$C_{30}H_{28}O_3$: C, 82.54; H, 6.46. Found: C, 82.49; H, 6.42.

1,1,2-Tris(4''-methoxyphenyl)-1-(4'-chlorophenyl)ethylene (8). Proportion of reactants: chlorobenzene (5.6 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), anisole (16.2 g) (0.15 mol). Compound **8** was eluted with petroleum ether–benzene (50:50) and crystallized from acetone: mp 178–180 °C; yield 9.57 g (42%); IR 1619, 1503, 1322, 1292, 1242, 1170, 1105, 1056, 831, 805, and 719 cm^{-1}; ^1H NMR δ 3.76 (s, 9 H, 3 × OCH_3), 6.64 (dd, 6 H, J = 2, 8 Hz, 3''-H, 5''-H), 6.92 (dd, 8 H, J = 2, 8 Hz, 2''-H, 6''-H, 3'-H, 5'-H), 7.0 (d, 2 H, J = 8 Hz, 2'-H, 6'-H); MS, m/z (relative intensity) 458 (M^+ + 2, 16), 456 (M^+, 48), 348 (6), 333 (9), 305 (29), 289 (19), 263 (29), 239 (54), 227 (67), 199 (100), 152 (96). Anal. Calcd for $C_{29}H_{25}ClO_3$: C, 76.22; H, 5.51. Found: C, 76.18; H, 5.45.

2',4'-Dimethyl-1',5'-bis[2,2-dichloro-1-(4''-methoxyphenyl)ethenyl]benzene (9). Proportion of reactants: *m*-xylene (5.3 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), anisole (10.8 g) (0.1 mol). The product was eluted with petroleum ether–benzene (75:25) and crystallized from MeOH: mp 146–147 °C; yield 9.61 g (38%); IR 1603, 1507, 1268, 1177, 1031, 966, 878, 854, 794, 769, and 720 cm^{-1}; ^1H NMR δ 2.12 (s, 6 H, 2 × CH_3), 3.80 (s, 6 H, 2 × OCH_3), 6.84 (d, 4 H, J = 8 Hz, 3''-H, 5''-H), 7.02 (s, 1 H, 3'-H), 7.14 (s, 1 H, 6'-H), 7.30 (d, 4 H, J = 8 Hz, 2''-H, 6''-H); MS, m/z (relative intensity) 510 (M^+ + 4, 52), 508 (M^+ + 2, 100), 506 (M^+, 76), 476 (7), 474 (21), 472 (24), 438 (12), 437 (19), 436 (18), 435 (21), 426 (5), 425 (10), 424 (10), 423 (19), 422 (10), 366 (5), 365 (7), 203 (17), 201 (29). Anal. Calcd for $C_{26}H_{22}Cl_4O_2$: C, 61.66; H, 4.38. Found: C, 61.60; H, 4.31.

2',4'-Dimethyl-1',5'-bis[2,2-dichloro-1-(2'',4''-dimethoxyphenyl)ethenyl]benzene (10). Proportion of reactants: *m*-xylene (5.3 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), dimethylresorcinol (13.8 g) (0.1 mol). Compound **10** was eluted with benzene and crystallized from ethyl acetate: mp 210–211 °C; yield 11.32 g (40%); IR 1608, 1576, 1502, 1414, 1308, 1287, 1211, 1175, 1127, 1086, 1033, 962, 917, 876, 849, 811, and 722 cm^{-1}; ^1H NMR δ 2.20 (s, 6 H, 2 × CH_3), 3.72, 3.80 (each s, 12 H, 4 × OCH_3), 6.42 (d, 2 H, J = 2 Hz, 3''-H), 6.46 (dd, 2 H, J = 2, 8 Hz, 5''-H), 6.94 (s, 1 H, 3'-H), 7.06 (s, 1 H, 6'-H), 7.18 (d, 2 H, J = 8 Hz, 6''-H); MS, m/z (relative intensity) 570 (M^+ + 4, 53), 568 (M^+ + 2, 100), 566 (M^+, 78), 534 (10), 533 (10), 532 (12), 531 (8), 500 (10), 498 (8), 497 (10), 496 (8), 495 (9), 365 (5), 363 (8), 284 (8), 283 (6), 161 (8), 148 (21). Anal. Calcd for $C_{28}H_{26}Cl_4O_4$: C, 59.36; H, 4.62. Found: C, 59.42; H, 4.57.

Crystallization and X-ray Experiments. Suitable single crystals of compound **10** were grown from ethyl acetate, and those of compound **8** were obtained from acetone. Crystal quality check and space-group determination were made from preliminary rotation and Weissenberg photographs.

Precise lattice constants and the intensity data of a quadrant were measured on a Stoe four-circle diffractometer with Ni-filtered Cu Kα radiation. The reflection intensities were recorded by the θ–2θ scan technique with variable scan range and variable scan speed. Two standard reflections which were measured every 90 min showed no significant variations during the whole data collection. A summary of crystallographic data is given in Table I (supplementary material).

Structure Determination and Refinement. Phase determination was carried out successfully with direct methods. SHELXS-86[12] was used for compound **10** and MULTAN[13] for compound **8**. Least-squares refinements were executed with the corresponding subprograms of the XTAL[14] (compound **10**) and XRAY[15] system (compound **8**). For compound **10**, hydrogens (in parts from difference syntheses and in parts on calculated positions) were included in the final stages of anisotropic refinement of non-H atoms. For compound **8**, hydrogens were not determined. For this structure a disorder of the chlorine and the terminal methoxy groups was observed. The positions given in Figure 1 are the most probable ones; however, there is some evidence for the chlorine to occupy in parts two further of the methoxy positions and that a methoxy group contributes also in parts to the present chlorine site. No attempt was made to investigate this disorder problem in detail. The final atomic parameters with Ueq values for compounds **8** and **10** are given in Tables II and III respectively (supplementary material).

