is significantly longer than the S(1)–N(1) bonds of (I)—(III), while the S(2)–N(1) bond [1·644(5) Å] is experimentally 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–S 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), 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 3) 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 asymmetric dispositions of the aromatic and sulphonyl groups, the torsion angle C(2)–C(1)–S(1)–O(1) being −11·2°. It is possible that this conformation is favoured to reduce steric interaction between C(2) and S(2) [C(2) ··· S(2) 3·91 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. That the value of 36·8° for the torsion angle

S(2)–N(1)–S(1)–O(1) is similar to those of 31·7 and 34·0° for this same angle in (II) and (III), is remarkable in view of the different substituent patterns and crystal environments of the three molecules, and it may be that the value of this torsion angle in these three molecules is related to the bonding within the S–N–S systems. The S(2)–N(1) projection reveals that the methyl substituents on S(2) are staggered with respect to the S(1)–N(1) bond, possibly as a result of steric effects.

Other features of the geometry of (I), are the approximately tetrahedral and pyramidal stereochemistries of S(1) and S(2) respectively, which are similar to the geometries previously observed for sulphur atoms in comparable environments.[3,4] Apart from the S(2) ··· C(2) short contact mentioned, the only other intramolecular contact of interest is that between S(2) and O(1) [2·94 Å]. Although this distance is less than the sum of the respective van der Waals' radii, the interaction is probably of much less significance than the corresponding short contacts observed in first-row ylides.[8,9] There are no abnormally short intermolecular contacts.

[8] A. F. Cameron, N. J. Hair, and D. G. Morris, J.C.S. Perkin II, 1972, 1071.

[9] A. F. Cameron, N. J. Hair, and D. G. Morris, J.C.S. Perkin II, 1972, 1331.

Catalysed Prototropic Rearrangements.† Part II.[1a] Metal Carbonyl-catalysed Isomerization of N-Allylamides to Prop-2-enyl Derivatives

By Andre J. Hubert,* Philippe Moniotte, Genevieve Goebbels, Roger Warin, and Philippe Teyssié, Univesité de Liège, Institut de Chimie, Sart Tilman, 4000 Liège, Belgium

The light-induced isomerization of olefins in the presence of pentacarbonyliron has been applied to nitrogen-containing compounds. Since the catalytic procedure was as effective in polar solvents (such as methanol and acetone) as in hydrocarbons, the isomerization of allylic compounds containing very polar functional groups (such as amides and ureas) into the corresponding propenyl derivatives could be effected in good yields. The reactions are however specific and whereas phenyl N-allylcarbamate was quantitatively isomerized to the expected N-propenylcarbamate, the allyl N-phenyl-ester did not react under the same conditions. As basic catalysts are, in general, not convenient for the isomerization of the title compounds, the procedure is of preparative interest.

In Part I,[1a] we studied the mechanism of the isomerization of allyl ethers under the influence of pentacarbonyliron and light according to Asinger's procedure.[2a] For nitrogen compounds, only the isomerization of N-allylimides into the corresponding N-prop-2-enyl-

† The series title has been generalized from the previous 'Base-catalysed Prototropic Rearrangements.'

[1] (a) Part I, A. J. Hubert, A. Georis, R. Warin, and Ph. Teyssié, J.C.S. Perkin II, 1972, 366; (b) P. W. Jolly, F. G. A. Stone, and K. Mackenzie, J. Chem. Soc. 1965, 6416.

imides by heating with pentacarbonyliron has been reported.[3,4]

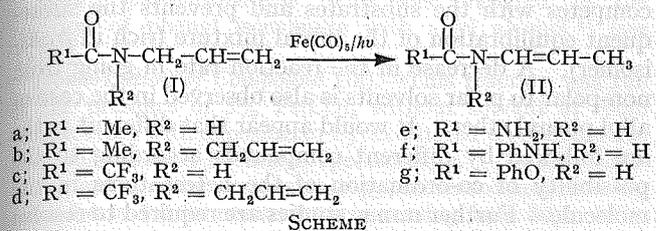In general, derivatives such as N-allylamides (Ia—d), ureas (Ie and f), and carbamate (Ig) are not isomerized by the classical basic catalysts. Consequently we have studied the isomerization of these compounds, induced

