Anal. Calcd for $C_{20}H_{20}N_2O_6$: C, 62.48; H, 5.25; N, 7.29. Found: C, 62.12; H, 5.23; N, 7.37.

***cis*-3-[[(1,1-Dimethylethoxy)carbonyl]amino]-4-(methoxycarbonyl)-1-(4-methoxyphenyl)-2-oxoazetidine (18).** A slurry of **13** (15 g, 39 mmol) in dichloromethane (200 mL) was cooled to 0 °C under argon and treated with methylhydrazine (6.2 mL, 117 mmol) dropwise. The procedure for the preparation of **16** was followed at this point, substituting di-*tert*-butyl pyrocarbonate for benzyl chloroformate (18.35 g, 82 mmol) and stirring the resulting mixture for 24 h. The mixture was washed with phosphate buffer, bicarbonate solution, and brine and dried. Filtration and concentration yielded a waxy solid which was triturated with ether. Filtration then yielded 9.7 g (71%) of the desired product as a white solid: IR 1765, 1720; NMR 7.3 (d, 2 H, J = 8), 6.9 (d, 2 H, J = 8), 5.4 (m, 2 H), 4.8 (d, 1 H, J = 5), 3.80 (s, 3 H), 3.73 (s, 3 H); mp 161–163 °C.

Anal. Calcd for $C_{17}H_{22}N_2O_6$: C, 58.27; H, 6.34; N, 8.00. Found: C, 57.66; H, 6.07; N, 7.92.

Acknowledgment. We thank Drs. C. M. Cimarusti, W. H. Koster, R. H. Mueller, and W. A. Slusarchyk for valuable discussions and assistance in preparing the manuscript.

Registry No. 3, 81767-89-7; **9**, 80542-41-2; **10**, 80542-40-1; **11**, 6780-38-7; **12**, 72079-55-1; **13**, 80542-45-6; **14**, 81741-01-7; **15**, 81741-02-8; **16**, 80542-46-7; **17**, 80542-47-8; **18**, 81741-03-9; **19**, 61964-83-8; **20**, 81741-04-0; **21**, 81741-05-1; *p*-anisidine, 104-94-9; *trans*-cinnamaldehyde, 14371-10-9; azidoacetic acid, 18523-48-3; methyl glyoxylate methyl hemiacetal, 19757-97-2.

Reactions of Phosphorus Compounds. 40. Alkylation and Acylation Reactions of Triphenylphosphonium 2-[(2-Oxo-1,2-diphenylethylidene)hydrazono]propylide. Examination of the Anomalous Pyridazine and Pyrazole Products from the Benzoylation Reaction

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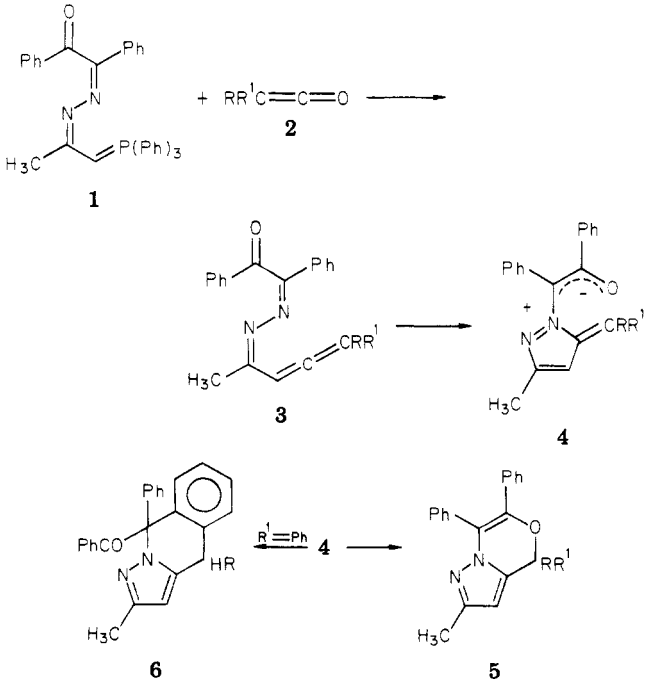
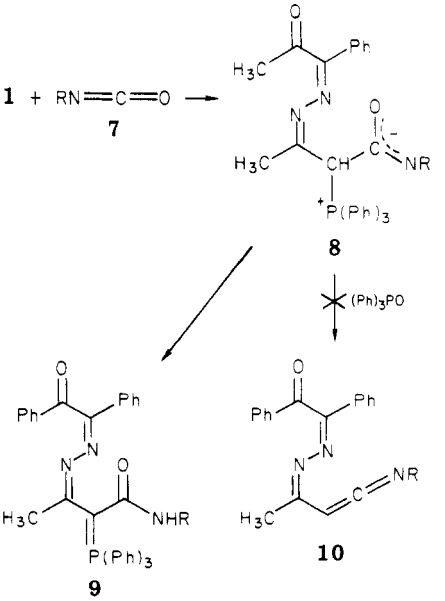
Received January 14, 1982

The title compound has been alkylated with methyl iodide, allyl bromide, and benzyl chloride, in acetonitrile, to give the corresponding salts. The title compound has been acylated with benzoyl chloride and ethyl chloroformate, in benzene, to give the corresponding ylides and hydrochloride salt of the title compound. Benzoylation of the title compound, in acetonitrile, gave two unexpected products, triphenyl[1-benzoyl-1-(3,4-diphenyl-6-pyridazinyl)methylene]phosphorane (**14**) and 2-(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)-1,2-diphenyl-1-(benzoyloxy)ethene (**24**), in addition to the expected benzoylated ylide and salt.