Supplementary Material Available: All X-ray data for compounds **8** and **10**, Tables I–III, as well as listings of complete atomic parameters with U_{ij} values, bond lengths, and bond angles (14 pages). Ordering information is given on any current masthead page.

(12) Sheldrick, G. M. SHELXS-86, program for crystal structure determination; University of Gottingen, Federal Republic of Germany, 1986.
(13) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declerq, S. P. MULTAN-77, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data; University of York, England and Louvain, Belgium, 1977.
(14) Stewart, J. M., Hall, S. R., Eds.; XTAL TR-1364. 2; Computer Science Center, University of Maryland, College Park, MD, 1986.
(15) Stewart, J. M.; Machin, P. A.; Ammon, H. L.; Dickinson, C. W.; Heck, H.; Flack, H. The XRAY-76 System, Technical Report TR-446; Computer Science Center, University of Maryland, College Park, MD, 1976.

Direct Synthesis of β-Keto Methylenetriphenylphosphoranes from Readily Available Phosphonium Salts

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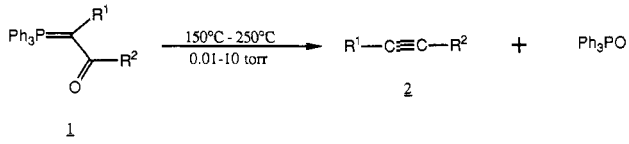
Thermolysis of β-keto methylenetriphenylphosphoranes **1** to give disubstituted acetylenes **2** and triphenylphosphine oxide (Scheme I), first investigated by Trippett and Walker,[1] is a particularly useful method for the preparation of (perfluoroalkyl)-substituted electron-deficient acetylenes.[2] The resultant acetylenes are valuable synthetic intermediates and can be employed in a variety of reactions as dipolarophiles[2c] or dienophiles[2g] for the preparation of fluorinated compounds. Reported methods for preparation of the phosphorane precursors, however, are rather cumbersome, requiring two steps from the readily available phosphonium salts and affording a mixture of the desired phosphorane and a phosphonium salt. An excellent method has been developed for the preparation of (β-ketoalkyl)phosphonates; however, this did not seem to us to be directly applicable to type **1** phosphoranes.[3] In order to prepare suitable quantities of the acetylenes, we endeavored to find a more convenient route to phosphoranes **1**.

Typically, phosphoranes **1** are prepared by treatment of mono-α-substituted methylenephosphoranes **4** with acid chlorides or anhydrides to afford an equimolar mixture of the desired phosphorane **1** and phosphonium salt **6** (Scheme II). Acylation of phosphorane **4** affords intermediate phosphonium salt **5**, which, via transylidation,[4]

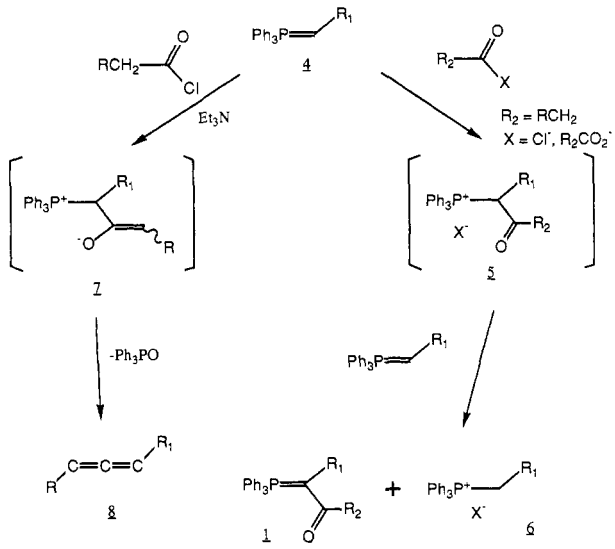
(1) Trippett, S.; Walker, D. M. *J. Chem. Soc.* **1959**, 3874.
(2) (a) Huang, Y. Z.; Shen, Y.; Ding, W.; Zheng, J. *Tetrahedron Lett.* **1981**, *22*, 5283. (b) Huang, Y.-T.; Shen, Y.; Xin, Y.; Fu, G.; Xu, Y. *Sci. Sin. Ser. B* **1982**, *25*, 21. (c) Kobayashi, Y.; Yamashita, T.; Takahashi, K.; Kuroda, H.; Kumadaki, I. *Tetrahedron Lett.* **1982**, *23*, 343. (d) Shen, Y.; Qiu, W.; Xin, Y.; Huang, Y. *Synthesis* **1984**, 924. (e) Shen, Y.; Xin, Y.; Cen, W.; Huang, Y. *Synthesis* **1984**, 35. (f) Braga, A. L.; Comasseto, J. V.; Petragnani, N. *Tetrahedron Lett.* **1984**, *25*, 1111. (g) Kobayashi, Y.; Yamashita, T.; Takahashi, K.; Kuroda, H.; Kumadaki, I. *Chem. Pharm. Bull.* **1984**, *32*, 4402. (h) Shen, Y.; Lin, Y.; Xin, Y. *Tetrahedron Lett.* **1985**, *26*, 5137. (i) Shen, Y.; Chen, W.; Huang, Y. *Synthesis* **1985**, 159. (j) Shen, Y.; Qiu, W. *Synthesis* **1987**, *42*. (k) Shen, Y.; Kheng, J. *J. Fluorine Chem.* **1987**, *35*, 513. (l) Shen, Y.; Cen, W.; Huang, Y. *Synthesis* **1987**, 626.
(3) Aboujaoude, E. E.; Collignon, N.; Teulade, M.-P.; Savignac, P. *Phosphorus Sulfur* **1985**, *25*, 57.
(4) Bestmann, H. J. *Chem. Ber.* **1962**, *95*, 58.

