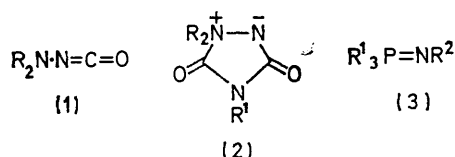


Reactions of $1\lambda^5\sigma^4,2,4$ -Triazoline-3,5-dione Decomposition Products with Organophosphorus Nucleophiles

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The reactions of 1,1-dialkyl-4-*t*-butyl- $1\lambda^5\sigma^4,2,4$ -triazoline-3,5-diones, under conditions known to produce *N*-isocyanato dialkylamines and *t*-butyl isocyanate, with various phosphorus compounds have been investigated. With phosphonium ylides the products depend on the phosphonium compound; highly stable or highly reactive ylides give products derived from *t*-butyl isocyanate, whereas ylides of intermediate stability react with the *N*-isocyanato-amine. The former products were independently synthesised from the phosphonium ylide and *t*-butyl isocyanate. Reactions with iminophosphoranes gave carbodi-imides, but only through reaction with *t*-butyl isocyanate; in no case were products derived from reaction with *N*-isocyanato-amine obtained. No evidence was observed for reaction with either *N*-isocyanato-amine or *t*-butyl isocyanate in experiments with a variety of phosphorus(III) compounds.

THE transient existence of *N*-isocyanato-amines (1) and their generation by photolysis of carbamoyl azides¹ and by thermolysis of 4-substituted 1,1-dialkyl- $1\lambda^5\sigma^4,2,4$ -triazoline-3,5-diones (2)² have been established. The highly reactive *N*-isocyanato-amines (1) may be trapped



in a number of ways: (a) by 1,3-dipolar addition,³ (b) by reaction of electrophiles with the amino-nitrogen atom, and (c) by nucleophilic addition to the isocyanato-group.¹ With regard to reactions of type (c), a study of organophosphorus nucleophiles appeared worthwhile since these compounds show a range of nucleophilicity and offer considerable synthetic potential.

Previous investigations of the reactions of isocyanates with phosphonium ylides have been confined to phenyl⁴ and benzoyl isocyanate.⁵ In each case initial attack occurred at the isocyanate carbonyl group and the nature of the final products depended on the ylide substituents. The reaction of isocyanates with iminophosphoranes (3) has been more extensively studied⁶ and shown to give carbodi-imides. By analogy similar reactions with *N*-isocyanato-amines should lead to aminocarbodi-imides.⁷ Tervalent phosphorus compounds generally catalyse trimerisation of aliphatic isocyanates,⁸ although in the specific case of compounds with P-N bonds the reactions are much more complex.⁹

RESULTS

Reactions with Phosphonium Ylides.—The reaction of the triazoline (5) with phosphonium ylides followed one of two pathways, depending on the phosphorane used.

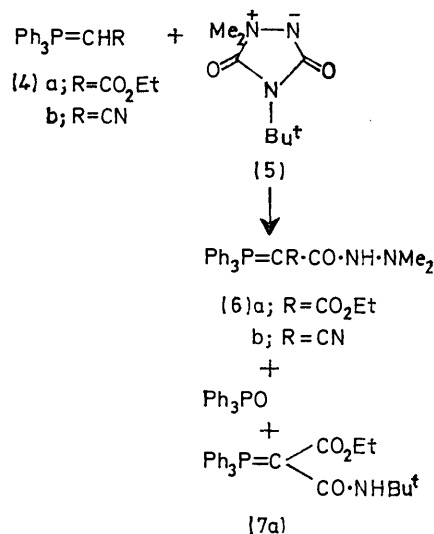
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¹ W. Lwowski, R. De Mauriac, T. W. Mattingly, jun., and E. Scheffle, *Tetrahedron Letters*, 1964, 3285.

² W. J. S. Lockley, V. T. Ramakrishnan, and W. Lwowski, *Tetrahedron Letters*, 1974, 2621.

³ W. S. Wadsworth and W. D. Emmons, *J. Org. Chem.*, 1967, **32**, 1279; W. Lwowski, R. De Mauriac, R. A. Murray, and L. Lunow, *Tetrahedron Letters*, 1971, 425.

Both ethoxycarbonyl- (4a) and cyano-methylenetriphenylphosphorane (4b) in benzene or ethyl acetate gave the corresponding [(3,3-dimethylcarbamoyl)methylene]triphenylphosphorane (6a or b), together with some triphenylphosphine oxide and, in the case of (4a), small amounts of [ethoxycarbonyl-(*t*-butylcarbamoyl)methylene]triphenylphosphorane (7a) (Scheme 1). The structures (6a and b) were assigned on the basis of n.m.r. (characteristic six-proton NMe signal at δ 2.6), i.r. (NH and CO stretching), and mass spectra and confirmed through the formation of perchlorate salts (8a and b) on



SCHEME 1

treatment with aqueous perchloric acid. Protonation in these salts appears to have taken place at the dimethylated nitrogen atom rather than at carbon since

⁴ H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635; S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1959, 3874.

⁵ Y. Ohshiro, Y. Mori, M. Komatsu, and T. Agawa, *J. Org. Chem.*, 1971, **36**, 2029.

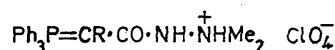
⁶ A. W. Johnson, 'Ylide Chemistry,' Academic Press, New York, 1966, pp. 226—229 and references therein.