We have previously reported[1] that pyrazolo[5,1-*c*]-1,4 oxazines, **5**, and/or 4,9-dihydropyrazolo[1,5-*b*]isoquinolines, **6**, may be prepared readily from conjugated azines, **3**. The azines, **3**, were prepared by allowing triphenylphosphonium 2-[(2-oxo-1,2-diphenylethylidene)hydrazono]propylide (**1**) to react with ketenes, **2**.



Continuing our interest in the reactions of conjugated azines to prepare fused pyrazolo ring systems,[1,2] we attempted the reaction of isocyanates **7** with the phosphorane **1**.[3] However, the intermediate betaine, **8**, did not

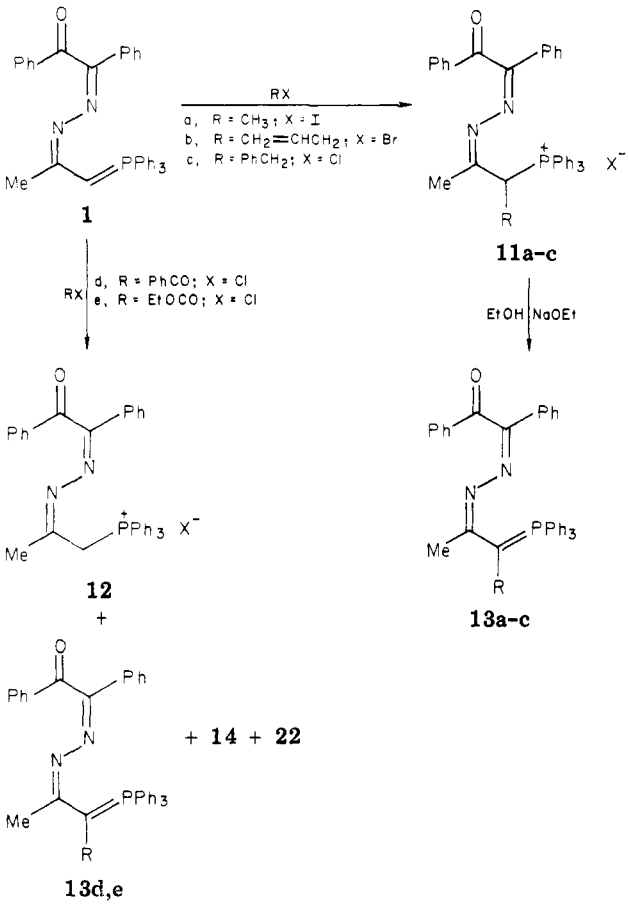


(1) E. E. Schweizer and S. Evans, *J. Org. Chem.*, **43**, 4328 (1978).

(2) (a) T. A. Albright, S. Evans, C. S. Kim, C. S. Labaw, A. B. Russiello, and E. E. Schweizer, *J. Org. Chem.*, **42**, 3691 (1977); (b) S. Evans, R. C. Gearhart, L. J. Guggenberger, and E. E. Schweizer, *ibid.*, **42**, 452 (1977).

0022-3263/82/1947-2768$01.25/0

Scheme I



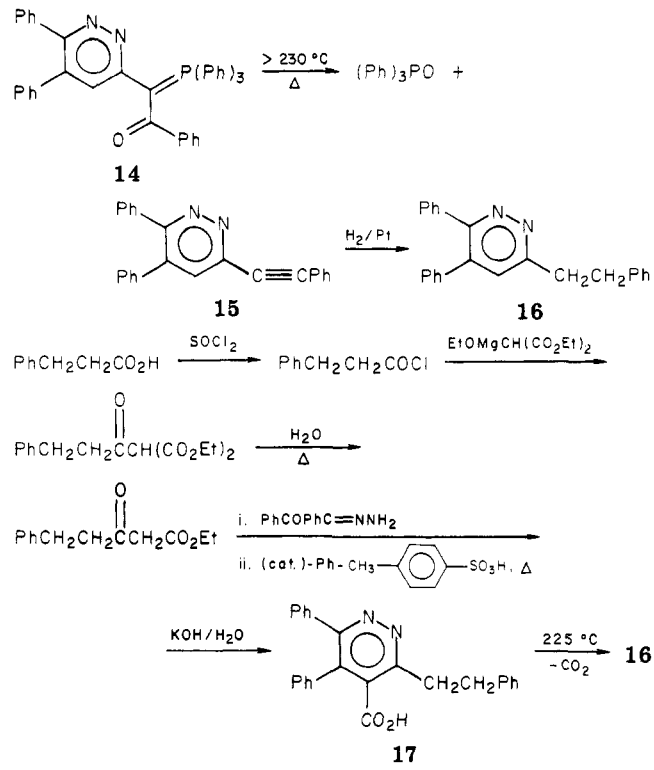
collapse to the hoped for ketimine, **10**, but transfered a proton to give the stabilized phosphorane, **9**. The transformation of the type **8** to **9** was originally uncovered by Trippett and Walker in 1959,[4] whereas early in this century Staudinger and Meyer[5] showed that phosphoranes without protons on the α-carbon atom underwent normal carbonyl olefination reactions. Therefore, it was decided that a study of the alkylation and acylation reactions of phosphorane, **1**, should be undertaken in order to acquire a suitable substituted phosphorane to use in the preparation of unsaturated azines.