0022-3263/88/1953-5558$01.50/0

Scheme I



Scheme II



reacts with another molecule of phosphorane 4 to afford the desired phosphorane 1 and phosphonium salt 6. This 1:1 mixture of components must be separated prior to thermolysis as appreciable amounts of the undesired phosphonium salt can considerably lower the yield of acetylene in the thermolysis step. In addition, at least half of the starting phosphorane is lost by conversion to phosphonium salt 6.

In principle, the presence of a suitable base in the reaction mixture can directly convert 5 to phosphorane 1 and thus avoid transylidation. However, for many acyl halides commonly used in this reaction, treatment with base gives rise to the formation of ketenes that readily react with 4 to afford allenes 8 by the intermediacy of phosphonium betaine 7. This route, using triethylamine as a base, has been explored to prepare allenes that are either substituted or unsubstituted in the α position.[5]

We now report a method for the one-step conversion of readily available phosphonium salts to the desired phosphoranes without the formation of undesired phosphonium salts. For acyl halides or anhydrides that do not afford ketenes in the presence of base (i.e., CF_3COCl, etc.), phosphorane 1 can be prepared directly by addition of base (Scheme III). While there are numerous examples of the preparation of (α-acylmethylene)phosphoranes 1 by transylidation, to our knowledge no reports have appeared describing the direct conversion of phosphonium salts to phosphoranes 1 in the presence of a base such as triethylamine. One report has appeared describing the conversion of an α-substituted methylenephosphorane 4 (R^1 = Ph, CN, or CO_2Et) to disubstituted phosphorane 1 (R^2 = PhC≡C) in the presence of triethylamine.[6] While this demonstrated that transylidation can be avoided by addition of an amine base, the finding was not extended to include the direct conversion from phosphonium salts.

(5) Lang, R. W.; Hansen, H.-J. *Helv. Chim. Acta* **1980**, *63*, 438. Lang, R. W.; Hansen, H.-J. *Org. Synth.* **1984**, *62*, 202.
(6) Gough, S. T. D.; Trippett, S. *J. Chem. Soc.* **1964**, 543.

Scheme III

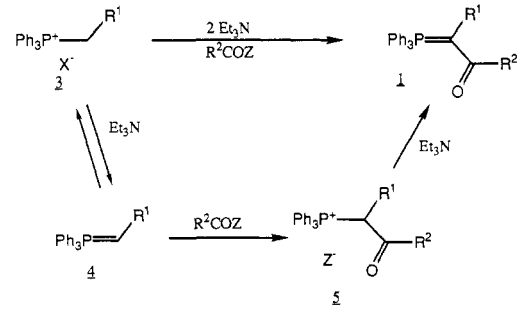


Table I. Preparation of (α-Acylmethylene)phosphoranes 1 from α-Substituted Methylphosphonium Salts 3

entry	R^1	R^2	yield[a] (%)
a	CO_2Et	CF_3	86
b	CO_2Et	CF_2CF_3	69
c	CO_2Et	CCl_2CH_3	85
d	CO_2Et	CCl_3	90
e	CN	CF_3	75
f	CO_2Bz	CF_3	98
g	CO_2CH_3	$CClF_2$	93
h	CO_2CH_3	CF_3	99
i	CO_2Et	$CFCl_2$	52
j	CO_2-*t*-Bu	CF_3	69
k	SCH_3	CF_3	49
m	CO_2Et	CF_2H	77
n	CO_2Et	$CHCl_2$	51
p[b]	$Si(CH_3)_3$	CF_3	30[c] 22[d]
q	C_6H_5	CF_3	24
r	H	CF_3	

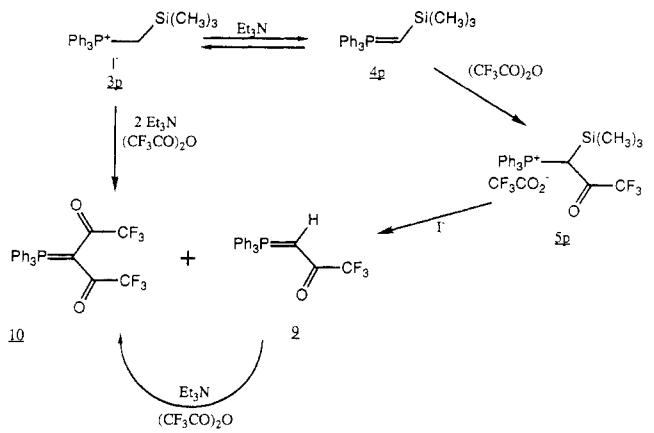
[a] All yields indicate amount of isolated materials. [b] A mixture of products is obtained as shown in Scheme IV. [c] Compound **9**. [d] Compound **10**.

Instead, phosphoranes such as 1 have been prepared almost exclusively by transylidation from monosubstituted methylenephosphoranes 4.[1,2,4,7] We have found that the addition of 2 equiv of triethylamine to methylphosphonium salts 3, followed by 1 equiv of acid chloride or anhydride gives (acylmethylene)phosphorane 1 in moderate to high yield (Table I). Compared to the transylidation route, this has the advantage of allowing conversion from a phosphonium salt rather than the stabilized phosphorane. This eliminates the need to prepare phosphoranes such as 4, which are hygroscopic and oftentimes not commercially available, in addition to simplifying the isolation of the desired product by eliminating phosphonium salt byproducts.