⁷ W. S. Wadsworth and W. D. Emmons, *J. Org. Chem.*, 1964, **29**, 2816; D. M. Zimmerman, Thesis, Pennsylvania State University, 1970 (*Diss. Abs.*, 1971, **32**, 193B).

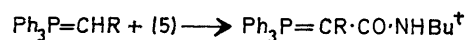
⁸ E. C. Juenge and W. C. Francis, *J. Org. Chem.*, 1961, **26**, 3334.

⁹ R. F. Hudson and A. Mancuso, *Phosphorus*, 1972, **1**, 265, 271 and references therein.

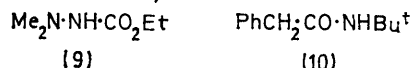
the NMe absorptions are shifted 0.4 p.p.m. downfield and no new CH resonance is observed, although a probable NH absorption appears at δ ca. 10.5. This idea is supported by the i.r. spectra, in which the



(8) a; R = CO₂Et
b; R = CN



(4) c; R = COPh (7) c; R = COPh
d; R = Ph d; R = Ph

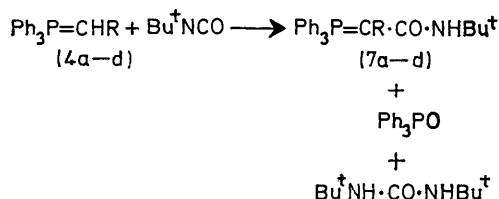


carbonyl absorptions undergo virtually no change on protonation (carbonyl-stabilised phosphonium ylides normally show a shift of the carbonyl absorption to shorter wavelength of $>150 \text{ cm}^{-1}$ and an increase in intensity with protonation on carbon or oxygen¹⁰), whereas the NH absorptions are markedly shifted.

Similar reactions of the triazoline (5) with phenacylidene- (4c) and benzyldiene-triphenylphosphorane (4d) gave the amides (7c and d). The reaction of (4c) was markedly solvent-dependent: it was not achieved by prolonged heating in ethyl acetate or benzene, but occurred readily in nitromethane. The structures (7c and d) were assigned on the basis of n.m.r. (Bu[†] at δ ca. 1.3 and NH at low field), i.r. (NH and characteristic ylide carbonyl absorptions), and mass spectra. The mass spectra were obtained only with difficulty since large pressure increases occurred in the mass spectrometer even at temperatures well below the m.p.s; this suggests thermal instability and may explain the unsatisfactory analysis obtained for (7d). Structures (7c and d) were confirmed by their synthesis from t-butyl isocyanate (see below).

Attempts to synthesise the ylides (6a and b) by the reaction of ethoxycarbonyl- or cyano-methylenetriphenylphosphorane with ethyl 3,3-dimethylcarbazate (9), either in refluxing toluene or neat at 160 °C, were unsuccessful.

Reactions with t-Butyl Isocyanate.—Heating the phosphonium ylides (4a—c) with t-butyl isocyanate in nitromethane gave the corresponding t-butylamides (7) and triphenylphosphine oxide in each case (Scheme 2). The



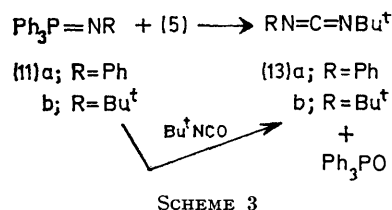
SCHEME 2

phosphoranes (7) were identified on the basis of their n.m.r. (Bu[†] at δ 1.33 and variable NH singlet), i.r. (NH

stretch), and mass spectra. Analogous reactions with phenyl isocyanate have been reported⁴ to give (phenyl-carbamoylmethylene)phosphoranes, but no phosphine oxide.

Small amounts of *NN'*-di-*t*-butylurea obtained from the reactions of the phosphoranes (4a—c) probably arise directly from t-butyl isocyanate by its hydrolysis.¹¹ The reaction of t-butyl isocyanate with the more reactive benzyldiene-triphenylphosphorane (4d) in benzene took place overnight at room temperature and gave, in addition to α -(*t*-butylcarbamoyl)benzyldiene-triphenylphosphorane (7d) small amounts of *N*-*t*-butylphenylacetamide (10). Pyrolysis of the phosphorane (7d) at 250 °C gave a high yield of triphenylphosphine oxide and traces of *N*-*t*-butylphenylacetamide.

Reactions with Iminophosphoranes.—The triazoline (5) reacted with 1 mol. equiv. of iminophosphorane (11a or b) to give *N*-phenyl-*N'*-*t*-butyl- (13a) and *NN'*-di-*t*-butyl-carbodi-imide (13b), respectively and in both



SCHEME 3

cases, triphenylphosphine oxide (Scheme 3). The carbodi-imides were identified by g.l.c. comparison with authentic samples and in the case of (13a) by conversion into the corresponding urea.

Similar reactions with 2 mol. equiv. of imine gave the same products, and in both cases triphenylphosphine oxide was obtained in higher yield than in the experiments involving 1 mol. equiv. of imine. However, while the yield of *NN'*-di-*t*-butylcarbodi-imide also increased, that of *N*-phenyl-*N'*-*t*-butylcarbodi-imide fell noticeably. In an attempt to trap the *N*-isocyanato-amine rather than the *t*-butyl isocyanate, triphenyl(phenylimino)-phosphorane was treated with the dimer (12) which is known to give transient *N*-isocyanatodimethylamine when heated in tetrachloroethylene;² however triphenylphosphine oxide was the only product isolated.

