1190. *Chemistry of the Metal Carbonyls. Part XXXII.*[1] *Isomerisation of Allyl Compounds and the Dimerisation of Norbornadiene*

By P. W. Jolly, F. G. A. Stone, and (in part) K. Mackenzie

Irradiation of allyl phenyl ether, allyl ethyl ether, and diallyl ether in the presence of pentacarbonyliron affords the corresponding propenyl ethers. Allylbenzene and allylperfluorobenzene are similarly isomerised.

Treatment of norbornadiene (I) with small amounts of dicarbonyldinitrosyliron results in a quantitative and rapid dimerisation of the hydrocarbon. Two known dimers are produced in 87 and 13% yield, respectively; unlike the reported reaction between (I) and pentacarbonyliron, no ketonic compounds are formed. The dimerisation of (I) by tricarbonylnitrosylcobalt, and the 7-t-butoxy-derivative of (I) by dicarbonyldinitrosyliron, are also described. The stereochemistry of the various norbornadiene dimers is discussed.

Reactions between dienes and iron carbonyl have been extensively studied, and many tricarbonyl-π-dieneiron complexes have been characterised.[2] In these reactions, substituted *cis*-dienes isomerise to the *trans*-form, and non-conjugated dienes become conjugated. Isomerisation occurs even when a tricarbonyliron π-complex is not isolated, *e.g.*, catalytic amounts of pentacarbonyliron quantitatively convert cyclo-octa-1,5-diene into the 1,3-diene,[3] a result reminiscent of the earlier report [4] that dodec-1-ene is isomerised by the same carbonyl. More recently, several mono-olefins have been isomerised in the presence of small quantities of dodecacarbonyltri-iron, enneacarbonyldi-iron, and pentacarbonyliron, either by warming [5] or by irradiation with ultraviolet light.[6] The internal olefins produced are stereoisomeric mixtures rich in the *trans*-forms, and the overall isomer distributions parallel the thermal equilibrium compositions.

Interest in the synthesis of alkenyl alkyl ethers [7-9] prompted examination of whether treatment of allyl ethers with catalytic quantities of pentacarbonyliron would produce the isomeric alkenyl compounds.

As shown in the Table, phenyl propenyl ether and ethyl propenyl ether are indeed formed quantitatively on irradiation of the allyl ethers in the presence of pentacarbonyliron. Similarly, an isomeric mixture of dipropenyl ethers is obtained from diallyl ether. However, irradiation of but-1-enyl methyl ether with pentacarbonyliron produced a mixture of compounds. This mixture consisted of 75% but-3-enyl methyl ethers (*cis*- and *trans*-isomers), the infrared spectrum of the remaining product being consistent with its being

Isomerisation of allyl compounds in the presence of 5% pentacarbonyliron

Reactant	Irradiation time (hr.)	Products (%)	
$CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$	$2\frac{1}{2}$	$CH_3{\cdot}CH{:}CH{\cdot}O{\cdot}C_6H_5$	*cis* 52, *trans* 48
$CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$	11	$CH_3{\cdot}CH{:}CH{\cdot}O{\cdot}C_2H_5$	*cis* 44, *trans* 56
$(CH_2{:}CH{\cdot}CH_2)_2O$	14	$(CH_3{\cdot}CH{:}CH)_2O$	*cis,cis* 26, *cis,trans* 43, *trans,trans* 31
$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_3$	35	$CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}O{\cdot}CH_3$	*cis* 34, *trans* 41
$CH_2{:}CH{\cdot}CH_2{\cdot}C_6H_5$	14	$CH_3{\cdot}CH{:}CH{\cdot}C_6H_5$	*cis* 5, *trans* 95
$CH_2{:}CH{\cdot}CH_2{\cdot}C_6F_5$	14	$CH_3{\cdot}CH{:}CH{\cdot}C_6F_5$	*cis* 2, *trans* 98

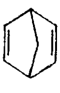
---

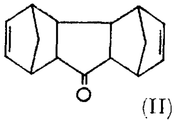
[1] Part XXXI, P. W. Jolly, M. I. Bruce, and F. G. A. Stone, *J.*, 1965, 5830.
[2] R. Pettit and G. F. Emerson, *Adv. Organometallic Chem.*, 1964, **1**, 1, and references cited therein.
[3] J. E. Arnet and R. Pettit, *J. Amer. Chem. Soc.*, 1961, **83**, 2954.
[4] F. Asinger and O. Berg, *Chem. Ber.*, 1955, **88**, 445.
[5] T. A. Manuel, *J. Org. Chem.*, 1962, **27**, 3941.
[6] F. Asinger, B. Fell, and K. Schrage, *chem. Ber.*, 1965, **98**, 372, 381.
[7] M. Farina, M. Peraldo, and G. Bressan, *Chimica e Industria*, 1960, **42**, 967.
[8] L. Brandsma and J. F. Aren, *Rec. Trav. Chim.*, 1962, **81**, 33.
[9] T. J. Prosser, *J. Amer. Chem. Soc.*, 1961, **83**, 1701.