Alkylation[6] and acylation[7,8] of phosphoranes have been reported in the past. Acylation, which produces a salt whose acidity is greater than its phosphorane precursor, is usually converted into its conjugate base (phosphorane), whereas the starting phosphorane is converted into its conjugate acid (phosphonium salt).[9]

Results and Discussion

The phosphorane, **1**, may be alkylated with alkyl halides, RX, in acetonitrile in relatively high yields (Scheme I).

Scheme II



The alkylated salts, **11a–c**, may be converted readily to the corresponding phosphoranes, **13a–c**, using ethanolic sodium ethoxide.

The reaction of the phosphorane, **1**, with benzoyl chloride in acetonitrile gave the expected stabilized benzoylated phosphorane,[9] **13d** (13% yield),[10] and the matching salt, **12**[9] (X = Cl; 91% yield),[10] as well as two unexpected products, **14** (50% yield)[10] and **22** (10% yield).[10]

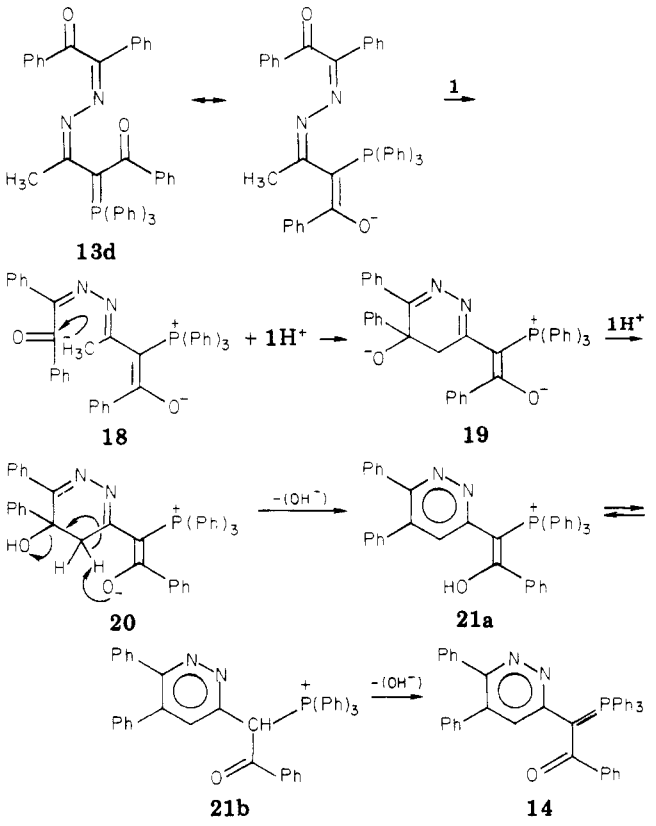
The structure of **14** was elucidated by the following experiments (Scheme II): (a) Pyrolytic cleavage of aryl-substituted benzoylphosphoranes is known to give acetylenes.[11] Heating of **14** for 15 min over 230 °C gave 3,4-diphenyl-6-(phenylethynyl)pyridazine (**15**) and triphenylphosphine oxide. Hydrogenation of **15** over platinum oxide gave 3,4-diphenyl-6-(2-phenylethyl)pyridazine (**16**). (b) An authentic sample of **16** was prepared via ethyl 3-oxo-5-phenylpentanoate, which on reacting with benzil monohydrazone by the procedure of Evans and Schweizer[12] gave 3,4-diphenyl-6-(2-phenylethyl)pyridazine-5-carboxylic acid (**17**). Compound **16** was obtained from **17** by heating and decarboxylating. (c) Mixture melting points and all of the analytical data for **16** produced from **15** or **17** were shown to be identical, thus proving the structure of **14**.

A proposed mechanism is shown in Scheme III. Proton transfer from the methyl to the ylide **1**, **13d** → **18**, may actually involve an intermolecular transfer of proton. An aldol condensation and dehydration to **21** follows with a subsequent reylidization, **21** → **14**. The reaction of **13d** and **1** would give the pyridazine product **14**.

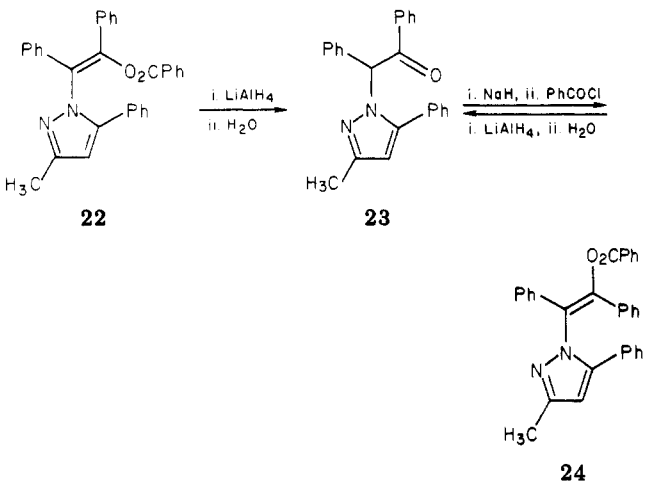
The minor product, **22**, is assumed to be in the *Z* configuration, as shown in Scheme IV. Support for its structure is as follows: (a) Reduction of **22** with $LiAlH_4$ gave the known[2a] 2-(3-methyl-5-phenyl-1*H*-pyrazol-1-

