Pergamon

Tetrahedron Letters, Vol. 35, No. 42, pp. 7759-7762, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01669-0

Dynamic Behavior of 2,2',6,6',9,9'-Hexa-*tert*-butyl-8,8'-dihydro-4,4'-bicyclohepta[def]fluorenylidene, a Substituted Bifluorenylidene

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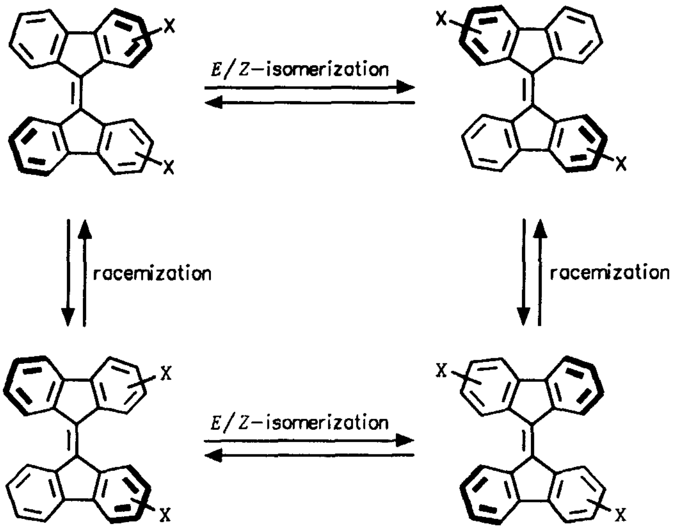
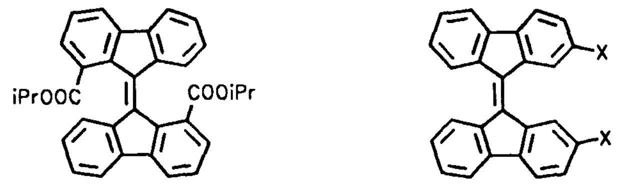
Abstract: The chiral title compound **5** has been synthesized by reductive coupling of 2,6,9-tri-*tert*-butyl-4-oxo-4,8-dihydrocyclohepta[def]fluorene (**4**). The free enthalpy of activation of the racemization of **5** was determined to 62.9 ± 0.8 kJ/mol by variable temperature NMR spectroscopy.

Bifluorenylidenes are twisted around the central double bond, and for the parent compound a twist angle of 43° has been determined by X-ray structure analysis[1]. Due to their non-planarity these compounds are chiral, and besides *E*/*Z*-isomerization a second dynamic process (racemization) is possible. Both processes should occur with all bifluorenylidenes, although they are observable only with appropriately substituted derivatives (Scheme 1).



Scheme 1: Dynamic processes of bifluorenylidenes

Whereas the *E*/*Z*-isomerization of these compounds is well documented[2,3] ($\Delta G^{\neq}$ can be as low as 79 kJ/mol for 1,1'-substituted or benzoannellated bifluorenylidenes), to the best of our knowledge there are only two literature reports on investigations of the racemization of bifluorenylidenes (Figure 1). The first one[2] states $\Delta G^{\neq}_{363}$ = 87.9 ± 0.8 kJ/mol for the racemization of diisopropyl bifluorenylidene-1,1'-dicarboxylate (**1**), but this compound undergoes *E*/*Z*-isomerization with a similar rate, and therefore this value may not be accurate. The second one[4] reports a barrier of 50 kJ/mol for the racemization of the (*Z*)-1,4-butanediyl bifluorenylidene-2,2'-dicarboxylate **2** and a similar barrier for the (*Z*)-bifluorenylidene-2,2'-dicarboxamide **3**.



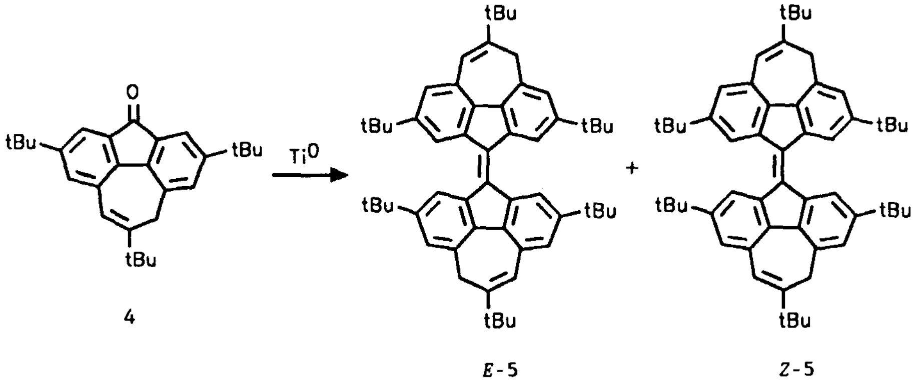
1

2: X = (*R*)-COOCH$_2$CHOMe

3: X = (*R*)-COONHCHMePh

Figure 1

In the course of our investigation of donor substituted cyclohepta[def]fluorenes[5] we synthesized ketone **4**, which could be coupled reductively using low valent titanium according to literature procedures[6] to give the substituted bifluorenylidene **5** (1:1 mixture of *E*- and *Z*-isomer) in nearly quantitative yield[7] (Scheme 2).



