was added dropwise as fast as possible without excessively vigorous reaction. After 12 h of stirring ether was evaporated and 450 ml of benzene added. The benzene solution was washed successively with 1 M hydrochloric acid, saturated solution of sodium carbonate and water. The solution was dried with Na_2SO_4, benzene evaporated and the residue distilled under reduced pressure. The fraction boiling at *ca.* 120 – 140 °C/2 mmHg solidified and was recrystallized from ethanol to give 67 g (65 %) of 2,3-diphenylpropionitrile, m.p. 55.5 – 56.5 °C (lit. 46 °C,[5] 58 °C[6]).

2-(1,2-Diphenylethyl)-2-imidazoline (4). A mixture of 2,3-diphenylpropionitrile (31.1 g, 0.15 mol) and 2-aminoethylammonium tosylate [3] (34.9 g, 0.15 mol) was heated at 203 – 205 °C until no more ammonia was evolved (*ca.* 2 h). The resulting solid was dissolved in 700 ml of boiling water and 6 g of sodium hydroxide dissolved in 25 ml of water was added. The oily precipitate solidified at 5 °C. It was dried and recrystallized from a mixture of toluene and light petroleum yielding 26.3 g (70 %) of white needles, m.p. 113 – 115 °C. The mass spectrum showed the parent peak at *m/e* 250.

2-[1-(o-Dihydroxyborylphenyl)-2-phenylethyl]-2-imidazoline (2). To a solution of 12 g (0.1 mol) of boron trichloride in 120 ml of ice-cold xylene 20 g (0.1 mol) of finely ground compound *4* was added. The mixture was stirred at 0 °C for 1 h and at room temperature for 2 h. Finely ground anhydrous aluminium chloride (12.8 g, 0.1 mol) was added and the mixture was refluxed with stirring under a slow nitrogen flow for 20 h. To the cooled solution 65 ml of 2 M hydrochloric acid was cautiously added. Stirring was continued until the sticky mass dissolved. Xylene was decanted off and *ca.* 300 ml of acetone was added to the water layer. The lower layer was separated and allowed to stay overnight in a refrigerator. The precipitate was washed with acetone, dried under reduced pressure and recrystallized from a mixture of 50 ml acetonitrile and 6 ml of water. The yield was 10 g (38 %) of white crystals with no definite melting or decomposition point. Anal. $C_{17}H_{19}BN_2O_2$.HCl:B. Neutralization equivalent, obs. 333.5, calc. 330.5.

No parent peak could be found in the mass spectrum of the compound *2*. A pyrocatechol derivative could be easily prepared as in the case of analogous boron compounds.[2] A thick white precipitate which formed when mixing aqueous solutions of the hydrochloride and pyrocatechol was filtered, washed with water and dried in a vacuum desiccator. The mass spectrum showed the parent peak at *m/e* 368.

1. Letsinger, R. L. *Adv. Chem. Ser. 42* (1964) 1.
2. Kankare, J. J. *Ann. Acad. Sci. Fenn. Ser. A 2 160* (1971).
3. Oxley, P. and Short, W. F. J. *J. Chem. Soc.* (1947) 497.
4. Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*, Butterworths, London 1965.
5. Jocelyn, P. C. *J. Chem. Soc.* (1954) 1641.
6. Liebermann, D. and Hengl, L. *Bull. Soc. Chim. Fr.* (1951) 974.

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A Stereoselectively Formed Dimer of 6-Benzoyloxy-6-phenylfulvene

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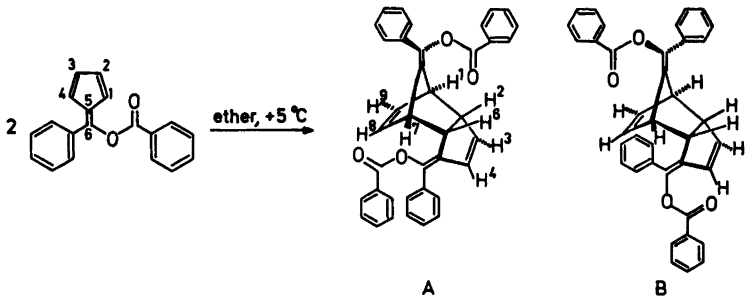
Fulvenes are known to take part in Diels-Alder reactions and other cycloadditions, both as dienes and dienophiles.[1,2] As dienophiles they can react both as 2π and 6π systems.[3] There are, however, few examples of Diels-Alder dimerisations of fulvenes.[2] The loss of the resonance energy in the fulvenes [2] makes these reactions energetically less favourable than the well-known dimerisation of cyclopentadiene. If substituted with different groups at the exocyclic carbon atom, a fulvene could either give a mixture of dimers or stereoselectively give only one dimer in a Diels-Alder reaction. In this paper the formation of such a dimer of 6-benzoyloxy-6-phenylfulvene is reported.

