A Simple Procedure for the Elaboration of Carbonyl Compounds into Homologous Alkynes [1]

By **Ernest W. Colvin** * and **Brendan J. Hamill**, Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

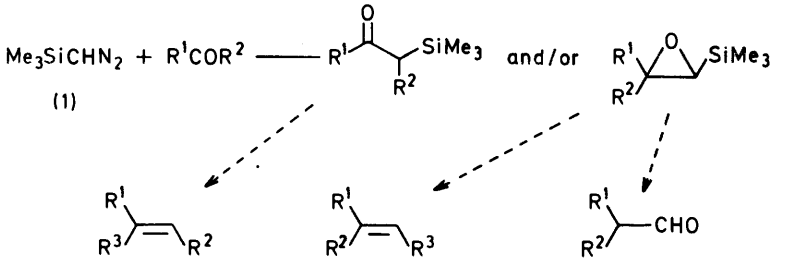
The base-induced reaction of diazomethyltrimethylsilane (1) or of the dialkyl diazomethylphosphonates (4) and (5) with aromatic carbonyl compounds leads directly to the corresponding homologous alkynes. The mechanism, scope, and limitations of this synthetically useful process have been investigated.

INTEREST [2,3] in the synthetic utility of organosilicon compounds prompted an investigation of the properties of diazomethyltrimethylsilane (1). Previous studies [4] on this compound had been limited to its copper(I)-catalysed decomposition to a trimethylsilylcarbenoid, which efficiently converted olefins into cyclopropanes. It was considered that the reaction of compound (1) with ketones, by analogy with the reactions of diazomethane itself, might provide routes to β-oxo-silanes or

[1] Preliminary report, E. W. Colvin and B. J. Hamill, *J.C.S. Chem. Comm.*, 1973, 151.
[2] G. Stork and E. Colvin, *J. Amer. Chem. Soc.*, 1971, **93**, 2080.
[3] G. Stork, M. E. Jung, E. Colvin, and Y. Noel, *J. Amer. Chem. Soc.*, 1974, **96**, 3684.
[4] D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Amer. Chem. Soc.*, 1968, **90**, 1080.

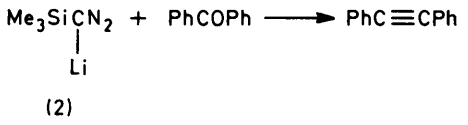
α-silyloxirans (Scheme 1), precursors of alkenes [5] and aldehydes.[2]

Initially, all attempts to induce the diazo-derivative (1) to react with a range of carbonyl substrates failed; the conditions employed ranged from the use of amine bases, including piperidinium acetate, to the addition of Lewis



SCHEME 1

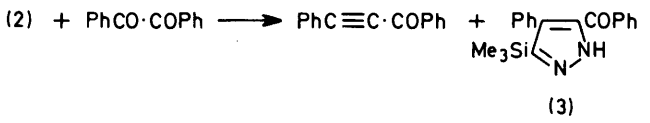
acid catalysts. However, the lithium salt (2), prepared from compound (1) with n-butyl-lithium in ether at 0 °C, reacted with benzophenone to give diphenylethyne in 80% yield (Scheme 2); the potassium salt, generated



SCHEME 2

analogously with potassium t-butoxide, reacted similarly. Although this result was unexpected, it did promise considerable synthetic utility. A preliminary study with other carbonyl substrates showed the conversion to be efficient, especially with diaryl ketones.

Although benzil underwent the desired rearrangement, the product alkynone was accompanied by the pyrazole (3), formed by further reaction with the reagent (Scheme 3); this pyrazole was initially [1] and erroneously assigned a silyl enol structure.

