

Sulfide Pyrolysis, I

Many Membered Hydrocarbon Cycles via Thermal Extrusion of Sulfide Sulfur

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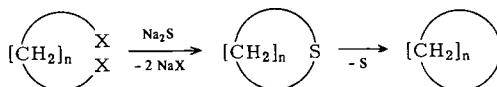
Sulfid-Pyrolyse, I

C–C-Bindungsknüpfung durch thermische Sulfidschwefel-Extrusion

Das Sulfid **1** konnte durch unkatalysierte Thermolyse bei 650°C unter Austritt des Schwefelatoms bei gleichzeitiger Rekombination der benzylicischen C-Atome in den cyclischen Kohlenwasserstoff **2** übergeführt werden.

Sulfone pyrolysis has come to be a useful tool for C–C bond formation in medium and large rings during the last few years¹⁾. As a rule, the sulfones to be pyrolysed are obtained by oxidation of the corresponding sulfides. A direct, thermal removal of the sulfur from the sulfide would make the oxidation step seem superfluous. However, such a sulfide sulfur extrusion has up to date only been successful in a few cases where it is carried out *photochemically* in the presence of thiophilic phosphorus compounds^{2–4)}.

We looked for suitable molecular skeletons from which the sulfide sulfur could be purely *thermally* extruded without necessitating any intermediate oxidation to the sulfone or photochemical excitation. Our purpose was to carry out the formation of C–C bonds in such systems also containing photochemically sensitive groups or groups unstable towards oxidation. Thus, by way of a nucleophilic substitution with Na₂S or dithiolates¹⁾, which has proved its usefulness as opposed to the tedious one via metallorganic reagents or intermediates, new C–C bonds could be synthesized:



An appropriate molecular skeleton was furnished by the 1,8-diarylnaphthalinophane system⁵⁾, which proved to be useful during sulfone pyrolysis reactions. Though in the mass spectrum no significant M⁺ – S peak of the double benzylic sulfide **1** is found, in contrast to the M⁺ – SO₂ peak of the corresponding sulfone⁶⁾, we noted a smooth sulfide extrusion from **1** with subsequent

¹⁾ For references see: J. Grütze and F. Vögtle, Chem. Ber. 110, 1978 (1977); see also: F. Vögtle and L. Rossa, Tetrahedron Lett. 1977, 3577.

²⁾ J. Bruhin and W. Jenny, Tetrahedron Lett. 1973, 1215.

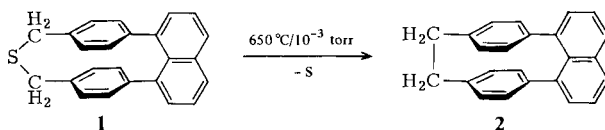
³⁾ V. Boelkeheide, I. D. Reingold, and M. Tuttle, J. Chem. Soc., Chem. Commun. 1973, 406.

⁴⁾ W. Rebařka and H. A. Staab, Angew. Chem. 85, 831 (1973); Angew. Chem., Int. Ed. Engl. 12, 776 (1973).

⁵⁾ W. Bieber and F. Vögtle, Angew. Chem. 89, 199 (1977); Angew. Chem., Int. Ed. Engl. 16, 175 (1977).

⁶⁾ Compare here with: R. C. Dougherty, Top. Curr. Chem. 45, 93 (1974).

C—C recombination to **2** with the help of the combined Curie point ⁷⁾ or pyroprobe ^{® 8)} pyrolyzator and gas chromatograph (see experimental part).



The above sulfide thermolysis could likewise be carried out on a preparative scale in pyrolysis apparatus. Temperatures of about 650°C and low pressures (10^{-3} torr) proved to be suitable. Under these conditions, **2** was obtained in a 5–10% yield after one passage of sulfide **1** through the pyrolysis ring ovens, 80–90% of the latter being recovered unchanged. Almost complete conversion may be achieved by repeated pyrolysis. Higher pyrolysis temperatures led to uncontrolled decomposition of **1**.

Any possible intermediate formation of the corresponding sulfone upon oxidation of the sulfide **1** by the air-oxygen in the pyrolysis apparatus under the prevailing thermolysis conditions was excluded: pyrolysis in apparatus flushed with nitrogen or argon led to the same results.

In order to check whether the thermal extrusion of the sulfide sulfur is facilitated by sulfur acceptors (e. g. by prior complex formation at the sulfur atom), we mixed sulfide **1** with metals and thiophilic phosphorus compounds under various conditions. However, vacuum pyrolysis of **1** did not give any appreciable improvement when mercury or triphenylphosphine vapour was present.

It is to be expected that the above thermal sulfide pyrolysis will also find application in other suitable molecular systems.

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Experimental Part

[2.0.0](1,4)Benzeno(1,8)naphthalino(1,4)benzenophane (**2**) by sulfide pyrolysis of 2-thia[3.0.0]-(1,4)benzeno(1,8)naphthalino(1,4)benzenophane (**1**): Prior to pyrolysis, the ring compound **1**, obtained by cyclisation of 1,8-bis[4-(bromomethyl)phenyl]naphthalene with Na_2S in *tert*-butyl alcohol, is thoroughly freed of any possible trace amount of the corresponding sulfone by column chromatography (silica gel⁹⁾, toluene).

Pyrolysis-gas chromatography (**1** → **2**): The pyrolysis apparatus used — Curie point ⁷⁾ and pyroprobe ^{®-190 8)} — were each directly connected to the injector of the gas chromatograph ¹⁰⁾. At constant temperatures between 450 and 900°C, 0.1–1 mg of **1** was successively pyrolysed during 10 s (intervals of 50°C being used). The retention times (column temperature 290°C; velocity of the carrier gas 30 ml/min) were 11.3 min for **2** and 25.5 min for **1**.

Preparative pyrolysis (**1** → **2**): 12 mg of **1** were pyrolysed in a quartz tube at 650°C/ 10^{-3} torr ¹¹⁾ in an apparatus equipped with several ring ovens¹⁾. Separation of sulfide **1** from accompanying unchanged hydrocarbon **2** in the sublimate was effected by column chromatography (silica gel): with *n*-hexane as eluant, 0.6–1.2 mg (5–10%) of **2** was at first obtained, subsequent use of toluene yielded 9–11 mg of **1**. **2** was unequivocally characterized by its melting point, mixed melting point, gas chromatographic retention time and ¹H-NMR data comparison with authentic samples⁵⁾.

⁷⁾ Fa. Fischer, D-5309 Meckenheim.

⁸⁾ Chemical Data Systems, Inc., Oxford, Pennsylvania, U.S.A.

⁹⁾ Silica gel Woelm, grain size 0.063–0.1 mm.

¹⁰⁾ F-22, Perkin-Elmer & Co. GmbH, D-7770 Überlingen; columns used: silicone oil OV17/chromosorb G, AW-DMCS, 80–100.

¹¹⁾ Vacuum pump: PD 170 AZw, Leybold-Heraeus GmbH & Co. KG, D-5000 Köln.