

Studies on Heterocyclic Chemistry. Part XV.¹ Synthesis of Phosphine *N*-Styrylimides by the Reaction of 2*H*-Azirines with Triphenylphosphine and a Tetrahalogenomethane, and their Transformation into Isoquinoline Derivatives²

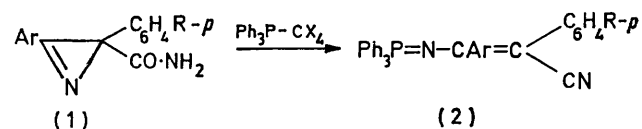
By Tarozaemon Nishiwaki* and Fusako Fujiyama, Department of Chemistry, Yamaguchi University, Yamaguchi City 753, Japan

Phosphine *N*-styrylimides are prepared by the ring-opening of 2,3-diaryl-2*H*-azirine-2-carboxamides or 2-alkoxy-carbonyl-3-aryl-2*H*-azirines with a combination of triphenylphosphine and a tetrahalogenomethane; mechanisms for the reaction are discussed. Phosphine *N*-(β -cyano- β -arylstyryl)imides afford 3-aryl-1-arylamino-4-cyano-isoquinolines when treated with aryl isocyanates.

DESPITE the recent development of the chemistry of 2*H*-azirines,³ which has been made feasible by their ready synthesis (by thermal or photochemical decomposition of vinylic azides^{4,5} and thermal⁶ or photochemical^{6,7} valence-bond isomerization of isoxazoles), 2*H*-azirines having a functional group other than carbonyl at C-2 or C-3 are little known. We were interested in studying the 2-cyano-derivatives. One convenient approach to these compounds is the dehydration of the corresponding carboxamides, but this reaction must be carried out under neutral conditions, since a 2*H*-azirine ring is easily cleaved by acidic reagents.³ We therefore studied the behaviour of 2*H*-azirine-2-carboxamides towards a combination of triphenylphosphine and carbon tetrachloride, which has been reported to dehydrate a number of carboxamides to nitriles.⁸

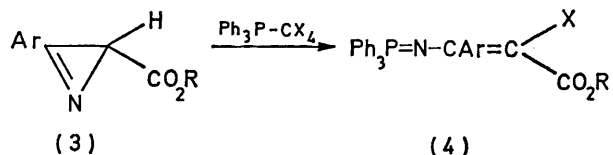
Treatment of 2,3-diphenyl-2*H*-azirine-2-carboxamide (1; Ar = Ph, R = H) with triphenylphosphine (2 equiv.)^{8a} and carbon tetrachloride (1 equiv.) in dry tetrahydrofuran at 50–60° gave a compound C₃₃H₂₅N₂P (10%), together with triphenylphosphine oxide and a further product not containing nitrogen which appears to be a quaternary phosphonium salt (its structure is as yet unknown). The nitrogen-containing material is a 1:1 adduct of triphenylphosphine and the dehydration product of the 2*H*-azirine (1; Ar = Ph, R = H); its i.r. spectrum exhibits strong absorptions at 2190 (C≡N) and 1388 cm⁻¹ (P=N stretching band⁹). The relatively low frequency of the C≡N band suggests the presence of an enamino-nitrile group.¹⁰ The n.m.r. spectrum displays an aryl multiplet only. From these observations the new compound was identified as phosphine *N*-(β -cyano- β -phenylstyryl)imide (2; Ar = Ph, R = H). Use of 3 equiv. of triphenylphosphine gave a higher yield (20%) of compound (2; Ar = Ph, R = H). Reactions with

other tetrahalogenomethanes (carbon tetrabromide and bromotrichloromethane) also afforded the same compound in comparable yield, whereas use of bromoform



did not produce the phosphine imide. Triphenylphosphine is known to react with bromoform at its boiling temperature to give a phosphonium salt Ph₃P⁺·CHBr₂ Br⁻,¹¹ but the high reaction temperature required discouraged us from further studies with this system. Similar reactions gave the phosphine *N*-(β -cyano- β -arylstyryl)imides (2; Ar = *p*-MeC₆H₄, R = H) and (2; Ar = Ph, R = Cl) in comparable yield (see Table 1), but we could not isolate 2-cyano-2*H*-azirine from any of these reactions.

We then studied the behaviour of 2-alkoxycarbonyl-3-aryl-2*H*-azirines towards triphenylphosphine and a tetrahalogenomethane. When the 3-phenyl methyl ester (3; Ar = Ph, R = Me) was treated with triphenylphosphine (2 equiv.) and carbon tetrachloride (1 equiv.) in dry tetrahydrofuran, a compound C₂₈H₂₃ClNO₂P was obtained (30%), together with a compound presumed to



be a phosphonium salt (not studied further). The former compound is a 1:1 adduct of the chlorination product of the 2*H*-azirine (3; Ar = Ph, R = Me) and triphenylphosphine, identified as phosphine *N*-(β -chloro- β -methoxycarbonylstyryl)imide (4; Ar = Ph, R = Me,

¹ Part XIV, T. Nishiwaki and F. Fujiyama, *Synthesis*, 1972, 569.

² Preliminary communication, T. Nishiwaki, *J.C.S. Chem. Comm.*, 1972, 565.

³ F. W. Fowler, *Adv. Heterocyclic Chem.*, 1971, **13**, 45.

⁴ G. Smolinsky, *J. Amer. Chem. Soc.*, 1961, **83**, 4483.