[2] (a) F. Asinger, B. Fell, and K. Schrage, Chem. Ber., 1965, 98, 372; (b) B. Fell, P. Krings, and F. Asinger, ibid., 1966, 59, 3688.
[3] P. Rossi and P. F. Barola, Ann. Chim. (Italy), 1969, 59, 268.
[4] P. Rossi and P. F. Barola, Ann. Chim. (Italy), 1969, 59, 762.

by pentacarbonyliron–u.v. light, the reactions being followed by i.r. and n.m.r. spectroscopy.

$$R^1\text{–}\overset{\displaystyle O}{\overset{\|}{C}}\text{–}\underset{\displaystyle R^2}{\overset{|}{N}}\text{–}CH_2\text{–}CH=CH_2 \xrightarrow{Fe(CO)_5/h\nu} R^1\text{–}\overset{\displaystyle O}{\overset{\|}{C}}\text{–}\underset{\displaystyle R^2}{\overset{|}{N}}\text{–}CH=CH\text{–}CH_3$$
$$(I) \qquad\qquad\qquad\qquad (II)$$

a; R^1 = Me, R^2 = H   e; R^1 = NH$_2$, R^2 = H
b; R^1 = Me, R^2 = CH$_2$CH=CH$_2$ f; R^1 = PhNH, R^2 = H
c; R^1 = CF$_3$, R^2 = H   g; R^1 = PhO, R^2 = H
d; R^1 = CF$_3$, R^2 = CH$_2$CH=CH$_2$

SCHEME

RESULTS

In the first instance, the experiments were performed neat with pentacarbonyliron as the solvent, or in benzene, but it rapidly became clear that this procedure, which was convenient for hydrocarbons,[2] ethers,[1] and simple amides was completely unsuitable for ureas which are solids, insoluble in hydrocarbons; however, methanol and acetone could be used successfully with these substrates. The reaction is sensitive to oxygen, a deep red colour developing, and isomerization did not take place. Under nitrogen, the solutions remain light yellow except in methanol where a red colour is observed under all conditions. As this red colour is not observed when oct-1-ene is isomerized in methanol, it is probably due to the bonding of the amido-group to a complex including methanol in its co-ordination sphere. Such a complex is not essential for the reaction as oct-1-ene is cleanly isomerized in methanol, but in the case of the amides, complexation of the amido-group probably plays an important role, as shown by the isomerization of allyl-substituted carbamates for which high reactivity is observed in the case of the N-allyl compound whereas the O-allyl isomer does not react at all. Despite the impossibility of measuring accurately the rate of isomerization under the conditions used, the following order of reactivity can be observed in methanol (approximate half-reaction times in parentheses): (Ig) (1 h) > (If) (2h) (Ie) (3 h) > (Ic) ≃ oct-1-ene > (Ia) (10 h) ≫ PhNHCO$_2$CH$_2$CH=CH$_2$, MeCO$_2$CH$_2$CH=CH$_2$ (24 h). N-Allyl-N'-phenyl(thiourea) was unchanged under various conditions.

These results should be compared with those for the attempted base-catalysed isomerization of amides, e.g. treatment of N-allylacetamide with potassium t-butoxide in t-butyl alcohol at 90 °C yields <10% of the rearranged product. Under more drastic conditions, decomposition takes place.

Geometrical Isomerism.—A mixture of cis- and trans-isomers is generally obtained (i.r. and n.m.r. spectroscopy) (see Experimental section). In contrast to the allyl ethers,[1] the trans-isomer is usually predominant; the cis : trans-ratio is ca. 0·43 in the case of N-allyl-N'-phenylurea in [²H₄]methanol or in [²H₆]acetone whereas the trans-isomer is exclusively formed from N-allyltrifluoroacetamide. The ratio of isomers depends on the nature of the solvent. In the case of phenyl N-allylcarbamate it is ca. 0·54 in [²H₆]benzene whereas a much smaller value (0·25) together with a slower reaction rate are observed in [²H₄]methanol.

