Photolysis of Diazocyclopentadiene in Alkyl Sulphides. Formation of Sulphonium Cyclopentadienylides

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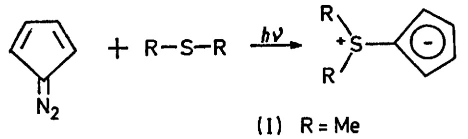
Summary Photolysis of diazocyclopentadiene in the presence of dimethyl, diethyl, and tetramethylene sulphides gave the corresponding sulphonium cyclopentadienylide; the ylide from di-t-butyl sulphide was unstable, and the reaction mixture gave the C–H and C–S insertion product from cyclopentadienylidene and the olefin elimination product.

Reactions of diazocyclopentadiene have been extensively studied,[1] but relatively few studies have been reported in which onium cyclopentadienylides are produced.[2,3] Carbenes are known to react with molecules containing heteroatoms to produce ylides. No ylide has hitherto been isolated from the reaction of cyclopentadienylidene in sulphides, although heating of diazotetraphenylcyclopentadiene in diphenyl sulphide gave the stable diphenylsulphonium tetraphenylcyclopentadienylide[3]

Diazocyclopentadiene was irradiated in various alkyl sulphides through Pyrex with light from a high pressure mercury lamp. Diazocyclopentadiene in dimethyl sulphide was photolysed completely in several hours and addition of light petroleum (b.p. 30—60°) to the cooled solution precipitated high yields of a pink solid, which gave colourless needles from benzene, and was shown to be the dimethylsulphonium cyclopentadienylide (I) by spectral comparison with an authentic sample.[4] Compound (I) had been prepared previously in only 15—20% yield by reaction of dibromocyclopentene with dimethyl sulphide followed by treatment with alkali. The carbene method gives yields of 40—50%.

Photolysis of diazocyclopentadiene in other sulphides was also studied. Irradiation in diethyl sulphide through Pyrex caused no observable precipitation. After addition of cold light petroleum and several hours in the cold diethyl-sulphonium cyclopentadienylide (II) appeared as brown needles, m.p. 85—86° (decomp.) (30%), which were separated by decanting and washed with light petroleum.

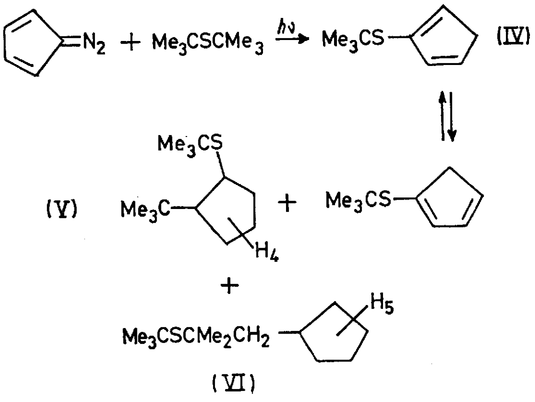


(I) R = Me
(II) R = Et
(III) R—R = -CH$_2$·CH$_2$·CH$_2$·CH$_2$−

Compound (II) slowly became brownish-black on exposure to light and air, or attempted recrystallisation. The chemical shift of the ring protons in compound (II) is very similar to that in other reported cyclopentadienylides.[5] Photolysis of diazocyclopentadiene in tetramethylene sulphide gave tetramethylenesulphonium cyclopentadienylide (III) in moderate yield.

The reaction of diazocyclopentadiene with alkyl sulphides may be envisaged as involving attack of the singlet state of the carbene on the lone pair of the sulphur atom.

In the photolysis of diazocyclopentadiene in di-t-butyl sulphide, di-t-butylsulphonium cyclopentadienylide was not isolated, and g.l.c. analysis indicated the probable formation of three products (IV)—(VI) in moderate yield. Their n.m.r. spectra were not those expected for single products, but rather in keeping with a mixture of 2 isomers.



For example, integration of the vinyl, allyl, and alkyl signals for (IV) gave a ratio of 3:2:9, respectively. These products, however, became black tars when left at room temperature. These results were to be expected, since it has been demonstrated that cyclopentadienylidene attacks on the sulphur atom to form the sulphonium cyclopentadienylide.

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