⁵ A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, 1968, **90**, 2869.

⁶ T. Nishiwaki, T. Kitamura, and A. Nakano, *Tetrahedron*, 1970, **26**, 453; T. Nishiwaki and T. Saito, *J. Chem. Soc. (C)*, 1971, 2648.

⁷ (a) B. Singh and E. F. Ullman, *J. Amer. Chem. Soc.*, 1967, **89**, 6911; (b) T. Nishiwaki, A. Nakano, and H. Matsuoka, *J. Chem. Soc. (C)*, 1970, 1825.

⁸ (a) E. Yamato and S. Sugawara, *Tetrahedron Letters*, 1970, 4383; (b) R. Appel, R. Kleinstück, and K.-D. Ziehn, *Chem. Ber.*, 1971, **104**, 1030.

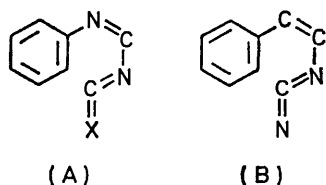
⁹ (a) G. Singh and H. Zimmer, *Organometallic Chem. Rev.*, 1967, **2**, 279; (b) W. Wiegräbe and H. Bock, *Chem. Ber.*, 1968, **101**, 1414.

¹⁰ S. Baldwin, *J. Org. Chem.*, 1961, **26**, 3288; R. A. Mitsch, *J. Amer. Chem. Soc.*, 1967, **89**, 6297.

¹¹ F. Ramirez and N. McKelvie, *J. Amer. Chem. Soc.*, 1957, **79**, 5829; A. J. Burn and J. I. G. Cadogan, *J. Chem. Soc.*, 1963, 5788.

X = Cl) from spectral evidence and chemical reactions. The i.r. spectrum shows strong bands at 1672 (C=O) [cf. the value¹² for the phosphine imide (4; Ar = Me, R = Et, X = H)], 1160 (C-O-C), and 1267 cm⁻¹ (P=N) * cm⁻¹. The n.m.r. spectrum consists of a methoxy-singlet (τ 6.56) and an aromatic multiplet (τ 2.4–3.4) indicating that halogenation had not occurred at the ester methyl group, in accord with the observation of Lee *et al.*¹³ The reactions of other 2-alkoxycarbonyl-3-aryl-2*H*-azirines [(3; Ar = Ph, R = Et) and (3; Ar = *p*-MeC₆H₄, R = Me) with triphenylphosphine and tetrahalogenomethanes proceeded similarly (see Table 2).

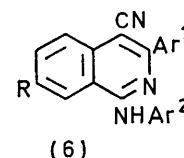
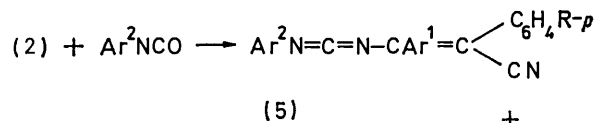
Chemical Reactions.—Imidoyl isothiocyanates¹⁴ and isocyanates¹⁵ having the partial structure (A) undergo valence-bond isomerisation to quinazoline-4-thiones and -4-ones, respectively. By analogy, the carbodi-imide of partial structure (B) (hitherto unknown¹⁶) would be expected to be converted into 1-aminoisoquinoline. As we considered that such a carbodi-imide might be obtained by the reaction of a phosphine *N*-(β -arylstyryl)-imide (2) with isocyanate according to the method of



Staudinger *et al.*,¹⁷ compound (2; Ar = Ph, R = H) was treated with phenyl isocyanate in benzene. Triphenylphosphine oxide, the carbodi-imide (5; Ar¹ = Ar² = Ph, R = H) (identified by i.r.), and a crystalline compound C₂₂H₁₅N₃ (the major product) were obtained. The last product is an isomer of the carbodi-imide (5; Ar¹ = Ar² = Ph, R = H) and has secondary amino- and cyano-groups (i.r. spectrum). Its u.v. spectrum shows it to be highly conjugated. The reactions of other phosphine imides [(2; Ar = Ph, R = Cl) and (2; Ar = *p*-MeC₆H₄, R = H)] with phenyl isocyanate, *p*-chlorophenyl isocyanate, and α -naphthyl isocyanate also produced mixtures of the corresponding carbodi-imide (5), its isomer, and triphenylphosphine oxide.

The isomers of the carbodi-imides (5) were identified as 1-arylamino-4-cyano-3-arylisquinolines (6) by close inspection of the out-of-plane aromatic CH deformation vibration region of their i.r. spectra and by high resolution mass spectrometry. The product derived from the compound (2; Ar = Ph, R = Cl) and phenyl isocyanate shows absorptions at 820 (two adjacent ring hydrogens) and 890 cm⁻¹ (one isolated ring hydrogen),¹⁸ whereas the

product derived from the compound (2; Ar = Ph, R = H) and *p*-chlorophenyl isocyanate has absorption at 825 cm⁻¹ but lacks a band associated with one isolated ring hydrogen atom. These features agree with structure (6). The mass spectrum of the compound (6; Ar¹ = Ar² = Ph, R = H) exhibits intense peaks at *m/e*



218-083, 203-073, 127-046, 103-045, and 92-053. These peaks are accounted for by the cleavages depicted, which are in keeping with the reported fragmentation patterns of isoquinoline derivatives.¹⁹