In the cases of N-allylacetamide [5% Fe(CO)₅; neat] and N-allylurea [5% Fe(CO)₅; methanol] the cis : trans-ratio increases with time and the trans-isomer is formed preferentially only during the early stages of the reaction (Figure). The same trend is observed by n.m.r. spectro-

scopy in the case of N-allyl-N'-phenylurea; the cis : trans-ratio varies from 0·22 (30 min; 5% conversion) to 0·43 (175 min; 20% conversion).

The allyl ethers show similar behaviour, the cis : trans-ratio of the products increasing from ca. 1·0 to 2·0 for the Fe(CO)₅–u.v. system [whereas a constant cis : trans-ratio of ca. 1·0 * was observed by heating the allyl ether at 140 °C with Fe(CO)₅ without light or only after preirradiation of the reaction mixture (a definite rate enhancement also being observed)]. These results suggest the possibility of geometrical isomerization, subsequent to the light-induced formation of active centres and position isomerization,
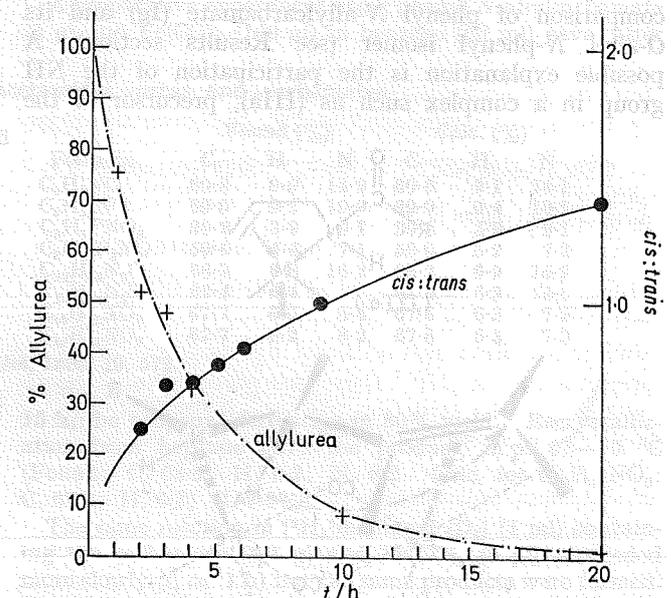
Isomerization of N-allylurea (Ie) in saturated methanol solution: catalyst 5% Fe(CO)₅–u.v. light; reaction followed by i.r. spectroscopy

which could also be catalysed by the metal–u.v. combination.

DISCUSSION

The route of the isomerization of N-allyl-N'-phenylurea (If) was studied for solutions in [²H₄]methanol and in [²H₆]acetone. In [²H₄]methanol rapid exchange of the NH protons takes place and the molecule which is actually isomerized is PhNDCONDCH₂CH=CH₂ as shown by n.m.r. spectroscopy (whereas in [²H₆]acetone it is possible to study the NH groups, see Experimental section). After irradiation for 10 min, a doublet of doublets is observed at δ 1·62 (CH₃ of the prop-2-enyl group is at δ 1·64 for the trans- and 1·60 for the cis-isomer), and a complex signal is found at δ ca. 2·6 (where the π-complex of the allyl ether group also absorbs[1a]). The presence of NCH₂ and of CHD₂OD absorptions (respectively at δ 3·77 and 3·29) prevents further study of this signal. After 265 min, the starting material completely disappeared and the multiplet at δ 2·6 largely decreased. The fact that no deuterium is incorporated into the propenyl groups indicates that

* The right-hand scale of Figure 3 in ref. 1a should be 0 to 1·0 instead of 1·0 to 2·0.