(3) S. Evans, Ph.D. Thesis, University of Delaware, Newark, DE, June, 1977.
(4) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 3874 (1959).
(5) H. Staudinger and J. Meyer, *Chem. Ber.*, **53**, 72 (1920).
(6) G. Wittig and M. Rieber, *Liebigs Ann. Chem.*, **562**, 177 (1949); H. J. Bestmann, E. Vilsmaier, and G. Graf, *ibid.*, **704**, 109 (1967).
(7) H. J. Bestmann, *Tetrahedron Lett.*, **4**, 7 (1960); H. J. Bestmann and B. Arnason, *Chem. Ber.*, **95**, 1513 (1962); H. J. Bestmann, *Angew. Chem.*, **77**, 651 (1965).
(8) H. J. Bestmann and H. Schulz, *Angew. Chem.*, **73**, 27 (1961); *Liebigs Ann. Chem.*, **674**, 11 (1964).
(9) S. Trippett, *Adv. Org. Chem.*, **1**, 83 (1960); H. J. Bestmann, *Chem. Ber.*, **95**, 58 (1962).
(10) Assuming quantitative (100%) yield is 50% conversion.
(11) S. Trippett and D. M. Walker, *J. Chem. Soc.* 3874 (1959); S. T. D. Gough and S. Trippett, *Proc. Chem. Soc.*, 302 (1961); S. T. D. Gough and S. Trippett, *J. Chem. Soc.* 2333 (1962); G. Markl, *Chem. Ber.*, **94**, 3005 (1961).
(12) S. Evans and E. E. Schweizer, *J. Org. Chem.*, **42**, 2321 (1977).

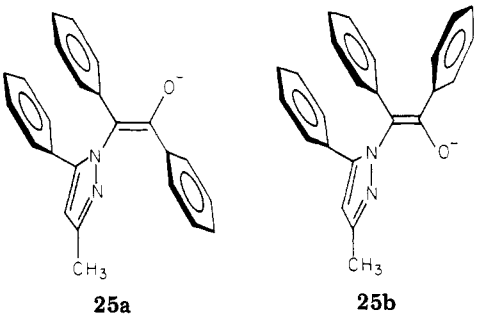
Scheme III



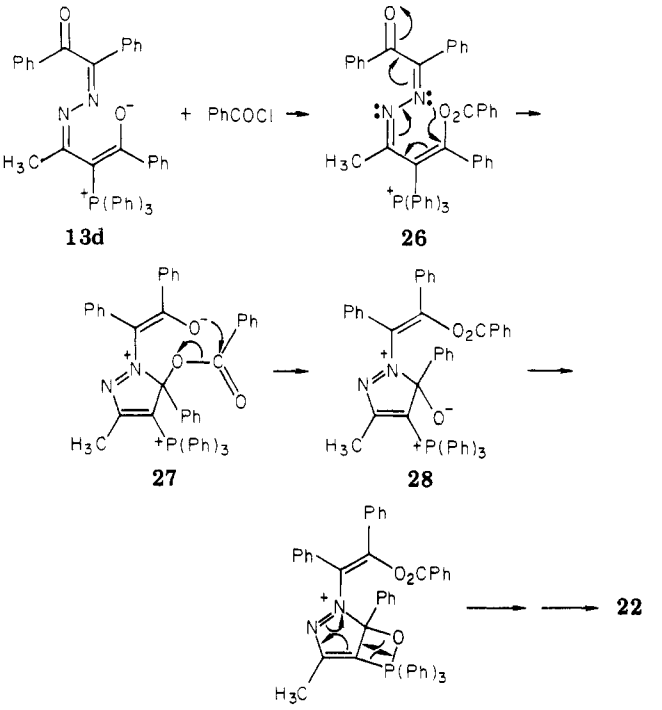
Scheme IV



Scheme V



Scheme VI



yl)-1,2-diphenylethanone (**23**) (cf. Scheme IV). (b) On benzoylating **23**, the expected product is (*E*)-2-(3-methyl-5-phenyl-1*H*-pyrazol-yl)-1,2-diphenyl-1-(benzoyloxy)ethene (**24**). The *E* configuration is expected because the (*E*)-enolate anion of the ketopyrazole derivative **25a** was shown by construction of models to have a much more available nucleophilic oxygen site, with the oxygen pointing away from the pyrazolyl nucleus, than the (*E*)-enolate anion **25b** (cf. Scheme V). The benzoylated product **24** gave essentially the same mass spectrum as the minor product **22**. The ^{13}C NMR was identical, except that all of the values differed by approximately 1 ppm (within experimental error). The IR is almost indistinguishable, and the ^1H NMR differed only by one absorption. Therefore, we believe that **22** has the *Z* configuration as shown in structure **22**.

A mechanism that is plausible which explains the *Z* orientation is shown in Scheme VI. If the enolate oxy anion in **13d** is benzoylated to yield **26**, the "criss-cross"[13] cycloaddition may take place to give the azomethinimine intermediate **27**. An intramolecular transfer of benzoyl group would only occur (**27** → **28**) if **27** had the *Z* configuration. The driving force for the Wittig reaction would of course be the formation of the pyrazole moiety.[14]

In an attempt to obtain the acylation product in higher yields, without the intrusion of side products, the reaction was undertaken in benzene. With benzoyl chloride, the phosphorane **13d**[9] was obtained in excellent yield (91%).[10] Ethyl chloroformate gave a poor yield (27%)[10] of **13e**.

