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Abstract

Full Text

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Decomposition of α-Ferrocenylcarbonium Ions to Fulvenes

Recently it was shown in our laboratory that N-methyl-2-ferrocenylpyridinium hydroxide decomposes in sunlight, as a result of which N-methyl-2-cyclopentadienylidene-pyridinium, cyclopentadiene, and Fe^{2+} are formed ([1]). It was suggested that a positive charge on an atom bonded to the ferrocene molecule weakens the iron–carbon bonds. It was found that triethylferrocenylammonium hydroxide, as well as ferrocenylamine, ethylferrocenylamine, diethylferrocenylamine, acetylferrocene, and its oxime in acidic aqueous solutions decompose in sunlight ([2]).

We have shown that this supposition is correct for certain α-ferrocenylcarbonium ions. The increased ease of their formation from the corresponding carbinols and their ethers is known, owing to the stabilizing influence of the free electron pair of iron ([3]). The carbocations formed from diphenylferrocenylcarbinol and 1,1′-bis-(α-oxybenzhydryl)-ferrocene in acetic acid in the presence of HCl proved to be exceptionally unstable and decomposed within several minutes:

$$\text{1,1'-bis(C(OH)}(C_6H_5)_2\text{)-ferrocene} \xrightarrow{H^+} [\text{ ferrocene bearing } C^+(C_6H_5)_2 \text{ groups in the 1,1' positions }] \longrightarrow 6$$

from the reaction mixture 6,6-diphenylfulvene was isolated.

In the case of diphenylferrocenylcarbinol, an intermediate reaction product was isolated—diphenylferrocenylcarbonium ferrichloride (I), which is decomposed by water in acetone to diphenylferrocenylcarbinol, and by conc. HCl to 6,6-diphenylfulvene.

The corresponding perchlorate of I is diamagnetic (e.p.r.).

Experimental Part

1. **Diphenylferrocenylcarbinol.** To phenyllithium iodide (from 1.05 g of iodobenzene and 0.13 g of magnesium in 15 ml of abs. ether) there is added 1.0 g of benzoylferrocene in 25 ml of abs. benzene; the reaction mixture is stirred for 2 hours, decomposed with 50 ml of 10% NH_4Cl, the organic layer is washed with water, dried over $MgSO_4$, the solvent is distilled off, and the residue is crystallized from heptane. Obtained: 0.98 g (77% of

theoretical) of diphenylferrocenylcarbinol, m.p. 130.5–131.5°. Literature data: m.p. 130–131° (4).

2. **6,6-Diphenylfulvene from diphenylferrocenylcarbinol.** To a solution of 0.2 g of diphenylferrocenylcarbinol in 10 ml of glacial acetic acid there is added one drop of conc. HCl. The orange solution becomes dark green. After 10 min the reaction mixture is extracted with ether and diluted with water. The ether layer is washed with water, 10% KOH, again with water, dried over $MgSO_4$, and the ether is distilled off. The residue is chromatographed in hexane on Al_2O_3. Obtained: 0.07 g (56% of theoretical) of 6,6-diphenylfulvene, m.p. 81.5–82° (from hexane); with an authentic sample it gives no depression of the melting point. Literature data: m.p. 81.5–82° (5).
3. **6,6-Diphenylfulvene from 1,1′-bis-(α-oxybenzylidryl)-ferrocene.** Similarly, from 0.2 g of 1,1′-bis-(α-oxybenzylidryl)-ferrocene (6), with a reaction time of 3–4 min, 0.11 g (65% of theoretical) of 6,6-diphenylfulvene was obtained, m.p. 81.5–82° (from hexane).

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REFERENCES CITED

[1] A. N. Nesmeyanov, V. A. Sazonova et al., DAN, **149**, 1354 (1963).
[2] A. N. Nesmeyanov, V. A. Sazonova, V. I. Romanenko, DAN, **152**, 1358 (1963).
[3] J. N. Richard, E. A. Hill, J. Am. Chem. Soc., **81**, 3484 (1959); E. A. Hill, J. N. Richard, J. Am. Chem. Soc., **83**, 3840, 4216 (1961); E. M. Arnett, R. D. Bashick, J. Org. Chem., **27**, 111 (1962).
[4] R. A. Benkeser, W. P. Fitzgerald, M. S. Melger, J. Org. Chem., **26**, 2569 (1961).
[5] G. Kresze, S. Rau et al., Lieb. Ann., **648**, 51 (1961).
[6] R. Riemschneider, D. Helm, Chem. Ber., **89**, 155 (1956).

Note: Figure translations are in progress. See original paper for figures.