The reaction is general for phosphonium salts with electron-withdrawing groups (R^1 = CO_2R, CN, etc.) and affords the highest yields when R^1 is an ester or nitrile group. In these cases the conversion of 3 to intermediate phosphorane 4 with triethylamine is nearly complete. Somewhat lower yields are observed with R^1 is a thiomethyl or phenyl substituent. In these cases the equilibrium between 3 and 4 favors the phosphonium salt. Unsubstituted methyltriphenylphosphonium salt (**3r**) did not afford phosphorane products even after prolonged reaction times of 14 days. Despite the presence of α-hydrogens, no allenic esters were detected when dichloro- and difluoroacetyl chlorides were employed (entries m and n). Instead, phosphoranes **1n** and **1m** were obtained in 51% and 78%

(7) (a) Märkl, G. *Chem. Ber.* **1961**, *94*, 3005. (b) Gough, S. T. D.; Trippett, S. *J. Chem. Soc.* **1962**, 2333. (c) Petragnani, N.; Schill, G. *Chem. Ber.* **1964**, *97*, 3293. (d) Bestmann, H. J.; Geismann, C. *Liebigs Ann. Chem.* **1977**, 282.

Scheme IV



yield, respectively.[8] Under the reaction conditions, the rate of reaction of the acid chlorides with phosphorane **4** must be greater than the rate of formation of betaine intermediate **7**.

The (trimethylsilyl)-substituted **3p** did not afford the expected phosphorane. Instead two phosphoranes, **9** and **10**, were separated by preparative liquid chromatography and obtained in a ratio of 57:43 (Scheme IV). Loss of the silyl group can occur by attack of intermediate phosphonium salt **5n** by I^- to afford **9**. Under the reaction conditions, we found that **9** is converted to (diacylmethylene)phosphorane **10** quantitatively. Thus, when only 1 equiv of the anhydride was employed in the reaction of the silyl phosphonium salt, a mixture of the mono- and diacyl products was obtained. The use of organolithium bases for preparation of (α-acylmethylene)phosphoranes has been utilized previously for the preparation of **9** from methylphosphonium salt **3r**.[9] Surprisingly, a small amount of **10** (8%) was also isolated from the preparation of **1e**, which may arise from loss of cyanate from an intermediate phosphonium salt. This impurity was not observed in any of the other reactions and does not account for the lower yields observed for **1k** and **1q**. In these cases, mass balance can be achieved by accounting for the presence of phosphonium salts.

As noted earlier, phosphonium salts having weakly electron withdrawing groups afford lower yields of the desired phosphoranes by using the present method. Alternative bases were investigated for the preparation of **1q**, an important intermediate for the preparation of arylacetylenes (Table II).[2c,g] The ratios of the phosphorane to the phosphonium salt were determined by analytical HPLC on a reverse-phase C18 column, allowing monitoring of both the salt and the phosphorane in addition to analysis of ^{31}P NMR spectra of the crude reaction mixtures. Use of 2 equiv of triethylamine (entry 1) afforded a 1:1 ratio of the phosphonium salt and **1q**. Due to problems associated with isolation when there is a significant amount of phosphonium salt present, only 25% isolated yield of phosphorane was achieved. Nearly identical results are obtained when either 1 equiv of phenyllithium or an equivalent of phenyllithium followed by triethylamine is employed (entries 2 and 3), affording a 30% yield of isolated **1q**. Comparison of amine bases shows that a hindered base such as DBU or Hünig's base (entries 4 and 5) resulted in a negligible amount of **1q**.

(8) In a related case, Lang and Hansen (ref 5) prepared a dichloroallene from (α,α-disubstituted-methylene)phosphorane 1 (R_1 = CH_3; R_2 = OEt) and dichloroacetyl chloride in 10% yield.

(9) Miyano, M.; Stealey, M. A. *J. Org. Chem.* **1975**, *40*, 2840.

Table II. Effect of Various Bases on the Ratio of Phosphorane 1q to Phosphonium Salt 6q Obtained from 3q by Trifluoroacetylation[a]

entry	base	ratio (1q:6q)[b]	yield (%)
1	1.1 equiv of PhLi	71:29	30[c]
2	DBU	8:92	
3	Et_3N	50:50	25
4	1.1 equiv PhLi/1.1 equiv Et_3N	76:24	
5	Hünig's base	0:100[d]	
6	DABCO	79:21	57
7	DMAP	58:42	
8	Lutidine	0:100[d]	
9	pyridine	0:100[d]	

[a] Reactions were run by treating 1 equiv of **3q** in CH_2Cl_2 with 2 equiv of base (unless otherwise stated), cooling the mixture in ice–water, and adding a 10% molar excess of trifluoroacetic anhydride. [b] Ratios were determined by both ^{31}P NMR and analytical HPLC. The agreement between the two methods was within 5%. [c] With only 1 equiv of base, the reaction stoichiometry affords a 1:1 mixture of **1q** and **6q**. Based on this stoichiometry, the yield is 59%. [d] Less than 2% of **1q** was present in the reaction mixture.

Pyridine type bases (entries 7, 8, and 9) afforded little or no desired product with the exception of DMAP, which proved to be slightly better than triethylamine. Of all the bases tried, DABCO gave the highest ratio of phosphorane to phosphonium salt and, in addition, afforded the least amount of side products (in the runs with triethylamine, small amounts, approximately 5% each, of two unidentified phosphorus compounds were detected by ^{31}P NMR and analytical HPLC). Thus, **1q** was obtained in 60% overall yield when DABCO was used as a base.

In cases where the phosphonium salts are not readily available, it is advantageous to prepare the phosphorane in a two-step, one-pot sequence from triphenylphosphine. This is also particularly attractive for large-scale synthesis of phosphoranes, since all the reactions are nearly quantitative and the reagents inexpensive. Treatment of triphenylphosphine, in a minimum amount of tetrahydrofuran, with *tert*-butyl bromoacetate affords a slurry of the phosphonium salt, which can be dissolved by addition of methylene chloride and directly converted to phosphorane **1j** by addition of triethylamine and trifluoroacetic anhydride in 69% overall yield.