The work on the preparation of the fused pyrazolo species from these salts is being pursued.

Experimental Section

Melting points were obtained on a Thomas-Hoover Unimelt capillary apparatus and were uncorrected. IR spectra were recorded on a Unicap SP 1100 infrared spectrophotometer and calibrated by comparison with a standard polystyrene film sample. The ^1H NMR spectra of approximately 10% (w/v) solutions in $CDCl_3$, unless otherwise stated, were obtained on a Bruker Spectrospin Model WM 250. Chemical shifts are reported in parts per million (δ scale) vs. tetramethylsilane as an internal standard, and they were corrected for instrument drift/miscalibration by references to a standard solution containing approximately proton

(13) T. Wagner-Jauregg, *Synthesis*, 349 (1976).
(14) The authors recognize the incompleteness of the purely speculative mechanism.

equivalent amounts of Me_4Si, cyclohexane, 1,4-dioxane, and chloroform in $CDCl_3$. In reporting the NMR data, the following abbreviations have been employed: *J*, coupling constant; s, singlet; d, doublet; dd, doublet of doublets: t, triplet; q, quartet; p, pentet; m, multiplet. The ^{13}C NMR data were collected on a Bruker Spectrospin Model WM 250 at 62.9 MHz in $CDCl_3$ solution [ca. 15% (w/v)]. The ^{31}P NMR data were taken at the operating frequency of 101.27 MHz with the same machine. The ^{31}P chemical shifts are reported as referenced to external 85% H_3PO_4 with shifts occurring downfield from the reference taken as positive. All samples were run at 28 °C with broad-band ^1H decoupling.

Dry N_2 gas was routinely employed as the reaction atmosphere in all reactions. Acetonitrile was dried over calcium hydride, followed by its distillation over P_2O_5. Absolute ethanol was distilled over sodium metal and diethyl phthalate. Baker silica gel (60–200 mesh) for dry column chromatography was used throughout for product separation.

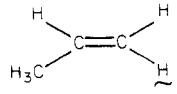
Precise mass spectra were recorded using a DuPont 21-492B instrument with a resolution of 3300. Elemental analyses were performed by Micro Analysis Inc., Wilmington, DE.

All glassware was baked at 110–120 °C for a minimum of 4 h before use. The numbering system used in the ^1H or ^{13}C NMR is as shown in ref 15.

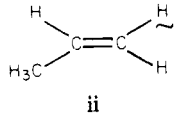
Preparation of Triphenyl[1-methyl-2-(phenylphenacylidenehydrazono)propyl]phosphonium Iodide (11a). To a 250-mL flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet were added 5.25 g (0.010 mol) of ylide **1**, 70 mL of dry acetonitrile, and 2.84 g (0.020 mol) of methyl iodide. The mixture was heated under reflux with stirring for 24 h. The solution was allowed to cool and then added to 300 mL of ethyl ether, stirred at room temperature for 1 h, and filtered. The filter cake was recrystallized from CH_2Cl_2–Et_2O to yield 5.53 g (83%) of **11a** as a pale yellow solid: mp 101–103 °C; ^1H NMR δ 1.40 (dd, J_{HH} = 7.0 Hz, J_{PH} = 18.4 Hz, 3 H, C4 CH_3), 2.52 (s, 3 H, C3 CH_3), 5.88–5.96 (m, 1 H, C4 H), 7.29–7.75 (m, 25 H, aromatic); ^{13}C NMR δ 196.3 (Cl), 161.9 (C2), 167.6 (C3, J_{cp} = 7.9 Hz), 37.3 (C4, J_{cp} = 51.2 Hz), 20.1 (C3 CH_3, J_{cp} = 5.9 Hz), 15.0 (C4 CH_3), 118.5 (C5, J_{cp} = 86.6 Hz); ^{31}P NMR δ 27.9.

Anal. Calcd for $C_{36}H_{32}IN_2OP$: I, 19.04. Found: 18.60.

Preparation of Triphenyl[1-(2-propenyl)-2-(phenylphenacylidenehydrazono)propyl]phosphonium Bromide (11b). Ylide **1** (5.25 g, 0.010 mol) was allowed to react as above with 1.45 g (0.012 mol) of allyl bromide in 70 mL of acetonitrile for 3 days. The crude phosphonium salt was recrystallized from CH_2Cl_2–EtOAc to yield 5.29 g (82%) of **11b** as a pale yellow solid: mp 123–125 °C; ^1H NMR δ 2.25 and 2.69 (m, 1 H each, CH_2CH=CH_2), 2.45 (s, 3 H, CH_3), 4.80 (d, *J* = 16.3 Hz, 1 H, i), 4.94 (d, *J*



i



ii

= 9.9 Hz, 1 H, ii), 5.96 (m, 1 H, CH_2CH=CH_2), 6.22 (split triplet, 1 H, C4 H), 7.34–7.84 (m, 25 H, aromatic); ^{13}C NMR δ 196.4 (C1), 162,1 (C2), 167.5 (C3), 41.3 (C4, J_{cp} = 47.3 Hz), 22.2 (CH_3, J_{cp} = 3.9 Hz), 35.7 (CH_2CH=CH_2), 131.4 (CH_2CH=CH_2), 118.9 (CH_2CH=CH_2), 118.1 (C5, J_{cp} = 84.7 Hz); ^{31}P NMR δ 28.0.

Anal. Calcd for $C_{38}H_{34}BrN_2OP$: C, 70.70; H, 5.31. Found: C, 70.33; H, 6.23.

