Photoassisted Isomerisation of Olefins by Platinum Complexes

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Summary Photoassisted isomerisation of carbon–carbon double bonds has been effected for the first time in the presence of platinum complexes; pent-2-ene, hex-2-ene, and 1,2-dichloroethene can be *cis–trans* interconverted with high efficiency.

PHOTOASSISTED isomerisation of olefins initiated by transition-metal (*e.g.* Cu^{II} and Rh^{I}) complexes, or metal carbonyl complexes has been studied,[1,2] but, as far as we know, there is no example of the photoinitiation of an isomerisation by platinum complexes. We have studied[3] the photochemical reactivity of the complexes [$PtCl_2$(amine)(olefin)], and have shown that on irradiation at $254 \leqslant \lambda \leqslant 366$ nm the olefin is expelled, yielding an aminated dimer [$PtCl_2$(amine)]$_2$.

Although it appeared from previous experiments[3–5] that only a minor proportion of the olefin could be isomerised during its photochemical expulsion from the complex, such behaviour was interesting enough for us to attempt a possible photoassistance of olefin isomerisation. We thought it would be possible to inhibit the dimerisation of the complex by using an excess of the olefin in solution, as the photochemically obtained tri-co-ordinated species [$PtCl_2$(amine)] could recombine with the free olefin to yield the initial complex rather than dimerise. We have studied the *trans*-[$PtCl_2$(tmpy)(olefin)] complexes (**2**) (tmpy = 2,4,6-trimethylpyridine, olefin = dichloroethene, pentene, or hexene) for which there is no thermal olefin exchange, and which show photodimerisation as the only photoprocess.†

Several types of olefins have been studied: alkylated olefins such as *cis*- and *trans*-pent-2-ene and -hex-2-ene, and chlorinated olefins such as *cis*- and *trans*-1,2-dichloroethene. When a mixture of pent-2-ene isomers was irradiated in the presence of *trans*-[$PtCl_2$(tmpy)(C_2H_4)] (**1**), whatever the

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† Conditions: 40 ml of a 9×10^{-4} M solution of complex (**1**) and $3{\cdot}6 \times 10^{-2}$ or $3{\cdot}6 \times 10^{-1}$ M olefin in CH_2Cl_2 (40 or 400 equiv. of olefin per complex), deoxygenated and irradiated ($\lambda > 310$ nm) with a Hanau TQ 150 mercury vapour arc lamp, the olefin isomerisation being monitored by g.l.c. (12 m × 1/8 in column, 30% PPG on Chromosorb G).

composition of the initial olefin mixture, a photostationary equilibrium with a ratio of *trans*- to *cis*-pent-2-ene of 80:20 was obtained after 50 h. The *cis*- to *trans*-isomerisation process is the major photoassisted reaction, since the total amount of *cis*- and *trans*-pent-2-ene comprises 97% of the final mixture. Some minor processes gave pentane (*ca.* 2%), pent-1-ene (< 1%), and traces of penta-1,4-diene.

Irradiation of complex (**1**) in the presence of an excess of *cis*- or *trans*-hex-2-ene yielded analogous results. A photostationary equilibrium mixture (80:20) of *trans*- and *cis*-hex-2-ene was obtained, irrespective of the composition of the initial olefin. Hexane was also formed in small proportion, but hex-1-ene and hex-3-enes were present only as traces. Complex (**1**) was irradiated in the presence of pent-1-ene, in order to establish that no hydrogen migration takes place across the carbon chain. After 65 h irradiation, the mixture consisted of 97% of pent-1-ene, 1·5% of *cis*- and *trans*-pent-2-ene, 1·3% of pentane, and < 0·2% of penta-1,4-diene.