Experimental Section

All reactions involving air- or moisture-sensitive reagents and all atmospheric distillations were run under a nitrogen atmosphere. The solvents and reactants were reagent grade. Anhydrous solvents were obtained from Aldrich (Sureseal bottles). Normal-phase HPLC analysis was performed with 250 mm × 0.46 mm i.d. columns containing 5-μm silica, using hexane/2-propanol mixtures as the mobile phase. Reverse-phase HPLC analysis was performed with 250 mm × 0.46 mm i.d. columns containing a 5-μm C-18 ODS bonded phase, using water/acetonitrile mixtures as the mobile phase. All melting points were recorded on a capillary melting point apparatus and are uncorrected. Proton and ^{13}C NMR resonances are reported relative to the internal tetramethylsilane in ppm, whereas ^{31}P resonances are reported relative to external standard 85% aqueous phosphoric acid and ^{19}F resonances relative to trichlorofluoromethane using trifluorotoluene (−63.763 ppm) as an external coaxial standard.

General Procedure for the Preparation of Phosphoranes. 4,4,4-Trifluoro-3-oxo-2-(triphenylphosphoranylidene)butanoic Acid, Ethyl Ester (1a). A slurry of (carbethoxymethyl)-triphenylphosphonium bromide (215 g, 0.5 mol) in 1.1 L of anhydrous THF was cooled in an ice–water bath and treated with triethylamine (150 mL, 1.1 mol). After being stirred for 15 min, the mixture was treated dropwise with trifluoroacetic anhydride (78 mL, 0.55 mol) and allowed to stir for 1 h. The mixture was filtered, the precipitate washed three times with cold THF, and the filtrate concentrated in vacuo to afford a yellow oily residue.

Trituration of the residue with 600 mL of water affords a crystalline product, which was collected, washed with water, and dried in vacuo to afford 192 g (86%) of a cream colored solid. A small sample was recrystallized from methanol–water to afford a white, crystalline solid: mp 125–127 °C (lit.[2b] mp 125–127 °C); ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3 H), 3.79 (q, 2 H), 7.43 (dt, 6 H), 7.52 (dd, 3 H), 7.66 (dd, 6 H); ^{13}C NMR ($CDCl_3$) δ 13.5, 59.8, 70.1 ($^1J_{CP}$ = 111 Hz), 117.8 (CF_3, $^1J_{CF}$ = 290 Hz, $^3J_{CP}$ = 14 Hz), 123.7 ($^1J_{CP}$ = 294 Hz), 128.6 ($^2J_{CP}$ = 13 Hz), 132.2, 132.9 ($^3J_{CP}$ = 10 Hz), 165.3, 174.4 ($^2J_{CF}$ = 34 Hz, $^2J_{CP}$ = 13 Hz); ^{19}F NMR ($CDCl_3$) δ −72.4 ($^3J_{PF}$ = 2 Hz); ^{31}P NMR ($CDCl_3$) δ 19.4. Anal. Calcd for $C_{24}H_{20}O_3F_3P$: C, 64.87; H, 4.54. Found: C, 64.96; H, 4.60.

4,4,4-Trifluoro-3-oxo-2-(triphenylphosphoranylidene)butanenitrile (1e). Trituration of the oily residue obtained from the reaction (0.15 mol) with methanol–water afforded a precipitate, which was collected and dried to yield 62.2 g of a yellow, crystalline solid. Recrystallization from methanol afforded 34.3 g (56.7%) of **1e**. An analytical sample was prepared by recrystallization from methanol to afford a cream colored crystalline solid: mp 191.0–192.5 °C (lit.[2a] mp 187–188 °C); ^{1}H NMR ($CDCl_3$) δ 7.50–7.75 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 48.7 (d, $^1J_{CP}$ = 123 Hz), 117.4 (dq, CF_3, $^1J_{CF}$ = 291 Hz, $^3J_{CP}$ = 13 Hz), 117.7 (CN, $^2J_{CP}$ = 12 Hz), 121.0 (C1, $^1J_{CP}$ = 94 Hz), 129.5 (C2, C6, $^2J_{CP}$ = 13 Hz), 133.6 (C3, C5, $^3J_{CP}$ = 10 Hz), 134.0 (C4), 176.8 (dq, C=O, $^2J_{CF}$ = 33 Hz, $^2J_{CP}$ = 5 Hz); ^{19}F NMR ($CDCl_3$) δ −72.7; ^{31}P NMR ($CDCl_3$) δ 22.4. Anal. Calcd for $C_{22}H_{15}ONF_3$: C, 66.50; H, 3.81; N, 3.53. Found: C, 66.50; H, 3.84; N, 3.53.

The mother liquors from the methanol recrystallizations of **1e** were combined and concentrated in vacuo. The resultant residue was purified by silica gel chromatography (2 × 22 in. column, 25% ethyl acetate in hexanes) to afford 11.9 g of **1e** (k' = 3.50), giving a combined yield of 45.2 g (74.7%). In addition, 6.0 g (7.9%) of **10**, a chromatographically less unretained material (k' = 1.15), was obtained.