neither the OD of the solvent nor the ND of the urea are involved in the prototropic transfer. Also the migration is intramolecular, at least in the complexed substrate as shown by Asinger's experiment with tritiated olefins.[2b] It is therefore difficult at present to find a mechanism accounting for all the phenomena involved in this reaction,[5,6] and it is quite probable 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-allylcarbamate (Ig) 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 (IIIa), precursor of the
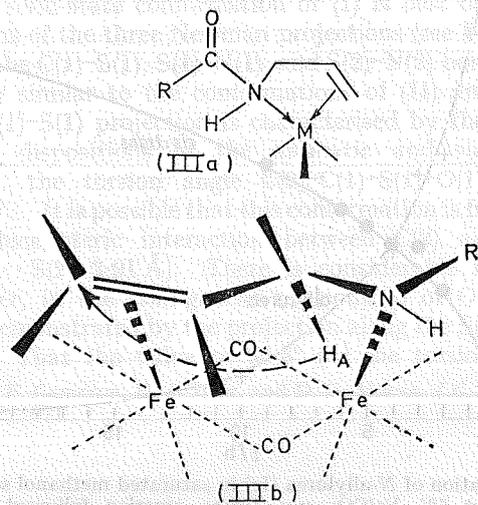
(IIIa)

(IIIb)

active centre, or possibly, a binuclear complex such as (IIIb) which could better explain the selectivity for the trans-isomer, as (IIIa) should rather favour the cis-isomer by analogy with the base catalysed isomerization of allyl ethers.[7] In fact, such a binuclear entity would not be unexpected as the formation of di-iron-nona-carbonyl is observed in the early stages of u.v. irradi-ation and as $Fe_2(CO)_9$ activates the isomerization of olefins even in the dark.[2a] Examples of the formation of binuclear complexes from pentacarbonyliron and various substrates are frequently encountered [e.g. from diphenylketen, $Fe(CO)_5$, and light,[8] and from isocyanate and $Fe(CO)_5$[9]].

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_2 group being de-activated as shown by the lack of reactivity of allyl acetate). When the co-ordinated NH group is far from the allyl group (e.g. in allyl N-phenylcarbamate), the reactive centre cannot interact with the double bond.*

* Further experiments indicate that this striking effect is also detected in the case of heterocyclic allyl amides.

[5] W. Klein, 'Transition Metals in Homogeneous Catalysis,' ed. G. N. Schrauzer, Dekker, New York, 1971, pp. 81—84.
[6] C. W. Bird, 'Transition Metal Intermediates in Organic Synthesis,' Logos Press, London, 1967, pp. 75—78.

The solvent effect in the case of N-allyl-N'-phenylurea may be due to co-ordination of the solvent, which competes with the substrates and prevents the subse-quent equilibration of the initial mixture (rich in trans-isomer). A decrease in the reaction rate in going from non-polar to polar solvents is also observed in the case of allyl phenyl ether. It would appear that different paths are followed by different compounds according to the possibility of co-ordination of the heteroatoms in the molecule. Further n.m.r. studies are required to resolve this problem.

Conclusion.—The pentacarbonyliron isomerization of N-allylamides proceeds particularly cleanly in the presence of u.v. light. The process is useful in the preparation of N-prop-2-enyl-amides, -ureas, and -carbamates as no side-products are formed. In some cases problems of isolation decrease the apparent yield. trans-Isomers are generally formed preferentially, at least during the early stages of the reaction.

The mechanism probably involves the intramolecular migration of an allylic proton via an unidentified inter-mediate co-ordination complex, probably similar to the π-complex detected in the case of allyl ethers, although more difficult to characterize. At present, it is not possible to choose between concerted or π-allyl type co-ordination mechanisms as too many non-quantified factors influence the course of the reaction.

EXPERIMENTAL

Technique of Isomerization.—The experimental conditions were those reported in Part I.[1a] Some experiments were conducted in CH_3OH or CD_3OD instead of C_6H_6 or C_6D_6. The course of the reactions was usually checked by n.m.r. spectroscopy, by following the characteristic absorptions of the allyl and propenyl groups. I.r. spectroscopy was used when the resolution of the n.m.r. spectra was too low for accurate measurements (the resolution was sometimes very low, mainly in the case of the experiments without solvent, because of the formation of paramagnetic species), exploit-ing the characteristic CH out-of-plane absorptions of the vinyl (e.g. 985 in the case of allylurea), of the trans-prop-2-enyl (940), and of the cis-prop-2-enyl (725 cm^{-1}) double bonds.