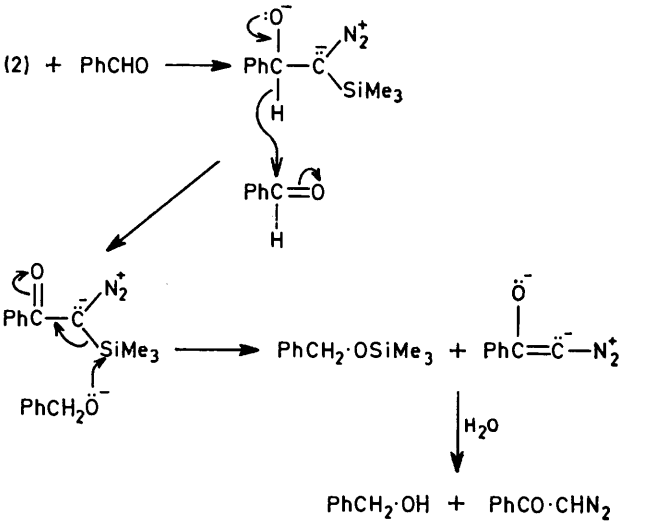


SCHEME 3

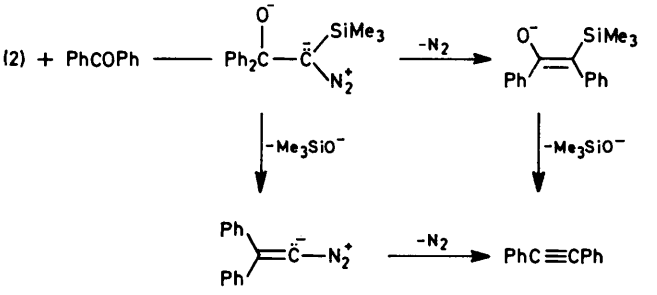
The adduct with benzaldehyde did not rearrange to phenylethyne, but instead transferred a hydride ion to unchanged benzaldehyde; this resulted in the ultimate production of benzyl alcohol and α-diazoacetophenone (Scheme 4).

All attempts to secure a reasonable yield of alkynes from aralkyl ketones, or any alkyne at all from aliphatic ketones, failed, presumably because of proton transfer between the enolisable substrate and the strongly basic reagent anion. Mechanistically, the conversion must involve two distinct stages after the initial condensation of diazo(trimethylsilyl)methanide ion with the ketone, namely Wolff rearrangement [6] with expulsion of nitrogen, and elimination of the trimethylsilanolate ion,[7] in either order, as shown for benzophenone in Scheme 5.

Diethyl and dimethyl diazomethylphosphonate, (4) [8] and (5),[9] are more acidic than diazomethyltrimethylsilane, as shown by the C*H*N$_2$ chemical shifts, *viz.* δ 2.2 for



SCHEME 4



SCHEME 5

the silicon reagent and *ca.* 4 for the phosphorus analogues, and should, therefore, have less basic anions. We ex-

[5] P. F. Hudrlik and D. Peterson, *Tetrahedron Letters*, 1972, 1785; P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, 1975, **40**, 2263.

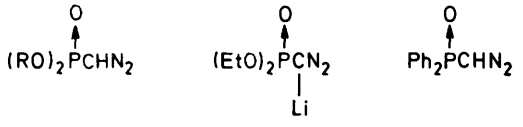
[6] W. E. Bachman and W. S. Struve, *Org. Reactions*, 1942, **1**, 38.

[7] D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780.

[8] M. Regitz, A. Liedhegener, U. Eckstein, M. Martin, and W. Anschutz, *Annalen*, 1971, **748**, 207.

[9] D. Seyferth, R. S. Marmor, and P. Hilbert, *J. Org. Chem.*, 1971, **36**, 1384.

pected the phosphorus reagents to be equally capable of the rearrangement sequence shown in Scheme 5, eliminating a dialkyl phosphate anion by analogy with the Wadsworth–Emmons modification [10] of the Wittig reaction.



