A General Electrocyclic Rearrangement of Sulphonium Ylids

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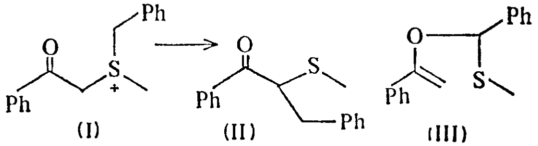
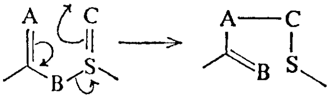
THE base-catalysed Stevens rearrangement of sulphonium salts has long been accepted as a general reaction pathway for these compounds, ever since Stevens reported the transformation of salt (I) into the sulphide (II)[1] This work, which has been much quoted[2] and repeated without further comment,[3] was reinvestigated by Ruiz who showed unequivocally that the substance described as (II) has in fact structure (III).[4] Later work has shown that an ylid is involved[5] and subsequently we[6] and others[7] have developed the reaction for allyl sulphonium salts.

We report that this reaction is only one example of what appears to be a very general electrocyclic mechanism for rearrangement of sulphonium ylids, which may be expressed in the general form of Scheme 1.† The driving force of these rearrangements is provided by the conversion of formally tetravalent sulphur to the divalent state. In this Scheme A, B, and C may be a variety of atomic types. This simple concept serves to unify and rationalize a large number of reactions of sulphonium compounds. (i) *A = B = C = Carbon*: In the preceding Communication we reported this transformation and have demonstrated its validity for a variety of substituting groups. In the same area may be grouped a number of reactions already in the literature, the transformation of tribenzyl sulphonium perchlorate,[8] the Sommelet Hauser rearrangement of benzyl sulphonium salts[9] and of 9-fluorenyl sulphonium salts,[10] the rearrangement of dialkyl allyl sulphonium salts,[7] and the reaction of allyl sulphides with dichlorocarbene, which have been postulated to proceed *via* the ylid.[11] All these proceed simply under mild conditions (Scheme 1). Also observed is the ring opening of the cyclic ylid (IV) to the unstable sulphide (V),[12] which differs only in the presence of an extra σ-bond in the cyclic π-array of the general system.

(ii) *A = Oxygen, B = C = Carbon*: The work of Ruiz,[4] and others[5] now demonstrates that the so-called Stevens rearrangement of sulphonium



(I) (II) (III)



SCHEME 1

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† We have chosen the extreme double-bonded representation for the ylid rather than the alternative dipolar form in order to express their similarities to the carbon electrocyclic processes. In this discussion either form may be used with equal ease, since both imply a cyclic reorganization of six electrons. For a recent review of the participation of *d*-orbitals in sulphur bonding see A. W. Johnson, "Ylide Chemistry," Academic Press, New York, 1966, p. 306.

salts is in fact an example of the general pathway suggested here. Subsequent investigations[5] demonstrated the intermediacy of the ylid (VI).

(iii) *A = C = Carbon, B = Oxygen*: The reaction of phenols with dimethyl sulphoxide in the presence of acylating agents proceeds through an intermediate ylid (VII), rearranging by the general mechanism to the intermediate dienone (VIII).[13]

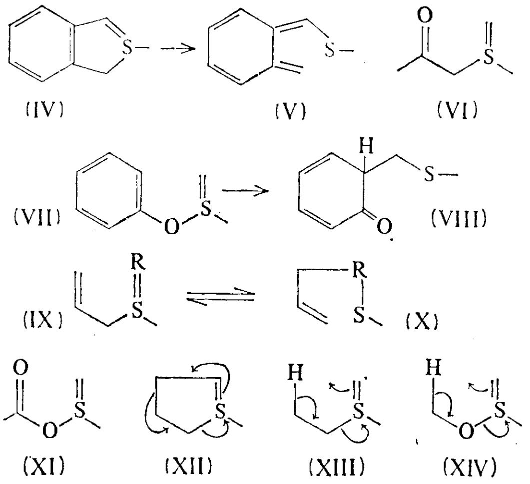
(iv) *A = B = Carbon, C = Oxygen*: Mislow has rationalized the racemization of allyl sulphoxides (IX; R = O) by equilibration with the allyl sulphenyl ester (X; R = O), the equilibrium favouring the sulphoxide.[14]

(v) *A = B = Carbon, C = Nitrogen*: The conversion of allyl sulphidi-imides (IX; R = NR) to the rearranged compounds (X; R = NR) was discovered by Challenger who has demonstrated the required reversal of the allyl group.[15]

(vi) *A = B = Oxygen, C = Carbon*: The well-known Pummerer reaction of sulphoxides may be seen as an example of the ylid rearrangement, by way of the acyloxy-ylid (XI). The present mechanistic evidence[16] is in agreement.

As in the carbon electrocyclic processes there are examples wherein a π-bond may be replaced by a σ-linkage, the sigmatropic processes,[17] so that in this heteroatomic mechanism we find a similar and analogous mechanism. (i) The observation by Weygand[18] that a tetrahydrosulphonium salt decomposes in basic media to fragmentation products is consistent with expression (XII), an analogue of the *retro*-Diels–Alder reaction.

(ii) Deuterium experiments of Franzen and Mertz[19] on the decomposition of sulphonium ylids support the pathway expressed by (XIII). Similarly its oxy-analogue (XIV) is consistent with the isotopic results of Moffatt on the mechanism of the dimethyl sulphoxide oxidation of alcohols.[20]



(IV) (V) (VI)

(VII) (VIII)

(IX) (X)

(XI) (XII) (XIII) (XIV)

We have shown how the simple electrocyclic process is useful in understanding a body of apparently unrelated reactions. By appropriate substitution of suitable atoms in the proposed cyclic array a number of, as yet unknown, processes are predictable and it is on these and the stereochemical aspects of this reaction that our present studies are concentrated.

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