N-Allylacetamides.—Compounds (Ia—d). These were prepared by reacting allylamine or diallylamine with the appropriate anhydride dissolved in the corresponding carboxylic acid. They were purified by distillation and identified by i.r. and n.m.r. spectroscopy. The analytical data are summarized in the Table.

Compound (Ie). This was from Fluka.

Compound (If) and N-allyl-N'-phenyl(thiourea). These were prepared by reacting the amine with phenyl isocyanate or thiocyanate[10] (see Table).

Compound (Ig). This was obtained by reacting allyl

[7] C. S. Price and W. H. Snyder, J. Amer. Chem. Soc., 1961, 83, 1773.
[8] O. S. Mills and A. D. Redhouse, Chem. Comm., 1966, 444.
[9] T. A. Manuel, Inorg. Chem., 1964, 3, 1703.
[10] See general procedure for urea and thiourea in A. I. Vogel, 'Textbook of Practical Organic Chemistry,' Longmans, London, 1967, p. 422.

isocyanate (Fluka) with phenol overnight at 50 °C, followed by distillation (see Table).

Allyl N-phenylcarbamate. This was prepared by the reaction of phenyl isocyanate with allyl alcohol[11] (see Table).

Isomerization of Compound (Ia).—This reaction was run in the presence of 5% $Fe(CO)_5$ without solvent at room temperature with exposure to Pyrex-filtered u.v. irradiation and was followed by n.m.r. spectroscopy. The cis : trans-ratio (measured by i.r. spectroscopy) increased progressively from 0·4 to 1·0 for conversions increasing from 20 to 70%.

The isomerized material was shaken with ferric chloride in order to destroy the remaining $Fe(CO)_5$,[3,4] the mixture was distilled in vacuo, and the volatile material was collected

Properties and analysis of allyl-acetamides, -ureas, and -carbamates

Compound	B.p. (°C at mmHg) [m.p.]	Yield (%)	Formula	Found (%) C	H	N	Calc. (%) C	H	N
(Ia) [a]	58 at 4	70	C_6H_9NO	60·8	9·0	14·9	60·6	9·1	14·1
(Ib)	50 at 4	80	$C_8H_{13}NO$	69·0	9·2	10·0	69·0	9·4	10·1
(Ic)	72 at 15	60	$C_5H_8FNO_3$	38·9	3·9	9·1	39·2	3·9	9·1
(Id)	32 at 2	60	$C_8H_{10}F_3NO$	50·6	4·4	7·1	50·0	5·2	7·2
(If)	[105]	50	$C_{10}H_{12}N_2O$	68·3	6·8	16·2	68·2	6·9	15·9
N-Allyl-N'-phenyl(thiourea)	[101]	60	$C_{10}H_{12}N_2S$	62·4	6·4		62·5	6·3	14·6
(Ig)	138 at 2 [25]	80	$C_{10}H_{11}NO_2$	67·7	6·0	8·4	67·8	6·3	7·9
Allyl N-phenylcarbamate	[71]	80	$C_{10}H_{11}NO_2$	67·7	6·2	8·2	67·8	6·3	7·9

[a] K. Chiari, Monatsh., 1898, 19, 572.

and analysed. Analysis of an isomerized sample containing 60% cis- and trans-N-propenylacetamide and 40% starting material (which could not be separated efficiently by t.l.c.) showed that the elemental composition was not affected and therefore that only a mixture of isomers was formed in this reaction.

Isomerizations of Compounds (Ib—e).—Treatment of compounds (Ib—d) with neat pentacarbonyliron under the conditions described above gave the prop-2-enyl isomer as before. The rearrangement of compound (Ic) was complete within 6 h, giving 100% trans-isomer, m.p. 60°.