(4) R = Et
(5) R = Me

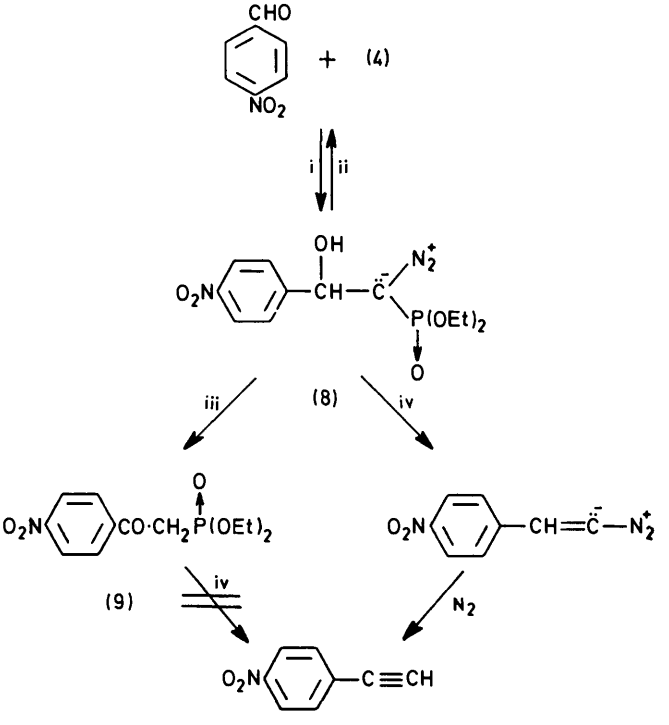
(6) (7)

The phosphorus-substituted diazomethanes were prepared and found to be rather more stable and more easy to handle than diazomethyltrimethylsilane. The corresponding anions were, surprisingly, much less stable and had to be generated at −78 °C; they both converted benzophenone into diphenylethyne in even higher yield than the silicon-based reagent.

A range of carbonyl substrates was subjected to this latter reaction; the results are summarised in the Experimental section. Once again, the reaction is quite general for diaryl ketones; substitution on the aromatic rings appears to have little effect. αβ-Unsaturated substrates are not converted into enynes, and α-dicarbonyl compounds give low yields of alkynone owing to subsequent 1,3-dipolar addition reactions; dicarbonyl compounds in which the carbonyl groups are mutually isolated react normally. Heteroaromatic ketones behave satisfactorily, although attempts to convert 2-benzoylfuran into the alkyne resulted in substrate polymerisation. The relatively high yield of alkyne from benzoylcyclohexane (25%) is noteworthy, and supports the idea that aralkyl ketones fail to react satisfactorily owing to competitive proton transfer, which will be less effective in this case than in the cases of acetophenone (22%) and phenyl benzyl ketone (0%).

The conversion of benzophenone into diphenylethyne was studied under various conditions. n-Butyl-lithium and potassium t-butoxide were equally effective in promoting reaction in tetrahydrofuran solution, other organometallic and metal alkoxide bases being less satisfactory. Amine bases, even strong ones such as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), were completely ineffective, although lithium di-isopropylamide was satisfactory, suggesting that an intermediate metal alkoxide is mandatory for rearrangement.

In the course of this work, a report [11] was published describing the preparation of ' aldol ' adducts of electrophilic carbonyl compounds with a range of phosphorus-substituted diazomethanes,by using a catalytic amount of base, usually triethylamine. In view of our earlier failure to induce any reaction at all under similar conditions, the work described in the report was re-investigated: it became apparent that amine bases will only catalyse adduct formation if the resulting adduct can be induced to precipitate from solution by suitable choice of solvent and substituted diazomethane. For example, 4-nitrobenzaldehyde reacted, under appropriate conditions, with diazo(diphenylphosphinoyl)methane (7) to give the corresponding adduct in quantitative yield, whereas the yield with diethyl diazomethylphosphonate (4) was only 50%. In contrast, the reaction of the lithium salt of diethyl diazomethylphosphonate with 4-nitrobenzaldehyde produced 4-nitrophenylethyne in 86% yield. Since this latter reaction must proceed through the lithium alkoxide derivative of the adduct (8), the stability of (8) to base was investigated, in the hope of determining the sequence of steps in the conversion. Treatment of the adduct (8) with 1,5-diazabicyclo[4.3.0]non-5-ene caused reversion to its components, whereas treatment with potassium t-butoxide