The carbodi-imides (5), when stored at room temperature or heated in benzene, gave no isoquinoline (6). This suggests that the carbodi-imide (5) is not an intermediate in the formation of (6), in contrast to the case in the isomerisation of imidoyl isothiocyanates¹⁴ and isocyanates.¹⁵ The 1,2-cycloaddition product²⁰ (7) from the phosphine imide (2) and aryl isocyanate probably gives the isoquinoline (6) with concerted elimination of triphenylphosphine oxide. Assignment of structure (6) also agrees with an observation that the phosphine *N*-styrylimide (4; Ar = *p*-MeC₆H₄, R = Me, X = Br), which lacks an aryl group at the β -position, gave only the carbodi-imide (8) [ν_{max} (film) 2130 (N=C=N) and 1722 cm⁻¹ (C=O)] and triphenylphosphine oxide when treated with phenyl isocyanate in benzene.

Phosphine imides are known to be susceptible to hydrolysis;^{9a} compound (4; Ar = Ph, R = Me, X = Cl) was also found to be decomposed to triphenylphosphine oxide, even by hydrazine hydrate, but the phosphine-imide (2; Ar = Ph, R = H) was recovered quantitatively after being heated with hydrazine hydrate. It appears that the P=N bond of the halogen-substituted phosphine imide (4) is easily cleaved by this reagent.

Mechanism.—The species which participates in the dehydration of carboxamides by triphenylphosphine-carbon tetrachloride is Ph₃P⁺Cl CCl₃⁻.^{8b} Electrophilic attack by this species on the carbonyl oxygen atom of the 2*H*-azirine (1) with concomitant loss of chloroform would produce an intermediate (9), which could eliminate

* A minor structural change causes a large shift of $\nu_{\text{max}}(\text{P}=\text{N})$.⁹

¹² G. R. Harvey and K. W. Ratts, *J. Org. Chem.*, 1966, **31**, 3907.

¹³ J. B. Lee and T. J. Nolan, *Canad. J. Chem.*, 1966, **44**, 1331.

¹⁴ H. M. Blatter and H. Lukaszewski, *Tetrahedron Letters*, 1964, 855; J. Goerdeler and D. Weber, *Chem. Ber.*, 1968, **101**, 3475.

¹⁵ L. Samaraj, W. A. Bondar, and G. I. Derkatsch, *Angew. Chem.*, 1967, **79**, 897.

¹⁶ F. Kurzer and K. Douraghi-Zadeh, *Chem. Rev.*, 1967, **67**, 107.

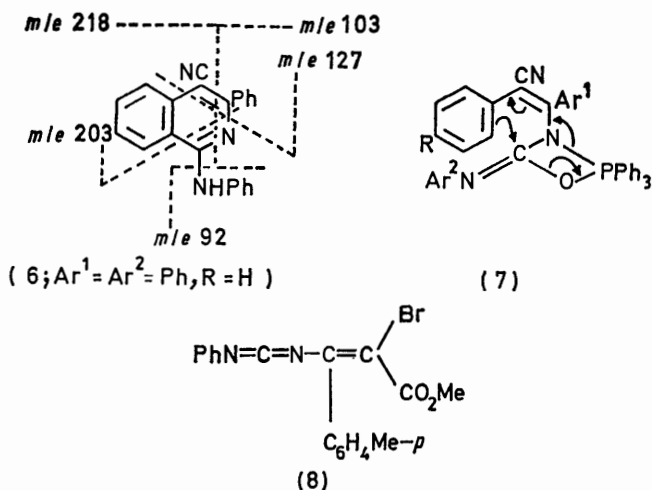
¹⁷ H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 1921, **4**, 861.

¹⁸ K. Nakanishi, 'Infrared Absorption Spectra (Japanese Edition)', Nankodo, Tokyo, 1960, p. 33.

¹⁹ Q. N. Porter and J. Baldas, 'Mass Spectrometry of Heterocyclic Compounds', Wiley-Interscience, New York, 1971, p. 398.

²⁰ H. Ulrich, 'Cycloaddition Reactions of Heterocumulenes', Academic Press, New York, 1967, p. 122.

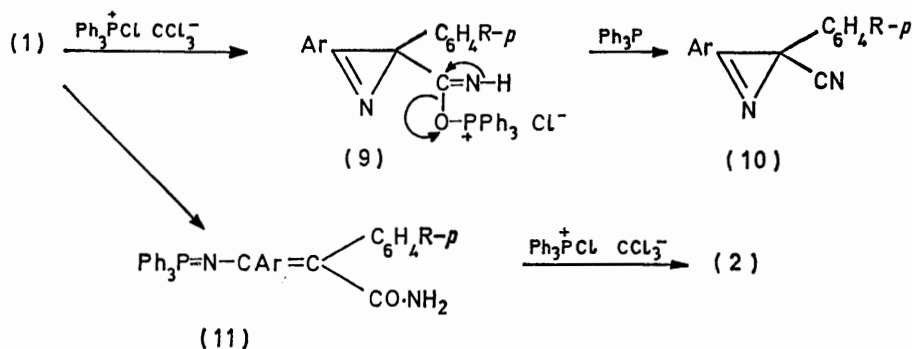
hydrogen chloride (trapped by triphenylphosphine) and triphenylphosphine oxide to produce a 2-cyano-2,3-diaryl-2*H*-azirine (10). But this 2*H*-azirine was not



isolated. We have stated earlier² that this azirine was detected by i.r. spectroscopy, but subsequent detailed studies have shown the absence of a nitrile band in the

