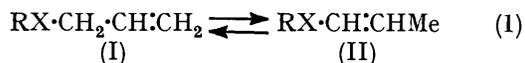


Base-catalysed Prototropic Rearrangement. Part I. Comparison of the Base-catalysed and the Metal Carbonyl-catalysed Isomerisation of Allyl Ethers

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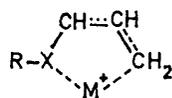
The light-induced isomerisation of allylic ethers in the presence of pentacarbonyliron has been compared with that brought about by a basic heterogeneous catalyst, $\text{KNH}_2\text{-Al}_2\text{O}_3$. The reaction on the basic catalyst proceeds through the usual *cis*-mechanism. In contrast, the carbonyliron reaction gives *cis*- and *trans*-isomers, in a 1:1 ratio in the case of allyl phenyl ether. A π -complex was detected (by n.m.r. spectroscopy) as an intermediate in the reaction. The formation of a catalyst which was particularly active for the thermal isomerisation of olefinic double bonds was detected during the irradiation of pentacarbonyliron in allyl phenyl ether. 3-Propoxycyclohexene was readily isomerised under these conditions, whereas it remained unchanged in the presence of very strong bases. Conformational effects of the ring were observed.

OLEFINIC compounds are isomerised under a great variety of conditions; catalysts such as acids, bases, and organometallic complexes are effective in promoting *cis-trans* isomerisation or the migration of double



bonds¹ [equation (1)]. The mechanism of the migration is well established.²

A general feature of these isomerisations is the initial rate-controlled formation of the *cis*-isomer during reaction (1). Compounds (II) have the *cis*-conformation during the early stages in the rearrangement of various olefins (e.g., X = CH_2 , O, NR' , or $[\text{CH}_2]_n$). As the di-substituted olefins are more stable than the mono-substituted ones, the equilibrium is displaced completely to the right in equation (1). The mechanism of the reaction has been explained in two different ways: first,^{2b,3} in terms of the greater stability of an allylic carbanion in the *cis*- than in the *trans*-conformation, and second, by supposing that the cation of the basic catalyst stabilises the *cis*-allylic carbanion by formation of a complex such as (III). The latter mechanism is more



(III)

plausible when X is a heteroatom having a lone pair of electrons able to interact with the positive charge of the cation.⁴

Amongst basic catalysts, the heterogeneous system

¹ For a review see A. J. Hubert and H. Reimlinger, 'The Isomerisation of Olefins, Part I, Base-catalysed Isomerisation of Olefins,' *Synthesis*, 1969, 97.

² (a) See D. Cram, 'Fundamentals of Carbonium Chemistry,' Academic Press, London, 1965; (b) G. J. Meiszwolf, J. A. A. Van Drunnen, and M. Kloosterziel, *Rev. Trav. chim.*, 1969, **88**, 1377; M. Kloosterziel and J. A. A. Van Drunnen, *ibid.*, 1970, **89**, 37.

³ S. Bank, A. Schriesheim, and C. A. Rowe, *J. Amer. Chem. Soc.*, 1965, **87**, 3244.

⁴ (a) T. J. Prosser, *J. Amer. Chem. Soc.*, 1961, **83**, 1701; (b) C. S. Price and W. H. Snyder, *Tetrahedron Letters*, 1962, 69; (c) P. Canbere and M. F. Hochu, *Bull. Soc. chim. France*, 1968, 459.

$\text{KNH}_2\text{-Al}_2\text{O}_3$, which isomerises olefins extremely rapidly and cleanly,⁵ has not yet been fully investigated.

As far as the metal carbonyl-catalysed reaction is concerned, many problems remain unsolved. Of the numerous catalysts belonging to this class,⁶ the most effective systems are the hydridometal carbonyls [e.g., $\text{HCo}(\text{CO})_4$,⁷ HFeCO_3^- ⁸] and pentacarbonyliron irradiated with u.v. light.⁹ These catalysts are *trans*-selective on the whole, although this does not seem to be well established, since the thermodynamic value of the *cis-trans* equilibria has not always been considered.

RESULTS AND DISCUSSION

We have studied the prototropic rearrangement of allyl ethers under the influence of pentacarbonyliron and u.v. radiation or heat, and of potassium amide on alumina. The rearrangement of allyl phenyl ethers to phenyl propenyl ethers is a particularly suitable system because: (a) the reaction is highly specific (95–100% of the *cis*-isomer is formed with catalysts such as potassium t-butoxide in dimethyl sulphoxide); (b) the products may be easily analysed by spectroscopic and chromatographic methods; (c) the electron-donating ether group will stabilise the intermediates so that they may be detected (or even trapped); (d) introduction of substituents into the aromatic ring will provide additional information through their electronic and steric effects.