Preparation of Triphenyl[1-benzyl-2-(phenylphenacylidenehydrazono)propyl]phosphonium Chloride (11c). Ylide **1** (5.25 g, 0.010 mol) was allowed to react as above with 1.9 g (0.015 mol) of benzyl chloride in 70 mL acetonitrile for 4 days. The crude phosphonium salt was recrystallized from CH_2Cl_2–Et_2O to yield 4.5 g (69%) of **11c** as a pale yellow solid: mp 219–221 °C; ^1H NMR δ 2.89 and 3.24 (br, t, 2 H, CH_2Ph), 3.04 (s, 3 H, CH_3), 5.97 (br, t, 1 H, C4 H), 7.17–7.85 (m, 30 H, aromatic); ^{13}C NMR δ 196.7 (C1), 162.8 (C2), 168.8 (C3, J_{cp} = 7.9 Hz), 44.2 (C4, J_{cp} = 45.3 Hz), 22.2 (CH_3, J_{cp} = 3.9 Hz), 37.7 (CH_2Ph), 118.0 (C5, J_{cp} = 84.7 Hz); ^{31}P NMR δ 28.1.

Anal. Calcd for $C_{42}H_{36}ClN_2OP$: Cl, 5.45. Found: Cl, 5.35.

Preparation of Triphenyl[1-methyl-2-(phenylphenacylidenehydrazono)propylidene]phosphorane (13a). In a 250-mL round-bottom flask was dissolved 0.50 g (0.022 mol) of sodium metal in 100 mL of absolute ethanol. This solution was cooled to between -15 and -10 °C (ice–acetone), and 13.4 g (0.020 mol) of **11a** was added with stirring. The deep-red solution was then stirred at ambient temperatures for 1.5 h, during which time an orange solid precipitated. Filtration and recrystallization from CH_2Cl_2–heptane afforded 8.7 g (81%) of **13a** as yellow-brown powder: mp 92–93 °C; ^1H NMR δ 1.69 (d, J_{PH} = 15.9, 3 H, C4 CH_3), 2.23 (s, 3 H, C3 CH_3), 6.41–7.49 (m, 23 H, aromatic), 7.80–7.83 (m, 2 H, aromatic ortho to C=O); ^{13}C NMR δ 192.2 (C1), 143.6 (C2), 173.7 (C3, J_{cp} = 7.9 Hz), 70.4 (C4, J_{cp} = 108.3 Hz), 14.6 (C3 CH_3, J_{cp} = 11.8 Hz), 14.4 (C4 CH_3); ^{31}P NMR δ 19.7.

Precise mass calcd for $C_{36}H_{31}N_2OP$: 538.217. Found: 538.217.

Preparation of Triphenyl[1-(2-propenyl)-2-(phenylphenacylidenehydrazono)propylidene]phosphorane (13b). Ylide **13b** (8.8 g, 78% yield) was prepared in the manner as **13a** with 12.9 g (0.020 mol) of **11b**. Recrystallization from acetonitrile afforded a red-orange analytical sample: mp 164–165 °C; ^1H NMR δ 2.46 (s, 3 H, CH_3), 2.67 (dd, J_{HH} = 5.6, J_{PH} = 20.2, 2 H, CH_2CH=CH_2), 4.74 (d, *J* = 1.7 Hz, 1 H, ii), 4.80 (d, *J* = 2.2 Hz, 1 H, i), 5.63 (m, CH_2CH=CH_2), 6.91–8.00 (m, 25 H, aromatic); ^{13}C NMR δ 201.5 (C1), 146.3 (C2), 172.9 (C3, J_{cp} = 7.9 Hz), 54.1 (C4, J_{cp} = 108.3 Hz), 14.4 (CH_3, J_{cp} = 9.8 Hz), 32.3 (CH_2CH=CH_2, J_{cp} = 13.8 Hz), 140.3 (CH_2CH=CH_2), 113.1 (CH_2CH=CH_2); ^{31}P NMR δ 18.2.

Precise mass calcd for $C_{38}H_{33}N_2OP$: 564.233. Found: 564.235.

Preparation of Triphenyl[1-benzyl-2-(phenylphenacylidenehydrazono)propylidene]phosphorane (13c). Ylide **13c** (9.1 g, 74% yield) was prepared in the same manner as **13a** with 13.0 g (0.020 mol) of **11c**. Recrystallization from acetonitrile afforded a red-orange analytical sample: mp 149–150 °C; ^1H NMR δ 2.46 (s, 3 H, CH_3), 3.37 (d, J_{PH} = 20.6, CH_2Ph), 6.92–7.90 (m, 30 H, aromatic); ^{13}C NMR δ 201.5 (C1), 146.5 (C2), 173.4 (C3, J_{cp} = 5.9 Hz), 55.7 (C4, J_{cp} = 108.3 Hz), 14.9 (CH_3, J_{cp} = 11.8 Hz), 34.2 (CH_2Ph, J_{cp} = 15.8); ^{31}P NMR δ 18.6.

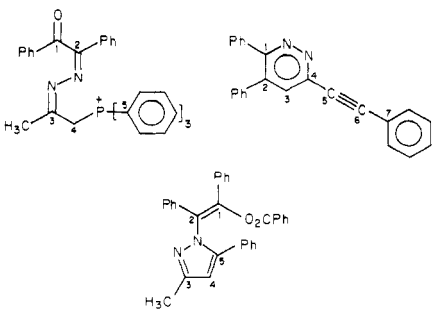
Precise mass calcd for $C_{42}H_{35}N_2OP$: 614.249. Found: 614.252.