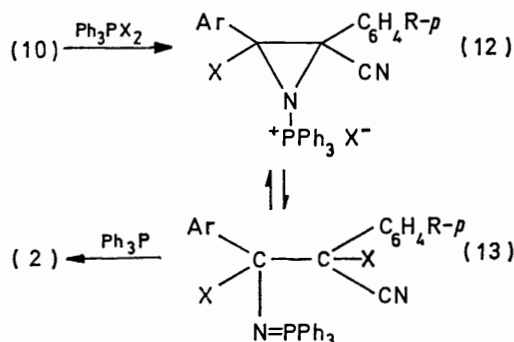
been observed, the phosphine imide (11; Ar = Ph, R = H) was not isolated.

Rabinowitz²¹ and Ramirez²² and their co-workers have reported that the reaction of triphenylphosphine with a tetrahalogenomethane produces a dihalogenotriphenylphosphorane as well as a dihalogenomethylenetriphenylphosphorane, and Horner *et al.* had previously succeeded in converting amides into nitriles using dihalogenotriphenylphosphorane itself, generated by the reaction of triphenylphosphine with a halogen.²³ If a dihalogenotriphenylphosphorane is the species participating in the dehydration of compound (1) and in the conversion of the 2-cyano-2*H*-azirine (10) into the phosphine imide (2), the following mechanism can be envisaged. Electrophilic attack of dihalogenotriphenylphosphorane on the ring nitrogen of the compound (10) will produce the intermediate (12). According to Hassner *et al.*²⁴ an aziridin-1-ylphosphonium halide having one phenyl group on the ring is in equilibrium with its open-chain isomer. If this is so, the intermediate (12) will equilibrate with its isomer (13), and the latter will readily undergo dehalogenation by triphenylphosphine to give compound (2). There are several



region where the cyano-group of the 2*H*-azirine (10) is expected to absorb (2250—2200 cm⁻¹). We withdraw our earlier statement, but we still believe that the 2-cyano-2*H*-azirine (10) is an intermediate for the formation of compound (2) from a 2*H*-azirine-2-carboxamide (1), because formation of an appreciable quantity of triphenylphosphine oxide is explicable only in terms of the process (1) \rightarrow (9) \rightarrow (10). If compound (1) were to be transformed into the phosphine imide (11) possessing an amide function by any of the mechanisms discussed later, and the latter were to undergo dehydration to give compound (2), the formation of triphenylphosphine oxide would be explained. Compound (11) is expected to be stable and to be present in a fair quantity in the reaction mixture before or shortly after the C \equiv N band of (2) begins to develop. However, even when the reaction was stopped about 20 min after the C \equiv N band of compound (2; Ar = Ph, R = H) had

reports of the dehalogenation of 1,2-dihalides by triphenylphosphine.²⁵



To test this hypothesis, the 2*H*-azirine (1; Ar = *p*-MeC₆H₄, R = H) was treated with dibromotriphenylphosphorane in the presence of triphenylphosphine (1

²¹ R. Rabinowitz and R. Marcus, *J. Amer. Chem. Soc.*, 1962, **84**, 1312.

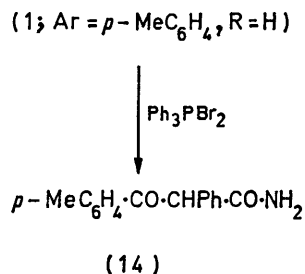
²² F. Ramirez, N. B. Desai, and N. McKelvie, *J. Amer. Chem. Soc.*, 1962, **84**, 1745.

²³ L. Horner, H. Oediger, and H. Hoffmann, *Annalen*, 1959, **626**, 26.

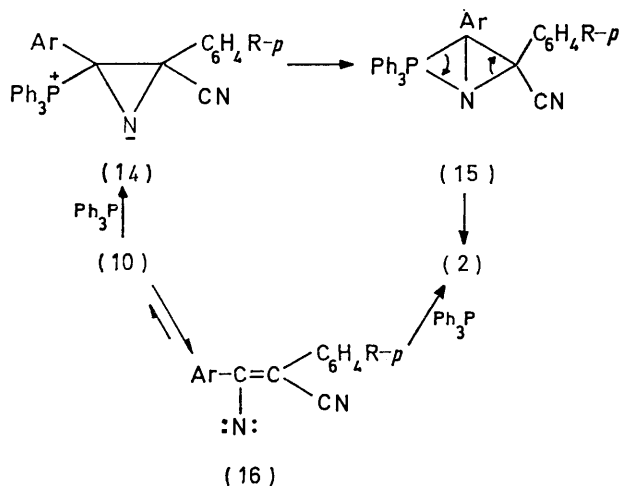
²⁴ A. Hassner and J. E. Gale, *J. Amer. Chem. Soc.*, 1970, **92**, 3733.