The isomerisation of allyl phenyl ether by irradiation with u.v. light has been reported¹⁰ to give a *cis-trans* product ratio of 52:48. However, we have found, by following the reaction by n.m.r. spectroscopy, that this ratio increases slowly as the reaction proceeds and reaches a value of ca. 2:1 at equilibrium (see Figure 1). The same ratio of isomers was obtained when pure

⁵ A. J. Hubert, *Chem. and Ind.*, 1968, 975.

⁶ For a review see A. J. Hubert and H. Reimlinger, 'The Isomerisation of Olefins, Part II,' *Synthesis*, 1970, 405.

⁷ (a) L. Roos and M. Orchin, *J. Amer. Chem. Soc.*, 1965, **87**, 5502; (b) R. W. Goetz and M. Orchin, *ibid.*, 1963, **85**, 1549.

⁸ H. W. Sternberg, R. Markby, and J. Wendler, *J. Amer. Chem. Soc.*, 1956, **78**, 5704.

⁹ F. Asinger, B. Fell, and K. Schrage, *Chem. Ber.*, 1965, **98**, 372.

¹⁰ P. W. Jolly, F. G. A. Stone, and K. MacKenzie, *J. Chem. Soc.*, 1965, 6416.

phenyl *cis*-propenyl ether or a mixture rich in the *trans*-isomer was isomerised in the presence of iodine. Thus, during the course of the reaction with pentacarbonyliron

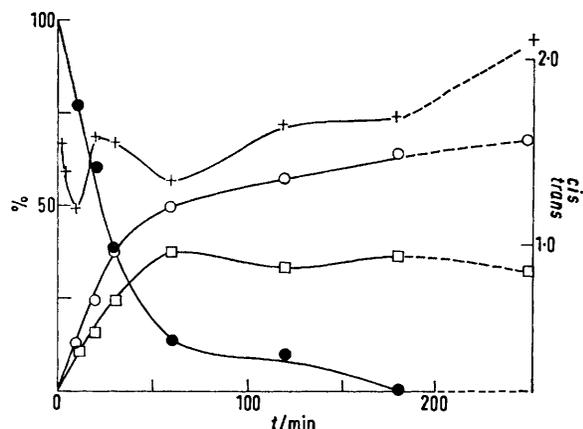
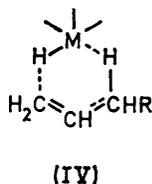


FIGURE 1 Photochemical isomerisations with pentacarbonyliron ($\lambda > 290$ nm) at 25°C: ●, allyl phenyl ether; ○, phenyl *trans*-propenyl ether; □, phenyl *cis*-propenyl ether; +, *cis*-*trans* ratio of phenyl propenyl ether (reaching thermodynamic equilibrium)

and light, the *trans*-isomer is formed in greater proportion than would be expected on thermodynamic grounds.

The formation of π -complexes in the metal-catalysed isomerisation of olefins has been established.^{4a,8,11-14} Such complexes have been isolated,¹¹ and hydrido-complexes have been recognised as particularly active catalysts.¹²⁻¹³ Complexes of the type (IV) have been postulated as intermediates in these isomerisations.^{4a}



Pentacarbonyliron and allyl compounds can give a hydrido-complex by hydrogen abstraction;⁸ the fact that $\text{DCo}(\text{CO})_4$ isomerises allylbenzene without incorporation of deuterium¹⁴ means that the π -complex is formed in the rate-determining step, which is followed by intramolecular transfer of hydrogen without intervention of the deuterium.

Our results may be interpreted in terms of the intermediacy of a π -complex. The n.m.r. spectrum of an irradiated solution of allyl phenyl ether containing pentacarbonyliron shows additional signals at δ 4.0 (allylic CH_2), 3.4 (olefinic CH), and 2.4 (vinylic CH_2) p.p.m., whose intensity is a function of the concentration of the catalyst (see Figure 2). The corresponding

signals from the starting material are at δ 4.3, 6.0, and 5.2 p.p.m. Thus the olefinic protons have undergone a large chemical shift, suggesting that they have become co-ordinated to the metal. The signals disappear when all the starting material has been consumed.