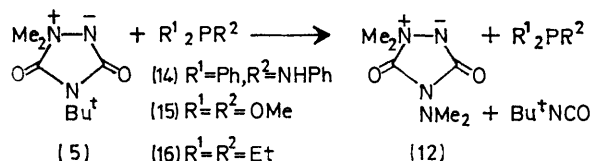
The carbodi-imides (13a and b) and triphenylphosphine oxide were also obtained from reactions of phenylimino- and *t*-butylimino-phosphoranes with *t*-butyl isocyanate (Scheme 3).

Reactions with Phosphorus(III) Compounds.—Attempts to trap the transient *N*-isocyanatodimethylamine with phosphorus(III) compounds were unsuccessful. Reactions of the triazoline (5) with anilindiphenylphosphine (14), trimethyl phosphite (15), and triethylphosphine (16) gave only the dimer (12) and unchanged P^{III} compound in each case (Scheme 4). In reactions of trimethylphosphine with *t*-butyl isocyanate only starting materials were recovered. The reaction of *t*-butyl

¹⁰ A. W. Johnson, 'Ylide Chemistry,' Academic Press, New York, 1966, p. 68 and references therein.

¹¹ W. Lwowski, unpublished results.

isocyanate with anilindiphenylphosphine in either ethyl acetate or nitromethane gave small yields of *NN'*-di-*t*-butyl- and *N*-phenyl-*N'*-*t*-butylurea, probably from hydrolysis of the *t*-butyl isocyanate by traces of water.

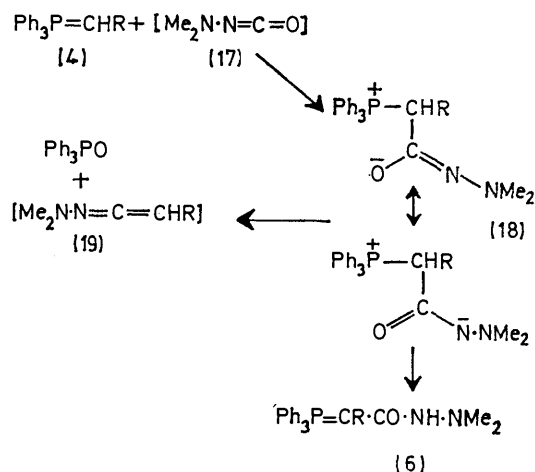


SCHEME 4

In no case was any trace found of the isocyanate dimers or trimers, although phosphorus(III) compounds are known to cause oligomerisation of a variety of isocyanates.^{8,12}

DISCUSSION

The reactions of the phosphonium ylides (4a and b) with the triazoline (5) are best interpreted in terms of nucleophilic attack by the phosphorane on the transient isocyanate (17) to give initially the zwitterion (18), which on proton transfer affords the product (6) (Scheme 5). The phosphine oxide formed may arise from the alternative mode of zwitterion decomposition by a Wittig-type elimination to give the vinylideneamine (19). Although no direct evidence for vinylideneamine formation was obtained in these reactions, *N*-*t*-butylphenylacetamide was isolated in small yield from the reaction of *t*-butyl isocyanate with the benzylidene ylide (4d) (see below). Direct reaction of the triazoline (5) with phosphonium ylides seems unlikely since nucleophiles would presumably attack the carbonyl group adjacent to the positively charged nitrogen in (5)

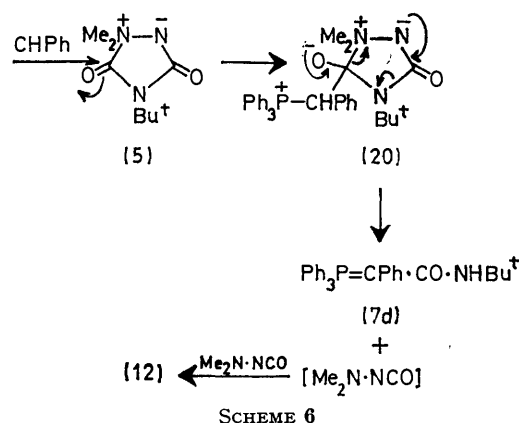


SCHEME 5

to give ultimately the products (7), formally derived from *t*-butyl isocyanate, whereas traces of these products were obtained in only one case. This is supported by the formation of (7a and b) in the reaction of *t*-butyl isocyanate with the ylides (4a and b). The low yield or absence of products (7), derived from *t*-butyl isocyanate, in these reactions is presumably due to the lower re-

activity of *t*-butyl isocyanate than of *N*-isocyanodimethylamine.

That the phenacylidene phosphorane (4c) reacts with the triazoline (5) to give products derived from *t*-butyl isocyanate rather than from *N*-isocyanatodimethylamine is presumably due to the lower nucleophilicity of the phosphorane (4c) than of the phosphoranes (4a and b). This allows dimerisation of the *N*-isocyanatoamine to (12) before reaction with the phosphorane takes place, and so only reaction with *t*-butyl isocyanate is observed; the dimer (12) is thermally stable under the reaction conditions. The analogous product (7d), obtained from the triazoline (5) with the reactive benzylidene phosphorane (4d) probably arises from direct reaction with the triazoline (5) rather than with its decomposition products, since the reaction takes place at room temperature. Attack of the carbanion on the



SCHEME 6

most reactive carbonyl group in the triazoline (5) [a mechanism already excluded for reactions of the ylides (4a and b)] followed by elimination of *N*-isocyanatodimethylamine provides a rationale for the products of this reaction (Scheme 6). The absence of products derived from reaction of the ylide (4d) with *N*-isocyanatodimethylamine suggests a slow elimination step from a stable intermediate (20).

