

LASER INDUCED SYNTHESIS :  
SELECTIVE FORMATION OF CYCLOHEXENE EPISULPHIDE FROM MOLECULAR SULPHUR S<sub>8</sub>

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Abstract : 1,2-Epithiocyclohexane was obtained selectively by irradiation of a mixture of cyclohexene and sulphur with a pulsed laser (266 nm).

It is known that the episulphide ring, like that of the epoxides, opens easily in various conditions, offering interesting opportunities for synthesis.

1,2-Episulphides cannot be synthesised by simple heating of an alkene and molecular sulphur because of their instability at the temperature required to obtain atomic sulphur in useful abundance.

Classically, these compounds are obtained by transformation of oxiranes<sup>(1)</sup>. In photochemistry, the formation of 1,2-epithioalkanes from ethylenic compounds and various sources of atomic sulphur<sup>(2)</sup> (for example, carbon disulphide, isothiocyanate derivatives, thiotriazols and carbon oxysulphide) has been studied.

In the case of COS, photolysis in the vapour phase ( $\lambda$  max = 225 nm) gives atomic sulphur in a singlet state <sup>1</sup>D or in the ground state <sup>3</sup>P. It has been demonstrated that atomic sulphur in the singlet state can lead to insertions in the C-H bonds or to the formation of 1,2-epithio compounds, whereas atomic sulphur in the triplet state leads only to the latter. This greater selectivity of S(<sup>3</sup>P) atom has been demonstrated notably through the use of carbon dioxide<sup>(3)</sup> to trap S(<sup>1</sup>D) atom and consequently to inhibit the formation of thiols.

The synthesis of episulphides from molecular sulphur by irradiation using a mercury lamp has only been reported in the case of caryophyllene and humulene<sup>(4)</sup>. In this case, we estimated that the quantum yield was less than 10<sup>-4</sup>.

More recently, it has been shown that ethylene episulphide can be produced by laser irradiation of a mixture composed of molecular sulphur and ethylene<sup>(5)</sup>, a mechanism of formation of S(<sup>3</sup>P) being suggested.

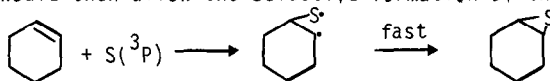
The object of the present work is to study the action of molecular sulphur S<sub>8</sub> on cyclohexene, in a heterogeneous solid-liquid phase, with laser interaction.

The laser used is a Nd-YAG delivering pulses of 13 nsec duration and 25 mJ energy at 266 nm with a beam diameter of 7 mm. Irradiation is carried out in a cylindrical cell made of Suprasil (length : 26 mm, diameter : 10 mm) placed vertically, the laser beam being directed from outside through the bottom optical window coated with a 1 mm (approx.) layer of sulphur S<sub>8</sub>.

After irradiation, the formation of 1,2-epithiocyclohexane is noted. The analysis was carried out using the GC/MS coupling ; the nature of the product is confirmed by comparison with a genuine sample. The reaction appears to be selective, as no thiol formation is detectable.

The quantum yield of the conversion appears to be high. However, its experimental value ( $\sim 0.15$ , i.e. 15 molecules formed per 100 photons) is still lower than the real value, since marked episulphide instability is observed on irradiation at 266 nm. This is clearly responsible for an equilibrium between its formation and degradation, leading to a chemical yield of only 1.1%. A promising optimisation of the latter may thus be expected, for instance, using a flowing system.

In view of the high degree of absorption of S<sub>8</sub> molecules at 266 nm<sup>(6)</sup> and the characteristics of the light source (peak power : 5 MW/cm<sup>2</sup>), it is suggested that a stepwise absorption process is involved, leading to S(<sup>3</sup>P) atom. The interaction of atomic sulphur in the triplet state with cyclohexene would then allow the selective formation of the episulphide by way of a biradical<sup>(3)</sup>:



The episulphide can then absorb one or several photons to give back cyclohexene and sulphur in an undetermined state.

This formation of cyclohexene episulphide appears to be a new and promising method of synthesis. The simplicity of the conditions, the use of a very cheap reagent (molecular S<sub>8</sub>) and the selectivity noted suggest that this reaction could be used on a series of alkenes and on more complex molecules where a selective reaction is extremely useful. The application of this synthesis to paramenthadienic hydrocarbons, for example, appears to be of particular interest, leading in a second stage to compounds with organoleptic properties.

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