Preparation of Triphenyl[1-benzoyl-2-(phenylphenacylidenehydrazono)propylidene]phosphorane (13d). To a 250-mL flask equipped with a magnetic stirrer, reflux condenser, dropping funnel, and nitrogen inlet were added 10.5 g (0.020 mol) of ylide **1** and 60 mL of anhydrous benzene, and the mixture was heated at reflux. To the above red-orange solution was added dropwise 1.40 g (0.010 mol) of freshly distilled benzoyl chloride in 20 mL of benzene over ca. 30 min. A precipitate formed. The hazy solution was refluxed for 4 h and allowed to cool and filtered. The filter cake was washed with benzene and recrystallized from CH_2Cl_2–ether to afford 5.1 g (91%) of **12** as a pale yellow solid: mp 219–221 °C; ^1H NMR δ 2.49 (d, J_{PH} = 0.86 Hz, 3 H, CH_3), 5.40 (d, J_{PH} = 13.3 Hz, 2 H, $CH_2P^+Ph_3$), 7.20–7.95 (m, 25 H, aromatic). The filtrate was concentrated to dryness in vacuo, and the residue was solidified with ether. Recrystallization from EtOAc–Et_2O afforded 4.5 g (85%) of **13d** as a yellow crystal: mp 190–191 °C; IR (KBr) 1670, 1590, 1575, 1520, 1440 cm^{-1}; ^1H NMR δ 1.98 (s, 3 H, CH_3), 7.23–7.85 (m, 30 H, aromatic); ^{13}C NMR δ 198.5 (C1), 159.1 (C2), 168.1 (C3, J_{cp} = 7.9 Hz), 78.7 (C4, J_{cp} = 108.2 Hz), 188.7 (COPh, J_{cp} = 5.9), 22.6 (CH_3, J_{cp} = 5.9 Hz), 126.7 (C5, J_{cp} = 92.5 Hz); ^{31}P NMR δ 19.5.

Precise mass calcd for $C_{42}H_{33}N_2OP$: 628.228. Found: 628.228.

Preparation of Triphenyl[1-carbethoxy-2-(phenylphenacylidenehydrazono)propylidene]phosphorane (13e). Ylide

(15) The numbering systems used in the ^1H or ^{13}C NMR is as shown below:



1 (5.25 g, 0.010 mol) was allowed to react in the same manner as **13d** with 0.54 (0.005 mol) of ethyl chloroformate for 2 h (prolonged reaction time gave no increase in yield). The filter cake was washed with benzene and recrystallized from CH_2Cl_2–ether to afford 0.8 g (28.6%) of **12** as a pale yellow solid: mp 219–221 °C. The filtrate was concentrated to dryness in vacuo, and the residue was solidified with ether and filtered. The solid was unreacted starting ylide 1 (3.9 g), mp 181–182 °C. Carbethoxy ylide **13e** (0.8 g, 27%) was separated from etherate by column chromatography [silica gel (3.5 × 40 cm, 80 g, 1:1 *n*-hexane–EtOAc)]: mp 162–163 °C; IR (KBr) 1685, 1670, 1600, 1490, 1440 cm^{-1}; ^1H NMR δ 0.63 (t, J = 7.3 Hz, 3 H, $CO_2CH_2CH_3$), 2.79 (s, 3 H, C3 CH_3), 3.66 (q, J = 7.3 Hz, 2 H, $CO_2CH_2CH_3$), 7.12–7.49 (m, 25 H, aromatic); ^{13}C NMR δ 199.2 (C1), 156.3 (C2), 168.9 (C3, J_{cp} = 13.8 Hz), 58.9 (C4, J_{cp} = 114.2), 18.5 (C3 CH_3, J_{cp} = 7.9 Hz), 172.8 ($CO_2CH_2CH_3$, J_{cp} = 3.9 Hz), 57.9 ($CO_2CH_2CH_3$) 13.9 ($CO_2CH_2CH_3$); ^{31}P NMR δ 19.6.

Precise mass calcd for $C_{38}H_{33}N_2O_3P$: 596.223. Found: 596.220.

Preparation of Triphenyl[1-benzoyl-1-(3,4-diphenyl-6-pyridazinyl)methylene]phosphorane (14) and (*Z*)-2-(3-Methyl-5-phenyl-1*H*-pyrazol-1-yl)-1,2-diphenyl-1-(benzoyloxy)ethene (22). To a 250-mL flask were added 8.75 g (0.0167 mol) of ylide 1, 100 mL of dry acetonitrile, and 2.35 g (0.00835 mol) of freshly distilled benzoyl chloride. The mixture was heated at reflux with stirring for 7 days and concentrated to dryness in vacuo. The product was extracted with hot benzene (500 mL), and the remaining undissolved residue solidified and was filtered. Recrystallization from CH_2Cl_2–Et_2O afforded 4.26 g (91%) of **12** as a pale yellow solid: mp 219–221 °C; ^1H NMR δ 2.49 (d, J_{PH} = 0.86 Hz, 3 H, CH_3), 5.40 (d, J_{PH} = 13.3 Hz, 2 H, $CH_2P^+Ph_3$), 7.20–7.95 (m, 25 H, aromatic).