The reaction of the phosphoranes (4) with *t*-butyl isocyanate presumably involves addition followed by proton transfer (Scheme 7). The *N*-*t*-butylphenylacetamide formed in the reaction of the benzylidene phosphorane (4d) may arise from the initially formed zwitterion (21), which undergoes elimination to give the vinylideneamine (22) followed by hydrolysis during chromatography. The *N*-*t*-butylphenylacetamide does not arise *via* hydrolysis of the phosphorane (7d) on the column, since rechromatography of a pure sample of (7d) gave no detectable amide. The appreciable amount of triphenylphosphine oxide isolated in each of the reactions of the phosphoranes (4a–d) with *t*-butyl isocyanate may also arise *via* elimination from the zwitterion (21), although in no case other than that of

¹² R. G. Arnold, J. A. Nelson, and J. J. Verbanc, *Chem. Rev.*, 1957, **57**, 47; A. A. R. Sayigh, J. H. Tilley, and H. Ulrich, *J. Org. Chem.*, 1964, **29**, 3344; C. A. Brown, R. F. Hudson, V. Rice, and A. R. Thompson, *Chem. Comm.*, 1971, 1255.

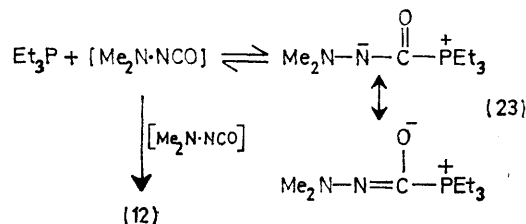
(4d) was any evidence for vinylideneamine formation found. This is not surprising since elimination of phosphine oxide from the zwitterion (21) must compete with proton transfer; this transfer is presumably slowest when $R = \text{Ph}$ owing to the lower acidity of the α -proton. The effect of R on the rate of vinylideneamine formation is less readily predicted.

Our inability to trap the transient *N*-isocyanato-dimethylamine with iminophosphoranes is again presumably due to isocyanato-amine dimerisation being competitive, owing to the relatively low nucleophilicity of the imine. Since the reactions with phosphonium ylides were shown to be highly sensitive to changes in nucleophilicity, the more nucleophilic *t*-butyliminophosphorane (11b) seemed more likely to react in the desired way. The failure to trap the isocyanato-amine in this case may be due to steric effects, although the highly sterically hindered reaction of the imine with *t*-butyl isocyanate takes place readily.

Failure to trap the isocyanato-amine by using 2 mol. equiv. of iminophosphorane indicates it is the rate competition with dimerisation, rather than with the *t*-butyl isocyanate reaction, that is important. Reaction of the excess of imine with carbodi-imide accounts for the reduced yield in reactions with 2 mol. equiv. of anilinophosphorane; the more sterically hindered di-*t*-butylcarbodi-imide apparently does not react since its yield is increased in a similar reaction.

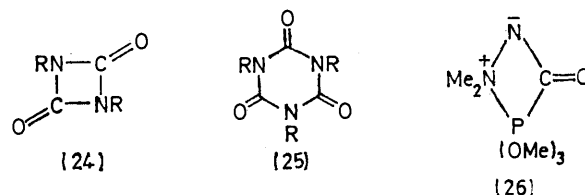
The failure to trap the *N*-isocyanato-amine with a variety of phosphorus(III) nucleophiles is at first sight surprising, especially in the case of triethylphosphine

formed, but reversibly, and this ultimately leads to complete irreversible dimerisation to the triazoline (12) and hence no apparent reaction (Scheme 8). The



SCHEME 8

relatively low stability of the adducts derived from isothiocyanato-amines supports this suggestion. The absence of isocyanate dimers (24) or trimers (25) from these reactions is probably due to the ease of formation of the alternative dimer (12) in the case of *N*-isocyanato-



dimethylamine and to steric effects in the case of *t*-butyl isocyanate (trimers of *t*-butyl isocyanate have not been reported).

The absence of phosphorus(v) derivatives of the type (2b) from reactions with trimethyl phosphite is disappointing, since similar compounds are known to be stabilised by electronegative substituents and by the fact that the phosphorus atom is contained in a small ring system.¹⁴

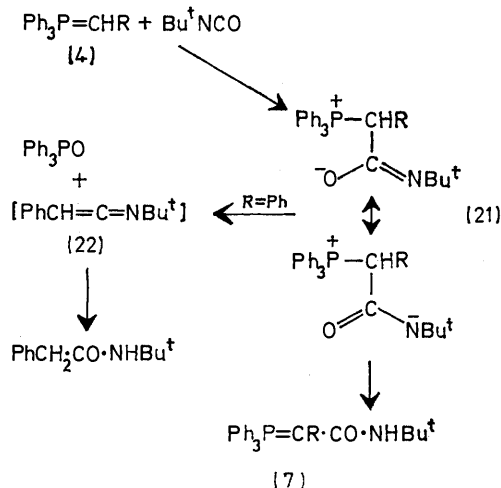
EXPERIMENTAL

M.p.s were determined with a Melt-Temp apparatus. N.m.r. spectra were determined with a JEOL Ps-100 spectrometer (at 100 MHz) (Me_4Si as internal standard), i.r. spectra with a Perkin-Elmer 621 spectrophotometer (calibrated with carbon dioxide and water absorptions at 2350 and 1560 cm^{-1}), and mass spectra with a Hitachi-Perkin-Elmer RMU-6E spectrometer. G.l.c. was carried out on an Aerograph P-3 instrument. A dry nitrogen atmosphere was used for all experiments involving air-sensitive phosphines and similar compounds. Reagent grade solvents were used directly, except that benzene and hexane were dried over sodium. Microanalyses were performed by Baron Consulting Co., Orange, Connecticut, U.S.A.