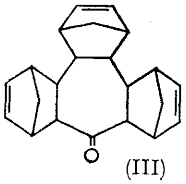
but-2-enyl methyl ether. Allylbenzene and allylperfluorobenzene are also quantitatively isomerised either by irradiation or by heating in the presence of pentacarbonyliron. It is interesting that, whereas allyl phenyl ether is quantitatively isomerised when irradiated for only $2\frac{1}{2}$ hours in the presence of pentacarbonyliron, it is only 60% isomerised after prolonged heating with the catalyst; in each case the isomer distribution of the product approaches the thermal equilibrium value.[10] Hex-1-ene is similarly isomerised, the photolytic and thermal [5] product exhibiting identical isomer distributions.

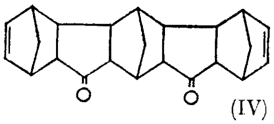
Interestingly, enneacarbonyldi-iron failed to isomerise the allyl ethers in the absence of irradiation at 50° (the reactant temperature in the successful irradiation experiments). The mechanism of the isomerisation described here and those described earlier [5,6] is not known, but two routes have been proposed for reactions of this type. Because certain mono-olefins form tetracarbonyl-π-olefiniron complexes in reactions with enneacarbonyldi-iron [11] it has been suggested [6] that the isomerisations proceed through an intermediate tetracarbonyliron π-complex and subsequent hydride shift. Alternatively, a tricarbonylhydrido-π-allyliron complex formed by hydride transfer could act as an intermediate,[5] it having been shown [12] that allyl halides, on irradiation in the presence of pentacarbonyliron, transfer halogen to iron forming tricarbonylhalogeno-π-allyliron complexes.

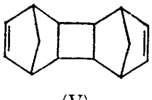
In addition to bringing about isomerisation of non-conjugated dienes and mono-olefins, pentacarbonyliron is known to react with norbornadiene (I) to give four dimers of (I) and five polycyclic ketones.[2,13] Representative structures for some of the compounds obtained are given by (II)—(VII). It had also been shown previously that tetracarbonylnickel dimerises (I) in inert solvents to give two further dimers, of which a compound having structure (VIII) has been reported, and that bis(acrylonitrile)nickel converts (I) into (V) and (VIII).[14] Stereochemical features have been proposed in appropriate cases only for compounds (II) and (V); the *endo-trans-endo*-configuration has been suggested [13,15]

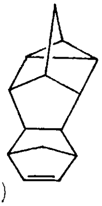

(I)

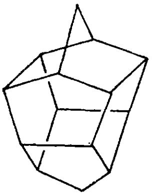

(II)

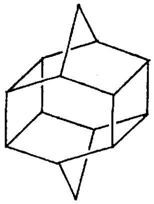

(III)

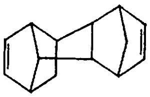

(IV)

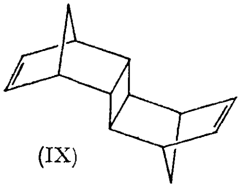

(V)

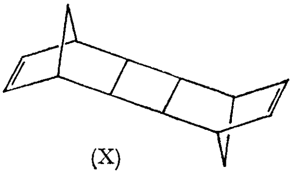

(VI)

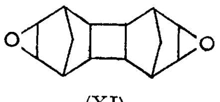



(VII)


(VIII)


(IX)


(X)


(XI)

---

[10] C. C. Price and W. H. Snyder, *J. Amer. Chem. Soc.*, 1961, **83**, 1773.

[11] H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, 1963, **56**, 1588.

[12] R. F. Heck and C. R. Boss, *J. Amer. Chem. Soc.*, 1964, **86**, 2580.

[13] C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters*, 1961, 373.

[14] G. N. Schrauzer, *Adv. Organometallic Chem.*, 1964, **2**, 1, and references cited therein.

