Laser Irradiation of a Diphosphene: Evidence for the First *cis–trans* Isomerization

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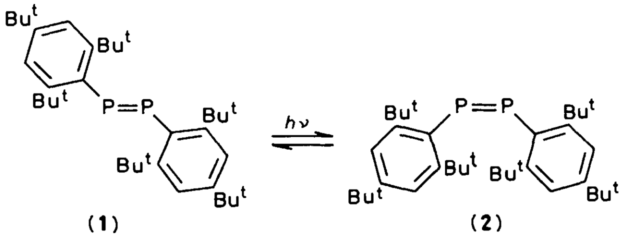
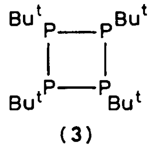
Low temperature laser irradiation of *trans*-diphosphene (**1**), followed using u.v., and ^{31}P and ^{1}H n.m.r. spectroscopy, gives an equilibrium between (**1**) and the unstable *cis*-isomer (**2**): the activation free energy of the (**2**)→(**1**) reaction is 20.3 kcal mol^{-1} (1 kcal = 4.18 kJ).

Isomerization reactions are well known in photochemistry. Geometrical isomerizations easily carried out under u.v. irradiation provide a suitable method for obtaining highly hindered isomers like the diazene or disilene series,[1] and organophosphorus analogues have been prepared and studied during the last two years. By introducing very bulky substituents Yoshifuji *et al.*[2] isolated bis(2,4,6-tri-t-butylphenyl)diphosphene (**1**), attracting a great deal of interest.[3] Structural determination indicated that (**1**), like all known diphosphenes, exhibits a *trans* configuration. The present article reports spectroscopic evidence for the formation of the unstable *cis*-diphosphene (**2**) by visible irradiation of the *trans* isomer (**1**).

Direct irradiation (514.5 nm) of a toluene solution of (**1**) at low temperature (−78 °C) with an argon ion laser, induces various changes which were studied by ^{31}P and ^{1}H n.m.r. and u.v. spectroscopy.



(**1**) (**2**)



(**3**)