Reactions of 1,1-Dimethyl-4-*t*-butyl-1 $\lambda^5\sigma^4$,2,4-triazoline-3,5-dione (5) with Phosphonium Ylides. (a) Ethoxycarbonylmethylenetriphenylphosphorane (4a).¹⁵ The triazoline (5) (0.62 g) and the phosphorane (1.16 g) in benzene (50 ml) were refluxed for 8 h. Evaporation left a solid which was

¹⁴ P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. P. Johl, F. Ramirez, E. A. Tsohis, and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 687; F. Ramirez, I. Ugi, and D. Marquarding, *ibid.*, 1973, **12**, 91.

¹⁵ W. Considine, *J. Org. Chem.*, 1962, **27**, 647.



SCHEME 7

where low steric effects and high nucleophilicity should facilitate reaction. However, in similar work with isothiocyanato-amines Anthoni¹³ was only able to trap *N*-isocyanatodi-isopropylamine, in the case of which steric hindrance to dimerisation allows isolation of the monomer. In view of the nucleophilicity of triethylphosphine it seems likely that the adduct (23) is

¹³ U. Anthoni, O. Dahl, C. Larsen, and P. H. Nielsen, *Acta Chem. Scand.*, 1969, **23**, 943.

recrystallised from chloroform-ethyl acetate to give [(3,3-dimethylcarbazoyl)(ethoxycarbonyl)methylene]triphenylphosphorane (6a) (1 g, 70%), m.p. 166–167°; ν_{\max} (dil. soln. in CHCl_3) 3330, 1630, 1595, and 1540 cm^{-1} ; δ (CDCl_3) 0.52 (3H, t), 2.58 (6H, s), 3.68 (2H, q), and 7.2–8.0 (15H, m); m/e 434 (M^+) (Found: C, 69.35; H, 6.15; N, 6.3. $\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_3\text{P}$ requires C, 69.15; H, 6.2; N, 6.45%).

Evaporation of the mother liquors provided a solid, m.p. 110–115° which, from its i.r. spectrum, appeared to be a mixture of (6a) and triphenylphosphine oxide. Its mass spectrum showed the presence of small amounts of [ethoxycarbonyl-(*t*-butylcarbamoyl)methylene]triphenylphosphorane (7a) (M^+ 447). Chromatography on silica gel gave triphenylphosphine oxide (eluted by 1:1 hexane-ether) (0.14 g), m.p. 156–158°, and (6a) (eluted by ether) (0.08 g).

Perchlorate of (6a). The phosphorane (6a) (100 mg) was dissolved in the minimum amount of methanol and treated with a few drops of aqueous 60% perchloric acid. Addition of water gave crystals of the *perchlorate* (70 mg), m.p. 190–191° (from methanol-water); ν_{\max} (Nujol) 3250, 3080, 1630, and 1600 cm^{-1} ; δ [$(\text{CD}_3)_2\text{SO}$] 0.42 (3H, t), 3.0 (6H, s), 3.59 (q), 7.5–7.9 (15H, m), and 10.70 (1H, s) (the integration of the signal at δ 0.42 is unsatisfactory owing to interference from the lock signal; the absorption at δ 3.59 overlaps with the broadened water signal) (Found: C, 56.05; H, 5.15; Cl, 6.95; N, 5.1. $\text{C}_{25}\text{H}_{27}\text{ClN}_2\text{O}_7\text{P}$ requires C, 56.3; H, 5.05; Cl, 6.65; N, 5.25%).

(b) *Cyanomethylenetriphenylphosphorane (4b).*¹⁶ The triazoline (5) (0.62 g) and the phosphorane (1.0 g) in benzene (or ethyl acetate) (40 ml) were refluxed for 8 h, during which time a solid separated. Evaporation gave [cyano-(3,3-dimethylcarbazoyl)methylene]triphenylphosphorane (6b) (0.85 g, 66%), m.p. 209–210° (decomp.) (from chloroform); ν_{\max} (dil. soln. in CHCl_3) 3255, 2170, and 1610 cm^{-1} ; δ (CDCl_3) 2.60 (6H, s), 6.30br (1H, s), and 7.60 (15H, m); m/e 387 (M^+), 329, and 328 (Found: C, 71.4; H, 5.85; N, 10.9. $\text{C}_{23}\text{H}_{22}\text{N}_3\text{OP}$ requires C, 71.35; H, 5.7; N, 10.85%).

Perchlorate of (6b). The phosphorane (6b) (300 mg) was dissolved in the minimum amount of methanol and treated with a few drops of aqueous 60% perchloric acid. After a few seconds crystals of the *perchlorate* (320 mg) separated, m.p. 248–250° (from methanol-water); ν_{\max} (Nujol) 3700–3100, 2183, and 1630 cm^{-1} ; δ [$(\text{CD}_3)_2\text{SO}$] 3.00 (6H, s), 7.50–7.90 (15H, m), and 10.40 (1H, s) (Found: C, 56.45; H, 4.75; Cl, 7.56; N, 8.55. $\text{C}_{23}\text{H}_{22}\text{ClN}_3\text{O}_5\text{P}$ requires C, 56.7; H, 4.5; Cl, 7.3; N, 8.65%).