SCHEME 6 Reagents: i, Et_3N; ii, DBN; iii, $Cu(acac)_2$; iv, $KOBu^t$

in tetrahydrofuran gave the alkyne in 64% yield (Scheme 6). These findings provide further evidence that the conversion of carbonyl compounds into homologous alkynes is a property shown only by metal salts of suitable substituted diazomethanes and not simply by their conjugate bases, although this is probably not due to co-ordination of the alkoxide with the metal cation hindering collapse of the initial adduct to starting materials, since potassium and lithium salts seem equally effective. In the unsuccessful cases where amine bases were employed, the conjugate acid * of the amine could catalyse reversal to starting components by protonation

* We thank a referee for this suggestion.

[10] W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, 1961, **83**, 1733.

[11] W. Disteldorf and M. Regitz, *Chem. Ber.*, 1976, **109**, 546; we thank Professor Regitz for a pre-print of this paper.

of the diazo carbon atom; t-butyl alcohol is apparently insufficiently acidic to do this.

It appears that the decisive stage in alkyne formation if the elimination of alkali metal phosphate from the initially formed adduct (8); if this does not occur the reaction will not proceed and, therefore, this step must precede Wolff rearrangement. To test this hypothesis, the adduct (8) was induced to undergo Wolff rearrangement, giving the β-oxo-phosphonate (9); no change, apart from proton abstraction, occurred when (9) was treated with potassium t-butoxide in tetrahydrofuran.[12] These mechanistic conclusions, outlined in Scheme 6, can presumably be extended to the silicon system.

To summarise, this reaction provides a useful method for the efficient preparation of diaryl-alkynes and -alkynones from the corresponding carbonyl compounds. It appears to be relatively insensitive to substitution on the aromatic rings. Its application to aromatic aldehydes appears to be limited to highly electrophilic cases, and it cannot be applied to the preparation of aralkyl-alkynes, unless the alkyl group is secondary; in no case studied was it possible to prepare a dialkylalkyne. Even with these limitations, the method is superior to most alternative sequences,[13,14] especially in ease of handling and speed of reaction; it is a simple ' one-pot ' process, purification being facilitated by the water-solubility of unwanted co-products. A wide range of carbonyl substrates is readily available, and the diazoalkanes (1), (4), and (5) are easily prepared and can be stored under refrigeration for long periods without deterioration.

EXPERIMENTAL

M.p.s were recorded with a Kofler hot-stage apparatus, i.r. spectra with a Pye Unicam SP 100 or a Perkin-Elmer 225 double beam spectrophotometer (for liquid films, unless otherwise stated), u.v. spectra with a Unicam SP 800 instrument, ^{1}H n.m.r. spectra with a Varian T-60 (60 MHz) or HA100 (100 MHz) spectrophotometer (tetramethylsilane as internal reference), ^{13}C n.m.r. spectra with a Varian XL-100-12 Fourier transform spectrophotometer, and mass spectra with an A.E.I.–G.E.C. MS12 spectrometer. Analytical g.l.c. was performed with a Perkin-Elmer F11 gas chromatograph.

Kieselgel (Merck) was used for analytical t.l.c., and Kieselgel HF_{254} or GF_{254} (Merck) for preparative t.l.c. All organic solutions were dried over anhydrous magnesium sulphate. Solvents were removed with a rotary evaporator. Tetrahydrofuran (THF) was distilled from lithium aluminium hydride immediately prior to use.

Diazomethyltrimethylsilane (1).—This compound, prepared by a published procedure,[4] was obtained as a yellow oil, b.p. 94—95° at 755 mmHg, $\nu_{max.}$ 2 060, 1 250, 1 030, and 840 cm^{-1}, δ($CDCl_3$) 0.3 (9 H, s) and 2.2 (1 H, s).