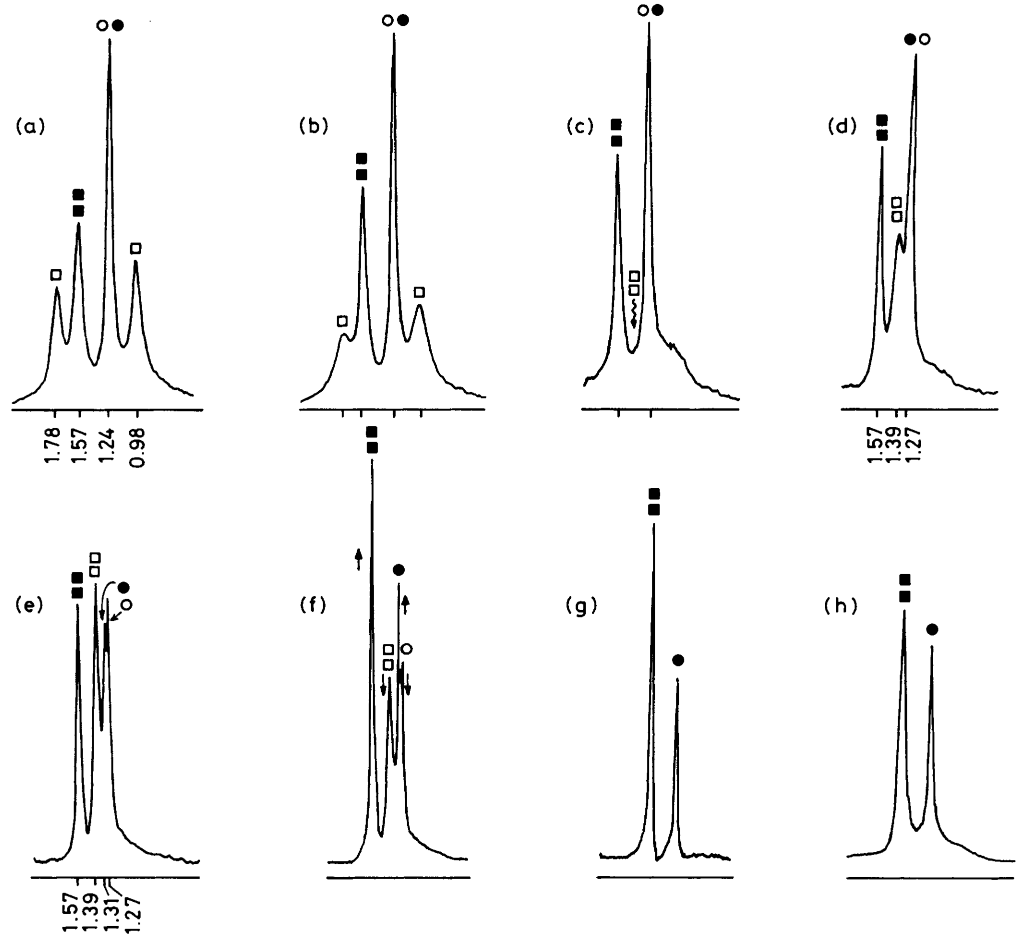


Figure 1. ^{1}H N.m.r. spectra of irradiated solutions of (**1**): (a) −70 °C, (b) −50 °C, (c) −40 °C, (d) −20 °C, (e) 0 °C, (f) 0 °C, +30 min, (g) +30 °C, (h) (**1**), not irradiated, at −70 °C. (**1**): ■ Me (*ortho*), ● Me (*para*); (**2**): □ Me (*ortho*), ○ Me (*para*).

The ^{31}P n.m.r. spectra, obtained at −80 °C, of a C_7D_8 solution of (**1**) (2×10^{-2} M) irradiated for 65 min showed only two peaks [δ (p.p.m. relative to H_3PO_4) +492 (30%) and +368 (70%)† corresponding to (**1**) and (**2**) respectively]. On increasing the temperature, the signal at δ 368 p.p.m. decreased whereas the signal at δ 492 p.p.m. increased. At room temperature only the signal corresponding to the starting material (**1**) was observed. The back reaction (**2**)→(**1**) was followed by ^{31}P n.m.r. at 0 °C, giving the first order rate constant of this reaction, k as 2.88×10^{-4} s^{-1} ($\Delta G^{\ddagger} = 20.35$ kcal mol^{-1}).‡

The ^{1}H n.m.r. spectra of the irradiated solution of (**1**) recorded at 0 °C (Figure 1e) shows four signals for the methyls of the Bu^t groups: δ 1.57 and 1.31 (2 : 1 ratio), *ortho* and *para* methyl groups of (**1**); δ 1.39 and 1.27 (2 : 1 ratio) for compound (**2**). The rate constant of the back reaction (**2**)→(**1**) (as determined by ^{1}H n.m.r. spectroscopy), k was 2.7×10^{-4} s^{-1} ($\Delta G^{\ddagger} = 20.38$ kcal mol^{-1} at 0 °C). Unexpectedly, the ^{1}H n.m.r. spectra of the mixture (**2**)–(**1**) changed between −70 and 0 °C. The −70 °C ^{1}H n.m.r. spectrum has four peaks at δ 0.98, 1.24, 1.57, and 1.78 (Figure 1a). When the temperature was increased the signals at δ 0.98 and 1.78 broadened and coalesced at −40 °C (Figure 1c) to give only one signal at δ 1.39. This phenomenon is reversible. At 0 °C the previously described spectrum was recovered. The coalescence pattern can be interpreted as a result of the hindered rotation of the Bu^t groups in the *ortho* position for the more crowded compound (**2**). The free activation energy for the hindered rotation $\Delta G^{\ddagger}$ was 11.2 kcal mol^{-1} at −40 °C.

An aliquot of the above irradiated solution was observed by u.v. spectroscopy. Spectral changes with time of this solution were followed at +2.5 °C. The $\lambda_{max.}$ at 452 and 347 nm shifted to 463 and 343 nm respectively, whereas two isosbestic points were observed at λ 449 and 365 nm. The rate of (**2**)→(**1**) interconversion monitored at 420 nm, k was 3.2×10^{-4} s^{-1} ($\Delta G^{\ddagger} = 20.5$ kcal mol^{-1} at 2.5 °C).

All information obtained from the three different methods indicated that irradiation of (**1**), at low temperature, leads to the selective formation of a new unstable compound (**2**). At room temperature (**2**) quantitatively returned to the starting material. This suggests the *cis* ⇌ *trans* isomerization. For the two geometrical isomers, the difference of ^{31}P chemical shift observed was very large (Δδ = 124 p.p.m.). However, the value δ 368 p.p.m. is consistent with a dico-ordinated phosphorus compound, so the possibility of dimerization [a dimer compound like (**3**) shows a ^{31}P resonance at δ −58 p.p.m.][4] and rearrangement involving a methyl group,[5] can be ruled out. Since similar results were obtained when oxygen or argon was bubbled through solutions of (**1**) in toluene or dichloromethane, it can be assumed that this

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† In fact the ratio 70 : 30 seems to represent, under the experimental conditions, the photo stationary equilibrium already obtained after 10 min.

‡ 1 kcal = 4.18 kJ.

reaction does not involve either solvation by toluene or photo-oxidation.

Theoretical calculations[6] suggest that there is a small but significant difference between the two isomers which at room temperature is sufficient for the compound to be largely (say over 99%) in the form of (**1**). This, coupled with the low interconversion barrier, is probably the reason why previous irradiation experiments[7] carried out at room temperature did not show the presence of species other than (**1**).

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