(c) *Phenacylidetriphenylphosphorane (4c).*¹⁷ (i) Refluxing equivalent amounts of the phosphorane and the triazoline (5) in benzene or ethyl acetate overnight gave, on evaporation, only starting phosphorane, m.p. and mixed m.p. 185–187°.

(ii) A solution of the phosphorane (0.31 g) and the triazoline (5) (0.16 g) in nitromethane (20 ml) was heated to 90 °C for 12 h. Cooling and trituration with a small amount of ethyl acetate gave α -(*t*-butylcarbamoyl)phenacylidetriphenylphosphorane (7c) (0.25 g), m.p. 228–230° (with gas evolution) (from ethyl acetate); ν_{\max} (Nujol) 3265, 3070, 1610, and 1520 cm^{-1} ; δ (CDCl_3) 1.36 (9H, s) and 6.8–7.9 (20H, m); m/e 479 (M^+), 464, 422, and 305

(Found: C, 77.35; H, 6.2; N, 2.65. $\text{C}_{31}\text{H}_{30}\text{NO}_2\text{P}$ requires C, 77.6; H, 6.25; N, 2.9%).

(d) *Benzylidetriphenylphosphorane (4d).*¹⁸ The triazoline (5) (0.23 g) was added in batches to a solution of the phosphorane [from the phosphonium chloride (0.48 g) and 2.3M-phenyl-lithium (0.55 ml)] in benzene (30 ml). The mixture was stirred overnight at room temperature, during which time a colour change from red to pale yellow occurred. Filtration gave benzyltriphenylphosphonium chloride¹⁹ (0.10 g), m.p. and mixed m.p. 334–336°. The filtrate was concentrated to give an amorphous precipitate of α -(*t*-butylcarbamoyl)benzylidetriphenylphosphorane (7d) (0.25 g), which could be recrystallised with difficulty from chloroform-ethyl acetate; m.p. 216–218° (decomp.); ν_{\max} (dil. soln. in CHCl_3) 3200, 1665, 1560, and 1110 cm^{-1} ; δ (CDCl_3) 1.25 (9H, s), 6.90–7.70 (20H, m), and 9.50 (1H, s); m/e 451 (M^+), 379, 262, and 57. A satisfactory analysis could not be obtained: values variably low in carbon and hydrogen, and high in nitrogen for $\text{C}_{30}\text{H}_{30}\text{NOP}$ were repeatedly observed.

Reactions of the Phosphoranes (4a and b) with Ethyl 3,3-Dimethylcarbazate.—(a) The phosphorane (4b) (0.16 g) and the carbazate (0.067 g) in toluene (10 ml) were refluxed for 6 h. Evaporation gave crystals of the starting phosphorane, m.p. and mixed m.p. 194–196°. A similar experiment with the phosphorane (4a) also gave only starting phosphorane, m.p. and mixed m.p. 126–128°.

(b) Heating either phosphorane (4a or b), with a large excess of the carbazate at 160 °C for 4 h gave, on evaporation, a black oil. Chromatography on silica gel gave only traces of sweet-smelling oils.

Reactions of the Triazoline (5) with Iminophosphoranes.—(a) *Anilinotriphenylphosphorane.*²⁰ (i) The imine (1.52 g) and the triazoline (5) (0.74 g) in benzene (40 ml) were refluxed for 14 h. Evaporation gave a semi-solid which was extracted with hexane (2 × 30 ml). The hexane-insoluble portion was recrystallised from ethyl acetate to give triphenylphosphine oxide (0.96 g, 80%), m.p. and mixed m.p. 157–158°. G.l.c. of the hexane fraction on a 15% QF-1 column at 120 °C gave *N*-phenyl-*N'*-*t*-butylcarbodi-imide²¹ (40% yield from g.l.c. trace); ν_{\max} (dil. soln. in CHCl_3) 2980, 2110, and 1600 cm^{-1} ; δ (CDCl_3) 1.40 (9H, s) and 7.2 (5H, m); m/e 174 (M^+), 118, 91, 77, and 57.

A solution of the carbodi-imide in ethyl acetate was treated with aqueous formic acid (88%) and set aside overnight at room temperature. Evaporation gave *N*-phenyl-*N'*-*t*-butylurea, m.p. 167–169° (lit.,²² 168–169°).

(ii) A similar experiment with a two-fold excess of imine gave triphenylphosphine oxide (100% yield calculated on the basis of reaction of 1 mol. equiv. of imine) and *N*-phenyl-*N'*-*t*-butylcarbodi-imide (29%).

(b) *Triphenyl-*t*-butyliminophosphorane.*²³ (i) The imine (0.83 g) and the triazoline (5) (0.46 g) in benzene (30 ml) were refluxed for 9 h. The solvent was evaporated off under reduced pressure at 10 °C and the residue was extracted with hexane (2 × 20 ml). The hexane-insoluble portion was recrystallised from ethyl acetate to give triphenylphosphine oxide (0.50 g, 73%), m.p. and mixed m.p. 157–158°. G.l.c. of the hexane extract on a 15% QF-1 column at 80 °C gave *NN'*-di-*t*-butylcarbodi-imide²⁴

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(60% yield from g.l.c. trace); ν_{\max} (dil. soln. in CHCl_3) 2115, 2095, 2080, 1370, and 1210 cm^{-1} ; m/e 154 (M^+), 139, 99, 97, 83, 57, and 56.