Diethyl Diazomethylphosphonate (4).—This compound was prepared by a modification of a published procedure.[8] A solution of the crude product in ether was filtered through a short column of alumina (Woelm neutral, Grade III), and the eluate was concentrated *in vacuo* at 30 °C prior to distillation; this minimised the chance of explosive decomposition on distillation. It was obtained as a yellow oil, b.p. 52° at 0.1 mmHg, $\nu_{max.}$ 2 113 and 1 253 cm^{-1}, δ_H($CDCl_3$) 1.1 (6 H, t of d, J 6 and 2 Hz), 4.0 (4 H, d of q, J 15 and 6 Hz), and 3.85 (1 H, d, J 10 Hz). δ_C(C_6D_6) 16.29 (d, $^3J_{P,C}$ 6.6 Hz, CH_3), 29.64 (d, $^1J_{P,C}$ 225.9 Hz, CHN_2), and 62.44 (d, $^2J_{P,C}$ 5.1 Hz, CH_2).

Dimethyl Diazomethylphosphonate (5).—This compound, prepared by a published procedure [9] with the same modification as described above, was obtained as a yellow oil, b.p. 59° at 0.1 mmHg, $\nu_{max.}$ 2 110 and 1 250 cm^{-1}, δ_H($CDCl_3$) 3.7 (6 H, d, J 11.5 Hz) and 4.5 (1 H, d, J 11 Hz).

Conversion of Benzophenone into Diphenylethyne.—(a) *Silicon-based reagent.* A solution of the silane (1) (170 mg, 1.5 mmol) in ether (6 ml) was treated, at 0 °C in an atmosphere of nitrogen, with n-butyl-lithium (2.1M in hexane; 0.76 ml, 1.5 mmol); the yellow colour of the solution faded, and a fine white precipitate was formed. A solution of benzophenone (182 mg, 1 mmol) in ether (6 ml) was added, and the cooling bath removed. After 2 h, the solution was poured onto water (10 ml). The organic layer was separated, the aqueous layer was extracted with ether (2 × 5 ml), and the organic extracts were combined, washed with brine, and dried. Removal of solvent, followed by preparative t.l.c. (20% ethyl acetate–hexane) gave diphenylethyne (143 mg, 0.8 mmol, 80%), m.p. 60—61° (lit.,[15] 62.5°), identified by g.l.c. (1% OV-17; 150 °C) and mixed m.p. comparison with an authentic sample.

A solution of the silane (1) (230 mg, 2 mmol) in benzene (5 ml) was treated, at 0 °C in an atmosphere of nitrogen, with potassium t-butoxide (227 mg, 2 mmol). After 5 min, a solution of benzophenone (365 mg, 2 mmol) in benzene (4 ml) was added. By the procedure given above, diphenylethyne (178 mg, 1 mmol, 50%) and unchanged benzophenone (61 mg, 0.34 mmol) were isolated.

(b) *Phosphorus-based reagents.* A solution of the phosphonate (4) (112 mg, 0.63 mmol) in THF (5 ml) was treated, at −78 °C in an atmosphere of nitrogen, with n-butyllithium (2.1M in hexane; 0.3 ml, 0.63 mmol); the colour of the solution changed from yellow to red. A solution of benzophenone (52 mg, 0.29 mmol) was added, and the cooling bath removed. After 16 h, the solution was poured onto water (5 ml) and extracted with ether (3 × 5 ml). The organic extracts were combined, washed with brine, and dried. Removal of solvent followed by preparative t.l.c. gave diphenylethyne (46 mg, 0.27 mmol, 94%).

A solution of the phosphonate (4) (181 mg, 1.02 mmol) in THF (5 ml) was treated, at −78 °C in an atmosphere of nitrogen, with a slurry of potassium t-butoxide (119 mg, 1.06 mmol) in THF (5 ml). A solution of benzophenone (107 mg, 0.59 mmol) was added, and the cooling bath removed. After 16 h, isolation as above afforded, after preparative t.l.c., diphenylethyne (81 mg, 0.45 mmol, 77%).

Virtually identical behaviour was shown by the dimethyl phosphonate (5).