Results and discussion. A cool diethyl ether solution of 6-benzoyloxy-6-phenylfulvene [4] slowly deposits a white precipitate. Analysis and MS show that this precipitate has the same composition as the fulvene. The compound was found to contain one single isomer, whose structure was elucidated by its ^{1}H NMR spectrum (Scheme 1). The spectrum showed the 1/1 ratio of olefinic to tertiary protons as expected for a normal Diels-Alder dimer. Decoupling experiments gave the chemical shifts and coupling constants for the eight protons in the tricyclo [5.2.1.$0^{2,6}$]decadiene ring system. The coupling constants $J_{1,2}$ and $J_{6,7}$ (4.2 Hz) show that the dimer has an *endo* configuration.[5] The remaining structural problem, the configuration at the exocyclic double bonds, was solved by means of a shift reagent. The chemical shifts for the eight protons increased on addition of a shift reagent (Eu fod_3) to the fulvene dimer. A rigorous treatment of the problem is very complex and was not carried out. However, the following qualitative argument should be satisfactory. One can hardly explain the induced shifts without assuming that both ester groups coordinate with the europium salt. Rotation around the single bond between



Scheme 1.

the ester groups and the tricyclic skeleton is essentially free and should decrease the importance of the angle-dependent term [6] on the induced chemical shift. The distance-dependent term [6] should dominate. H-1 and H-7 show the largest induced shifts. Thus the ester groups should be close to these protons as in isomer A, Scheme 1. The induced chemical shifts of the other protons are also consistent with this simple picture.

The selective formation of only one of the many possible dimers of 6-benzoyloxy-6-phenylfulvene could be reasonably well rationalized by frontier orbital arguments. The *endo* selectivity is readily rationalized and well documented in most Diels-Alder reactions, although cycloadditions with fulvenes frequently give *exo* products in thermodynamically controlled reversible reactions.[2,3] The periselectivity, *i.e.* the selective reactivity of the dienophile as a 2π system, using one of the double bonds in the ring, is less readily explained. The lowest unoccupied molecular orbital (LUMO) in fulvenes has a large coefficient at the exocyclic carbon, where the reaction should take place.[3] However, in most cases electrocyclic reactions do not occur at the exocyclic carbon but with one of the double bonds in the ring. Neglecting the possibility of reactions at the exocyclic carbon, one can understand the regiospecificity of the dimerisation. The perturbation of the LUMO and HOMO in the fulvene, caused by the unsymmetrical substitution pattern, should have opposite effects on the coefficients in the LUMO and HOMO. Thus, the new bonds should form between carbons 1 and 4′ or 1′ and 4, resulting in the dimers *A* and *B* (Scheme 1), respectively. Isomer *B* is less likely than isomer *A* for steric reasons. The interaction between one of the phenyl rings and carbons and protons 7 and 8 is substantial in isomer *B*.

Experimental. 6-Benzoyloxy-6-phenylfulvene,[4] prepared from cyclopentadienylcopper tributylphosphine and benzoyl chloride, was kept in the refrigerator (+5 °C) as an ether solution (initially *ca.* 5 %). An almost white precipitate (15–25 %) slowly formed during several weeks, while the red solution turned brown. Thin layer chromatography showed no other major product. Recrystallisation from ethanol or acetic acid gave white crystals (m.p. 155–157 °C). Analysis: C, H. IR (KBr): 1725 (s), 1601 (m), 1495 (m), 1450 (m), 1260 (s), 1218 (m), 1092 (s), 1070 (m), 780 (m), 768 (m), 712 (s), 704 (s), 697 (s) cm^{-1}. UV (ethanol): λ_{max} 283 nm ($\varepsilon = 24\,500$) and 230 (45 000). MS (70 eV): *m/e* 274 (M/2+, 5 %), 106 (8), 105 (100), 77 (38) and 51 (9). The dimer is cleaved on attempted sublimation. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.22 (m), 8.14 (m), 7.71–7.43 (m), 7.36–7.27 (m), 7.15 (m) and 7.05 (m), aromatic protons, 6.51 (d of d, H-4), 6.22 (d of d, H-8), 6.01 (d of d, H-9), 5.95 (d of d, H-3), 3.86 (m, H-7), 3.77 (m, H-6), 3.60 (m, H-2) and 3.41 (m, H-1). The following coupling constants were obtained, mainly from decoupling experiments: $J_{1,2}$ 4.2 Hz, $J_{1,8}$ 0.8, $J_{1,9}$ 3.0, $J_{2,3}$ 2.6, $J_{2,4}$ 1.6, $J_{2,6}$ 6.0, $J_{3,4}$ 5.8, $J_{6,7}$ 4.2, $J_{7,8}$ 3.0, $J_{7,9}$ 0.5 and $J_{8,9}$ 6.0. On addition of Eu(fod)$_3$ linear induced shifts of the protons were observed. A fivefold excess (by weight) of the shift reagent gave the following induced shifts (ppm): H-1 = 0.80, H-2 0.36, H-3 0.06, H-4 0.19, H-6 0.57 H-7 0.70, H-8 0,32 and H-9 0.16.

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1. Bergmann, E. D. *Chem. Rev. 68* (1968) 41.
2. Yates, P. *Adv. Alicyclic Chem. 2* (1968) 59.
3. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*, Wiley, London 1976, and references therein.
4. Lundin, R., Moberg, C., Wahren, R. and Wennerström, O. *Acta Chem. Scand. 26* (1972) 2045.
5. Jackman, L. M. and Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon, Oxford 1969, p. 288.
6. Cockerill, A. F., Davies, G. L. O., Harden, R. C. and Rackham, D. M. *Chem. Rev. 73* (1973) 553.

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