The *cis*-*trans* product ratio is also related to the concentration of catalyst and approaches the thermodynamic equilibrium value at high concentration (Figures 1 and 2). In the i.r. spectrum of the irradiated solution, a sharp band is observed at 4.80 μ , whose intensity decreases at the completion of the reaction. The band was not affected by the addition of deuterio-methanol, suggesting that it was not due to a metal-hydrogen bond. It may, therefore, be assigned to a carbonyl absorption though not one found in penta- or ennea-carbonyl-iron (formed during irradiation) or the π -complex.

Attempts to isolate the complexes (*e.g.*, the π -complex) failed. When the reaction was followed by g.l.c. at 200°, we observed that isomerisation took place during the chromatography, even though allyl phenyl ether is stable to heat alone. Allyl phenyl ether, when heated in the presence of pentacarbonyliron without irradiation, gives only 5–6% of phenyl propenyl ether. However we found that initial irradiation followed by thermal isomerisation gives faster overall transformation of allyl phenyl ether. For example, when allyl phenyl ether-pentacarbonyliron (9:1) is irradiated for 30 min at 15°C and then subjected to g.l.c. 58% of the starting

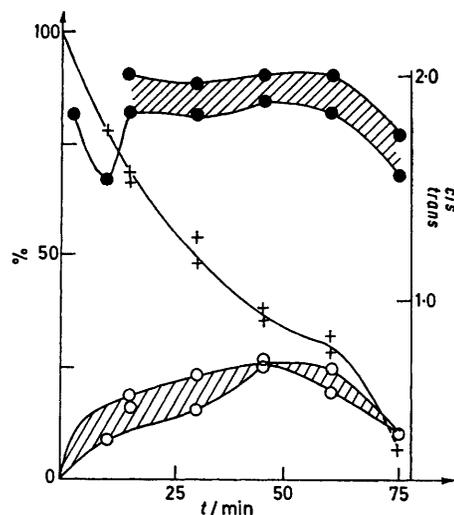


FIGURE 2 Photochemical isomerisations with pentacarbonyliron: ●, phenyl *cis*- and *trans*-propenyl ether; ○, π -complex; +, allyl phenyl ether

material is consumed, whereas if the irradiation procedure is used throughout this time, only 25% of the allyl phenyl ether is isomerised.

The *cis*-*trans* product ratio is the mean of the photochemical (Figure 1) and thermal (*ca.* 1.5 decreasing to

¹¹ C. S. Price and W. H. Snyder, *J. Amer. Chem. Soc.*, 1961, **83**, 1773.

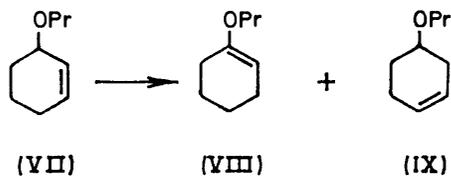
¹² S. J. Rhoades, J. K. Chattopadhyay, and E. E. Walli, *J. Org. Chem.*, 1970, **35**, 3352.

¹³ E. Korner von Gustorf, M. C. Henry, and C. DiPietro, *Z. Naturforsch.*, 1966, **21b**, 42.

¹⁴ G. L. Karapinka and M. Orchin, *J. Amer. Chem. Soc.*, 1961, **28**, 4187.

trans-selectivity (*cis-trans* ratio 1:1 compared with equilibrium value of 1.21:1).¹⁷

Cyclohexen-3-yl propyl ether (VII) does not undergo base-catalysed isomerisation,¹⁸ presumably because it cannot form an anion of the type (III). However, on treatment with pentacarbonyliron and light the 1- (VIII) and 4- (IX) isomers are formed. Initially the



4-isomer (IX) is the major product but after long reaction times, the vinyl ether (VIII) becomes predominant. The reaction is not sensitive to thermal catalysis during g.l.c. The vinyl ether (VIII) is the thermodynamic

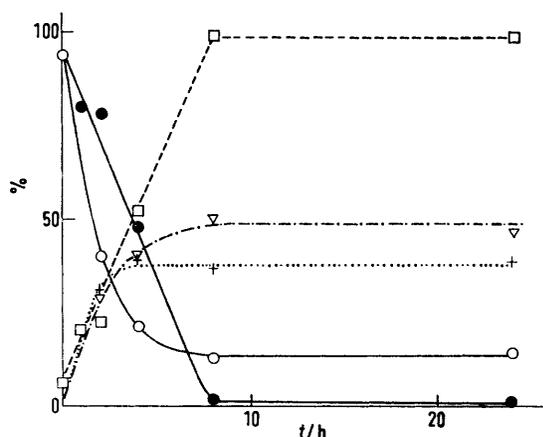
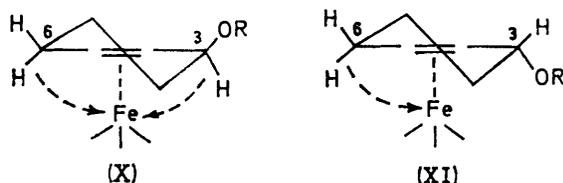