[15] C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. and Ind.*, 1960, 20.

for (II), but n.m.r. studies [16] support the *exo-trans-exo*-form. Compound (V) has also been assigned the former stereochemistry.[13]

In earlier studies [17] it was observed [18] that (I) was rapidly converted into a white solid when treated with dicarbonyl dinitrosyl iron. We have investigated this reaction and find that the product contains no ketonic components, but is a mixture of the dimers (V) (87%) and (VIII) (13%). The dimerisation occurs rapidly in the presence of about 4% of the nitrosyl carbonyl compound. During the reaction, which can be followed spectroscopically, the appearance of a peak at 1745 cm.$^{-1}$ in the infrared suggests the transient formation of a complex between a nitrosyliron group and (I), but no organoiron complex could be isolated. From the large number of dinitrosyliron complexes that can be prepared from dicarbonyldinitrosyliron,[17,19,20] it is clear that the carbonyl groups are more easily replaced than the nitrosyl groups. In this connexion it is interesting that the complex $(Ph_3P)_2Fe(NO)_2$ which can be made very easily by replacement of carbon monoxide in dicarbonyldinitrosyliron, does not dimerise (I). In general unsaturated hydrocarbons often displace carbonyl groups from carbonylmetal complexes, but they do not displace triphenylphosphine ligands. The opposite in fact is true. Further, treatment of a mixture of (I) and norbornene with dicarbonyldinitrosyliron gives no cross-dimers, and no dimers are obtained from cyclohexene, cyclohexa-1,3-diene, cycloheptatriene, norbornene, quinone, or dicyclopentadiene under similar conditions.

The 7-t-butoxy-derivative of (I) is, however, dimerised by dicarbonyldinitrosyliron, but the yield is much reduced (16% after 3 hours), suggestive of a steric effect which inhibits dimerisation or formation of an intermediate.

The function of the dicarbonyldinitrosyliron in these reactions is unknown, but a dinitrosylirondinorbornadiene complex may be formed by successive replacement of carbon monoxide by norbornadiene. Significantly perhaps, the dimer (V) corresponds to *exo*-addition to each of the norbornadiene molecules (see below), the preferred stereochemical mode of attack in the norbornadiene series. It could be visualised that successive replacement of norbornadiene ligands by substrate results in splitting off of relatively long lived activated homoconjugatively stabilised norbornadiene molecules, which then dimerise; but such a process appears to be energetically unfavourable. The alternative view is that dimerisation occurs between two norbornadiene ligands intramoleularly, in a sterically critical tetrahedral complex; although only one π-bond from each norbornadiene molecule is formally involved, the specificity observed suggests that the second π-bond of the organic ligand also contributes in the transition state.

Tricarbonylnitrosylcobalt also dimerises (I), giving mainly (V) and (VI) together with a trace of (VIII) in overall conversion of 30%; again no ketonic compounds are formed.

An attempt was made to establish the stereochemistry of (V) because of doubts expressed [16] about the *endo-trans-endo* assignment [13] for (II), and the absence of convincing evidence in favour of a similar configuration for (V). For (V), six stereoisomers are possible depending on whether the two norbornene fragments are fused *cis* or *trans* to each other, and whether they are *exo* or *endo* fused. The *endo-cis-endo*-form is perhaps unlikely on steric grounds, and no cage structures are isolated [*e.g.*, (VII)].

Compounds which are sterically overcrowded at the bridge-methylene show an anomalously high C–H stretching frequency (>3030 cm.$^{-1}$) in the infrared range; [21] the product of hydrogenation of (V), however, showed no high-frequency C–H bands, and the *exo-cis-exo-* and *endo-cis-exo*-forms of (V) may therefore be excluded. The n.m.r. spectrum of (V) consists of bands centred at 4·03 τ (olefin protons), 7·36 τ (bridgehead protons), 8·66 τ (cyclobutane ring protons,) and doublets at 8·31 and 8·77 τ (bridge-methylene

---

[16] M. Green and E. A. C. Lucken, *Helv. Chim. Acta*, 1962, **45**, 1870.

[17] D. W. McBride, S. L. Stafford, and F. G. A. Stone, *Inorg. Chem.*, 1962, **1**, 386.

[18] S. L. Stafford and F. G. A. Stone, unpublished observations.

[19] L. Malatesta and A. Arȧneo, *J.*, 1957, 3803.

[20] R. B. King, *Inorg. Chem.*, 1963, **2**, 1275.

