

## The formation of triarylsulfonium salts through a photochemical route

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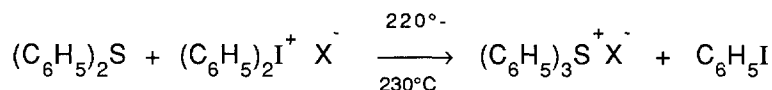
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### Summary

An original method of synthesizing triarylsulfonium salts through UV light excitation of diphenylsulfides in presence of diphenyliodonium salts is described.

### INTRODUCTION

Recently, diaryliodonium and triarylsulfonium salts have received much attention as photoinitiators in cationic polymerization (1,2). Various methods for the preparation of these salts have been reported (3-5). Crivello prepared triarylsulfonium salts using trace amounts of copper (II) compound as a catalyst (6). Nesmeyanov *et al* (7) reported that diphenylsulfide (DPS) can be directly arylated with diphenyliodonium salt at 220-230°C to obtain the corresponding sulfonium salt, as shown in the following equation :



However, the reaction requires a fivefold excess of diphenylsulfide. Knapczyk and McEwan (8) reported similar results. They conducted the reaction at 180°C for 35 hours. All experiments were, thus, carried out under fairly severe conditions. To the best of our knowledge, no photochemical method for preparing triarylsulfonium salt has been reported, so far, in the literature.

In the present study, we attempted to carry out the above reaction under light excitation. The diaryliodonium salts used as a starting materials were synthesized as reported in reference 1. They included diphenyliodonium hexafluorophosphate and 4,4'-dinitrodiphenyliodonium hexafluoroarsenate. Diphenyl sulfide was purchased from Aldrich as reagent grade and the methyl viologen was supplied by Tokyo Kasai. All solvents used in this work were spectroscopic grade.

### EXPERIMENTAL

The photochemical reactions were carried out as follows. After deaeration by bubbling purified nitrogen for 10 minutes, the solution of the iodonium salt (0.00027 M) and diphenyl sulfide (0.00037 M) in acetonitrile (5 ml) was irradiated for 4 hours at  $\lambda \geq 300$  nm, using

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a medium pressure Hg lamp (HPK 125 W). The iodobenzene by-product and the unreacted diphenyl sulfide were removed by washing several times with ethyl ether. The remaining insoluble product was examined by direct inlet mass spectroscopy (Nermag/Sider).

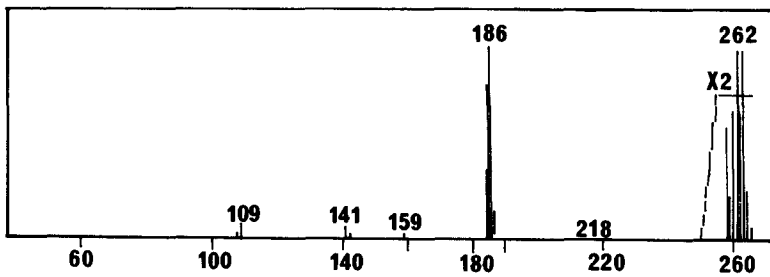


Figure 1: Direct-inlet mass spectrum of photochemical reaction product of diphenyl iododiuim salt and diphenyl sulfide.