FIGURE 4 Isomerisations of cyclic ethers with pentacarbonyliron at 25 °C: ●, 2,5-dihydrofuran; ○, 3-propoxycyclohexene; +, 4-propoxycyclohexene; ▽, 1-propoxycyclohexene; □, 2,3-dihydrofuran

product because of the stabilisation induced by conjugation of the oxygen lone-pair with the double bond. In the intermediate complexes (X) and (XI) there is always a hydrogen atom at C-6 available to migrate to the metal to form the π -allyl complex, but only in one case (X) can a hydrogen atom migrate from C-3. Thus



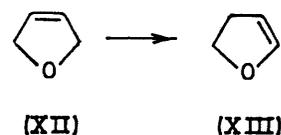
the formation of the kinetic product (IX) is initially favoured on statistical grounds. The 4-isomer (IX) is more stable than the 3-isomer (VII), because, as in the case of methylcyclohexanes,¹⁹ it can accommodate the

¹⁷ R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 4023.

¹⁸ M. Wrighton, G. S. Hammond, and H. R. Gray, *J. Amer. Chem. Soc.*, 1970, **92**, 6068.

¹⁹ J. Herling, J. Shabtai, and E. Gil-Av, *J. Amer. Chem. Soc.*, 1965, **87**, 4107.

propoxy-group in an equatorial position more readily than the 3-isomer.²⁰ 2,5-Dihydrofuran (XII), which can form



an ion of the type (III), is converted by potassium amide on alumina into the 2,3-dihydro-isomer (XIII). This is also the sole product of the rearrangement in the presence of pentacarbonyliron and light, the reaction being complete in 10 h.

Comparison of the results for the cyclic ethers (VII) and (XII) (see Figure 4) shows that base catalysis does give a *cis*-intermediate but that the metal-catalysed reaction can proceed by other paths.

EXPERIMENTAL

The work was performed in collaboration with M. KLEINEN and M. LALMAND.

Allyl Ethers.—Allyl phenyl ether and allyl methyl ether were prepared by reactions of stoichiometric quantities of allyl bromide with the corresponding sodium alkoxides.^{21,22}

Phenyl cis-Propenyl Ether.—This compound was obtained by isomerisation of allyl phenyl ether by potassium *t*-butoxide in dimethyl sulphoxide.²²

3-Propoxycyclohexene.—This compound was prepared according to the general procedure reported;²³ ν_{\max} 9.20 μ (ether linkage).

2,5-Dihydrofuran and pentacarbonyliron (Fluka) and enneacarbonyliron (Alpha Inc.) were commercially available.

Photochemical Isomerisation of Allyl Ethers.—Pentacarbonyliron was dissolved in the allyl ether. The mixtures were irradiated through Pyrex ($\lambda > 290$ nm) under argon in a bath at 15–20 °C with a u.v. lamp (Philips HPK 125 W) cooled by a water-jacket. Most of the experiments were performed without solvents and with mixtures containing 10% pentacarbonyliron. The results were practically identical for experiments conducted in benzene or heptane or without solvents, but since the n.m.r. resolution was better in deuteriobenzene, this solvent was used in some cases for n.m.r. studies. As the general pattern remained the same in all these cases, the results reported here are those without solvent.

The course of the reaction was dependent on the concentration of pentacarbonyliron. To isolate the π -complex, an excess of pentacarbonyliron had to be used. The n.m.r. spectrum of this complex and the kinetic results (see Figure 2) were obtained with equimolar amounts of pentacarbonyliron and allyl phenyl ether. The reaction was followed by g.l.c. and by n.m.r. and i.r. spectra of samples of the irradiated solution withdrawn through a septum with a syringe. N.m.r. spectroscopy gave information on the photochemical isomerisation while g.l.c. was useful for the thermal isomerisation. To study the π -complexes, the reaction was followed by n.m.r. directly.

In the isomerisation of allyl phenyl ether, the n.m.r.

