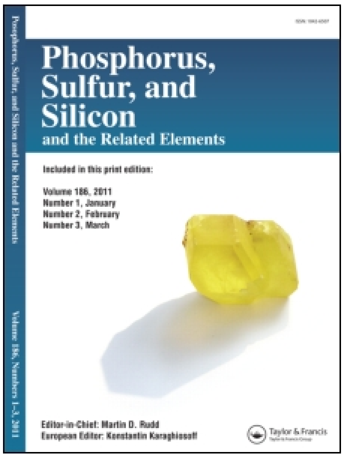


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE ISOMERIZATION OF Δ^3-TO Δ^2-PHOSPHOLENES PROMOTED BY ETHYL ACRYLATE

Paul D. Beer[a]; Philip J. Hammond[a]; C. Dennis Hall[a]
[a] Department of Chemistry, King's College, University of London, Strand, London

To cite this Article Beer, Paul D. , Hammond, Philip J. and Hall, C. Dennis(1981) 'THE ISOMERIZATION OF Δ^3-TO Δ^2-PHOSPHOLENES PROMOTED BY ETHYL ACRYLATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 10: 2, 185 — 189

To link to this Article: DOI: 10.1080/03086648108077504

URL: http://dx.doi.org/10.1080/03086648108077504

Phosphorus and Sulfur, 1981, Vol. 10, pp. 185–190
0308-664X/81/1002-0185$06.50/0

THE ISOMERIZATION OF Δ^3- TO Δ^2-PHOSPHOLENES PROMOTED BY ETHYL ACRYLATE

PAUL D. BEER, PHILIP J. HAMMOND and C. DENNIS HALL

Department of Chemistry, King's College, University of London, Strand, London WC2R 2LS.

(Received September 19, 1980)

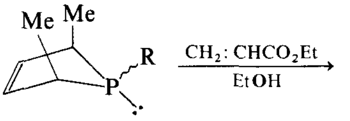
Diastereomerically pure *cis*- or *trans*-1-methyl (or 1-phenyl)-2,5-dimethyl-Δ^3-phospholenes (**1ab** and **2ab**) react with ethyl acrylate in benzene and in the presence of ethanol to produce mixtures of the diastereomeric 1-substituted-2,5-dimethyl-Δ^2-phospholenes (**3ab** and **4ab**). A mechanism is proposed involving a pentaco-ordinate intermediate which achieves a relief of strain by isomerisation of the double bond.

Trico-ordinate phosphorus compounds are known to behave as nucleophiles towards activated double (or triple) bonds by the reversible formation of betaines which may be trapped as the phosphonium salts by protonation (Eq. 1).[1–3] In the presence of alcohols the betaines form pentaco-ordinate phosphorus compounds especially when the trico-ordinate phosphorus compound is either a phosphinite or a phosphonite and the alcohol is primary.[4]

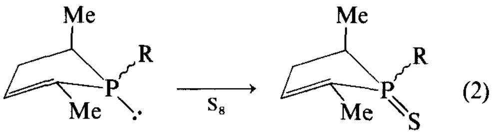
$$R_3P + CH_2{=}CHY \rightleftharpoons R_3\overset{+}{P}CH_2{-}\overset{-}{C}HY \xrightarrow{HCl} R_3\overset{+}{P}CH_2CH_2Y\ \ \overset{-}{Cl} \qquad (1)$$

Y = electron withdrawing group, e.g. $-CO_2R$ or $-CN$.

As a result of this work and with the knowledge that pentaco-ordinate phosphorus compounds are often stabilised by incorporating small (4- or 5-membered) rings to span the apical-equatorial positions of the incipient tbp, we decided to investigate the reactions of Δ^3-phospholenes with the activated olefin, ethyl acrylate. The reactions were followed by ^{31}P nmr and the results for *cis*- and *trans*-1,2,5-trimethyl-Δ^3-phospholene (**1a** and **1b** respectively) and *cis*- and *trans*-1-phenyl-2,5-dimethyl-Δ^3-phospholene (**2a** and **2b**) are shown in Table I. In all four cases a quantitative conversion to a mixture of diastereomeric Δ^2-phospholenes was observed (Eq. 2). The products were identified by ^{31}P nmr and the structures were confirmed by treatment of the reaction mixtures with sulphur to produce the corresponding sulphides (**5ab** and **6ab**) which were isolated by distillation under high vacuum (ca. 0.1 mm).† The sulphides offer a useful source of the Δ^2-phospholenes through reduction with hexachlorodisilane and hence one has a clean and facile entry into the Δ^2-phospholene series.‡