²⁵ A. J. Speziale and C. C. Tung, *J. Org. Chem.*, 1963, **28**, 1353; K. C. Pande and G. Trampe, *ibid.*, 1970, **35**, 1169; C. J. Delvin and B. J. Walker, *J.C.S. Perkin I*, 1972, 1249.

equiv.). However, the phosphine imide (2; Ar = *p*-MeC₆H₄, R = H) was not obtained; instead a crystalline material was isolated to which we assign the *p*-toluoylphenylacetamide structure (14) on the basis of i.r. spectral evidence [ν_{\max} (Nujol) 3370 and 3150 (NH₂) and 1684 and 1640 cm⁻¹ (C=O)]. We conclude that a dihalogenotriphenylphosphorane cannot dehydrate the 2*H*-azirine-2-carboxamide (1), and that the reaction pathway (10) → (12) → (13) → (2) is inoperative under the conditions used.



We have recently described the reactions of 2*H*-azirine-2-carboxamides and 2-alkoxycarbonyl-2*H*-azirines with trialkyl phosphites to give the corresponding aziridin-2-ylphosphonates, and postulated the intermediacy of a betaine.²⁶ If triphenylphosphine attacks the C=N bond of compound (10) to produce a betaine (14), the latter may well cyclise to the phosphazabicyclo[1.1.0]butane derivative (15), which could rearrange to the phosphine imide (2). However, triphenylphosphine was found to be unreactive towards 2,3-diaryl-2*H*-azirine-2-carboxamides (1) and 2-alkoxycarbonyl-3-aryl-2*H*-azirines (3), and there is no reason to believe that only the short-lived 2-cyano-2*H*-azirine (10) can react with triphenylphosphine.



Abramovitch^{27a} and Cadogan^{27b} and their co-workers have suggested that 7-azabicyclo[4.1.0]hepta-2,4,6-triene (a bicyclic 2*H*-azirine) is in equilibrium with phenylnitrene. No relevant experiments are reported regard-

²⁶ T. Nishiwaki and T. Saito, *J. Chem. Soc. (C)*, 1971, 3021.

²⁷ (a) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **64**, 149; (b) J. I. G. Cadogan and M. J. Todd, *J. Chem. Soc. (C)*, 1969, 2808.

ing the occurrence of equilibration between a monocyclic 2*H*-azirine and the corresponding vinylnitrene. However, there are two observations which bear on this question. Photochemical valence-bond isomerisation of 2-benzoyl-3-aryl-2*H*-azirines to 3-aryl-5-phenylisoxazoles has been suggested to proceed *via* the corresponding vinylnitrene,^{7a} and Boyer has pointed out²⁸ that hydrogenation of 2-ethoxycarbonyl-3-methyl-2*H*-azirine to ethyl 3-aminocrotonate¹² could proceed *via* the corresponding vinylnitrene. If the 2-cyano-2*H*-azirine (10) equilibrates with the corresponding vinylnitrene (16) in favour of the latter, this could then be converted into the phosphine imide (2); trivalent phosphorus compounds can readily couple with nitrenes.²⁹ To test this hypothesis, the reaction of 2,3-diphenyl-2*H*-azirine-2-carboxamide (1; Ar = Ph, R = H) with triphenylphosphine (3 equiv.) and carbon tetrachloride (excess) was carried out in the presence of cyclohexene. The yield of compound (2; Ar = Ph, R = H) decreased to only 4%, but no product arising from the insertion of (16) into cyclohexene was characterised.

A fourth process to be considered is the cleavage of a 2-cyano-2,3-diaryl-2*H*-azirine ring (10) by a phosphonium salt Ph₃P⁺Cl⁻ or Ph₃P⁺CCl₃⁻. Although this is one of the likely pathways leading to the phosphine imide (2), we cannot envisage a reasonable mechanism at present and we have little relevant experimental evidence. At least two observations cited already, namely, increase of the yield of (2; Ar = Ph, R = H) when the quantity of free triphenylphosphine is increased, and the decrease in the yield of (2; Ar = Ph, R = H) when cyclohexene is present, mitigate against the involvement of such a phosphonium salt.

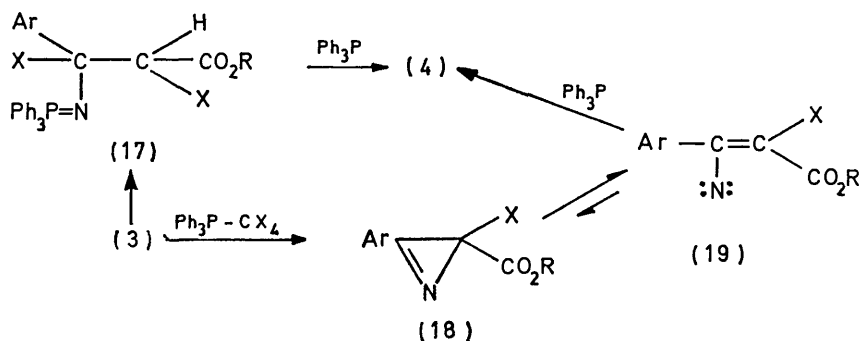
The situation concerning the formation of the halogen-containing phosphine imide (4) is more complicated. We again reject the involvement of a dihalogenotriphenylphosphorane, although elimination of hydrogen halide from such an intermediate as (17) (*see before*) is an acceptable explanation for the presence of halogen in compound (4). This is borne out by an independent reaction of the compound (3; Ar = Ph, R = Me) with dibromotriphenylphosphorane in the presence of triphenylphosphine (1 equiv.); this reaction gave no significant amount of the compound (4; Ar = Ph, R = Me, X = Br).

