Tetrahedron Letters Vol. 22, pp 1097 - 1100
© Pergamon Press Ltd. 1981. Printed in Great Britain

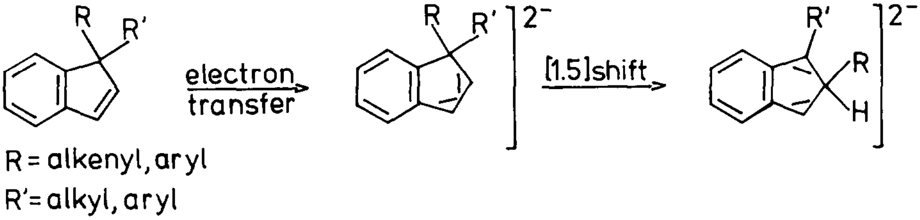
0040-4039/81/0315-1097$02.00/0

HOMO- AND SPIROCONJUGATIVE EFFECTS IN THE SIGMATROPIC REARRANGEMENT OF 1,1'-SPIROBIINDENES

Herbert Kiesele
Fakultät für Chemie der Universität Konstanz
Postfach 5560, D-7750 Konstanz, West Germany

Summary: Due to homoconjugative interactions 2,3-dihydro-1,1'-spirobiindene and 1,1'-spirobiindene yield isomeric benzofluorenes in thermal, photochemical, and electron transfer induced rearrangement.

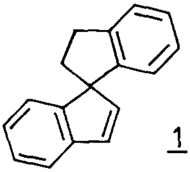
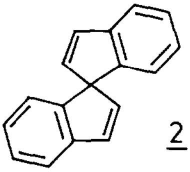
Recently it was shown that the electron transfer induced rearrangement of 1,1-disubstituted indenes proceeds by a dianion[1], following a concerted, suprafacial pathway[2].

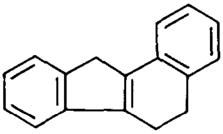


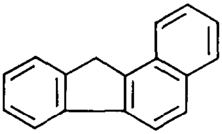
The exceedingly high reaction rates are in sharp contrast to the predictions of Woodward and Hoffmann[3]. Therefore we assumed homoconjugative assistance. An analogous interpretation has been given by McCullough for the "forbidden" photorearrangement of 1-arylindenes[4] (see also [5,6]).

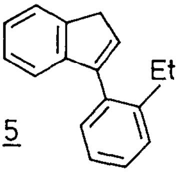
To test the influence of homo- and spiroconjugation on sigmatropic shifts we studied the thermal, photochemical, and electron transfer induced rearrangements of 2,3-dihydro-1,1'-spirobiindene 1 and 1,1'-spirobiindene 2. With competing alkyl-, alkenyl-, and aryl-substituents, a geometry allowing for homo- and spiroconjugative interactions[7], and three electronically very different rearrangement mechanisms, 1 and 2 seemed especially suitable for that purpose. The experimental results are summarized in Table I and will be discussed with the aid of HMO-calculations. The yields listed in Table I refer to chromatographically purified products.

Table I

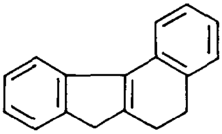
Educt	Products		
	Δ	hν	e⁻
 1	3 79 % 4 7 %	3 74 % 4 13 %	3 28 % 4 48 % 5 15 %
 2	7 92 %	7 61 %	7 90 %

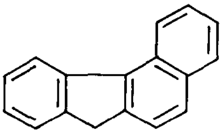

3


4



5


6


7

The "allowed" thermal isomerization of 2,3-dihydro-1,1'-spirobiindene 1, performed at 200°C in diphenylether as a solvent, specifically yields 6,11-dihydro-5H-benzo[a]fluorene 3 by aryl migration and succeeding hydrogen transfer [4,8]. 3 is partially oxidized to 11H-benzo[a]fluorene 4. Just the same products are obtained in the "forbidden" photorearrangement, which was realized by irradiation of 1 in cyclohexane at 10°C with a high pressure mercury lamp. Reduction of 1 with freshly distilled potassium in 1,2-dimethoxyethane[1] and hydrolysis of the resulting fluorenyl salts again produces 3 together with 4, the latter being formed by intermolecular hydrogen transfer[2]. The small amounts of 3-(2-ethylphenyl)-indene 5 arise from a radicalic side reaction which may also produce 6,7-dihydro-5H-benzo[c]fluorene 6 under different conditions[2].

The thermal, photochemical, and electron transfer induced rearrangement of 1,1'-spirobiindene 2 results in isomeric 7H-benzo[c]fluorene 7, the experimental conditions being the same as above. 7 is obtained in high yields by sigmatropic [1.5] shift of the alkenyl group, followed by hydrogen migration or hydrogen abstraction and protonation of the fluorenyl anion (see above). No 11H-benzo[a]fluorene $\underline{4}$ was detected, though $\underline{4}$ is thermodynamically more stable than the sterically hindered 7H-benzo[c]fluorene $\underline{7}$[9].

These findings fully agree with HMO calculations which include homo- and spiroconjugative interactions. The latter are schematically represented in Figure 1 for the dianions of $\underline{1}$ and $\underline{2}$.