1a, R = *cis*-Me **2a**, R = *cis*-Ph
1b, R = *trans*-Me **2b**, R = *trans*-Ph



3ab, R = Me **5ab**, R = Me
4ab, R = Ph **6ab**, R = Ph

It is obvious from Table I that the *cis*- and *trans*-1,2,5-trimethyl-Δ^3-phospholenes each give the same mixture of diastereomeric Δ^2-phospholenes (**3ab**) whereas with the 1-phenyl-2,5-dimethyl-Δ^3-phospholenes, the *cis*-isomer gives a predominance of *cis*-Δ^2 (**4a**) and the *trans*-isomer a predominance of *trans*-Δ^2 (**4b**).

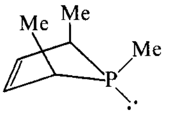
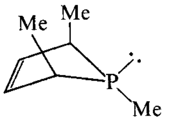
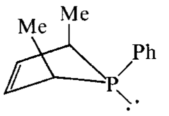
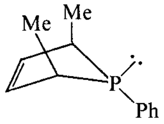
The results may be rationalised by assuming the existence of a pentaco-ordinate intermediate (**7**)

---

† The preparation and nmr data of mixtures of the diastereomeric phosphines (**3ab** and **4ab**) and their oxides and sulphides are reported elsewhere.[5]

‡ Unfortunately, fractional distillation of the mixture of Δ^2-phospholenes and ethyl acrylate failed to separate the components efficiently.

TABLE I

Initial phospholene		Products ($\delta^{31}P$, %)	
		Δ^2-phospholenes	Δ^2-phospholene sulphides
	**(1a)**	**3a** (−8,2, 33); **3b** (4.7, 67)	**5a** (63.3, 33); **5b** (66.0, 67)
	**(1b)**	**3a** (−8.3, 34); **3b** (4.6, 66)	**5a** (63.0, 36); **5b** (66.0, 64)
	**(2a)**	**4a** (9.9, 59); **4b** (22.6, 41)	**6a** (68.6, 53); **6b** (69.6, 47)
	**(2b)**	**4a** (9.9, 36); **4b** (22.6, 64)	**6a** (68.4, 36; **6b** (69.4, 64)