To examine the possible implication of a phosphonium salt Ph₃P⁺X⁻ or Ph₃P⁺CX₃⁻ in this reaction, 1 equiv. each of triphenylphosphine and carbon tetrabromide were heated in benzene at 60° for 30 min, and the phosphonium salt formed was mixed, without isolation, with 2-methoxycarbonyl-3-aryl-2*H*-azirine (3; Ar = Ph, R = Me) and heated for 2 h. No phosphine imide (4; Ar = Ph, R = Me, X = Br) was obtained, in contrast to the reaction using 2 equiv. of triphenyl-

²⁸ J. H. Boyer, 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, vol. II, Interscience, New York, 1969, p. 267.
²⁹ P. A. S. Smith, 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, p. 99; J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.

phosphine and 1 equiv. of carbon tetrabromide (*see before*), and g.l.c. of the supernatant liquid showed that 20–30% of the starting 2*H*-azirine was unchanged. Thus the presence of free triphenylphosphine appears essential for the formation of (4).

The vinylnitrene (19) is again one of the most likely intermediates, and could be generated from a 2-alkoxycarbonyl-3-aryl-2-halogeno-2*H*-azirine (18). But even if one accepts this reaction course, the question regarding the incorporation of halogen remains unanswered. 2-Halogeno-2*H*-azirine derivatives are reported to be



unstable,³⁰ but their fate is unknown. A combination of triphenylphosphine and tetrahalogenomethane has often been used in the conversion of a hydroxy-group into a halogeno-substituent,³¹ but substitution of a saturated CH group by halogen with this reagent has not been recorded. We hope to clarify these questions in the future.*

The low material balance and the uncertain role of the phosphonium salt Ph₃P⁺X CX₃⁻ or Ph₃P⁺CX₃ X⁻ do not permit a definitive statement concerning the mechanism of the reactions of the 2*H*-azirine derivatives (1) and (3) with triphenylphosphine-tetrahalogenomethane. Further studies are required to establish the occurrence of equilibration between the short-lived 2*H*-azirine and the corresponding vinylnitrene.

EXPERIMENTAL

Petroleum used had b.p. 30–70°. N.m.r. spectra were run at 100 Hz for solutions in CDCl₃. Molecular weights were determined from high resolution mass spectra by use of the 'element map' technique.

Reaction of 2,3-Diphenyl-2*H*-azirine-2-carboxamide (1; Ar = Ph, R = H) with Triphenylphosphine and Carbon Tetrachloride.—A mixture of the 2*H*-azirine (2.36 g, 0.01 mol), triphenylphosphine (7.86 g, 0.03 mol), carbon tetrachloride (1.6 g, 0.01 mol), and dry tetrahydrofuran (50 ml) was stirred at 50–60° for 3 h in nitrogen. The precipitate (0.98 g) was filtered off. This was readily soluble in water, gave triphenylphosphine oxide among other products on treatment with aqueous sodium hydroxide, had an intense i.r. absorption at 1112 cm⁻¹ (quaternary phosphonium

* The reaction of 2-alkoxycarbonyl-2,3-diaryl-2*H*-azirine with triphenylphosphine-tetrahalogenomethane will clarify these questions to some extent. Failure to obtain the isoxazole intermediates has impeded our study in this field.

† Triphenylphosphine oxide was eluted by the first and the second eluants only.

salt³²), and had no u.v. absorption above 300 nm. The filtrate was evaporated and the residue was chromatographed on silica gel with petroleum-carbon tetrachloride (3:1), petroleum-chloroform (10:1), petroleum-chloroform (3:1), ether, ether-ethyl acetate (3:1), and ethyl acetate as eluants. Phosphine N-(β-cyano-β-phenylstyryl)-imide (2; Ar = Ph, R = H) was eluted by the third and the fourth eluants and was washed with cold ethanol (*see Table 1*). Triphenylphenylphosphine oxide was eluted by the first and the second eluants (1.32 g) and the fifth eluant (0.04 g). The product from the fifth eluant may have arisen by hydrolysis of phosphonium salt on the column.

Use of carbon tetrabromide (3.32 g, 0.01 mol) in place of carbon tetrachloride afforded 25% yield of compound (2; Ar = Ph, R = H). When the reaction was carried out using trichlorobromomethane (2.0 g, 0.01 mol) and anhydrous benzene, the yield of the phosphine imide was 9%.

Reaction of 2-*p*-Chlorophenyl-3-phenyl-2*H*-azirine-2-carboxamide (1; Ar = Ph, R = Cl) with Triphenylphosphine and Carbon Tetrachloride.—A mixture of the 2*H*-azirine (5.74 g, 0.021 mol), triphenylphosphine (16.50 g, 0.063 mol), carbon tetrachloride (30 ml; excess), and dry tetrahydrofuran (100 ml) was stirred at 60° for 2 h in nitrogen, and the precipitate (6.81 g) was filtered off. Work-up as before gave the phosphine imide (2; Ar = Ph, R = Cl) (*see Table 1*) and triphenylphosphine oxide (2.26 g, 38%).†

Reaction of 2-Phenyl-3-*p*-tolyl-2*H*-azirine-2-carboxamide (1; Ar = *p*-MeC₆H₄, R = H) with Triphenylphosphine and Carbon Tetrachloride.—A mixture of the 2*H*-azirine (5.00 g, 0.02 mol), triphenylphosphine (15.72 g, 0.06 mol), carbon tetrachloride (30 ml; excess), and dry tetrahydrofuran (100 ml) was stirred at 55–60° for 2 h in nitrogen, and the precipitate (6.58 g) was filtered off. Work-up as before gave the phosphine imide (2; Ar = *p*-MeC₆H₄, R = H) (*see Table 1*) and triphenylphosphine oxide (2.13 g, 38%).†