1,1,1-Trifluoro-3-(triphenylphosphoranylidene)-2-propanone (9) and 1,1,1,5,5,5-Hexafluoro-3-(triphenylphosphoranylidene)-2,4-pentanedione (10). To a suspension of **3p** (22.8 g, 47.9 mmol) in 100 mL of anhydrous THF was added triethylamine (15 mL, 108 mmol). The suspension was cooled in an ice–water bath and treated with trifluoroacetic anhydride (7.5 mL, 53 mmol). After being stirred overnight, the reaction mixture was filtered and concentrated in vacuo. The resultant oily residue was triturated with water and the precipitate collected to afford 13.0 g (61.1%) of a 57:43 mixture of **10** and **9**, respectively. The two compounds were separated by silica gel chromatography (2 × 22 in. column, 25% ethyl acetate in hexanes) to afford 6.78 g (30.2%) of **10** (R_f 0.26) and 4.0 g (22.4%) of **9** (R_f 0.10). An analytical sample of **9** was obtained by recrystallization from methanol to afford a white, crystalline solid: mp 227–228 °C (lit.[9] mp 233 °C); ^{1}H NMR ($CDCl_3$) δ 4.28 (d, 1 H, $^2J_{HP}$ = 20 Hz), 7.40–7.70 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 52.3 ($^1J_{CP}$ = 111 Hz), 118.8 (CF_3, $^1J_{CF}$ = 291 Hz, $^3J_{CP}$ = 22.8 Hz), 124.8 (C1, $^1J_{CP}$ = 91 Hz), 129.2 (C2, C6, $^2J_{CP}$ = 13 Hz), 132.9 (C4, $^4J_{CP}$ = 1.7 Hz), 133.0 (C3, C5, $^3J_{CP}$ = 11 Hz), 173.5 (C=O, $^2J_{CF}$ = 32 Hz, $^2J_{CP}$ = 4 Hz); ^{19}F NMR ($CDCl_3$) δ −74.4 ($^4J_{FP}$ = 3 Hz); ^{31}P NMR ($CDCl_3$) δ 16.9; MS(EI), m/z (relative intensity) 372 (M^+, 11), 303 (CF_3, 100); MS(DP/CI isobutane), m/z 373 (M + 1). Anal. Calcd for $C_{21}H_{16}OF_3P$: C, 67.74; H, 4.33. Found: C, 67.81; H, 4.38.

The high R_f material **10** was recrystallized from methanol to afforded a yellowish white crystalline solid: mp 144–145 °C (lit.[2d] mp 142–143 °C); ^{1}H NMR ($CDCl_3$) δ 7.5–7.7 (m, 15); ^{13}C NMR ($CDCl_3$) δ 75.9 (J_{CP} = 104 Hz), 116.6 (dq, CF_3, $^1J_{CF}$ = 292 Hz, $^3J_{CP}$ = 11 Hz), 122.3 (Cl, $^1J_{CP}$ = 93 Hz), 129.2 (C2, C6, $^2J_{CP}$ = 13 Hz), 133.3 (C4, $^4J_{CP}$ = 3 Hz), 133.6 (C3, C5, $^3J_{CP}$ = 9.5 Hz), 177.9 (dq, C=O, $^2J_{CF}$ = 36.5 Hz, $^2J_{CP}$ = 5 Hz); ^{19}F NMR ($CDCl_3$) δ −73.7 ($^4J_{PF}$ = 1 Hz); ^{31}P NMR ($CDCl_3$) δ 21.8; MS(EI), m/z (relative intensity) 468 (M^+, 7), 399 (CF_3, 100), 281 (31). Anal. Calcd for $C_{23}H_{15}O_2PF_6$: C, 58.99; H, 3.23. Found: C, 58.92; H, 3.24.

[2-(1,1-Dimethylethoxy)-2-oxoethyl]triphenylphosphonium Bromide (3j). To a solution of triphenylphosphine (88 g, 0.336 mol) in 75 mL of THF cooled in an ice bath was added *tert*-butyl bromoacetate (65.45 g, 0.336 mol). The mixture was stirred overnight and the resultant slurry used without purification for the preparation of **1j**. An analytical sample was obtained by removing 6 g of crude material from the reaction mixture and recrystallizing the slurry from chloroform–ethyl acetate. The precipitate was collected, washed with ethyl acetate, and dried to afford 3.1 g of a white, crystalline solid; mp 190–192 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 9 H), 5.26 (d, 2 H, $^2J_{PH}$ = 14 Hz), 7.71–7.94 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 27.5, 34.0 (CH_2, $^1J_{CP}$ = 54 Hz), 84.7, 117.9 (C1′, $^1J_{CP}$ = 89 Hz), 130.3 (C2′, C6′, $^2J_{CP}$ = 13 Hz), 133.9 (C3′, C5′, $^3J_{CP}$ = 10 Hz), 135.2 (C4′, $^4J_{CP}$ = 3 Hz), 162.8 (C=O, $^2J_{CP}$ = 4 Hz); ^{31}P NMR ($CDCl_3$) δ 19.2. Anal. Calcd for $C_{24}H_{26}O_2BrP$: C, 63.03; H, 5.73. Found: C, 63.12, H, 5.76.

