is significantly longer than the S(1)-(N(1)) bonds of (I)—
(III), while the S(2)-(N(1)) bond [1.64(4) Å] is experi-
mentally identical to the corresponding bonds in the other three molecules. While there are fundamental differences between (IV) and (I)—(III) which make direct comparison difficult (e.g. IV is formally a charged species, whereas (I)—(III) are not), we nevertheless note that whereas the nitrogen atom of (IV) has only one lone-pair of electrons which may be considered initially in a p-type orbital approximately perpendicular to the S-N plane, the nitrogen atoms of (I)—(III) all bear two lone-pairs of electrons. The removal of one of these lone-pairs of electrons by N-alkylation apparently produces a marked effect in the S(1)—N(1) bond, but not in the S(2)—N(1) bond.

The solid-state conformation of (I) is best described in terms of the three Newman projections (see Figure 2) along the C(1)—S(1), S(1)—N(1), and S(2)—N(2) bonds, and is very similar to the conformations of (II) and (III). The C(1)—S(1) projection is characterised by the asym-
metrical disposition of the aromatic and sulphonyl groups, the torsion angle C(1)C(2)C(3)S(1) being —11.7°. It is possible that this conformation isfavoured to reduce steric interaction between C(2) and S(2) [C(1)C(2)C(3)S(2) 30.9(1) Å]. There is considerable interest, however, in the semi-gauche relationship of O(1) and S(2), demonstrated by the projection along the S(1)—N(1) bond, which is 35.7° for the other two.

Computations were performed on the Glasgow University TRIP 9 computer using programs developed by the Glasgow group. We thank the Carnegie Trust for the Universities of Scotland for the provision of a post-graduate award (to N. J. H.).

Part II.

Metal Carbonyl-catalysed Isomerisation of N-Allylaldimines to Prop-2-enyl Derivatives

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The light-induced isomerisation of olefins in the presence of pentacarbonyl manganese has been applied to nitrogen-
containing compounds. Since the catalytic procedure was as effective in polar solvents (such as methanol and acetonitrile) as in hydrocarbons, the isomerisation of allylic compounds containing very polar functional groups (such as amines and amides) into the corresponding propenyl derivatives could be effected in good yields. The method is however specific and whereas phenyl N-allylcarbamate was quantitatively isomerized to the expected N-propenyl derivative, the same compound reacted under the same conditions with propargyl alcohol and imines the formation of active centres and position isomerisation, which could also be catalysed by the metal-carbonyl combination.

DISCUSSION
The route of the isomerization of N-allyl-N'-phenyl-
urea (I) was studied for solutions in D$_2$O and in methanol. In D$_2$O, the isotope effect is significant, but it is possible to study the NH groups, see Experimental section). After irradiation for 10 min, a doublet of doublets is observed at 6.07 (1H, the N-allyl group) and 1.14 (2H, the isopropyl group) indicating that the NH and NH$_2$ protons take place and the molecule which is 8.86% is also isomerized is PANDONCONHCH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$ as shown by n.m.r. spectroscopy (whereas in H$_2$O the 5.5% isomer is present in the 1H$_2$O, whereas a much smaller amount (0.2%) is observed). The decrease in the intensity of the reaction mixture (a definite rate enhancement is observed). These results suggest the possibility of the formation of active centres and position isomerisation, which could also be catalysed by the metal-carbonyl combination.

Imisonation of N-allylurea (Ia) in methanol solution:

- catalyst 5% Fe(acac)$_3$; u.v. light; reaction followed by i.r. and n.m.r. spectroscopy.

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- catalyst 5% Fe(acac)$_3$; u.v. light; reaction followed by i.r. and n.m.r. spectroscopy.
neither the OD of the solvent nor the ND of the urea are involved in the prototropic transfer. Also the migration is not only, but also, in the complexed substrate as shown by Amos's experiment with tritiated olefins.\(^9\) It is therefore difficult at present to find a mechanism accounting for all the phenomena involved in this reaction.\(^9\) and it is quite possible that different paths are followed according to the conditions, e.g. nature of the substrates or the solvents.

For example, we have shown that the NH group plays an important role in the reaction, as shown by the comparison of phenyl N-allylcarnbamate (I) and its O-allyl N'-phenyl isomer (See Results section). A possible explanation is the participation of the NH group in a complex such as (III), precursor of the active centre, or possibly, a binuclear complex such as (III) which could better explain the selectivity for the trans-isomer, as (IIIA) should rather favour the cis-isomer by analogy with the base catalysed isomerisation of allyl ethers.\(^9\) In fact, such a binuclear entity would not be unexpected as the formation of divinyl monomercyanide is observed in the early stages of u.v. irradiation and as Fe(CO)\(_5\) activates the isomerisation of olefins even in the dark.\(^10\) Examples of the formation of binuclear complexes from penta(allylidyne) and various substrates are frequently encountered [e.g. from diphenylketone, Fe(CO)\(_5\), and Fe, and from isocyanate Fe(CO)\(_5\), Fe, and Fe].

We therefore assume that the difference of behaviour is due essentially to the co-ordination of the metal with the nitrogen of the carbamate (the CO group being de-activated as shown by the lack of reactivity of allyl acetates). When the co-ordinated NH group is far from the allyl group (e.g. in allyl N-phosphoramide), the reactive centre cannot interact with the double bond.\(^10\)

\(^9\) Further experiments indicate that this striking effect is also reflected by the reaction of alkyl allyls.

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