Reaction of 2-Phenyl-3-*p*-tolyl-2*H*-azirine-2-carboxamide (1; Ar = *p*-MeC₆H₄, R = H) with Dibromotriphenylphosphorane.—A solution of the 2*H*-azirine (1.50 g, 0.006 mol) and dry benzene (30 ml) was added to a cold mixture of dibromotriphenylphosphorane and benzene [prepared by adding a solution of bromine (1.0 g, 0.006 mol) in dry benzene (10 ml) to a solution of triphenylphosphine (3.14 g, 0.012 mol) in dry benzene (20 ml)] and heated under reflux for 30 min. Solid was filtered off and dissolved in water

³⁰ J. Ciabattini and M. Cabell, *J. Amer. Chem. Soc.*, 1971, **93**, 1482.

³¹ J. B. Lee, *J. Amer. Chem. Soc.*, 1966, **88**, 3440; J. B. Lee I. M. Downie, *Tetrahedron*, 1967, **23**, 359; R. G. Weiss and E. I. Snyder, *J. Org. Chem.*, 1970, **35**, 1627.

³² G. Witschard and C. E. Griffin, *Spectrochim. Acta*, 1963, **19**, 1905.

(50 ml). The filtrate was evaporated and the residue was chromatographed on silica gel with the same series of eluants as before. Ether eluted a small quantity of an oil which did not crystallise even when stored for a long time. The presence of the phosphine imide (2; Ar = *p*-MeC₆H₄, R = H) in this oil was revealed by t.l.c. and i.r. absorptions at 2190 and 1390 cm⁻¹. The aqueous solution was extracted with chloroform, and the extract was dried (CaCl₂) and evaporated. Silica gel chromatography of the residue with chloroform-ether (2:1) as eluant gave a solid (0.24 g). Crystallisation from aqueous ethanol gave *p*-toluoylphenylacetamide as needles, m.p. 184–185° (Found: C, 75.7; H, 6.0; N, 5.5; O, 12.9. C₁₆H₁₅NO₂ requires C, 75.9; H, 6.0; N, 5.5; O, 12.6%), λ_{max} (EtOH) 257 nm (log ε 4.10).

having the same alkyl group as the starting 2*H*-azirine for washings.

*Reaction of Methyl 3-Phenyl-2*H*-azirine-2-carboxylate* (3; Ar = Ph, R = Me) with *Dibromotriphenylphosphorane*.—A solution of the 2*H*-azirine (1.0 g, 0.006 mol) in dry benzene (5 ml) was added to a mixture of triphenylphosphine (3.14 g, 0.012 mol), bromine (1.0 g, 0.006 mol), and dry benzene (60 ml) and the product was heated under reflux for 45 min. The precipitate was filtered off and dissolved in water. The filtrate was evaporated leaving a small amount of an oil. Its i.r. spectrum and t.l.c. showed the presence of the starting 2*H*-azirine and the phosphine imide (4; Ar = Ph, R = Me, X = Br). The aqueous solution was extracted with chloroform and the extract was worked up as before.

TABLE 1

Phosphine *N*-(β-cyano-β-arylstyryl)imides (2)^{a,b}

Ar	R	M.p. (°C)	Cryst. solvent *	Yield (%)	Found (%)				Formula	Required (%)				ν _{max} /cm ⁻¹		λ _{max} /nm (log ε)
					C	H	N	P		C	H	N	P	C≡N	P=N	
Ph	H	178–179	CCl ₄	20	82.2	5.4	5.6	6.3	C ₃₃ H ₂₅ N ₂ P	82.5	5.2	5.8	6.45	2190	1388	324(4.12)
Ph	Cl	208–209	PhH-LP	20	76.9	4.8	5.25	6.2	C ₃₃ H ₂₄ ClN ₂ P	77.0	4.7	5.4	6.0	2200	1390	331(4.11)
<i>p</i> -MeC ₆ H ₄	H	195–197	CCl ₄ -LP	13	82.65	5.6	5.5	6.1	C ₃₄ H ₂₇ N ₂ P	82.6	5.5	5.7	6.3	2180	1385	329(4.30)

^a All compounds crystallised as pale yellow rods or plates. ^b I.r. and u.v. spectra were determined for solutions in chloroform.

* LP = Light petroleum.

