# Synthesis of Benzothiet from Benzo[*b*]thiophen 1,1-dioxide

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*Summary* Benzothiet, the parent member of a new class of compounds, has been obtained by the vacuum flash pyrolysis of benzo[*b*]thiophen 1,1-dioxide; it is fairly stable at room temperature but dimerizes above 100 °C giving 6*H*,12*H*-dibenzo[*b*,*f*][1,5]dithiocin.

Although thiet dioxides have been extensively investigated,[1] attempts to prepare thiets failed[2] until recently when Meier *et al.*[3] prepared methyl benzothiet-2-carboxylate by photolysis of 3-diazobenzo[*b*]thiophen-2(3*H*)-one. We here report a convenient way of synthesizing the parent benzothiet. Flash vapour-phase pyrolysis (1000 °C, $5 \times 10^{-2}$ mmHg) of benzo[*b*]thiophen 1,1-dioxide (**4**) through a quartz tube (20 × 2 cm) gives benzothiet (**2**) in *ca.* 45% yield,† together with some benzene (8%), benzo[*b*]thiophen (2%), and a trace of benzo[*b*]furan;‡ $CO_2$ (28% yield)

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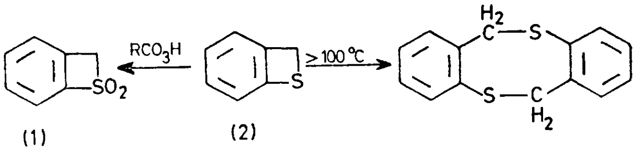
† In order to determine the yield of benzothiet (**2**) by n.m.r. spectroscopy, we condensed the mixture of the pyrolysis products in a cold trap containing a weighed amount of 1,3,5-trimethoxybenzene dissolved in $CDCl_3$. After removal of the solvent, benzothiet was further concentrated to a purity of *ca.* 70% (main contaminant benzene) by means of bulb-to-bulb distillation.

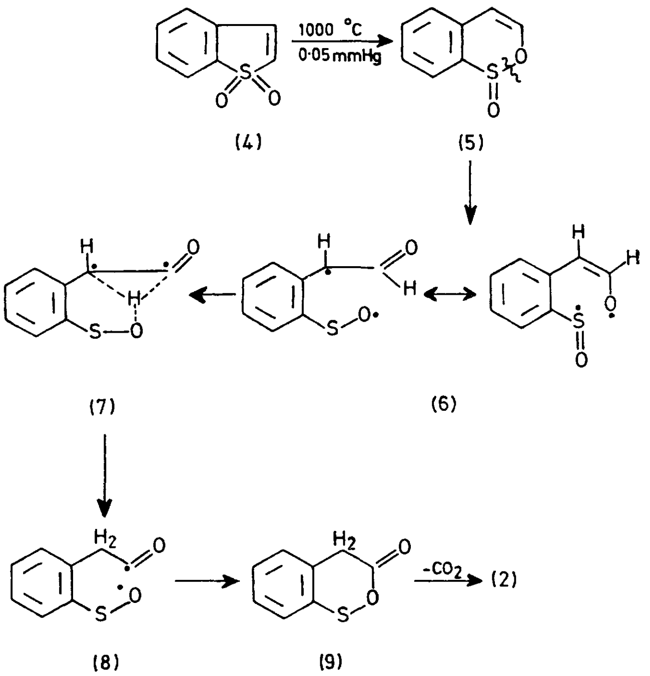
‡ Usually, furans are the main products obtained on pyrolysis of substituted thiophen 1,1-dioxides; ref. 6.

and some $SO_2$ (3%) were also identified. Benzothiet was identified on the basis of its spectral properties: $^{1}$H n.m.r.: $\delta$ 4·28 (s) and 6·8—7·8 (m); $^{13}$C n.m.r.: $\delta$ 36·43 p.p.m. (s; changes into t on partial decoupling), 121·0, 122·7, 123·9, 128·5, 139·6, and 144·8 p.p.m. (all s); i.r.: *ortho*-substituted aromatic bands, and 735 br cm$^{-1}$ (C–S); mass spectrometry: $M^{+}$ at *m/e* 122·0190 (84%) ($C_7H_6S$ 122·0186); *m/e* 121 (100%). The structure assignment was supported by oxidation of (**2**) with peracid to the known[4] benzothiet 1,1-dioxide (**1**).



(1) (2) (3)

In contrast to non-annulated thiets, which are too unstable to be isolated,[5] benzothiet is stable for several days at room temperature. At higher temperatures (> 100 °C) it dimerizes to 6*H*,12*H*-dibenzo[*b*,*f*][1,5]dithiocin (**3**), apparently *via* $H_2C$–S bond rupture. The structure of (**3**) was assigned on the basis of the following spectral data: $^{1}$H n.m.r.: $\delta$ 4·14, broadened singlet which showed further broadening on cooling (no exchange with $D_2O$); mass spectrometry: $M^{+}$ 244·0385 ($C_{14}H_{12}S_2$ 244·0380); *m/e* 121 (100%), and 104 ($C_8H_8$)(< 2%); *m/e* 140 ($C_6H_4S_2$) absent; i.r.: *ortho*-substitution patterns, C–S stretching at 730 cm$^{-1}$.



Scheme.

Benzothiet formation is suggested to proceed *via* the sequence of reactions in the Scheme. The sulphone–sulphite rearrangement and subsequent rupture of the O–S bond to give the diradical (**6**) are the same as those occurring in furan formation.[6] The rather unusual[7] 1,2-hydrogen shift (**6** → **8**) is believed to involve a transfer of the hydrogen atom *via* the neighbouring sulphenoxyl radical.§ Intramolecular recombination then leads to compound (**9**), which upon loss of $CO_2$ affords (**2**). The pyrolysis of different but related thiophen dioxides, such as dibenzothiophen 1,1-dioxide, takes a different course, leading to furan formation, because of the lack of transferable hydrogen in the 2-position.

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§ The diradical (**7**) is not likely to exist as a free diradical, since in that case keten formation would have to be expected. In our opinion the sulphenoxyl radical only mediates the transfer of hydrogen. In this connection it is worth mentioning that sulphenic acids such as (**7**) are extremely good donors of hydrogen atoms even to alkoxyl radicals, see ref. 8.

[1] J. E. McCoskie, P. L. Chang, T. R. Nelsen, and D. C. Dittmer, *J. Org. Chem.*, **1973**, **38**, 3963, and refs. cited therein.

[2] D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, 1962, **84**, 399.

[3] E. Voigt and H. Meier, *Angew. Chem.*, 1976, **88**, 94.

[4] D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, 1967, **32**, 3872.

[5] D. C. Dittmer, K. Takanishi, and F. A. Davis, *Tetrahedron Letters*, **1967**, **4061**. See also ref. 2.

[6] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, 1966, **88**, 2836. See also W. J. M. van Tilborg and R. Plomp, *Rec. Trav. chim.*, in the press.

[7] P. de Mayo, 'Molecular Rearrangements,' Wiley, New York, 1963, p. 427.

[8] P. Koelewijn and H. Berger, *Rec. Trav. chim.*, 1972, **91**, 1275.