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

By **A. J. Hubert,* A. Georis, R. Warin, and P. Teyssié,** Laboratoire de chimie macromoléculaire et de catalyse organique, University of Liége, Sart–Tilman, 4000 Liege, Belgium

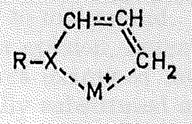
The light-induced isomerisation of allylic ethers in the presence of pentacarbonyliron has been compared with that brought about by a basic heterogeneous catalyst, $KNH_2–Al_2O_3$. The reaction on the basic catalyst proceeds through the usual *cis*-mechanism. In contrast, the carbonyliron reaction gives *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

$$\underset{(I)}{RX{\cdot}CH_2{\cdot}CH{:}CH_2} \rightleftharpoons \underset{(II)}{RX{\cdot}CH{:}CHMe} \qquad (1)$$

bonds[1] [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 $[CH_2]_n$). As the disubstituted olefins are more stable than the monosubstituted 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 $KNH_2–Al_2O_3$, 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.*, $HCo(CO)_4$,[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 reported [10] 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 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 and light, the *trans*-isomer is formed in greater proportion than would be expected on thermodynamic grounds.

---

[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.

[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.

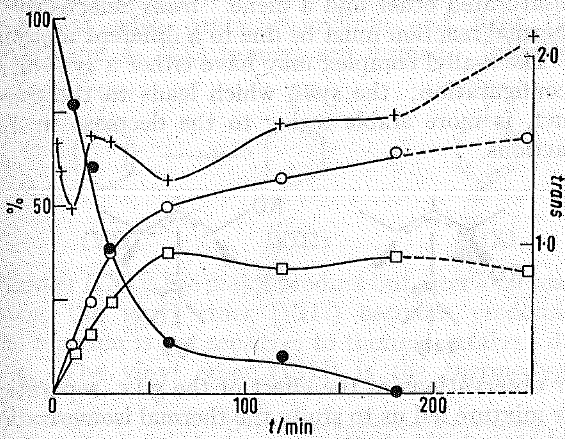
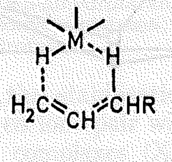


FIGURE 1 Photochemical isomerisations with pentacarbonyliron (λ > 290 nm) at 25 °C: ●, allyl phenyl ether; ○, phenyl *trans*-propenyl ether; □, phenyl *cis*-propenyl ether; +, *cis–trans* ratio of phenyl propenyl ether (reaching thermodynamic equilibrium)

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]



(IV)

Pentacarbonyliron and allyl compounds can give a hydrido-complex by hydrogen abstraction;[8] the fact that $DCo(CO)_4$ isomerises allylbenzene without incorporation of deuterium [14] 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 deuteriomethanol, 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 material is consumed, whereas if the irradiation procedure is used throughout this time, only 25% of the allyl phenyl ether is isomerised.

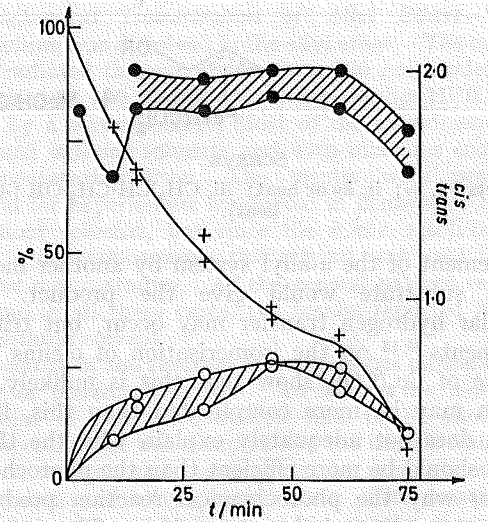


FIGURE 2 Photochemical isomerisations with pentacarbonyliron: ●, phenyl *cis*- and *trans*-propenyl ether ratio; ○, π-complex; +, allyl phenyl ether

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.