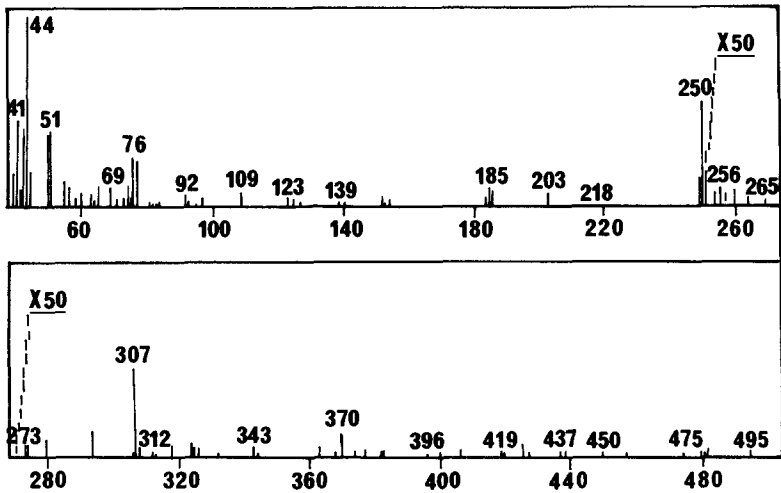


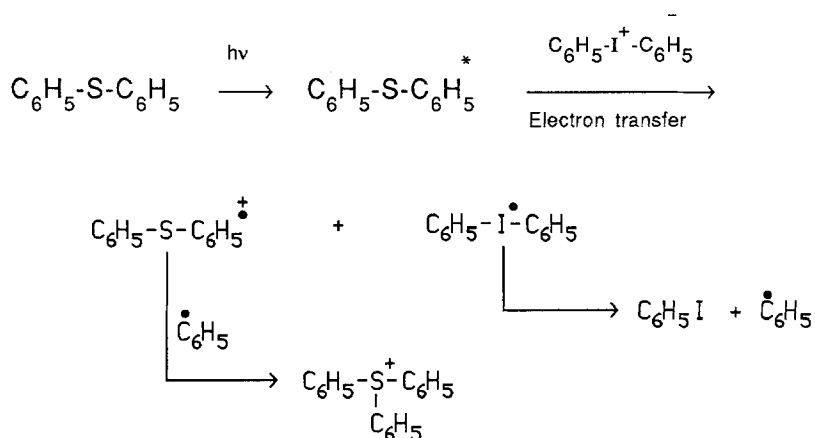
Figure 2: Direct-inlet mass spectrum of photochemical reaction product of 4,4'-dinitro-diphenyliodoniuim salt.

## RESULTS AND DISCUSSION

The direct-inlet mass spectrum of the reaction product is shown in Figure 1. It is apparent that the triphenylsulfonium cation species is fairly abundant ( $m/e$  262) with the parent peak being diphenyl sulfide ( $m/e = 186$ ). Since the sample was washed repeatedly with ethyl ether and the quantity of diphenyl sulfide used approached molar equality with the diphenyliodonium salt, it can be assumed that the diphenyl sulfide observed in the spectrum is a fragmentation product resulting from the ionic bombardment in the spectrometer.

In Figure 2, the same conclusion may be drawn from the mass spectrum of the photochemical product prepared by reacting diphenyl sulfide with the 4,4'-dinitrodiphenyliodonium salt. The mononitro- triphenylsulfonium cation can also be observed in the spectrum ( $m/e = 307$ ). But, since the reaction does not go to completion, the iodonium salt and its fragmentation products can still be observed in the same spectrum.

The results of these experiments can be explained by the following electron transfer mechanism.



In this case, the excited diphenyl sulfide acts as an electron donor and transfers an electron to the iodonium salt, thus, forming the diphenyl sulfide cation-radical and reducing the iodonium cation to a radical species. Because of its instability, the diphenyliodide radical decomposes in a subsequent step to iodobenzene and the phenyl radical. The latter can react further with the diphenyl sulfide cation radical to form the triphenylsulfonium salt as shown.

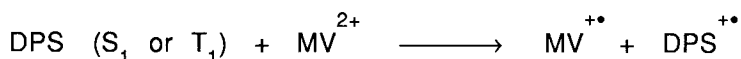
About fifteen years ago, Knapczyk (9) reported that, when diphenyl sulfide is added to a triarylsulfonium salt solution prior to irradiation, the photolysis reaction leads to a marked increase in the recovery of the triarylsulfonium salt. This phenomenon is in agreement with the result of the present study. Knapczyk, however, did not use the iodonium salt or suggest an electron transfer to explain this reaction.

The data obtained in the present study supports an electron transfer mechanism. This assumption is based on thermodynamic grounds. According to the Rehm-Weller equation(10), the free energy change  $\Delta G$  involving an electron transfer is given by :

$$\Delta G = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} - \Delta E_{0,0}$$

where  $E_{1/2}^{\text{ox}}$  is the oxidation potential of the electron donor,  $E_{1/2}^{\text{red}}$  is the reduction potential of the acceptor and  $\Delta E_{0,0}$  is the electron excitation energy of the excited species. For diphenyl sulfide  $E_{1/2}^{\text{ox}} = 34$  Kcal/mole (11) and  $\Delta E_{0,0} = 89$  Kcal/mole (12), while for diphenyliodonium salt,  $E_{1/2}^{\text{red}}$  is - 5 Kcal/mole. According to the Weller equation  $\Delta G = - 45$  Kcal/mole. It is well-known that the magnitude of the free energy ( $\Delta G$ ) should be negative (i.e. exothermic) in such a case, by at least 10 Kcal/mole. Calculations therefore show that the electron transfer is within the range of possibility.

This conclusion is also supported by the fact that diphenyl sulfide (DPS) behaves as an electron donor. It is well-known that methyl viologen is a cation species and its reduction product - the corresponding cation radical has a characteristic absorption at a long wavelength of 610 nm (13). Accordingly, if an electron transfer takes place between diphenyl sulfide and methyl viologen the characteristic absorption of the methyl viologen cation radical should be observed. Laser excitation of diphenyl sulfide in the presence of methyl viologen  $MV^{2+}$  (with a 3 ns pulse delivered by a YAG/Nd laser (14) at 353 nm) leads to the generation of  $MV^{\bullet+}$ . The following electron transfer can, therefore, be considered :



In conclusion, it was found that the electron transfer effect can provide an explanation of the recorded data. It, therefore, seems reasonable to assume that other types of triarylsulfonium salts may be prepared in this same manner.

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