[21] D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Amer. Chem. Soc.*, 1961, **83**, 2938.

protons). These assignments are made in comparison with n.m.r. studies on norbornene derivatives [22] and are in agreement with other work (below).[23] The relative simplicity of the n.m.r. spectrum of (V) indicates a high degree of symmetry and that it has either the *endo-trans-endo-* (IX) or the *exo-trans-exo*-configuration (X). If the two double bonds were in different environments, it would be expected that the spectrum would show two groups of olefin proton signals.

In order to test these deductions, the *exo*-diepoxide (XI) was prepared for dipole-moment measurements. A diepoxide derived from (IX) or (X) should have a zero or small dipole moment, whereas a diepoxide formed from one of the other non-centrosymmetric isomers would have a substantial moment (estimated from models to be greater than 1 D). The observed small moment of the diepoxide (0·57 D) is in accord with (V) having either of the structures (IX) or (X) but does not permit a distinction between the two. However, comprehensive n.m.r. studies [23] involving several dimers of norbornadiene and norbornene have established that (V) has the *exo-trans-exo*-form (X).

EXPERIMENTAL

Isomerisation Reactions.—The volatile products were separated by vapour-phase chromatography using a Perkin-Elmer A52 instrument and a di-isodecyl phthalate column. Before use the purity of the allyl compounds was checked by chromatography. The radiation source was a 50 w Hanovia mercury lamp, and the isomerisations were carried out under nitrogen. Products were identified where appropriate by their infrared spectra, by their refractive indices, by analysis, and by coupling constants from the proton n.m.r. spectra. *trans*-Proton–proton coupling constants are always greater than *cis* in the group (H)C:C(H).[24]

(*a*) Phenyl *cis*-propenyl ether (n_D^{20} 1·5232; J_{cis} = 6·0 c./sec.); phenyl *trans*-propenyl ether (n_D^{20} 1·5238; J_{trans} = 11·3 c./sec.). For a mixture of *cis*- and *trans*-isomers, n_D^{19} = 1·525.[25]

(*b*) Ethyl *cis*-propenyl ether (n_D^{20} 1·3984; lit.,[7] 1·3986); ethyl *trans*-propenyl ether (n_D^{20} 1·3977; lit.,[7] 1·3977).

(*c*) cis,cis-*Dipropenyl ether* (n_D^{20} 1·4350, J_{cis} = 7·5 c./sec.) (Found: C, 73·3; H, 10·3. $C_6H_{10}O$ requires C, 73·5; H, 10·2%); trans,trans-*Dipropenyl ether* (n_D^{20} 1·4336; J_{trans} = 12·5 c./sec.) (Found: C, 73·7; H, 10·3%); *cis,trans*-Dipropenyl ether (n_D^{20} 1·4340) (Found: C, 73·7; H, 10·3%). The proton n.m.r. spectrum was similar to that obtained by superimposing the spectra of the *cis,cis*- and *trans,trans*-isomers.

(*d*) *cis*- and *trans*-But-3-enyl methyl ether were identified by their infrared spectra.[7]

(*e*) *trans*- and *cis*-Propenylbenzene were identified by their infrared and ultraviolet spectra.[26]

(*f*) *trans*-Propenylperfluorobenzene was identified by its infrared and ultraviolet spectra.[27] The spectrum of the small amount of the other product was consistent with its being the *cis*-isomer.

Dimerisation of Norbornadiene.—Dicarbonyldinitrosyliron and tricarbonylnitrosylcobalt were prepared as described elsewhere.[28] Molecular weights were determined in benzene using a Mechrolab vapour-pressure osmometer. For gas chromatography a 2-m. silicone grease column was used at 180°. With a helium flow of 100 c.c./min. retention times were 11·9 min. for (V), 13·0 min. for (VIII), and 14·5 min. for (VI).

Reaction between Norbornadiene and Dicarbonyldinitrosyliron.—Freshly distilled (I) (2·5 g., 27 mmoles) and dicarbonyldinitrosyliron (0·1 g.) were refluxed under nitrogen in cyclohexane (30 ml.). The reaction was followed by infrared spectroscopy and by vapour-phase chromatography and was complete in 30 min. The red solution was evaporated, and the dark solid taken up in dichloromethane (10 ml.) and filtered through a 5-cm. alumina column. The resultant white solid (2·46 g., 98%) was shown by gas chromatography to consist of (V) (86·5%) and

---

[22] P. Laszlo and P. R. Schleyer, *J. Amer. Chem. Soc.*, 1964, **86**, 1171.

[23] D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, 1965, **87**, in the press.

