% yield. The amount of the magnesium compound was crucial in obtaining the product in a good yield because the excess caused contamination with unidentified materials and the less caused recovery of the unreacted aldehyde. It was recrystallized from acetonitrile, mp 120.0—121.0 °C. Found: C, 81.87; H, 6.94%. Calcd for $C_{28}H_{28}OSi$: C, 82.30; H, 6.91%. ^{1}H NMR (CDCl$_3$) δ=−0.40 (9H, s), −0.05 (1H, app d, J=14.7 Hz), 0.76—0.91 (2H, m), 3.80 (1H, app d, J=11.5 Hz), 6.13 (1H, s), 7.14—7.95 (13H, m), 8.49—8.53 (1H, m).

The *sp*-form, mp 110.0—111.0 °C, was obtained much more easily than the *ap*-form: the usage of 1.0 mol of trimethylsilylmethylmsgnesium chloride per 1 mol of the aldehyde sufficed to give 93% yield of the product. It was recrystallized from methanol. Found: C, 82.29; H, 6.85%. Calcd for $C_{28}H_{28}OSi$: C, 82.30; H, 6.91%. ^{1}H NMR (CDCl$_3$) δ=0.08 (9H, s), 1.40—1.60 (2H, m), 1.97 (1H, br d, J=2.9 Hz), 5.70—5.80 (1H, m), 5.97 (1H, s), 6.38—8.00 (14H, m).

Elimination Reactions. Elimination reactions of **2** were carried out under the same conditions described for the competitive reactions below except that a single rotational isomer was submitted to the reaction conditions. It was confirmed that *ap*- or *sp*-9-(2-vinyl-1-naphthyl)fluorene (**3**)[5] was the exclusive product, the yield being over 95% in every case.

Competitive Debrominations. a) Debromination with Zinc. To a solution of 10.0 mg each of *sp*- and *ap*-**2** (X=Y=Br) in 30 mL of ether were added 3.0 mL of acetic acid and 30 mg of zinc dust and the whole was stirred for ca. 10 min at room temperature. The solid material was removed by filtration and the filtrate was washed with water and then with aqueous sodium hydrogencarbonate. After drying over magnesium sulfate, the solvent was evaporated and the residue was submitted to analysis.

b) Debromination with Lithium Tetrahydridoaluminate. To a solution of 10.0 mg each of *sp*- and *ap*-**2** (X=Y=Br) in 50 mL of tetrahydrofuran was added the specified amount of lithium tetrahydridoaluminate and the mixture was allowed to react for the time interval shown below. The reaction was quenched by cooling the mixture at −78 °C, water was added to the mixture at this temperature, and the temperature was allowed to rise to 0 °C. It was confirmed that the reaction was negligibly slow at −78 °C. Then dilute hydrochloric acid was added to the mixture which was extracted with ether. The ether extract was treated as above. The reaction temperature, the amount of the lithium tetrahydridoaluminate used, and the reaction period are given below.

Temperature/°C	Amount of LiAlH$_4$/mg	Period/min
ca. −15	30	30
0	25	30
40	20	4

c) Debromination with Telluride. A sodium telluride solution was prepared in the following way.[9,13] Tellurium (18 mg or 0.14 mmol) and 240 mg (1.56 mmol) of sodium hydroxymethanesulfinate dihydrate were added to 2 mL of 1 mol L^{-1} aqueous sodium hydroxide and 5 mL of dioxane and the mixture was stirred for ca. 10 min at 70 °C to give a dark red to purple solution. To this solution was added a solution of 10.0 mg each of *ap*- and *sp*-**2** (X=Y=Br) in 3.0 mL of dioxane and the mixture was stirred for 5—6 min at room temperature under a nitrogen atmosphere. The reaction was quenched by introducing air or adding water and ether to the reaction mixture. The formed tellurium was removed by decantation and the product was extracted with ether. The product was treated similarly as above.

Since debromination from 1,2-dibromoethane derivatives with a sulfinate was reported,[14] the dibromide was treated with a sodium hydroxymethanesulfinate solution under the same conditions. However, no sign of formation of the olefin was detected.

Competitive Peterson Reaction. To a solution of 10.0 mg each of *sp*- and *ap*-rotamer of **2** (X=OH, Y=$Si(CH_3)_3$) in 30 mL of tetrahydrofuran was added 4 drops of concentrated sulfuric acid and the mixture was stirred for 15 min at 15 °C or for 30 min at 0 °C. The reaction was quenched by adding aqueous sodium hydrogencarbonate. The treatment of the mixture hereafter was the same with that described above.

Acquisition and Treatment of Data in Competitive Reactions. The reactions were quenched at less than 50% completion of the reaction, if both the isomers were counted, and the unreacted compounds were analyzed by ^{1}H NMR with the use of a JEOL GX270 NMR spectrometer. The relative rates (k_{rel}) were obtained by the following equation. The results shown in Table 1 are the averages of two to three runs.

$$k_{\mathrm{rel}} = \frac{k_{ap}}{k_{sp}} = \frac{[\ln(a_0 - a)/a_0]_{sp}}{[\ln(a_0 - a)/a_0]_{ap}}$$

References

1) For Part XXV, see K. Moriyama, M. Nakamura, N. Nakamura, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **62**, 485 (1989).

2) S. Murata, S. Kanno, Y. Tanabe, M. Nakamura, and M. Ōki, *Angew. Chem., Int. Ed. Engl.*, **20**, 606 (1981); *Bull. Chem. Soc. Jpn.*, **57**, 525 (1984).

3) M. Ōki and R. Saito, *Chem. Lett.*, **1981**, 649: R. Saito and M. Ōki, *Bull. Chem. Soc. Jpn.*, **55**, 3267 (1982).

4) K. B. Wiberg, "Oxidation by Chromic Acid and Chromyl Compounds," in "Oxidation in Organic Chemistry," Part A ed by K. B. Wiberg, Academic Press, New York (1965), pp. 142—178.

5) M. Ōki, J. Tsukahara, Y. Sonoda, K. Moriyama, and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **61**, 4303 (1988).

6) R. A. Y. Jones, "Physical and Mechanistic Organic Chemistry," 2nd ed, Cambridge University Press, Cambridge (1984), pp. 175—195.

7) I. M. Mathai, K. Schug, and S. I. Miller, *J. Org. Chem.*, **35**, 1733 (1970).

8) W. M. Schubert, B. S. Rabinovitch, N. R. Larson, and V. A. Sims, *J. Am. Chem. Soc.*, **74**, 4590 (1952).

9) W. H. Perkin, *J. Chem. Soc.*, **24**, 37 (1871).

10) H. Suzuki and M. Inouye, *Chem. Lett.*, **1985**, 225.

11) D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968).

12) P. F. Hudrlik and D. Peterson, *J. Am. Chem. Soc.*, **97**, 1464 (1975).

13) L. Tschugaeff and W. Chlopin, *Ber.*, **47**, 1269 (1914).

14) R. Otto, *J. Prakt. Chem.*, **53**, 1 (1896): R. Otto and F. Stoffel, *Ber.*, **30**, 1799 (1897).