²⁰ M. S. Newman, 'Steric Effects in Organic Chemistry,' Wiley, 1956, 30.

²¹ H. L. Goering and R. R. Jacobson, *J. Amer. Chem. Soc.*, 1958, **80**, 3278.

²² C. H. De Pury, R. W. King, and D. H. Froemsdorf, *Tetrahedron Letters*, 1959, **7**, 123.

²³ A. Berlande, *Bull. Soc. chim. France*, 1942, **9**, 644.

signal at δ 4.3 p.p.m. (allylic CH_2) was used to follow the disappearance of the starting material. Multiplets at 4.7 (*cis*-olefinic protons) and 5.2 (*trans*-olefinic protons) were observed, respectively, for the phenyl *cis*- and *trans*-propenyl ether. The isomerisation of 3-propoxycyclohexene was followed by observing the disappearance of the δ 5.72 p.p.m. signal for the starting material, and the appearance of signals at δ 5.62 and 5.82 p.p.m. respectively for the 1- (VIII) and 4- (IX) isomers.

G.l.c. was carried out on a Varian Series 1800 machine with a column of diethylene glycol succinate (4 ft \times $\frac{1}{4}$ in). In a typical experiment with allyl phenyl ether, after 5 min at 70 °C, the machine was programmed to raise the temperature to 190 °C at 10 deg min⁻¹. The temperature of the injection port was 200 °C, that of the detector 300 °C. If the temperature of the injection port was too low, contamination of the tungsten filament of the catharometer with the metal carbonyls took place. At this temperature, a thermal reaction could be observed besides the photochemical isomerisation.

The isomerisations of 3-propoxy-cyclohexene and -cyclopentene, and 2,5-dihydrofuran were followed by g.l.c. [10% Plastinol (a polyester-type stationary phase from U.C.B., Belgium) on Chromosorb AW; 8 ft \times $\frac{1}{4}$ in] at 120 °C with the other conditions as before.

Thermal Isomerisation of Allyl Phenyl Ether.—Allyl phenyl ether and pentacarbonyliron (10%) were irradiated for 15 min. The mixture was then analysed by n.m.r. spectroscopy and g.l.c. The mixture was then heated to 150 °C and the reaction was followed by g.l.c. and n.m.r. For comparison, non-irradiated tubes containing penta- and ennea-carbonyliron were heated at the same temperature.

Determination of the Thermodynamic cis-trans Equilibrium

of Phenyl Propenyl Ethers.—A solution of pure phenyl *cis*-propenyl ether (1 mmol) in cyclohexane (0.5 ml) was heated at 70 °C in the presence of iodine (0.5 mmol) during 19 h. The ratio of *cis*- to *trans*-isomers was 2 : 17 (from g.l.c.). The same experiment was performed with a mixture of phenyl *cis*- and *trans*-propenyl ether (obtained by isomerisation) in which the *cis-trans* ratio was 1.12 : 1.

After isomerisation with iodine, we obtained a ratio of 1.80 : 1. Both n.m.r. spectroscopy and g.l.c. show that the *cis-trans* isomerisation of pure phenyl *cis*-propenyl ether in the presence of pentacarbonyliron and light gives a ratio of ca. 2.05 : 1 after prolonged irradiation. It is obvious that this composition is close to the real equilibrium composition.

2-Propoxycyclohexene.—A sample of this compound was isolated by preparative g.l.c. (on a column of Plastinol) from a mixture of the 1-, 3-, and 4-isomers resulting from isomerisation of 3-propoxycyclohexene with pentacarbonyliron and light. The i.r. spectrum showed the typical absorption of the olefinic group at 6.02 μ and of the vinyl ether group at 8.45 μ . The absorption at 6.02 is strong because of the presence of an alkoxy-substituent on the double bond. 4-Propoxycyclohexene was also isolated by preparative g.l.c., and had an i.r. spectrum similar to that of the 3-isomer.

Isomerisation of Allyl Phenyl Ether on $\text{KNH}_2\text{-Al}_2\text{O}_3$.—Allyl phenyl ether (5 ml) in heptane (50 ml) was added to the catalyst¹ (22 g). The reaction was followed by g.l.c. After completion of the isomerisation, the catalyst was filtered off, the solvent was evaporated, and the residue was distilled *in vacuo* at 70° and 2 mmHg. Phenyl *cis*-propenyl ether was contaminated with some *trans*-isomer (5% after 2 min of reaction, 26% after 24 h) as shown by g.l.c.

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