

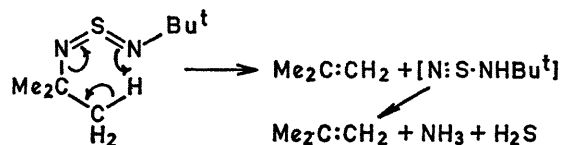
The Pyrolysis of Sulphur Di-imides

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Summary The pyrolysis of diphenylsulphur di-imide gave azobenzene while di-*t*-butylsulphur di-imide pyrolysed to 2-methylpropene, ammonia, and hydrogen sulphide.

We report a new, potentially useful, two-step olefin synthesis from dialkylsulphur di-imides. When di-*t*-butylsulphur di-imide was pyrolysed in a sealed tube at 265° for 24 hr., approximately 60% 2-methylpropene was formed (Scheme). Sulphur di-imides are easily obtained from the reaction of a primary amine and either sulphur dichloride,¹ sulphur tetrafluoride,² or ditolylsulphonylsulphur di-imide.³



SCHEME

The pyrolysis of diphenylsulphur di-imide at 200° for 0.5 hr. gave 66% azobenzene. However, a detailed examination of the products from pyrolysis of di-*t*-butylsulphur di-imide at 265° revealed small amounts of carbon disulphide, 2-methyl-2-propanethiol, and 2,2,4,4-tetramethyl-3-thiapentane in addition to isobutene, ammonia, and hydrogen sulphide (Table 1).

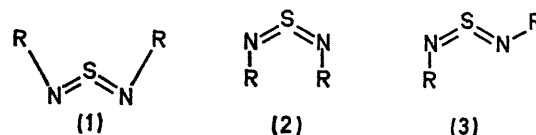
TABLE 1. Pyrolysis of di-*t*-butylsulphur di-imide

<i>T</i>	<i>t</i> hr.	% Me ₂ C=CH ₂	% NH ₃	% H ₂ S
200°	24	0	0	0
265	4	41	26	28
265	24	59	40	34
350	2	47	29	35

Bis-azo-2-methyl-2-propane or its decomposition products might be expected from the pyrolysis of di-*t*-butylsulphur

di-imide. However, the pyrolysis of bis-azo-2-methyl-2-propane gave mainly molecular nitrogen and 2-methylpropane. We found no nitrogen or isobutane, and concluded that bis-azo-2-methyl-2-propane was not formed in the pyrolysis of di-*t*-butylsulphur di-imide. Clearly, the 2-methyl-2-propyl radical is not an intermediate in the pyrolysis since this radical⁴ disproportionates to isobutane and a trace of isobutene. However, the 2-methyl-2-propyl cation may be an intermediate or the reaction may be concerted (Scheme).

The possibility of geometrical isomers for sulphur



di-imides has not been considered in the past. If nitrogen and sulphur are *sp*² hybridized then there are three potential isomers—*cis*, *syn*-(1), *cis*, *anti*-(2), and *trans*-(3). When R is large, such as 2-methyl-2-propyl, models show isomer (2) to be highly strained. Only isomer (3) is consistent with a concerted reaction. However, the ¹H n.m.r. spectrum¹ of di-*t*-butylsulphur di-imide shows only one peak at δ 1.38, a fact which is consistent with isomer (1) and not with (3). The possibility of interconversion between isomers (1) and (3) is being studied at various temperatures. The mass spectrum of di-*t*-butylsulphur di-imide had an *M* - 56 (*m/e* = 118) and *M* - 112 (*m/e* = 62) peak. These peaks correspond to the ions [Me₃C-NH-S≡N]⁺ and [H-N=S=N-H]⁺, respectively. These ions arise from a concerted cyclic transition state and since the temperature of the ion source is 250° isomer (3) must be capable of existence at this temperature.

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