(ii) A similar experiment with a two-fold excess of imine gave triphenylphosphine oxide (106% calculated on the basis of reaction of 1 mol. equiv. of imine) and NN' -di-*t*-butylcarbodi-imide (100%). G.l.c. of the reaction mixture on a Carbowax column at 60 °C showed a small amount of an unidentified component very close to the solvent peak. Attempts to isolate this were unsuccessful.

Reaction of 4-Diethylamino-1,1-diethyl-1 $\lambda^5\sigma^4$,2,4-triazoline-3,5-dione with Anilinotriphenylphosphorane.—The imine (0.70 g) and the triazoline (0.18 g) were heated in tetrachloroethylene at 97 °C for 24 h. Cooling and filtration gave triphenylphosphine oxide (0.1 g), m.p. and mixed m.p. 157—158°, as the only isolated product.

*Reactions of *t*-Butyl Isocyanate with Phosphonium Ylides.*
—(a) *Ethoxycarbonylmethylenetriphenylphosphorane.* The phosphorane (3.48 g) and *t*-butyl isocyanate (1.1 g) in nitromethane (80 ml) were heated to 100 °C for 36 h. Cooling and evaporation gave [*ethoxycarbonyl-(t-butyl-carbamoyl)methylene*]triphenylphosphorane (7a) (1.6 g, 36%), m.p. 172—173° (from ethyl acetate); ν_{\max} (dil. soln. in CHCl_3) 3300, 3050, 1610, 1565, and 1525 cm^{-1} ; δ (CDCl_3) 0.50 (3H, t), 1.33 (9H, s), 3.62 (2H, q), 7.20—7.80 (15H, m), and 8.60 (1H, s); m/e 447 (M^+), 390, 374, 348, 262, 108, and 57 (Found: C, 71.7; H, 6.6; N, 3.05. $\text{C}_{27}\text{H}_{30}\text{NPO}_3$ requires C, 72.5; H, 6.7; N, 3.1%). Chromatography of the mother liquors on silica gel gave NN' -di-*t*-butylurea (eluted by 4 : 1 hexane-ether) (0.20 g), m.p. >200° (sublimes), more amide (7a) (eluted by 1 : 1 hexane-ether) (0.5 g, total yield 47%), and triphenylphosphine oxide (0.35 g), m.p. and mixed m.p. 157—158°.

(b) *Cyanomethylenetriphenylphosphorane.* The phosphorane (3 g) and *t*-butyl isocyanate (2 g) in nitromethane (80 ml) were heated at 95 °C for 36 h. Cooling and evaporation gave [*cyano-(t-butylcarbamoyl)methylene*]triphenylphosphorane (7b) (2 g, 50%), m.p. 191—192° (decomp.) (from ethyl acetate); ν_{\max} (dil. soln. in CHCl_3) 3415, 3050, 2990, 2145, 1600, and 1510 cm^{-1} ; δ (CDCl_3) 1.34 (9H, s), 5.54 (1H, s), and 7.2—7.8 (15H, m); m/e 400 (M^+), 385, 360, 328, 108, 93, and 57 (Found: C, 75.25; H, 6.35; N, 7.15. $\text{C}_{25}\text{H}_{25}\text{N}_2\text{OP}$ requires C, 75.0; H, 6.25; N, 7.0%). Chromatography of the mother liquors on silica gel gave NN' -di-*t*-butylurea (eluted by 4 : 1 hexane-ether) (0.12 g), m.p. >200° (sublimes) and more amide (7b) (eluted by 1 : 1 hexane-ether) (0.6 g, total yield 65%).

(c) *Phenacylidetriphenylphosphorane.* The phosphorane (0.74 g) and *t*-butyl isocyanate (0.6 g, 3 mol. equiv.) in nitromethane (30 ml) were refluxed for 24 h. Cooling and filtration gave α -(*t*-butylcarbamoyl)phenacylidetriphenylphosphorane (7c) (0.45 g), m.p. 228—230°. The concentrated filtrate was chromatographed on silica gel to give NN' -di-*t*-butylurea (eluted by 6% ethyl acetate-hexane) (0.04 g), m.p. >200° (sublimes), more amide (7c) (eluted by 1 : 1 hexane-ethyl acetate) (0.16 g, total yield 65%), m.p. 228—230°, and triphenylphosphine oxide (0.10 g), m.p. and mixed m.p. 157—158°.

(d) *Benzylidenetriphenylphosphorane.* *t*-Butyl isocyanate (0.55 g) was added to a solution of the phosphorane [from the phosphonium chloride (1.90 g) and 2.3-*M*-phenyl-lithium (2.18 ml)] in benzene (60 ml) at room temperature. The

mixture was then heated at 40 °C overnight, evaporated, and chromatographed on silica gel to give *N*-*t*-butylphenylacetamide (eluted by 1 : 1 hexane-ethyl acetate) (0.02 g), m.p. and mixed m.p. 109—111° (from hexane) (lit.,²⁵ 111—113°) [ν_{\max} (dil. soln. in CHCl_3) 3430, 3410, 3000, and 1660 cm^{-1} ; δ (CDCl_3) 1.30 (9H, s), 3.44 (2H, s), 5.3br (1H, s), and 7.28 (5H, m); m/e 191 (M^+)], triphenylphosphine oxide (eluted by ethyl acetate) (0.15 g, 11%), m.p. and mixed m.p. 157—158°, a small amount of an unidentified yellow oil (eluted by ethyl acetate), and α -(*t*-butylcarbamoyl)benzylidenetriphenylphosphorane (7d) (eluted by 3% methanol-ethyl acetate) (1.57 g, 71%), m.p. 216—218° (decomp.). A sample of α -(*t*-butylcarbamoyl)benzylidenetriphenylphosphorane rechromatographed on silica gel gave no detectable *N*-*t*-butylphenylacetamide.