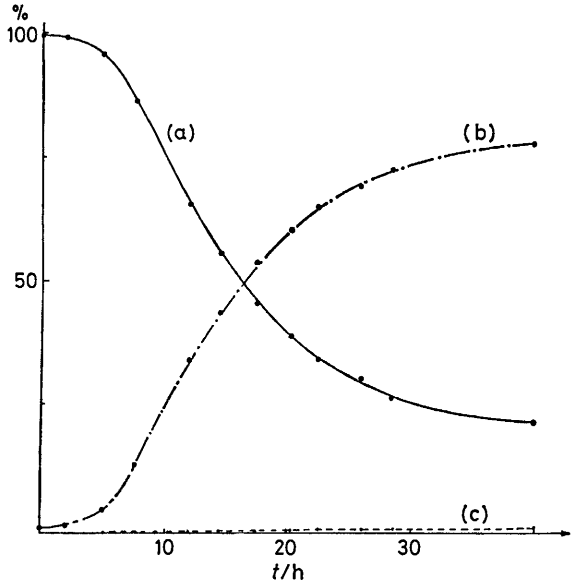

FIGURE. Isomer distribution during irradiation of a 9 × 10^{-4} M solution of complex (**1**) in CH_2Cl_2 in the presence of 0·36 M *cis*-pent-2-ene: (a) *cis*-pent-2-ene; (b) *trans*-pent-2-ene; (c) pentane.

A photoassisted *cis–trans*-isomerisation is also possible when electron-attracting groups are present, such as chlorine. Irradiation of complex (**1**) in the presence of an excess of *cis*- or *trans*-1,2-dichloroethene (40 equiv. of olefin per complex) led to a clean photoassisted isomerisation of the double bond; in this case, the photostationary equilibrium was attained more rapidly (3 h) and it favoured the *cis*-dichloro-olefin (70:30 *cis*:*trans* ratio).

All the compounds studied showed an induction period, which is short for the 1,2-dichloroethenes (7—10 min), and somewhat longer for the other olefins (4—8 h depending on the olefin; see Figure for *cis*-pent-2-ene). This suggests that the complex which initiated the isomerisation is not *trans*-$[PtCl_2(tmpy)(olefin)]$ (**2**), but a species derived from it on irradiation. We have not been able to identify the species as yet, but the transformations of the initial complex (**1**) have been followed by irradiation in the presence of an excess of olefin. The steps in the Scheme have been established for the photoreactions of complex (**1**).[3,6]

$$\begin{tikzcd}
\underset{(\mathbf{1})}{trans\text{-}[PtCl_2(tmpy)(C_2H_4)]} \arrow[r, "h\nu", "\text{olefin excess}"'] & \underset{(\mathbf{2})}{trans\text{-}[PtCl_2(tmpy)(olefin)]} \arrow[d, "h\nu"] \\
\underset{(\mathbf{4})}{[PtCl_3(tmpy)]^- \ [Htmpy]^+} & \underset{(\mathbf{3})}{cis\text{- and } trans\text{-}[PtCl_2(tmpy)]_2} \arrow[l, "h\nu"']
\end{tikzcd}$$

SCHEME

Each step of this sequence has been independently established and the same photoassisted olefin isomerisations as just described have been performed starting from either the *trans*-dimer $[PtCl_2(tmpy)]_2$ (**3**) or the ionic complex $[PtCl_3(tmpy)]^-$ $[Htmpy]^+$ (**4**).[3] An induction period is observed in these cases also, which indicates that none of these complexes is the direct initiator of the photoassisted isomerisations. We were able to establish that these olefin isomerisations have no thermal origin from a species photochemically generated in solution, as the isomer proportion does not change when the irradiation is stopped.

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[1] R. G. Salomon, in 'Inorganic and Organometallic Photochemistry,' ed. M.S. Wrighton, Advances in Chemistry Series 168, American Chemical Society, Washington D.C., 1978, p. 174, and references cited therein.

[2] G. L. Geoffroy and M. S. Wrighton, 'Organometallic Photochemistry,' Academic Press, New York, 1979.

[3] R. Rumin and P. Courtot, *J. Organomet. Chem.*, 1979, **169**, 225, and previous papers.

[4] P. Courtot, R. Pichon, and J. Y. Salaün, unpublished results.

[5] P. Courtot, R. Rumin, and A. Peron, *J. Organomet. Chem.*, 1978, **144**, 357.

[6] P. Courtot, J. Y. Salaün, and R. Pichon, to be published.