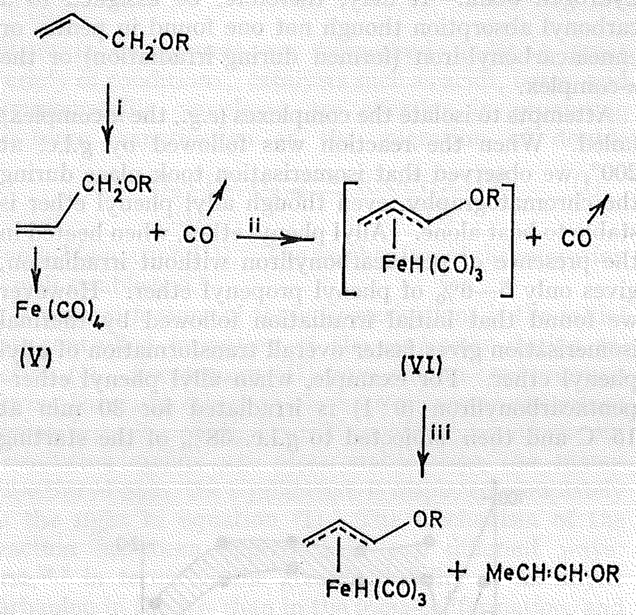
[13] E. Korner von Gustorf, M. C. Henry, and C. DiPietro, *Z. Naturforsch.*, 1966, **21***b*, 42.

[14] G. L. Karapinka and M. Orchin, *J. Amer. Chem. Soc.*, 1961, **26**, 4187.

ca. 1·0 for 30—50% conversion) isomerisation ratios because under the conditions of the chromatography, as control experiments revealed, the rearrangement of allyl phenyl ether to products is faster than *cis–trans* isomerisation.

The possibility that the reaction might be a radical one was discounted by the results of addition of large amounts of scavenger, *o*-methyl-*p*-t-butylphenol. No effect was observed other than a slight decrease in rate.

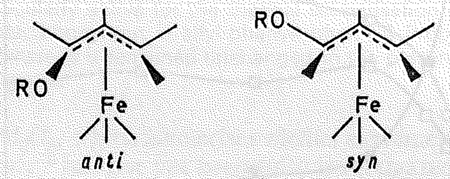
These results may be summed up by the mechanism shown in the Scheme. The π-complex (V) is formed first, by the action of u.v. light, followed by the π-allyl complex (VI), formed by u.v. light or by heat. Then, displacement of the π-allyl system by another molecule of the substrate would give the product. Intermolecular hydrogen transfer may occur, but tritiation experiments [7b,15] on the isomerisation of olefins in the presence of $Co_2(CO)_8$ show that this is unlikely. The reaction may be more complicated than this, for the scheme does not adequately explain why the thermal process should be more efficient than the photochemical one, nor why the photochemical reaction produces a greater proportion of the *cis*-product. The data show that the key step in the mechanism is the first one, *i.e.* the formation of the π-complex.



SCHEME

Reagents: i, *hν*; ii, *hν* or heat; iii, $CH_2{:}CH{\cdot}CH_2{\cdot}OR$ (+*hν* or heat).

The *trans*-selectivity (*i.e.*, greater proportion of *trans*-isomer than predicted by thermodynamic consideration) which we have observed is not so well established a phenomenon in metal-catalysed isomerisations as is claimed. However, it was observed in the photoisomerisation of penta-1,3- and hexa-2,4-diene in the presence of carbonyltungsten [7a] and it was suggested that in the intermediate the co-ordinated diene had an *S-cis*-configuration, which may decompose to a *trans*-product. In our case the oxygen lone-pair may perform the same role as the unco-ordinated π-bond in the diene, thus leading to *trans*-selectivity. However it is not clear to what extent an analogy can be drawn between an unsaturated ether and a diene. *trans*-Selectivity in the thermal reaction must be due to a different mechanism. The π-allyl complex may have either a *syn*- or an *anti*-configuration; the *syn*-, which leads to the *trans*-product, is more stable owing to the decrease in 1,3-interactions.



Our observations of the effect of the g.l.c. separation on the mixture led us to study the thermal isomerisation of allyl phenyl ether in the presence of pentacarbonyliron more closely. At 150 °C, after initial irradiation, the reaction proceeded rapidly and gave much *trans*-product (Figure 3). The reaction could not be forced to completion, suggesting that the catalyst is thermally unstable. As before, it was found that initial irradiation improved the efficiency of the rearrangement with both penta- and ennea-carbonyliron as catalysts, and that rearrangement proceeds more rapidly than *cis–trans* isomerisation. The base-catalysed rearrangement of allyl phenyl ether in dimethyl sulphoxide gave pure phenyl *cis*-propenyl ether with $t_{1/2}$ *ca.* 2 min.[16] With potassium amide on alumina as catalyst the reaction is complete within 2 min.