Figure 1

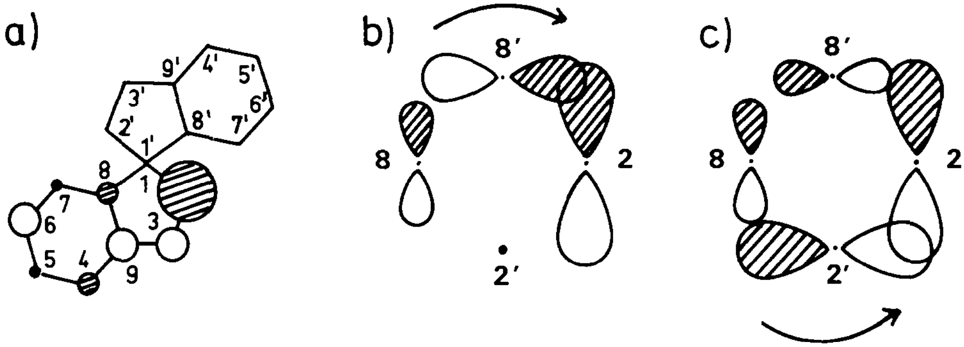


Figure 1a shows the LUMO of one indene moiety in HMO approximation together with the enumeration of the 1,1'-spirobiindene system. The coefficients, characterized by the radius (amount) and the hatching (sign) of each circle, are in good agreement with ESR data of 1,1-disubstituted indene radical anions[10].

Coupling of an indene dianion with a benzene ring or an other (neutral) indene by homo- or spiroconjugative interaction significantly decreases the total π-electron energies of $\underline{1}^{2-}$ and $\underline{2}^{2-}$[11]. Nevertheless, the right-angled orientation of the interacting p-orbitals represents a maximum π-electron energy for the spirobiindene dianions. As is easily shown by first order perturbation theory twisted configurations are more favourable. Because of the very large coefficient in position 2 and the much smaller one in position 8, $\underline{1}^{2-}$ tends towards the intermediate 6,11a-dihydro-5H-benzo[a]fluorene dianion (Figure 1b), whereas $\underline{2}^{2-}$ tends towards the intermediate 6aH-benzo[c]fluorene dianion (Figure 1c). As an example Table II shows some numerical data for the 1,1'-spirobiindene dianion, calculated with standard parameters[12] and varying spiro resonance integrals β'. For the right-angled configuration we assumed $\beta' = 0.2\ \beta_0$, as proposed by Simons and Fukunaga[13]. The twisted configurations, representing the very beginning of the rearrangement, were simulated by a synchronous decrease and increase of β' from $\beta' = 0.20\ \beta_0$ to $\beta' = 0.15\ \beta_0$ and $\beta' = 0.25\ \beta_0$. Even with this cautious parametrization the results clearly show, that the rearrangement towards benzo[c]fluorene is favoured by the dianion $\underline{2}^{2-}$. Analogous results were obtained for all other reactions listed in Table I. The close correlation between migratory aptitude (alkenyl > aryl > alkyl) and homoconjugative interaction strongly supports our starting hypothesis.

Table II Spiroconjugative Interactions in 1,1'-Spirobiindene Dianion $\underline{2}^{2-}$

configuration	spiro resonance integral $[\beta_o]$				total π-electron energy [eV]
	$\beta'_{2,2'}$	$\beta'_{8,8'}$	$\beta'_{2,8'}$	$\beta'_{2',8}$	
right-angled	0.00	0.00	0.00	0.00	-43.6788
right-angled	0.20	0.20	0.20	0.20	-47.1066
twisted towards benzo[a]fluorene	0.15	0.15	0.25	0.25	-47.1731
twisted towards benzo[c]fluorene	0.25	0.25	0.15	0.15	-47.3012

References:

1. H. Kiesele, Angew. Chem. in press
2. H. Kiesele, to be published
3. R.B. Woodward and R. Hoffmann, Angew. Chem. 81, 797 (1969).
4. J.J. McCullough, Acc. Chem. Res. 13, 270 (1980).
5. M.F. Semmelhack, H.N. Weller, and J. Clardy, J. Org. Chem. 43, 3791 (1978).
6. D.J. Field, D.W. Jones, and G. Kneen, J.C.S. Perkin I 1978, 1050
7. A. Schweig, U. Weidner, R.K. Hill, and D.A. Cullison, J. Am. Chem. Soc. 95, 5426 (1973).
8. L.L. Miller and R.F. Boyer, J. Am. Chem. Soc. 93, 650 (1971).
9. M. Orchin and R.A. Friedel, J. Am. Chem. Soc. 71, 3002 (1949).
10. H. Kiesele, Chem. Ber. 111, 1908 (1978).
11. neglecting electron-electron repulsion
12. E. Heilbronner and H. Bock, Das HMO-Modell und seine Anwendung, p. 84, Verlag Chemie GmbH, Weinheim/Bergstr. (1968).
13. H.E. Simmons and T. Fukunaga, J. Am. Chem. Soc. 89, 5208 (1967).

(Received in Germany 26 November 1980)