TABLE 2

Phosphine *N*-(β-halogeno-β-alkoxycarbonylstyryl)imides (4)^{a,b}

Ar	R	X	M.p. (°C)	Cryst. solvent	Yield (%)	Found (%)					Formula	Required (%)					ν _{max} /cm ⁻¹		λ _{max} /nm (log ε)
						C	H	N	P	X		C	H	N	P	X	C=O	P=N	
Ph	Me	Cl	190–191	MeOH	30	71.1	5.0	2.8	6.85	7.6	C ₂₈ H ₂₄ ClNO ₂ P	71.3	4.9	3.0	6.7	7.5	1672	1267	310(4.09)
Ph	Et	Cl	177–179	EtOH	13	71.8	5.3	2.7	6.9	7.3	C ₂₉ H ₂₆ ClNO ₂ P	71.7	5.2	2.9	6.4	7.3	1665	1260	309(4.30)
Ph	Me	Br	191–192	MeOH	38	65.2	4.55	2.7	6.2	15.8	C ₂₈ H ₂₃ BrNO ₂ P	65.1	4.5	2.7	6.0	15.5	1672	1260	314(4.20)
Ph	Et	Br	187–188	EtOH	13	65.4	4.9	2.65	5.9	15.1	C ₂₉ H ₂₅ BrNO ₂ P	65.7	4.75	2.6	5.8	15.1	1664	1267	313(4.28)
<i>p</i> -MeC ₆ H ₄	Me	Br	220–221	MeOH	51	65.4	4.95	2.5	6.0	14.8	C ₂₉ H ₂₄ BrNO ₂ P	65.7	4.75	2.6	5.8	15.1	1670	1260	313(4.30)

^a All compounds crystallised as yellow rods or needles. ^b I.r. and u.v. spectra were determined for solutions in chloroform.

TABLE 3

3-Aryl-1-arylamino-4-cyanoisoquinolines (6)^{a,b}

Ar ¹	Ar ²	R	M.p. (°C)	Cryst. solvent	Yield (%)	Found (%)			Formula	Required (%)			ν _{max} /cm ⁻¹		λ _{max} /nm (log ε)
						C	H	N		C	H	N	NH	C≡N	
Ph	Ph	H	259–260	PhH	19	81.9	4.8	13.0	C ₂₃ H ₁₅ N ₃	82.2	4.7	13.1	3330	2190	224(4.49), 255(4.38), 364(4.38)
Ph	Ph	Cl	243–244	PhH	13	74.55	3.7	11.9	C ₂₃ H ₁₄ ClN ₃	74.3	4.0	11.8	3390	2200	238(4.74), 255(4.65), 372(4.46)
Ph	<i>p</i> -ClC ₆ H ₄	H	289–290	PhH	31	74.1	3.9	11.8	C ₂₃ H ₁₄ ClN ₃	74.3	4.0	11.8	3380	2210	223(4.51), 256(4.50), 362(4.45)
<i>p</i> -MeC ₆ H ₄	Ph	H	213–215	AcOEt	18	82.15	4.9	12.5	C ₂₃ H ₁₅ N ₃	82.4	5.1	12.5	3340	2210	223(4.57), 262(4.46), 363(4.31)
Ph	<i>α</i> -Naphthyl	H	207	PhH	19	84.4	4.8	10.9	C ₂₄ H ₁₇ N ₃	84.1	4.6	11.3	3330	2200	255(4.85), 351(4.62)

^a All compounds crystallised as pale yellow or yellow needles. ^b I.r. spectra were determined for Nujol mulls, u.v. spectra for solutions in ethanol.

*Reaction of Methyl 3-Phenyl-2*H*-azirine-2-carboxylate* (3; Ar = Ph, R = Me) with *Triphenylphosphine and Carbon Tetrachloride*.—A mixture of the 2*H*-azirine (2.6 g, 0.015 mol), triphenylphosphine (7.82 g, 0.03 mol), carbon tetrachloride (2.6 g, 0.015 mol), and dry tetrahydrofuran (50 ml) was stirred at 60° for 3 h in nitrogen. The precipitate (2.14 g), which had no u.v. absorption above 300 nm, was filtered off, and the filtrate was concentrated to a small volume and mixed with cold methanol (5 ml). The phosphine imide (4; Ar = Ph, R = Me, X = Cl) was thus obtained (see Table 2).

This phosphine imide (0.330 g), hydrazine hydrate (85%; 1.0 ml), and methanol (10 ml) were heated under reflux for 1 h. The u.v. absorption of the phosphine imide disappeared completely and evaporation of the solvent gave only triphenylphosphine oxide (0.16 g).

Reactions of other 2-alkoxycarbonyl-3-aryl-2*H*-azirines with triphenylphosphine and a tetrahalogenomethane were carried out similarly but with use of dry benzene for the reaction with carbon tetrabromide and with the alcohol

The only compound identified was triphenylphosphine oxide (0.87 g).

Reaction of the Phosphine Imide (2; Ar = Ph, R = H) with *p*-Chlorophenyl Isocyanate.—A mixture of the phosphine imide (0.48 g, 0.001 mol), *p*-chlorophenyl isocyanate (0.153 g, 0.001 mol), and dry benzene (10 ml) was heated under reflux for 1.5 h. The isoquinoline (6; Ar¹ = Ph, Ar² = *p*-ClC₆H₄, R = H) was precipitated during the reaction and was purified as indicated in Table 3. The filtrate was concentrated to a small volume and mixed with ether (5 ml), giving triphenylphosphine oxide (0.08 g, 30%). The subsequent filtrate was evaporated, leaving a viscous oil, showing intense i.r. absorptions at 2125 (N=C=N) and 2200 cm⁻¹ (C≡N), indicative of the carbodi-imide (5; Ar¹ = Ph, Ar² = *p*-ClC₆H₄, R = H). The other isoquinolines (6) (Table 3) were prepared in a similar way but by use of silica gel chromatography [ether-benzene (1:1)] for compounds (6; Ar¹ = *p*-MeC₆H₄, Ar² = Ph, R = H) and (6; Ar¹ = Ph, Ar² = *α*-naphthyl, R = H).

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