Conversion of Carbonyl Compounds into Alkynes.—A set of standard conditions was employed, exemplified by the

[12] S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 1962, 233.
[13] G. Köbrich and P. Buck, ' Chemistry of Acetylenes,' ch. 2, ed. H. G. Viehe, Dekker, New York, 1969.
[14] C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, 1966, **31**, 4071, and references therein; (*b*) E. J. Corey and P. L. Fuchs, *Tetrahedron Letters*, 1972, 3769; (*c*) H. P. Hogan and J. Seehafer, *J. Org. Chem.*, 1972, **37**, 4446; (*d*) H. Reimlinger, *Chem. and Ind.*, 1969, 1306; (*e*) J. H. Hargis and W. D. Alley, *J.C.S. Chem. Comm.*, 1975, 612.
[15] L. I. Smith and H. H. Hoehn, *J. Amer. Chem. Soc.*, 1941, **63**, 1180.

conversion of benzophenone into diphenylethyne by using the lithium salt (6) of the phosphonate (4) in THF. The following conversions were achieved. 4,4'-Dimethylbenzophenone reacted with the lithium salt (6) (2 equiv.) to give di-*p*-tolylethyne (97%), m.p. 134—135° (lit.,[16] 135—136°); 4-chlorobenzophenone with (6) (2 equiv.) gave 4-chlorophenyl(phenyl)ethyne (82%), m.p. 82—83° (lit.,[17] 83—84°); 4-methoxybenzophenone with (6) (2.4 equiv.) gave 4-methoxyphenyl(phenyl)ethyne (66%), m.p. 58—59° (lit.,[16] 59—60°); 3-nitrobenzophenone with (6) (2.4 equiv.) gave 3-nitrophenyl(phenyl)ethyne (38%), m.p. 56—57° (lit.,[18] 70—71°), $\nu_{max.}$ (CCl_4) 3 080, 2 220, 2 200, 1 595, 1 520, and 1 350 cm^{-1}, $\delta(CDCl_3)$ 7.5 (5 H, m), 7.8 (2 H, m), and 8.3 (2 H, m), M^+ 233; di-2-naphthyl ketone with (6) (10 equiv.) gave di-2-naphthylethyne (75%), m.p. 225—226° (lit.,[19] 228—229°); 4-benzoylbenzophenone with (6) (3.6 equiv.) gave two products, separated by preparative t.l.c. (20% ethyl acetate–hexane) into 1,4-bis(phenylethynyl)-benzene (13%), m.p. 178—179° (lit.,[20] 181—182°), and 4-(*phenylethynyl*)*benzophenone* (66%) as yellow crystals, m.p. 121—122° (from hexane), $\nu_{max.}$ (CCl_4) 3 080, 3 060, 3 040, 2 230, 1 665, and 1 600 cm^{-1}, M^+ 282 (Found: C, 89.25; H, 5.1. $C_{21}H_{14}O$ requires C, 89.35; H, 5.0%).

2-Benzoylthiophen with (6) (2.7 equiv.) gave 2-(phenylethynyl)thiophen (44%), m.p. 48—49° (from aq. ethanol), $\nu_{max.}$ (CCl_4) 3 100, 3 070, 2 190, 1 590, and 1 210 cm^{-1}, $\delta(CCl_4)$ 7.0 (1 H, m) and 7.4 (7 H, m), M^+ 184 (Found: C, 78.1; H, 4.25. $C_{12}H_8S$ requires C, 78.25; H, 4.4%). 3-Benzoylpyridine with (6) (4.2 equiv.) gave 3-(phenylethynyl)pyridine (38%), m.p. 46—47° (lit.,[14a] 47—48°); benzoylcyclohexane with (6) (3.8 equiv.) gave starting material (45%) and cyclohexyl(phenyl)ethyne (25%), b.p. 160° at 14 mmHg, $\nu_{max.}$ 3 060, 2 930, 2 860, 2 235, and 1 600 cm^{-1}, $\delta(CCl_4)$ 1.75 (11 H, m) and 7.3 (5 H, m), M^+ 184.

Attempted conversion of 2-benzoylfuran into the corresponding alkyne resulted in substrate polymerisation. No reaction was observed with cinnamaldehyde, benzyl phenyl ketone, dibenzyl ketone, dicyclohexyl ketone, or di-t-butyl ketone, starting material being recovered in each case.