4,4,4-Trifluoro-3-oxo-2-(triphenylphosphoranylidene)butanoic Acid, 1,1-Dimethylethyl Ester (1j). To a suspension containing 150 g (0.328 mol) of crude phosphonium salt **3j**, obtained directly from the reaction without purification, was added 500 mL of methylene chloride. The solution was cooled in an ice–water bath and treated with triethylamine (100 mL, 0.722 mol). A slurry results, which is treated dropwise with trifluoroacetic anhydride (51 mL, 0.361 mol). After stirring overnight, the suspension was concentrated, dissolved in 800 mL of methanol, and treated with 500 mL of water to afford a crystalline solid. The entire sample was recrystallized from methanol–water to afford 107.14 g (69.2%) of a white, crystalline solid: mp 126.5–127.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H), 7.43–7.72 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 27.7, 71.3 (d, $^1J_{CP}$ = 110 Hz), 80.2, 118.2 (CF_3, dq, $^1J_{CF}$ = 290 Hz, $^3J_{CP}$ = 15 Hz), 124.3 (C1′, $^1J_{CP}$ = 93 Hz), 128.8 (C2′, C6′, $^2J_{CP}$ = 13 Hz), 132.4 (C4′, $^4J_{CP}$ = 3 Hz), 133.3 (C3′, C5′, $^3J_{CP}$ = 11 Hz), 165.0 (CO_2, $^2J_{CP}$ = 13 Hz), 174.0 (C=O, dq, $^2J_{CF}$ = 33 Hz, $^2J_{CP}$ = 6 Hz); ^{19}F NMR ($CDCl_3$) δ −75.5; ^{31}P NMR ($CDCl_3$) δ 18.0; MS(EI), m/z (relative intensity) 472 (M^+, 12), 416 (C_4H_8, 8), 399 ($OC(CH_3)_3$), 11), 347 (100). Anal. Calcd for $C_{26}H_{24}O_3F_3P$: C, 66.10; H, 5.12. Found: C, 66.11; H, 5.16.

1,1,1-Trifluoro-3-phenyl-3-(triphenylphosphoranylidene)-2-propanone (1q). A suspension of benzyltriphenylphosphonium chloride (9.95 g, 26 mmol) in 25 mL of anhydrous CH_2Cl_2 was prepared under nitrogen and cooled to −10 °C. The stirred suspension was treated with 1,4-diazabicyclo[2.2.2]octane (6.9 g, 62 mmol). After the suspension was stirred for 15 min, the mixture was treated dropwise with trifluoroacetic anhydride (4.0 mL, 28 mmol), such that the reaction temperature was kept below 10 °C. The resultant mixture was stirred overnight, quenched with water, and extracted thrice with ethyl acetate. The combined extracts were dried and concentrated in vacuo to afford a crude solid. This solid was dissolved in 25 mL of hot methanol, filtered, and treated with 10 mL of water. After standing overnight, the crystalline product was collected, washed with methanol–water (1:1), and dried to afford 6.5 g (56%) of a white crystalline solid: mp 219.5–220.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.01 (m, 5 H), 7.37 (m, 6 H), 7.50 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 72.6 ($^1J_{CP}$ = 105 Hz), 119.5 (CF_3, dq, $^1J_{CF}$ = 291 Hz, $^3J_{CP}$ = 20 Hz), 124.4 (C1′, $^1J_{CP}$ = 91 Hz), 126.4 (C3, C5, $^4J_{CP}$ = 3 Hz), 127.4 (C2, C6, $^3J_{CP}$ = 4 Hz), 128.8 (C2′, C6′, $^2J_{CP}$ = 12 Hz), 132.2 (C4′, $^4J_{CP}$ = 3 Hz), 133.6 (C3′, C5′, $^3J_{CP}$ = 10 Hz), 134.0 (C1, $^2J_{CP}$ = 7 Hz), 134.9 (C4, $^3J_{CP}$ = 3 Hz), 170.1 (dq, C=O, $^2J_{CF}$ = 30 Hz, $^2J_{CP}$ = 9 Hz); ^{19}F NMR ($CDCl_3$) δ −67.8 ($^4J_{FP}$ = 2.7 Hz); ^{31}P NMR ($CDCl_3$) δ 19.9. Anal. Calcd for $C_{27}H_{20}OPF_3$: C, 72.32; H, 4.50. Found: C, 72.33; H, 4.52.

1,1,1-Trifluoro-3-phenyl-3-(triphenylphosphoranylidene)-2-propanone (1q) and Benzyltriphenylphosphonium Trifluoroacetate (6q). A suspension of benzyltriphenylphosphonium chloride (99.93 g, 257 mmol) in 250 mL of methylene chloride was prepared under nitrogen and cooled to −5 °C. The stirred suspension was treated with triethylamine (79.5 mL, 570 mmol) at once and subsequently treated dropwise with trifluoroacetic anhydride (40 mL, 283 mmol). After addition was complete, the reaction was stirred overnight and filtered and the filtrate was concentrated. The resultant oily solid was dissolved in 250 mL of methanol and treated with 200 mL of water to afford a crystalline precipitate. The precipitate was collected, washed with water, and dried to afford 27.3 g (23.7%) of **1q**. Treatment of the aqueous filtrates with 1 L of water afforded an oily precipitate. The filtrate was extracted three times with CH_2Cl_2 and combined extracts were concentrated, dissolved in 200 mL of CH_2Cl_2, stirred, and treated portionwise with 200 mL of hexanes to afford a white crystalline solid. After collecting and washing the solid with CH_2Cl_2 in hexaanes (1:1), the solid was dried to afford 25.9 g (21.6%) of **6q**. An analytical sample was prepared by dissolving 2 g in hot $CHCl_3$ and adding ethyl acetate to afford

a white, crystalline solid: mp 183.0–183.5 °C; ^{1}H NMR ($CDCl_3$) δ 4.98 (d, 2 H, $^2J_{HP}$ = 14 Hz), 6.98 (d, 2 H), 7.11 (t, 2 H), 7.22 (t, 1 H), 7.63 (m, 12 H), 7.76 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 30.2 (d, $^1J_{CP}$ = 48 Hz), 117.4 (CF_3, $^1J_{CF}$ = 86 Hz), 127.0, 128.5, 128.8, 130.2, 131.3, 134.0, 135.1, 160.6 (C=O, $^2J_{CF}$ = 33 Hz); ^{19}F NMR ($CDCl_3$) δ −73.9; ^{31}P NMR ($CDCl_3$) δ 23.1. Anal. Calcd for $C_{27}H_{22}PO_2F_3$: C, 69.53; H, 4.75. Found: C, 69.60; H, 4.79.