Pyrolysis of α -(t-Butylcarbamoyl)benzylidenetriphenylphosphorane.—The phosphorane (0.20 g) was heated at 250 °C for 1 min to give on cooling a yellow solid. Extraction with hot hexane and evaporation of the extract gave *N*-*t*-butylphenylacetamide (0.01 g), m.p. and mixed m.p. 109—111°. The hexane-insoluble portion was recrystallised from ethyl acetate to give triphenylphosphine oxide (0.1 g, 81%), m.p. and mixed m.p. 157—158°.

Reactions of t-Butyl Isocyanate with Iminophosphoranes.
(a) *Anilinotriphenylphosphorane.* The imine (0.88 g) and *t*-butyl isocyanate (0.24 g) in benzene (30 ml) were refluxed for 16 h. Evaporation and trituration with hot hexane gave triphenylphosphine oxide (0.62 g, 95%), m.p. and mixed m.p. 157—158°. G.l.c. of the hexane fraction gave a single peak (other than the solvent), which had the same retention time as authentic *N*-phenyl-*N'*-*t*-butylcarbodi-imide on both Carbowax and 15% QF-1 columns (150 °C). The total yield of carbodi-imide was 58% (g.l.c. trace).

(b) *Triphenyl-(t-butylimino)phosphorane.* The imine (0.83 g) and *t*-butyl isocyanate (0.25 g) in benzene (30 ml) were refluxed for 7 h. G.l.c. of the mixture on a 15% QF-1 column at 75 °C gave a peak of the same retention time as authentic NN' -di-*t*-butylcarbodi-imide and indicated a 77% yield. The reaction mixture was evaporated under reduced pressure at 10 °C and the residue was extracted with hexane (2 × 20 ml). The hexane-insoluble portion was recrystallised from ethyl acetate to give triphenylphosphine oxide (0.57 g, 72%), m.p. and mixed m.p. 157—158°. G.l.c. of the hexane fraction on a 15% QF-1 column at 75 °C gave NN' -di-*t*-butylcarbodi-imide (72% yield from g.l.c. trace).

Reaction of Anilinodiphenylphosphine with the Triazoline (5).—The phosphine (0.7 g) and the triazoline (5) (0.46 g) in benzene (30 ml) were refluxed for 48 h. On cooling a solid separated, m.p. 170—172°, identical with an authentic sample of 4-dimethylamino-1,1-dimethyl-1 $\lambda^5\sigma^4$,2,4-triazoline-3,5-dione³ (12) (0.22 g). The filtrate was concentrated and chromatographed on silica gel to give anilinodiphenylphosphine (eluted by hexane) (0.52 g), m.p. 69—71° (lit.,²⁶ 70—72°).

Reaction of Anilinodiphenylphosphine with t-Butyl Isocyanate.—(a) The phosphine (1.45 g) and *t*-butyl isocyanate (0.90 g) in ethyl acetate (30 ml) were refluxed under nitrogen for 36 h. Concentration and chromatography on silica gel gave anilinodiphenylphosphine (eluted by hexane) (1.1 g), m.p. 69—70° (lit.,²⁶ 70—72°), and a yellow oil

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²⁶ R. F. Hudson, R. J. G. Searle, and F. H. Devitt, *J. Chem. Soc. (C)*, 1966, 1001.

(0.018 g) which from its n.m.r., i.r., and mass spectra appeared to be mainly aniline, although a peak at m/e 192 suggested the presence of some *N*-phenyl-*N'*-*t*-butylurea.

(b) The above reaction was repeated in nitromethane at 100 °C. Chromatography on silica gel gave traces of an unidentified yellow oil (eluted by 2% ethyl acetate-hexane) and *NN'*-di-*t*-butylurea (0.30 g) (eluted by 6% ethyl acetate-hexane). The mother liquors from recrystallisation of the *NN'*-*t*-butylurea gave a small amount of *N*-phenyl-*N'*-*t*-butylurea, m.p. 167–168° (lit.,²³ 168–169°). Further elution with 1:1 hexane-ethyl acetate gave anilino-diphenylphosphine (1.0 g), m.p. 238–240° (lit.,²⁶ 240–242°).

Reaction of Triethylphosphine with the Triazoline (5).—The phosphine (0.6 g) and the triazoline (0.92 g) were refluxed in benzene (20 ml) for 16 h. Cooling and evapor-

ation gave 4-dimethylamino-1,1-dimethyl-1λ⁵σ⁴,2,4-triazoline-3,5-dione (0.20 g) as the only isolated product.

Reaction of Trimethyl Phosphite with the Triazoline (5).—The phosphite (0.31 g) and the triazoline (0.46 g) were refluxed in benzene (15 ml) overnight. Cooling and evaporation gave 4-dimethylamino-1,1-dimethyl-1λ⁵σ⁴,2,4-triazoline-3,5-dione (0.14 g) as the only isolated product.

*Reaction of Trimethyl Phosphite with *t*-Butyl Isocyanate.*—The phosphite (2.5 g) and *t*-butyl isocyanate (2 g) were heated together overnight at 90 °C. Distillation gave *t*-butyl isocyanate, b.p. 78–80°, containing some trimethyl phosphite (by i.r.).

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