[24] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959.

[25] P. Bieber, *Ann. Chim. France*, 1954, **9**, 674.

[26] R. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, 1953, **75**, 4094.

[27] J. M. Birchall, T. Clark, and R. N. Haszeldine, *J.*, 1962, 4977.

[28] W. Hieber and H. Beutner, *Z. Naturforsch.*, 1960, **15b**, 323.

(VIII) (13·5%). This mixture was fractionally crystallised (hot ethanol), to afford (V) as colourless plates (Found: C, 91·3; H, 8·7%. *M*, 189. Calc. for $C_{14}H_{16}$: C, 91·3; H, 8·7%; *M*, 184), m. p. 66·5° (lit.,[23] 67°). The eighth fraction of the recrystallisation was a liquid, which was shown by gas chromatography to consist of 70% of (VIII). The infrared spectrum was identical with that of the dimer prepared by treating (I) with bis(acrylonitrile)nickel.

Dinitrosylbis(triphenylphosphine)iron was recovered unchanged after refluxing in (I) for 4 hr., and no dimerisation of (I) occurred. It was also shown experimentally that (I) was not dimerised by nitric oxide, a possible decomposition product of $Fe(CO)_2(NO)_2$.

Dimerisation of 7-t-Butoxynorbornadiene with Dicarbonyldinitrosyliron.—t-Butoxynorbornadiene [29] (2·5 g., 15 mmoles) dissolved in cyclohexane (30 ml.) was treated with dicarbonyldinitrosyliron (15 mg.) and refluxed under nitrogen. The reaction was followed spectroscopically. After 3 hr., when the $Fe(CO)_2(NO)_2$ had all been consumed, the solution was evaporated. Chromatography of a solution of the residue on alumina, using light petroleum (b. p. 60—80°) as eluant, afforded white *crystals* (430 mg., 16%) (Found: C, 80·5; H, 9·9%; *M*, 337. $C_{22}H_{32}O_2$ requires C, 80·5; H, 9·8%; *M*, 328).

Reaction between Norbornadiene and Tricarbonylnitrosylcobalt.—The yellow solution from (I) (2·5 g., 27 mmoles), tricarbonylnitrosylcobalt (0·1 g.), and cyclohexane (30 ml.) was refluxed under nitrogen for 8 hr., by which time the nitrosyl could not be detected in the mixture by its infrared spectrum. The solution was evaporated to give a brown liquid (700 mg., 28%) which was shown by gas chromatography to consist of (V) (48%), (VI) (52%), and a trace of (VIII). Compound (V) was identified as described above, and the dimers (VI)and (VIII) by their infrared spectra.[14]

An attempt was made to isolate a norbornadienecobalt complex by refluxing tricarbonylnitrosylcobalt (1·5 g., 8·7 mmoles) with (I) (5 g., 54 mmoles) in light petroleum (b. p. 40—60°) for 6 hr. However, no organometallic compound was obtained. It was also shown that refluxing (V) with $Co(CO)_3(NO)$ in cyclohexane did not convert (V) into (VI) or (VIII).

Preparation of the Diepoxide (XI).—A sample (2 g., 19 mmoles) of (V) in benzene (25 ml.) was added to a solution of peracetic acid, obtained from acetic anhydride (4·6 g.) and hydrogen peroxide (7·8 ml., 100 vol.) which had been stirred at 0° for 2 hr. After 15 hr. at room temperature the benzene layer was washed with dilute sodium hydroxide and with water, and dried ($MgSO_4$). Evaporation gave a white *solid* (2·3 g., 95%) which was obtained pure (m. p. 241°) by chromatography on Florisil using chloroform–ether as eluant (Found: C, 77·8; H, 7·4. $C_{14}H_{12}O_2$ requires C, 77·7; H, 7·4%). (XI) showed a characteristic epoxide band at 843 $cm.^{-1}$ in its infrared spectrum. We are indebted to Dr. P. Owston, of the I.C.I. Petrochemical and Polymer Laboratory, for the dipole moment of (XI).

The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and for providing P. W. J. with a pre-doctoral fellowship. They also thank Dr. D. R. Arnold for communicating results prior to publication and Dr. G. N. Schrauzer for the infrared spectra of compounds (VI) and (VIII).

SCHOOL OF CHEMISTRY, THE UNIVERSITY, BRISTOL 8. [*Received, June 3rd*, 1965.]

[29] P. Story, *J. Org. Chem.*, 1961, **26**, 287.