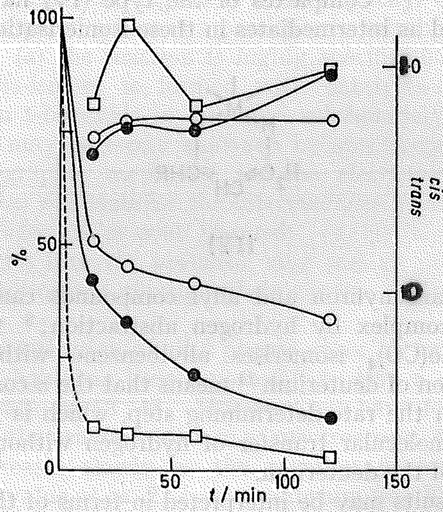
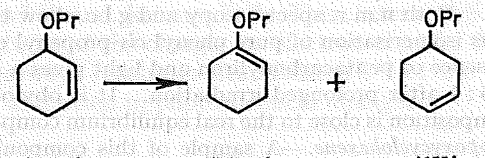


FIGURE 3 Thermal isomerisations of allyl phenyl ether at 150 °C: ●, with pentacarbonyliron (10%); ○, with enneacarbonyliron (10%); □, with pentacarbonyliron and irradiated for 15 min

The rearrangement of allyl methyl ether proceeds analogously to that of allyl phenyl ether and also shows *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 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 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.



(VII) (VIII) (IX)

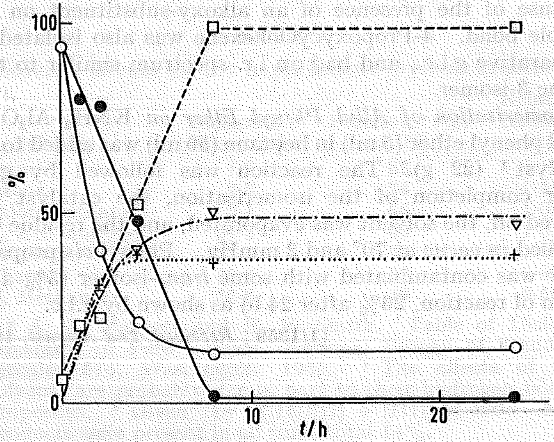
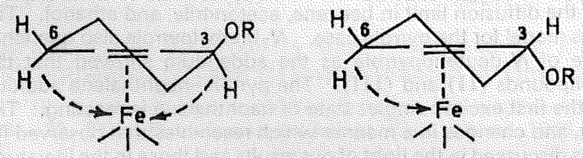
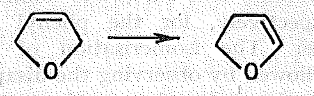


FIGURE 4 Isomerisations of cyclic ethers with pentacarbonyliron at 25 °C: ●, 2,5-dihydrofuran; ○, 3-propoxycyclohexene; +, 4-propoxycyclohexene; ▽, 1-propoxycyclohexene; □, 2,3-dihydrofuran



(X) (XI)



(XII) (XIII)

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 stoicheiometric 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.[4a]

3-*Propoxycyclohexene.*—This compound was prepared according to the general procedure reported;[23] $\nu_{max.}$ 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 (λ > 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.

---

[15] T. A. Manuel, *J. Org. Chem.*, 1962, **27**, 3941.

[16] B. Fell, P. Krings, and F. Asinger, *Chem. Ber.*, 1966, **99**, 3688.

[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.

[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 × ¼ 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 × ¼ 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 KNH$_2$–Al$_2$O$_3$.—Allyl phenyl ether (5 ml) in heptane (50 ml) was added to the catalyst[1] (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.

[1/1359 *Received, 2nd August,* 1971]

The Photoreaction of Naphthalene with Pyrrole; Products and Reaction Mechanism

By **J. J. McCullough,* W. S. Wu,** and **C. W. Huang,** Chemistry Department, McMaster University, Hamilton, Ontario, Canada

