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The formation of 1,2,3,4-tetrafluoronaphthalene in the co-pyrolysis of pentafluorobenzenesulphonyl chloride or pentafluoronitrobenzene with butadiene[1]

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Abstract

Co-pyrolysis of pentafluorobenzenesulphonyl chloride or pentafluoronitrobenzene with butadiene in a flow system at 500–635°C gave 1,2,3,4-tetrafluoronaphthalene. © 1999 Elsevier Science S.A. All rights reserved.

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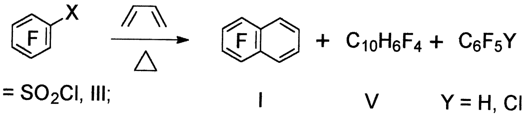
1. Introduction

1,2,3,4-Tetrafluoronaphthalene (I) was obtained by the thermolysis of tetrafluorobenzobicycloocta[2.2.2]triene (II) [1–3]. The latter was synthesized by the interaction of tetrafluorobenzyne with benzene [1–3]. Generation of tetrafluorobenzyne in its turn was realised by the decomposition of pentafluorophenylmagnesium chloride or bromide [1,2], as well as pentafluorophenyl lithium [3].

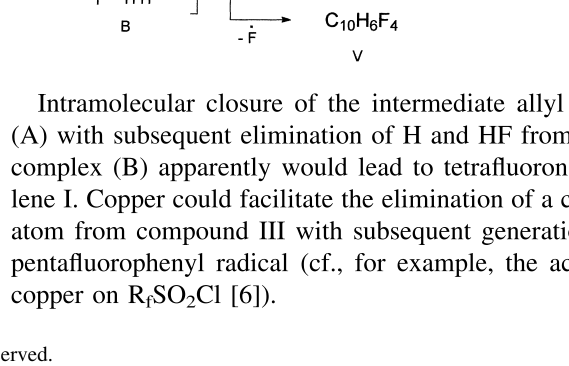
In this work, another route to tetrafluoronaphthalene I is described from the co-pyrolysis of pentafluorobenzenesulphonyl chloride (III) or pentafluoronitrobenzene (IV) with butadiene (see Table 1).



Yield of compound I in the co-pyrolysis of sulphonyl chloride III with butadiene may run to 40%. In this reaction, the formation of $C_{10}H_6F_4$ (V), pentafluorobenzene, chloropentafluorobenzene also occurred as the minor products (yield of each is approximately 2–4%). According to gas chromatography–mass spectrometry (GC–MS) data, the reaction mixture contains unfluorinated products as well. GC–MS data are consistent with 4-vinyl cyclohexene and 1,5-cyclooctadiene.

The co-pyrolysis of compound III with butadiene in the presence of copper or brass also gives tetrafluoronaphthalene I in 30–33% yields (see Table 1).

It is probable that pentafluorophenyl radical, generated by the thermolysis of compounds III and IV [4,5] or the high-temperature interaction of the first with copper (cf. [6]), takes part in the formation of the compound I by reacting with butadiene in the following manner:



Intramolecular closure of the intermediate allyl radical (A) with subsequent elimination of H and HF from the σ-complex (B) apparently would lead to tetrafluoronaphthalene I. Copper could facilitate the elimination of a chlorine atom from compound III with subsequent generation of a pentafluorophenyl radical (cf., for example, the action of copper on R_fSO_2Cl [6]).

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Table 1
Co-pyrolysis of polyfluoroaromatic compounds with butadiene[a]

Run	Starting compound (g)	Temperature (°C)	Time (min)	Metal addition (shaving) (g)	Yield of reaction mixture (g)	Content of (I) according to GLC (%)	Yield of (I) according to GLC (%)
1	III, 6.6	500–550	7	Copper, 12	2.0	75	30
2	III, 8	510–560	25	Brass, 12	2.6	77	33
3	III, 8.4	510–530	20	–	3.1	22	14
4	IV, 8.9	510–555	25	–	3.0	55	20
5	III, 9.9	550–570	21	–	7.1	33	31[b]
6	III, 17.2	550–585	40	–	7.6	63	37
7	III, 22	570–610	60	–	11.8	56	40
8	III, 6.4	620–635	30	–	3.2	38	30

[a] Gas was fed at the rate of 10 l/h.

[b] Solid product, 1.8 g, was filtered off from the reaction mixture. According to GLC content of I is 96%.

Tetrafluoronaphthalene I was also obtained by pyrolysis of compound II in a flow system at 530°C in accordance with [3]. IR-, ^{19}F, ^{1}H, ^{13}C NMR spectra of compound I obtained by the two methods agree with each other. Formula $C_{10}H_6F_4$[2] is ascribed on the basis of mass spectrometry data (found: M 202.0363; calculated: M 202.0406) of the mixture of compounds I and V which was isolated by distillation of reaction mixture (run 7, Table 1).

The ^{19}F, ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP-200SY and Bruker AC-200 instruments operating at 188.2, 200 and 50.3 MHz in $CDCl_3$ (10% solution of individual compounds). Internal standards were hexafluorobenzene and hexamethyldisiloxane. The IR spectra were recorded on a UR-20 instrument for solid samples as KBr pellets at a concentration of 0.25%. Molecular weights and molecular formulae of compounds were determined mass-spectrometrically on a Finnigan-MAT-8200 instrument. The nominal energy of ionizing electrons was 70 eV. GLC analyses were performed on a LHM-72 instrument with a thermal conductivity detector with a linear temperature program of 10°C/min. The carrier gas was helium with a flow rate of 10 ml/min. The stainless steel columns 4000×4 mm in dimensions (the solid carrier chromosorb W) with (a) silicon SKTFT-50, (b) silicon SKTFT-803. The ratio of stationary phase to solid carrier was 15:100, column temperature 50–270°C, detector temperature 250°C. GC–MS analyses were performed with a Hewlett-Packard 5890/II apparatus (70 eV) using a 30 m capillary column coated with an HP5 oil. A typical experimental procedure was as follows. The starting polyfluoroaromatic compound was passed dropwise in a stream of butadiene through a quartz tube (400×20 mm) placed into an electric oven which was heated to certain temperature (see Table 1). The reaction mixture was distilled with steam, treated by CH_2Cl_2, dried over $MgSO_4$ and analysed by GLC methods. The results of experiments are given in Table 1.

Compound I was isolated from the reaction mixture after evaporation of the solvent. The precipitate was filtered off and recrystallized from ethanol, m.p. 110–111°C (m.p. 110–111°C [7]). Found (%): C 60.0; H 2.0; F 38.5; Mol. weight 200.0248 (MS), $C_{10}H_4F_4$. Calculated (%): C 60.0; H 2.0; F 38.0; Mol. weight 200.0249. ^{19}F NMR (δ, ppm): F^1 11.09; F^2 2.44 (F^1 11.82; F^2 3.05 [8]). ^{1}H NMR (δ, ppm): H^5 7.95; H^6 7.53 (H^5 8.05; H^6 7.64 [8]).

Acknowledgements

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[2] Description of the structure will be published.