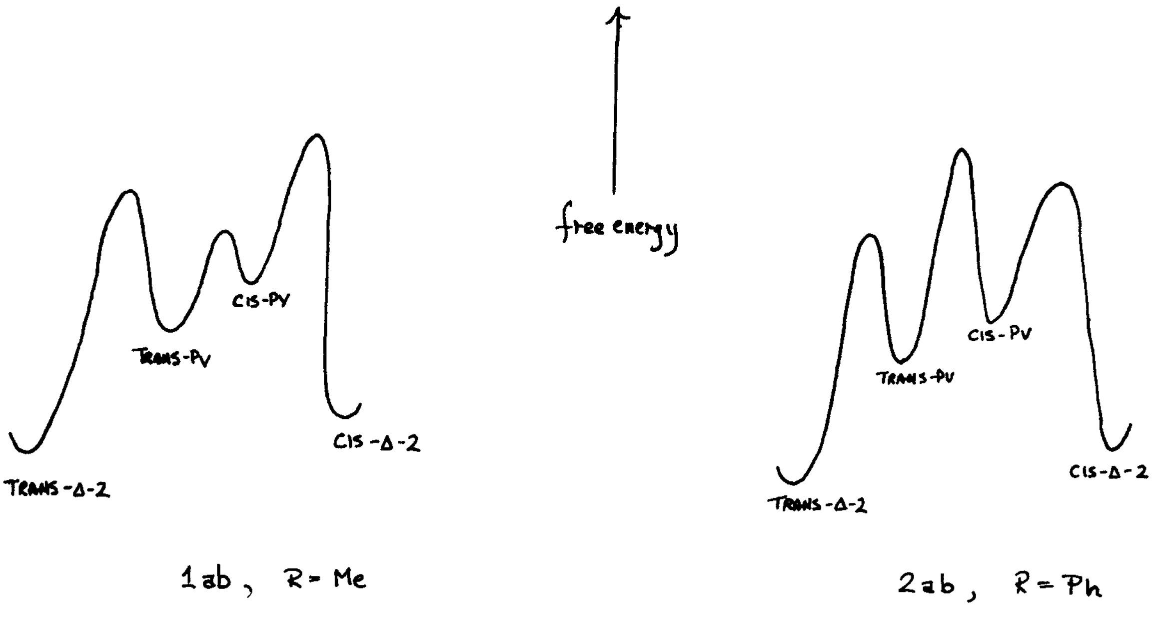
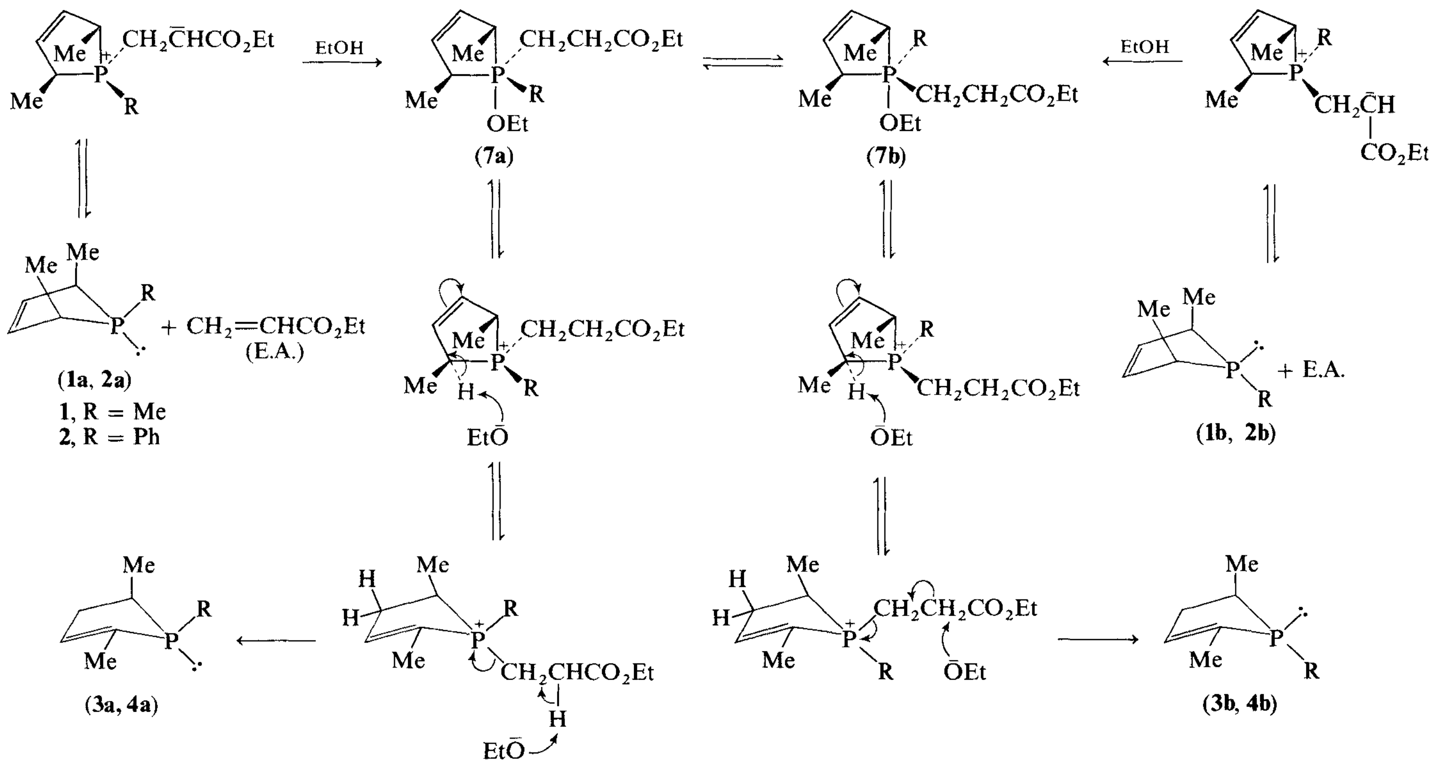
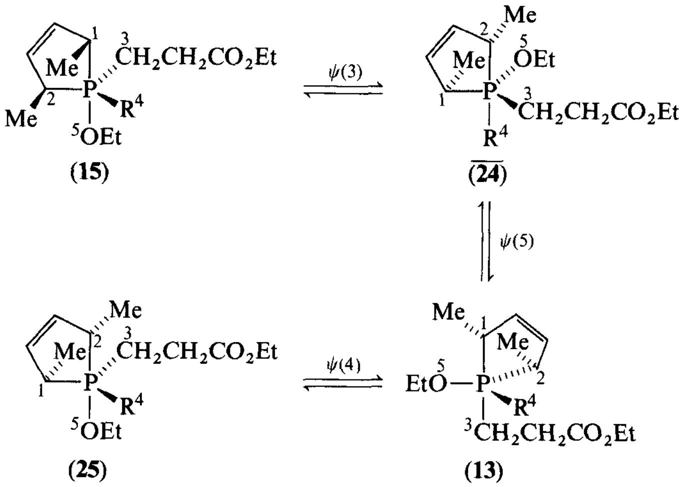


FIGURE 1 Energy profiles for the isomerisation of (**1ab**) and (**2ab**) via pentacoordinate intermediates.