Irradiation of naphthalene and pyrrole by u.v. light through Pyrex or at 310 nm affords 2-(1,4-dihydro-1-naphthyl)pyrrole (II) and 2-(1,2-dihydro-2-naphthyl)pyrrole (III). These products together comprise 85% of the mixture, the remainder consisting of two 3-(dihydronaphthyl)pyrroles. Products (II) and (III) were characterized by n.m.r. spectra, and by conversion into the stable, crystalline 5-ethoxycarbonyl derivatives. The mechanism of this addition was studied by use of fluorescence quenching, solvent effects, and a labelling experiment. Pyrrole quenches naphthalene fluorescence at a rate close to the diffusion limit in benzene, acetonitrile, and ethanol. The quenching is similar to that of amines, which is used as model for the pyrrole case. *N*-Methylpyrrole also quenches naphthalene fluorescence, but does not react. Use of *N*-deuteriopyrrole as the addendum showed that the deuterium is retained in the methylene groups of compounds (II) and (III). The pyrrole–naphthalene addition does not occur on triplet sensitization, implying that the first excited singlet state of naphthalene is reacting. The ratio of products (II) and (III) is solvent-dependent, and changes in a manner which resembles that observed for certain ground-state, ionic processes. A mechanism is discussed in the light of our results and those in the literature.

WE have been studying photoadditions of indene and naphthalene derivatives, from the viewpoint of the structures of the products and the reaction mechanism.[1-3] The report by Bryce-Smith and his co-workers of the reaction of benzene with pyrrole[4,5] to afford the dihydrophenylpyrrole (I) prompted us to investigate the photolysis of naphthalene and pyrrole.[6] The question of multiplicity is easier to answer for the

reactions of naphthalene than of benzene, and it seemed that the structural similarity between pyrrole and amines might enable us to use the considerable body of photochemical work with the latter substances[7-19] to formulate a mechanism for the reactions of pyrrole. Amines interact with excited states, singlets, and triplets of many molecules, including aromatic hydrocarbons[7-14] and ketones.[15-19] This interaction is believed to be of the charge- or electron-transfer type,[7-12] which always results in deactivation[7-13] of the excited states, and often in photochemical changes.

RESULTS AND DISCUSSION

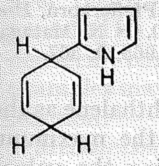
Irradiation of naphthalene and pyrrole in ethanol, acetonitrile, benzene, or hexane with light of wavelength >300 nm, resulted in the formation of four 1 : 1 adducts. Their proportions were solvent-dependent (see Table 1), but the two major products were 2-(1,4-dihydro-1-naphthyl)pyrrole (II) and 2-(1,2-dihydro-2-naphthyl)pyrrole (III).[6] The progress of the reaction and the ratios of products were monitored by g.l.c., and compounds (II) and (III) were isolated by chromatography on silica gel and characterized by spectroscopic methods [both showed *m/e* 195 (M^+)]. The n.m.r. spectrum[20] of the isomer (II) had resonances at δ 6·97 (4H, benzenoid), 6·29 (1H, 5-H), 5·88 (4H, 3-, 4-, 2′-, and 3′-H), 4·50 (1H, 1′-H), and 3·30 (2H, 4′-H$_2$) p.p.m. The last two peaks were multiplets, consistent with an ABX system. Irradiation of the resonance at δ 4·50 p.p.m. caused the methylene signal at δ 3·30 p.p.m. to simplify by the elimination of a coupling with *J* 6·2 Hz, thus pointing to a 1,4-dihydronaphthalene structure.[4,21] In the n.m.r. spectrum of (III), resonances appeared at δ 6·95 (4H, benzenoid), 6·26 (2H, 5- and 3′(4′)-H), 5·87 [3H, 3-, 4-, and 4′(3′)-H], 3·57 (1H, 2′-H), and 2·91 (2H, 1′-H$_2$). The u.v. spectra of compounds (II) and (III) were also consistent with these structures.

TABLE 1

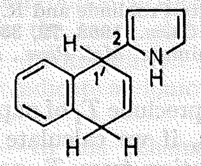
Solvent effects on the naphthalene–pyrrole reaction

Solvent	Dielectric constant (D) [a]	Fraction [c] (%) of (II)	Relative reaction rates
Hexane	1·9	82	
Benzene	2·3	74	1·45
Dichloromethane	9·1	66	1·08
95% Ethanol [b]	24·3	60	1·04
Acetonitrile	37·5	62	1·00
Methanol [b]	32·6	52	0·89
80% Methanol [b]	32·6	49	0·59

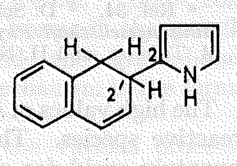
[a] A. A. Maryott and E. R. Smith, 'Table of Dielectric Constants of Pure Liquids,' National Bureau of Standards, Circular 514, Washington, 1951. [b] The effects of these solvents are probably due in part to their hydrogen bonding properties. [c] Given by [(II)/(II) + (III)] × 100; minor products were present in all runs, total 14%.



