The Pyrolysis of Sulphur Di-imides

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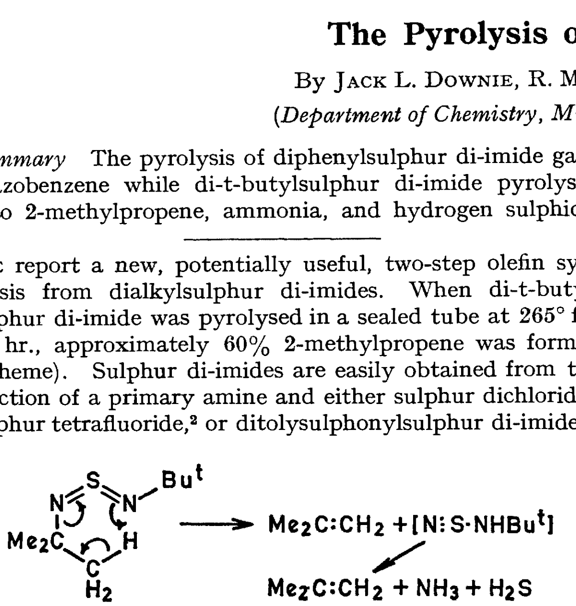
Summary The pyrolysis of diphenylsulphur di-imide gave azobenzene while di-t-butylsulphur di-imide pyrolysed to 2-methylpropene, ammonia, and hydrogen sulphide.

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 ditolysulphonylsulphur di-imide.[3]



SCHEME

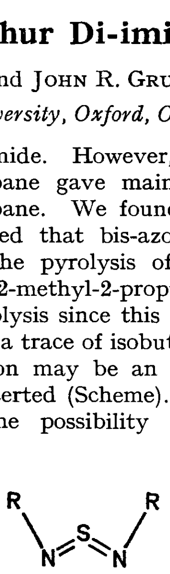
The pyrolysis of diphenylsulphur di-imide at 200° for 0·5 hr. gave 66% azobenzene. However, a detailed examination of the products from pyrolysis of di-t-butylsulphur di-imide at 265° revealed small amounts of carbon disulphide, 2-methyl-2-propanethiol, and 2,2,4,4-tetramethyl-3-thiapentane in addition to isobutene, ammonia, and hydrogen sulphide (Table 1).

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

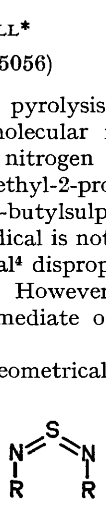
T	t hr.	% $Me_2C{=}CH_2$	%NH_3	%H_2S
200°	24	0	0	0
265	4	41	26	28
265	24	59	40	34
350	2	47	29	35

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-methyl propane. 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 radical[4] 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).

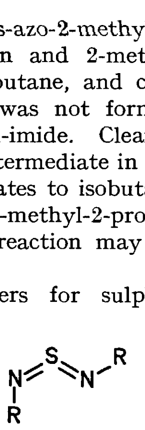
The possibility of geometrical isomers for sulphur di-imides has not been considered in the past. If nitrogen and sulphur are sp^2 hybridized then there are three potential isomers—*cis, syn*-(**1**), *cis, anti*-(**2**), and *trans*-(**3**). When R is large, such as 2-methyl-2-propyl, models show isomer (**2**) to be highly strained. Only isomer (**3**) is consistent with a concerted reaction. However, the ^1H n.m.r. spectrum[1] 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 $|Me_3C{-}NH{-}S{\equiv}N|^+$ 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.



(1)



(2)



(3)

(*Received, January 15th,* 1970; *Com.* 066.)

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