Conversion of Acetophenone into 1-*Phenylpropyne*.—Reaction of acetophenone with the salt (2) (1.1 equiv.) gave a trace of alkyne. Reaction with the salt (6) (1.1 equiv.) gave 1-phenylpropyne (9%); use of the potassium salt of (4) (2 equiv.) gave the alkyne in 22% yield. In each case, large amounts of acetophenone were recovered; the alkyne was identified by g.l.c. (1% OV-1; 125 °C) comparison with an authentic sample.

Conversion of Phenylethanal into 3-*Phenylpropyne*.—Phenylethanal reacted with the potassium salt of (4) (1 equiv.) to give 3-phenylpropyne (30%), identified by g.l.c. (1% OV-1; 125 °C) comparison with an authentic sample.

Reaction of the Salt (2) *with Benzaldehyde*.—A solution of the silane (1) (228 mg, 2 mmol) in benzene (5 ml) was treated, at 0 °C in an atmosphere of nitrogen, with n-butyl-lithium (2.1M in hexane; 0.96 ml, 2 mmol). A solution of freshly distilled benzaldehyde (212 mg, 2 mmol) in ether (5 ml) was added, and the cooling bath removed. After 18 h, normal isolation (see above) followed by preparative t.l.c. (10% ethyl acetate–hexane) afforded benzyl alcohol (97 mg, 0.9 mmol) and α-diazoacetophenone (124 mg, 0.85 mmol), $\nu_{max.}$ 2 140, 1 630, and 1 380 cm^{-1}, $\delta(CDCl_3)$ 4.3 (1 H, s) and 7.4 (5 H, m), both identified by comparison with authentic samples.

Direct g.l.c. (8% Carbowax; 80 °C) injection of the reaction mixture prior to aqueous treatment showed that benzyl alcohol was present as its trimethylsilyl ether (comparison with an authentic sample).

Conversion of Benzil into Diphenylpropynone.—(a) *Silicon-based reagent*. A solution of the silane (1) (137 mg, 1.2 mmol) in ether (5 ml) was treated, at 0 °C in an atmosphere of nitrogen, with n-butyl-lithium (2.3M in hexane; 0.6 ml, 1.38 mmol). A solution of benzil (164 mg, 0.75 ml) in ether (5 ml) was added, and the cooling bath was removed. After 10 min, the solution was black. Normal isolation (see above) gave a brown oil (220 mg), preparative t.l.c. (20% ethyl acetate–hexane) of which gave diphenylpropynone (90 mg, 0.44 mmol, 58%), identified by comparison with an authentic sample, and a more polar compound as a white solid (20 mg), m.p. 162—164° (from ether–pentane), $\nu_{max.}$ (CCl_4) 3 460, 3 260, 3 060, 2 960, 1 665, 1 245, 1 165, and 910 cm^{-1}, $\lambda_{max.}$ (EtOH) 253 (ε 7 450) and 212 nm (13 360), $\delta(CDCl_3)$ 0.3 (9 H, s), 7.3br (6 H, one H exchanges with D_2O), 7.5 (3 H, m), and 8.1 (2 H, m), M^+ 320, identified as 5-*benzoyl*-4-*phenyl*-3-*trimethylsilylpyrazole* (3) (Found: C, 70.9; H, 6.6; N, 8.4. $C_{19}H_{20}N_2OSi$ requires C, 71.2; H, 6.3; N, 8.75%).

(b) *Phosphorus-based reagent*. Benzil reacted with the salt (6) (4 equiv.) to give diphenylpropynone in 25% yield.

Reactions of 4-*Nitrobenzaldehyde*.—(a) *Conversion into* 4-*nitrophenylethyne*. 4-Nitrobenzaldehyde reacted with the salt (6) (2 equiv.) to give 4-nitrophenylethyne, m.p. 150—152° (lit.,[21] 152°) (86%).