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Supplementary Material Available: Experimental and spectral data for compounds **1b–d**, **1f–i**, **1k**, **1m,n**, and **3f** (5 pages). Ordering information is given on any current masthead page.

Reactions of Azines. 13. Thermal Rearrangements of 1,5,6-Triaza-1,2,4,6-heptatetraenes to 4,9-Dihydropyrazolo[5,1-*b*]quinazolines and *N*-α-Styryl-5-(phenylamino)pyrazoles

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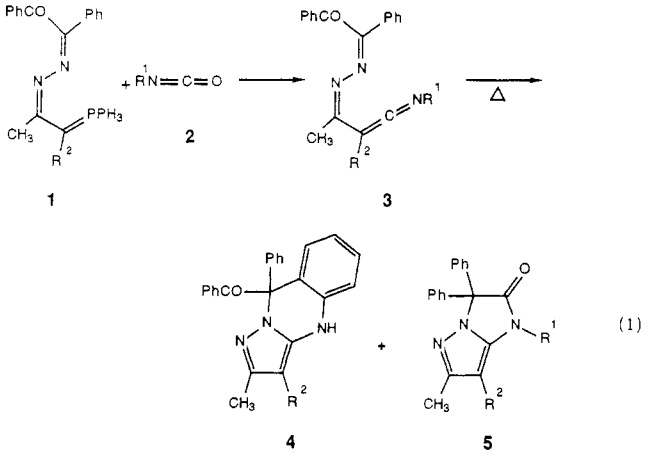
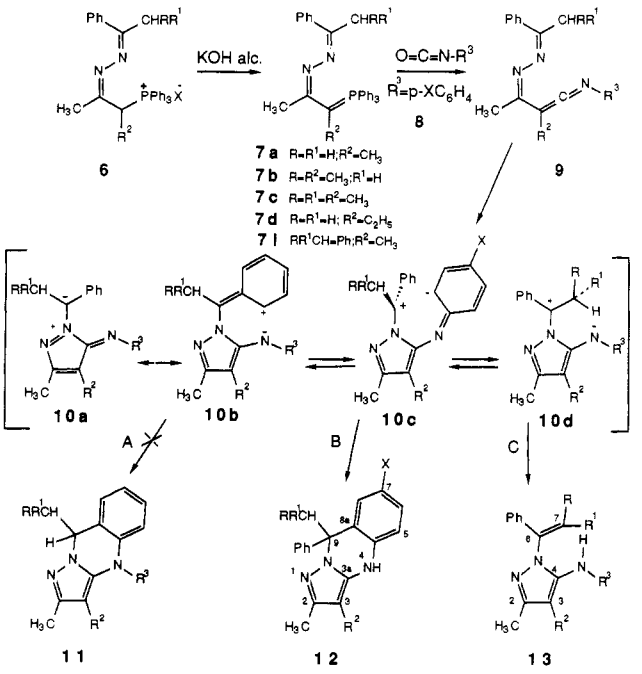
The thermal rearrangements of unsaturated azines **3** with cumulated double bonds in conjugation with the azine moiety have been shown[1-8] to provide excellent syntheses for a variety of pyrazolo fused heterocyclic compounds such as pyrazolo[5,1-*c*]oxazines and 4,9-dihydropyrazolo[1,5-*b*]isoquinolines,[1,2] 4*H*-pyrazolo[1,5-*c*][1,3,5]oxadiazines,[4] 4,5-dihydro- and 6,7-dihydropyrazolo[1,5-*a*]pyridines.[5] For example, the reaction of keto azine phosphoranes **1** with isocyanates **2** gave 4,9-dihydropyrazolo[5,1-*b*]quinazolines **4** and 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones **5** as shown in eq 1.[6]



(1)

We anticipated on the basis of the previous work that the thermal electrocyclic reactions of azine ketimines **9**, obtained from **7** and an isocyanate **8** (Scheme I), could give 4,9-dihydropyrazolo[5,1-*b*]quinazolines **11** and **12** and the *N*-α-styryl-5-(phenylamino)pyrazoles **13** via the resonance stabilized zwitterionic intermediates **10a–d**.

Scheme I



Results and Discussion

Trippet and Walker showed[9] that the reactions of isocyanates with phosphoranes with α-protons give betamines, which do not decompose to ketimines but transfer a proton to give stable phosphorane amides. Staudinger and Meyer had previously demonstrated[10] that phosphoranes without α-protons underwent normal carbonyl olefination reactions with isocyanates to yield ketimines. It was therefore necessary to use the α-alkylated phosphoranes **6** to prepare the desired ketimines **9**.

The phosphonium ylides **7** were prepared as previously reported[11] from the corresponding phosphonium salts **6** and ethanolic KOH. The phosphoranes **7** decomposed on standing; therefore, they were used immediately after their preparation.

The reactions of phosphoranes **7a–d,i** with aromatic isocyanates **8** in refluxing toluene led to the formation of two products along with triphenylphosphine oxide, as indicated by TLC. The presumed intermediate azine ketimines **9** were too unstable to isolate, so the thermolyses were carried out directly by briefly heating the reaction mixtures. The products were separated by column chromatography.[12]

The less polar products were isolated as orange oils and assigned as the *N*-α-styryl-5-(phenylamino)pyrazoles **13** on the basis of the following spectral data. A pyrazole ring was indicated by peaks[13] at δ 137–140 (C2), 107–111 (C3), and 143–146 (C4) in the ^{13}C NMR spectrum. There were

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(12) Chromatographic technique was that of Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.
(13) The numbering schemes used in the following discussions for the 4,9-dihydropyrazolo[5,1-*b*]quinazolines **12** and the *N*-α-styryl-5-(phenylamino)pyrazoles **13** are as shown in Tables II and III, respectively.

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