Scheme 2

The isomers could be separated by fractional crystallization from *n*-hexane (one isomer[8] [red crystals, mp 275-278°C] is considerably more soluble than the other[9] [red crystals, mp 296-298°C]), and no interconversion was observed after several hours in boiling *n*-hexane (69 °C). Therefore the barrier for *E*/*Z*-isomerization of **5**, as with other bifluorenylidenes unsubstituted at the 1/8-position, must be considerably high[3]. Due to the very small differences between the chemical shifts in the ^{1}H-NMR spectra of *Z*-**5** and *E*-**5** and also between the signals of the hydrogens in the peri positions to the central double bond in each isomer so far it could not be decided which isomer has the *E*- and which the *Z*-configuration.

Compound **5** is a good candidate for the investigation of the racemization of bifluorenylidenes, because **5** exhibits no interfering *E*/*Z*-isomerization at temperatures below 70 °C, and the diastereotopic methylene protons should serve as an ideal probe in ^{1}H-NMR spectroscopy.

At room temperature a quite broad signal for the methylene groups is observed, in accordance with the expected dynamic process[10]. On heating to 50 °C the signal sharpens and becomes a singlet, whereas at -25 °C it is an AB-system with a coupling constant of 15.0 Hz. The coalescence temperature was determined to be T_c = 309 K (36 °C). Numeric line shape analysis[11] afforded a value of $\Delta G^{\neq}_{309} = 62.9 \pm 0.8$ kJ/mol. The free energy of activation shows no significant temperature dependence between 25 and 40 °C, and therefore $\Delta S^{\neq}$ should be small.

It is reasonable that the energy barrier determined for compound **5** is considerably lower than in the case of the 1,1'-disubstituted bifluorenylidene **1**, because the transition state of the racemization is expected to be more sterically hindered in the latter case. Two reasons may account for the lower barrier determined for derivatives of bifluorenylidene-2,2'-dicarboxylic acid: Firstly, these compounds are tethered by an alkyl chain in the case of **2** or (probably) by a hydrogen bond in the case of **3**. The tether is expected to cause a smaller twist angle (compared to unsubstituted bifluorenylidene), thus lowering the barrier for racemization. Secondly, the *tert*-butyl groups in **5**, although not located in the peri position, may be large enough to interfere with each other in the transition state of the racemization, thus raising the energy barrier for this process.

Acknowledgements: This work has been generously supported by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *Degussa AG*, Frankfurt/Main. We thank the *Stiftung Stipendienfonds des Verbandes der Chemischen Industrie* for a Ph. D. fellowship to U. G..

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7. Experimental procedure: 0.35 ml (0.62 g, 3.26 mmol) of titanium(IV) chloride was added to a suspension of 0.43 g (6.52 mmol) of zinc-copper couple in 25 ml of dry THF and the resulting mixture was stirred for 15 min under nitrogen. Then a solution of 0.84 g (2.17 mmol) of 2,6,9-tri-*tert*-butyl-4-oxo-4,8-dihydrocyclohepta[def]fluorene (**4**) in 25 ml of dry THF was added and the mixture was refluxed for 1 h. After cooling to room temp. the mixture was filtered through a short column of alumina and the solvent was evaporated to yield 0.80 g (1.08 mmol, 99 %) of 2,2',6,6',9,9'-hexa-*tert*-butyl-8,8'-dihydro-4,4'-bicyclohepta[def]fluorenylidene (**5**) (1:1-mixture of *E*- and *Z*-isomer according to its ^{1}H-NMR spectrum). The isomers could be separated by fractional crystallization from *n*-hexane and gave correct elemental analyses.
8. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.33$ (s, 54 H, tBu), 3.46 (br., 2 H, 8-H), 3.60 (br., 2 H, 8-H), 6.52 (s, 2 H, 10-H), 7.13 (d, $J = 1.2$ Hz, 2 H, 1-H or 7-H), 7.24 (d, $J = 1.2$ Hz, 2 H, 1-H or 7-H), 8.28 (d, $J = 1.3$ Hz, 2 H, 3-H or 5-H), 8.31 (d, $J = 1.3$ Hz, 2 H, 3-H or 5-H).
9. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.33$ (s, 54 H, tBu), 3.47 (br., 2 H, 8-H), 3.60 (br., 2 H, 8-H), 6.52 (s, 2 H, 10-H), 7.14 (d, $J = 1.1$ Hz, 2 H, 1-H or 7-H), 7.23 (d, $J = 1.1$ Hz, 2 H, 1-H or 7-H), 8.29 (d, $J = 1.2$ Hz, 2 H, 3-H or 5-H), 8.30 (d, $J = 1.2$ Hz, 2 H, 3-H or 5-H).
10. A flipping of the methylene group up and down of the plane of the cyclohepta[def]fluorene system, which would be another possible dynamic process (but not a racemization), was observed neither in the case of **5** nor with **4** or any other derivative of 4,8-dihydrocyclohepta[def]fluorene[5].
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(*Received in Germany* 17 *August* 1994; *accepted* 25 *August* 1994)