Pyrolysis of Bicyclo[2.2.1]heptane-2-thiols: Evidence for a Carbene Intermediate in a Thermal Hydrogen Sulphide Elimination

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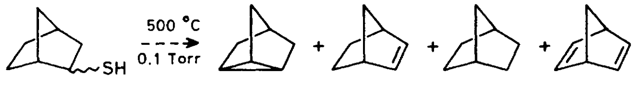
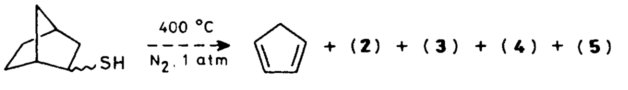
Pyrolysis of *endo*- and *exo*-bicyclo[2.2.1]heptane-2-thiols yields tricyclo[2.2.1.$0^{2,6}$]heptane and bicyclo[2.2.1]hept-2-ene *via* competing carbene and radical mechanisms.

The thermal chemistry of thiols has been largely ignored in spite of the occurrence of thiols in crude petroleum. Hydrogen sulphide and alkenes have been identified as reaction products in previous investigations of alkane thiol thermal reactions.[1] A variety of reaction mechanisms have been proposed to account for these transformations.[2] Recent kinetic studies of thiol thermal reactions have not clearly identified the reaction mechanism; radical and concerted 1,2-elimination mechanisms were proposed for the pyrolysis of 2-methylpropane-2-thiol.[3,4] This communication describes the reaction products



	(2)	(3)	(4)	(5)
(1x)	74%	23%	1%	2%
(1n)	75%	23%	1%	1%

Scheme 1. Yields are percentages of the pyrolysis mixture at 5% thiol conversion.



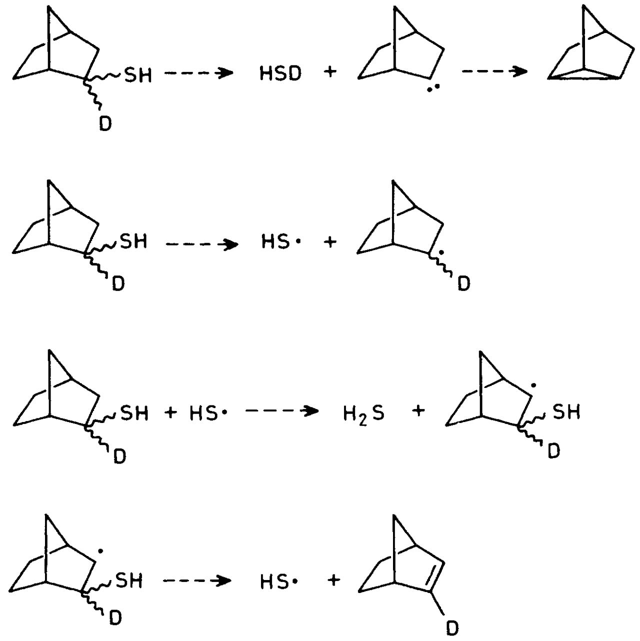
(1x)	51%	16%	27%	2%	4%
(1n)	53%	13%	26%	2%	4%

Scheme 2. Yields are percentages of the pyrolysis mixture at 5% thiol conversion.

from the pyrolysis of the isomeric bicyclo[2.2.1]heptane-2-thiols and experiments which indicate that these products are formed by competing reaction mechanisms.

Flash vacuum pyrolysis of *exo*-bicyclo[2.2.1]heptane-2-thiol (**1x**) and *endo*-bicyclo[2.2.1]heptane-2-thio (**1n**) in a well-seasoned quartz apparatus yields tricyclo[2.2.1.0^{2,6}]heptane (**2**) and bicyclo[2.2.1]hept-2-ene (**3**) as major products (Scheme 1). Products were identified by comparison of mass spectra obtained from gas chromatography–mass spectrometry analysis of the pyrolysis mixture with mass spectra obtained from the literature or from authentic samples. No evidence was obtained for formation of bicyclo[2.2.1]heptyl sulphides or disulphides. Higher thiol conversions were observed at higher pyrolysis temperatures, but the quantity of minor products in the pyrolysis mixture also increased. The similar product distribution observed in the pyrolysis of (**1x**) and (**1n**) indicated that the products were derived from common intermediates rather than from concerted elimination of hydrogen sulphide from (**1x**) and (**1n**).

Flow pyrolysis of benzene solutions of (**1x**) and (**1n**) in a nitrogen stream yielded cyclopentadiene and the same hydrocarbon products observed in the flash vacuum pyrolysis (Scheme 2). The change in product distribution was a result of the longer contact times in the flow system rather than changes in the surface area and surface composition of the pyrolysis apparatus. Thiol conversions were 5% under these conditions. Cyclopentadiene was a pyrolysis product of (**3**). The flow pyrolysis product distribution is sensitive to added reagents. Flow pyrolysis of benzene solutions of (**1x**) or (**1n**) and benzenethiol, an efficient hydrogen atom donor, resulted in increased yields of (**4**) and decreased yields of (**3**) without affecting the yield of (**2**). Flow pyrolysis of benzene solutions of (**1x**) or (**1n**) and azoisobutyronitrile, an efficient radical reaction initiator, resulted in increased yields of (**3**) without affecting the yield of (**2**). These results are consistent with formation of (**3**) *via* a radical chain mechanism which can be initiated by added radical sources or quenched by hydrogen atom donors.[3] The intermediate responsible for the formation of (**2**) was trapped when methanol solutions (**1x**) or (**1n**) were subjected to flow pyrolysis. The yield of (**2**) decreased and *exo*-2-methoxybicyclo[2.2.1]heptane was identified as a pyrolysis product. Methanol is stable under these pyrolysis conditions. These results are consistent with 1,1-elimination of hydrogen sulphide from (**1x**) or (**1n**) to form bicyclo-[2.2.1]heptan-2-ylidene which rearranges to (**2**) or inserts into the oxygen–hydrogen bond of methanol.[5]



Scheme 3

The presence of radical and carbene intermediates in the reaction was supported by the results of a deuterium labelling study. Lithium aluminium deuteride reduction of bicyclo[2.2.1]heptane-2-thione gave an 80:20 mixture of [$^2H_1$]-(**1n**) and [$^2H_1$]-(**1x**) with deuterium located at carbon-2. Isotopic incorporation was greater than 95%. The isomer mixture was subjected to flash vacuum pyrolysis and the reaction products were analysed by gas chromatography–mass spectrometry. Compound (**3**) was greater than 85% $^2H_1$ while (**2**) was essentially $^2H_0$. These results require the carbon-2 carbon–hydrogen bond to be broken during the formation of (**2**) but to remain intact during the formation of (**3**). A mechanism which accommodates all the experimental evidence is shown in Scheme 3.

The mechanism of thiol thermal reactions is dependent on the reaction conditions. Fast, radical-chain hydrogen sulphide elimination mechanisms dominate thiol thermal reactions in static or flow pyrolysis systems which support relatively high concentrations of reactants and radical intermediates.[3] Competing hydrogen sulphide elimination mechanisms are kinetically insignificant in the presence of rapidly propagating radical chains and can only be detected by varying reaction conditions.

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