(I)



(II)



(III)

The products resemble pyrrole in rapidly becoming coloured in air, and although the isomer (II) was obtained as a solid, it was not sharp melting and satisfactory analytical figures were not obtained. Both adducts were characterized by treatment with carbonyl chloride, followed by ethanol,[22] to afford the 5-ethoxycarbonyl derivatives, which were stable, crystalline compounds. Their n.m.r. spectra were consistent with the assigned structures.[23] Thus, the ester protons of the compound (II) derivative gave signals at δ 1·12 (t) and 4·39 (q, *J* 7·0 Hz) p.p.m.[23] Also, two protons assigned to the pyrrole nucleus gave signals at δ 6·0 and 6·72 p.p.m. These are at different chemical shifts but are both attributed to the β-protons, and are both shifted downfield relative to the analogous signals from compound (II).[23] Similarly, the ester from compound (III) showed signals at δ 1·62 (t) and 4·53 (q) p.p.m., respectively. The pyrrole protons (β-H) resonated at δ 6·34 and 7·10 p.p.m. The methine proton and the methylene group comprised an ABX system, and the methylene group gave a doublet at δ 3·50 p.p.m., in contrast to the corresponding signal for the isomer (III) which was a multiplet. The spectrum apparently belongs to the 'deceptively simple' type[24] for the ester of the isomer (III), meaning that the protons of the methylene group have almost the same chemical shift.

Dehydrogenation of compounds (II) and (III) gave different 2-(naphthyl)pyrroles in agreement with the structures assigned.

One of the minor adducts was isolated by column

---

[1] J. J. McCullough and C. W. Huang, *Canad. J. Chem.*, 1969, **47**, 757.

[2] R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Amer. Chem. Soc.*, 1970, **92**, 4106.

[3] R. M. Bowman and J. J. McCullough, *Chem. Comm.*, 1970, 948.

[4] M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Comm.*, 1967, 263.

[5] D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 147.

[6] J. J. McCullough, C. W. Huang, and W. S. Wu, *Chem. Comm.*, 1970, 1368. A preliminary report of our results is given there.

[7] H. Leonhardt and A. Weller, *Z. phys. Chem.* (*Frankfurt*), 1961, **29**, 277; *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 791.

[8] D. Rehm and A. Weller, *Israel J. Chem.*, 1970, **8**, 259.

[9] T. Miwa and M. Koizumi, *Bull. Chem. Soc. Japan*, 1966, **39**, 2588; K. Kaneta and M. Koizumi, *ibid.*, 1967, **40**, 2254.

[10] H. Yamashita, H. Kokubun, and M. Koizumi, *Bull. Chem. Soc. Japan*, 1968, **41**, 2312.

[11] N. Mataga and K. Ezumi, *Bull. Chem. Soc. Japan*, 1967, **40**, 1355; Y. Nakato, N. Yamamoto, and H. Tsubomura, *ibid.*, p. 2480.

[12] W. R. Ware and H. P. Richter, *J. Chem. Phys.*, 1968, **48**, 1595.

[13] M. G. Kuzmin and L. N. Guseva, *Chem. Phys. Letters*, 1969, **3**, 71.

[14] (*a*) R. S. Davidson, *Chem. Comm.*, 1969, 1450; (*b*) C. Pac and H. Sakurai, *Tetrahedron Letters*, 1969, 3829.

[15] R. C. Cookson, S. M. de B. Costa, and J. Hudec, *Chem. Comm.*, 1969, 753.

[16] S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, 1968, **90**, 165; S. G. Cohen and B. Green, *ibid.*, 1969, **91**, 6824.

[17] R. A. Caldwell, *Tetrahedron Letters*, 1969, 2121.

[18] C. Pac, H. Sakurai, and T. Tosa, *Chem. Comm.*, 1970, 1311.

[19] R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1969, 1098.

[20] *Cf.* the spectrum of 2-methylpyrrole, R. L. Hinman and S. Theodoropulos, *J. Org. Chem.*, 1963, **28**, 3052.

[21] S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.

[22] M. W. Roomi and S. F. MacDonald, *Canad. J. Chem.*, 1970, **48**, 139.

[23] M. W. Roomi and H. Dugas, *Canad. J. Chem.*, 1970, **48**, 2303.

[24] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, vol. 1, p. 363.