(b) *Preparation of diethyl* [1-*diazo*-2-*hydroxy*-2-(4-*nitrophenyl*)*ethyl*]*phosphonate* (8). A solution of the phosphonate (4) (487 mg, 2.74 mmol) and 4-nitrobenzaldehyde (370 mg, 2.45 mmol) in ether (5 ml) was treated with triethylamine (50 mg, 0.5 mmol), and left for 1 week at 5 °C. The solution was concentrated *in vacuo* at 30 °C, and the resulting crystals were triturated with ether to give the adduct (8) (395 mg, 1.2 mmol, 50%), m.p. 87—88° (rapid heating), $\nu_{max.}$ (CCl_4) 3 600, 3 300, 2 980, 2 070, 1 330, and 1 150 cm^{-1}, $\delta(CDCl_3)$ 1.4 (6 H, t, *J* 6 Hz), 5.7 (1 H, d, *J* 8 Hz), 4.2 (4 H, d of q, *J* 10 and 6.5 Hz), 4.6br (1 H, s, exchanges with D_2O), and 7.7 and 8.3 (4 H, ABq, J_{AB} 8 Hz). This adduct proved highly unstable to heat.

(c) *Reaction of the adduct* (8) *with potassium t-butoxide*. A solution of the adduct (8) (16 mg, 0.05 mmol) in THF (2 ml) was treated with a suspension of potassium t-butoxide (8 mg, 0.07 mmol) in THF (1 ml); the solution rapidly changed colour from yellow to deep red. After 30 min, normal isolation (see above) gave 4-nitrophenylethyne (5 mg, 0.032 mmol, 64%).

(d) *Reaction of the adduct* (8) *with* 1,5-*diazabicyclo*[4.3.0]-*non*-5-*ene*. A solution of the adduct (8) (59 mg, 0.18 mmol) in THF (3 ml) was treated with 1,5-diazabicyclo[4.3.0]non-5-ene (31 mg, 0.25 mmol). After 16 h, normal isolation, followed by preparative t.l.c. (ether), gave 4-nitrobenzaldehyde (25 mg, 0.165 mmol) and the phosphonate (4) (23 mg, 0.13 mmol), both identified by comparison with authentic samples.

[16] A. Jovtscheff and S. L. Spassov, *Monatsh.*, 1969, **100**, 328.
[17] A. R. Katritzky, A. J. Boulton, and D. J. Short, *J. Chem. Soc.*, 1960, 1519.
[18] C. W. Bird and A. F. Harmer, *Org. Prep. Procedures*, 1970, **2**, 79.
[19] K. Nakasuji, S. Akiyama, K. Akashi, and M. Nakagawa, *Bull. Chem. Soc. Japan*, 1970, **43**, 3567.
[20] W. Reid and A. Urschel, *Chem. Ber.*, 1958, **91**, 2459.
[21] V. Drewsen, *Annalen*, 1882, **212**, 150.

(e) *Reaction of the adduct* (8) *with bisacetylacetonatocopper*. A solution of the adduct (8) (157 mg, 0.48 mmol) in benzene (25 ml) was treated with bisacetylacetonatocopper (5 mg), and the mixture heated at reflux for 4 h. Concentration and preparative t.l.c. (ether) gave *diethyl 4-nitrophenacylphosphonate* (9) as a yellow oil (135 mg, 0.45 mmol, 93%), b.p. 135° at 0.4 mmHg, $\nu_{max.}$ 3 070, 2 980, 1 690, 1 600, 1 520, 1 340, and 1 250 cm^{-1}, $\delta(CDCl_3)$ 1.35 (6 H, t, *J* 7 Hz), 3.75 (2 H, d, *J* 22 Hz), 4.2 (4 H, d of q, *J* 10 and 7 Hz), and 8.3 (4 H, t, *J* 10 Hz) (Found: C, 47.95; H, 5.45; N, 4.6. $C_{12}H_{16}NO_6P$ requires C, 47.85; H, 5.35; N, 4.65%).

We thank Mrs. Harkness and her staff for microanalytical services, and Mr. A. Ritchie for mass spectral determinations. We are grateful to the University of Glasgow for a studentship (to B. J. H.).

[6/1444 *Received*, 22*nd July*, 1976]