A 30% solution of (Ic) in methanol was completely isomerized within 10 h. For compound (Ie) the cis : trans-ratio varied from ca. 0·4 to 1·4 over the conversion range 50—90%. The reaction was complete within 10 h.

Except in the case of compound (IIc) it did not prove possible to separate the isomers.

Isomerization of Compound (If).—The isomerization was carried out in methanol as before. Recrystallization from ethanol gave a crystalline compound (60%), m.p. 140 °C (Found: C, 68·0; H, 6·8; N, 15·8. Calc. for $C_{10}H_{12}N_2O$: C, 68·2; H, 6·9; N, 15·9%). N.m.r. spectra were measured in CD_3OD or in $(CD_3)_2CO$; in the latter case it was possible to study the variations in chemical shifts of the NH groups. The cis–trans isomerism of the propenyl group can be best studied by analysing the methyl resonance which appears, in acetone solution to be a triplet, because of the partial superposition of two doublets of doublets. The isomerism is best estimated for methanol solutions [trans, δ 1·64 (3H, ^3J 6·9, ^4J 1·7 Hz, CH_3); cis, δ 1·60 (3H, ^3J 7·0, ^4J 1·8 Hz, CH_3)] in which the four doublets are distinct. Integration of the signals gives a cis : trans-ratio of 0·43. During the

early stages of the reaction (5% conversion; 30 min) the cis : trans-ratio is lower (0·22) as in previous examples.

Isomerization of N-Allyl-N'-phenyl(thiourea).—Unchanged starting material was recovered under all experimental conditions.

Phenyl N-Prop-2-enylcarbamate (IIg).—Compound (Ig) (0·1 g) was isomerized in [²H₆]benzene (1 ml) containing $Fe(CO)_5$ (10 µl) during 1 h. The reaction was followed by n.m.r. spectroscopy. The typical absorptions of the allyl group disappeared completely and were replaced by two doublets characteristic of the methyl groups of the cis- and trans-N-prop-2-enyl groups.

A preparative experiment using phenyl N-allylcarbamate (1 g) and $Fe(CO)_5$ (100 µl) in benzene (60 ml) gave, after 15 h, the propenyl derivative in 80% yield. Recrystalliz-ation from heptane gave the product, m.p. 67—70 °C (Found: C, 68·5; H, 6·2; N, 8·2. Calc. for $C_{10}H_{11}NO_2$: C, 67·8; H, 6·3; N, 7·9%).

The same reaction in [²H₄]methanol (D₄) (1 ml) contain-ing the carbamate (0·1 g) and $Fe(CO)_5$ (5 µl) proceeded more slowly ($t_{\frac{1}{2}}$ ca. 1 h) but the same products were formed. The chemical shifts of the methyl resonances differed from those observed in [²H₆]benzene owing to a solvent effect. The signals were the characteristic doublets of doublets.

Isomerization of Allyl N-Phenylcarbamate.—This was isomerized under the same conditions as the N-allyl O-phenyl isomer. After 1 h no isomerization was detected; similarly, when the product was irradiated for 24 h in methanol, no reaction took place.

Isomerization of Allyl Acetate.—This was carried out in [²H₆]benzene under the same conditions as above. No reaction took place within 24 h; precipitates of iron-containing complexes were formed slowly.

Isomerization of Oct-1-ene.—For purposes of comparison a solution of oct-1-ene (3 ml) in methanol (7 ml) containing pentacarbonyliron (0·15 ml) was irradiated at 30 °C under argon in thin sealed tubes (diameter 5 mm). The reaction was followed by i.r. spectroscopy, the bands of the mono-substituted olefin (990 and 910 cm^{-1}) disappearing and the typical band of a trans-disubstituted double bond being observed at 965 cm^{-1}. N.m.r. spectroscopy showed methyl signals at δ 1·61 ($CH_3CH=$) and 0·91 ($CH_3[CH_2]_nCH=$). The reaction was complete within 10 h.

[11] See general procedure for carbamates in ref. 10, p. 264.