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The Hydroboration of Dibenzofulvenes(1)

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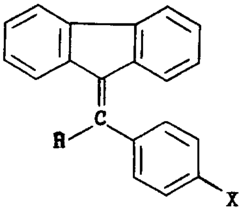
The semicyclic double bond of the fulvenes is in many respects different from other double bonds, undoubtedly due to its polar character[2,3]. We wish to report another unusual property of this double bond in ω-phenyl- or ω,ω-diphenyldibenzofulvenes (I). On treatment of these compounds with diborane, not hydroboration, but reduction takes place, leading to 9-benzyl- or 9-benzhydryl-fluorenes (II), respectively. These compounds are the sole reaction product whether the reaction mixture is decomposed with water, aqueous alkali or aqueous hydrogen peroxide. The reduction that takes place is simply a transfer of hydrogen atoms (or rather of H^- and H^+) to the semicyclic double bond.

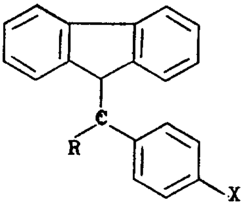
It is surprising that dibiphenyleneëthene (III) is not attacked by diborane, although in most respects it behaves like the fulvenes[2,3]. This difference is perhaps due to the steric structure of this hydrocarbon[2,3,4] which might prevent the initial addition of diborane to the central double bond. One must then conclude that the "hydrogenation" reaction of I to II is a hydrogen transfer within the addition complex formed primarily.

The experimental results with the dibenzofulvenes I, which were prepared according to the literature[5,6] are presented in the table.



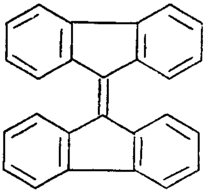
R= H or C_6H_5

I



R= H or C_6H_5

II



III

Procedure

In an atmosphere of nitrogen and at 0°, 5 ml of a 2.7 molar solution of diborane[7)] was added dropwise to a stirred solution of 1 gr of the dibenzofulvene (I) in 25 ml of tetrahydrofuran. After one additional hour at 0° and 10 hours at room temperature, the excess of diborane was destroyed with water and the solution dried with anhydrous potassium carbonate. The latter was removed by decantation and washed twice with 40 ml of methylene chloride, and the combined solutions were evaporated *in vacuo*. The solid residue was recrystallized, as indicated in the table.

The molecular weights of the products were determined by mass spectroscopy.

Dibenzofulvene	Product	Yield	Recryst. from	m.p.(°)	Analysis				
					C, calcd.	C, fd.	H, calcd.	H, fd.	mol. wt.
ω-Phenyl (I, R = H, X = H)	II, R = H, X = H	64	ethanol	134[a]	93.7	93.4	6.2	6.1	
ω-p-Bromophenyl (I, R = H, X = Br)	II, R = H, X = Br	65	ethanol	146	71.6	71.2	4.5	4.3[b]	336
ω-(p-Methoxyphenyl) (I, R = H, X = OCH3)	II, R = H, X =OCH3	60	ethanol	112	88.0	87.7	6.3	6.4	286
2-Bromo-ω-phenyl (as I, R = H, X = H)	9-Benzyl-2-bromofluorene (as II, R = H, X = H)	50	ethanol	115	71.6	72.0	4.5	4.2[c]	336
2-Bromo-ω-(p-methoxyphenyl) (as I, R = H, X = OCH_3)	9-(p-Methoxybenzyl)-2-bromofluorene (as II, R = H, X = OCH_3)	75	ethanol	122	69.0	69.4	4.7	4.6[d]	366
ω, ω-Diphenyl (I, R = C_6H_5, X = H)	9-Benzhydryl-fluorene (II, R = C_6H_5, X = H)	70	ligroin	216[e]	94.0	94.3	6.0	5.8	332

a) See ref. 4.
b) Br, calcd. 24.2; Br, fd. 24.4.
c) Br, calcd. 24.2; Br, fd. 24.3.
d) Br, calcd. 21.9; Br, fd. 22.3.
e) See ref. 8.

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