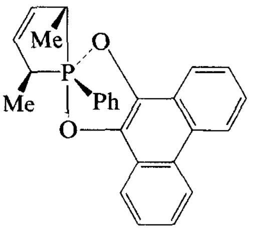

EtOH
EtOH
(7a)
(7b)
(1a, 2a)
1, R = Me
2, R = Ph
+ CH₂=CHCO₂Et
(E.A.)
(1b, 2b)
+ E.A.
(3a, 4a)
(3b, 4b)

SCHEME 1

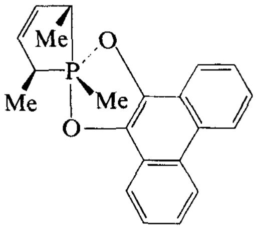


SCHEME 2

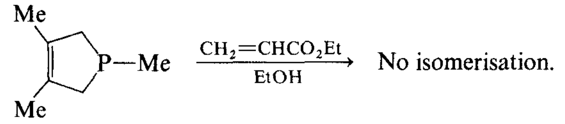
which in the case of R = Me may pseudorotate freely between the two diasteromers of lowest energy (**7a** and **7b**) and so produce an equilibrium mixture of the Δ^2-phospholenes (**3a** and **3b**) from (**1a**) or (**1b**)-Scheme 1. With R = Ph however, the energy barrier to pseudorotation must be slightly higher than that for the isomerisation process since the same mixture of the Δ^2-phospholenes is *not* produced from each Δ^3-phospholene. It has been established from work on the fragmentation of phosphoranes derived from Δ^3-phospholenes,[6] that steric compression plays a significant role in the stability of phosphoranes so that (**8**) derived from (**2a**) is less stable than the analogous (**9**) derived from (**1a**). Since 1,3,4-trimethyl-Δ^3-phospholene (**10**) does not isomerise to the Δ^2-phospholene in the presence of ethyl acrylate,† it seems likely that steric factors also play a significant role in the *isomerisation* and hence it is not surprising that the energy barrier for isomerisation of the double bond should be *lower* for R = Ph than for R = Me. On the other hand, the energy barriers facing pseudorotation from (**7a**) to (**7b**) and *vice-versa* are likely to be higher for R = Ph than for R = Me. This can be seen quite readily if one considers the most likely pseudorotation pathway which avoids placing the five-membered ring diequatorial (Scheme 2). The high-energy isomer is 24 with the ethoxy group equatorial and the R group apical. Since the phenyl group is less apicophilic than the methyl group[1,7] one can expect a slower rate of pseudorotation for R = Ph. Thus both energy factors favour isomerisation rather than pseudorotation for R = Ph and hence the equilibration of (**4a**) and (**4b**) is never complete. The two, slightly different free energy profiles for (**1ab**) and (**2ab**) are represented by Figure 1.



(**8**)



(**9**)



(**10**)

ACKNOWLEDGEMENT

We thank the S.R.C. for financial support.

REFERENCES

1. J. Emsley and C. D. Hall, *The Chemistry of Phosphorus*, Chap. 4, Harper and Row, 1976.
2. M. A. Shaw and R. Ward, *Topics in Phosphorus Chemistry*, Vol. 7, Wiley Interscience, 1972.

---

† Polymerisation of the ethyl acrylate is observed over several hours at ambient.

3. a) Z. Rappoport and S. Gertler, *J. Chem. Soc.*, 1360 (1961).
   b) R. L. Powell and C. D. Hall, *J. Chem. Soc.*, **C**, 2336 (1971).
4. P. D. Beer, R. C. Edwards, C. D. Hall, J. R. Jennings, and R. J. Cozens, *J. Chem. Soc., Chem. Com.*, 351 (1980).
5. P. J. Hammond, J. R. Lloyd, and C. D. Hall, "The reactions of Δ^3-phospholenes with sulphenate esters and sulphenamides," *Phosphorus and Sulphur*, in press.
6. P. J. Hammond, J. R. Lloyd, and C. D. Hall, "The fragmentation of phosphoranes," *Phosphorus and Sulphur, in press.*
7. R. K. Oram and S. Trippett, *J. Chem. Soc.*, Perkin **I**, 1300 (1973).