The benzene solution showed the formation of three products by TLC (silica gel, hexane–EtOAc, 1:1). After the solvent was removed in vacuo, the crude reaction mixture was chromatographed on a 3.5 × 80 cm silica gel (150 g) column eluting with *n*-hexane–EtOAc (4:1). This yielded the following in order of elution.

(a) **22** (0.41 g, 10%) as a white solid. Recrystallization from ethanol yielded a white analytical sample: mp 153–154 °C; IR (KBr) 1745, 1600, 1495, 1450 cm^{-1}; ^1H NMR δ 2.19 (s, 3 H, C_3 CH_3), 6.12 (s, 1 H, C_4 H), 7.01–7.56 (m, 18 H, aromatic), 7.88 (d, J = 7.9 Hz, 2 H, aromatic ortho to C=O); ^{13}C NMR δ 163.6 (OCOPh), 149.6 (C1), 77.2 (C2), 145.4 (C3) 106.3 (C4), 144.7 (C5), 13.6 (CH_3).

Anal. Calcd for $C_{31}H_{24}N_2O_2$: C, 81.55; H, 5.30; N, 6.14. Found: C, 81.71; H, 5.13; N, 6.29.

(b) **13d** (0.70 g, 13%): analytical data were identical with an earlier sample.

(c) **14** (2.51 g, 50%): isolated as an amber resinous solid. Crystallization from EtOAc–Et_2O afforded a colorless analytical sample: mp 228–229 °C; IR (KBr) 1580–1480 (many peaks overlap), 1440, 1405, 1350 cm^{-1}; ^1H NMR δ 6.69–7.84 (m, 31 H, aromatic); ^{13}C NMR (Me_2SO-d_6) δ 153.6 (C1), 142.5 (C3, J_{cp} = 9.8 Hz), 159.4 (C4, J_{cp} = 9.8 Hz), 70.7 (C5, J_{cp} = 114.2 Hz), 186.5 (C6, J_{cp} = 5.9 Hz); ^{31}P NMR δ 19.2.

Anal. Calcd for $C_{42}H_{31}N_2OP$: C, 82.60; H, 5.12; N, 4.59; P, 5.07. Found: C, 82.59; H, 5.26; N, 4.88; P, 4.75.

Preparation of Triphenyl[1-benzoyl-1-(3,4-diphenyl-6-pyridazinyl)methylene]phosphorane (14). To a 50-mL flask were added 1.0 g (0.00159 mol) of ylide **13d**, 0.1 g (0.00019 mol) of ylide 1, and 15 mL of dry acetonitrile. The mixture was heated at reflux with stirring for 7 days and concentrated to dryness in vacuo. The title compound **14** (0.54 g, 55.6%) was separated by column chromatography [silica gel (100 g), *n*-hexane–EtOAc (4:1)]. Analytical data were identical with an earlier sample.

Preparation of 3,4-Diphenyl-6-(phenylethynyl)pyridazine (15). The pyridazine ylide **14** (1.5 g, 0.00245 mol) was placed in a thick-walled glass tube, capped, and heated in an oil bath at 230–235 °C for 15 min. After cooling to room temperature, the crude products were dissolved in a minimum amount of CH_2Cl_2 and chromatographed on a 3.5 × 40 cm silica gel (50 g) column eluting with *n*-hexane–EtOAc (1:1) to afford 0.78 g (96%) of **15** as a colorless solid and 0.63 g (93%) of Ph_3PO. Recrystallization from ether yielded **15** as a colorless analytical sample: mp 164.5–165.5 °C; IR (KBr) 2225 (C≡C), 1602, 1575, 1495, 1445, 1395 cm^{-1}; ^1H NMR δ 7.25–7.68 (m, aromatic); ^{13}C NMR δ 157.7 (C1), 136.2 (C2), 132.2 (C3), 146.6 (C4), 94.0 (C5), 86.0 (C6), 121.7 (C7), 138.4 (ipso carbon of C1 phenyl), 136.4 (ipso carbon of C2 phenyl).

Precise mass calcd for $C_{24}H_{16}N_2$: 332.131. Found: 332.133.

Hydrogenation of 15. Preparation of 3,4-Diphenyl-6-(2-phenylethyl)pyridazine (16). A solution of 0.15 g (0.00045 mol) of pyridazinylacetylene compound **15** in 20 mL of ethyl acetate was placed in the bottle of a Burgess–Parr reduction apparatus, a catalytic amount of platinum oxide catalyst was added, and the mixture was shaken in an atmosphere of hydrogen under an initial pressure of 40 psi for 4 h. When the reduction was complete, the catalyst was removed by suction filtration, and the filtrate was evaporated to dryness. Recrystallization of the residue from ether–petroleum ether afforded 0.14 g (93%) of **16** as a colorless solid: mp 114–115 °C; mmp with an authentic sample was identical; ^1H NMR δ 3.20 (m, 2 H, CH_2CH_2Ph), 3.37 (m, 2 H, CH_2CH_2Ph), 7.09–7.44 (m, 16 H, aromatic); ^{13}C NMR δ 158.0 (C1), 136.9 (C2), 126.2 (C3), 161.2 (C4), 37.7 (C5), 35.7 (C6), 140.9 (C7), 138.9 (ipso carbon of C1 phenyl), 137.0 (ipso carbon of C2 phenyl).

Precise mass calcd for $C_{24}H_{20}N_2$: 336.163. Found: 336.164.

Preparation of Diethyl 3-Phenylpropionylmalonate. 3-Phenylpropionyl chloride (16.8 g, 0.1 mol), prepared from 3-phenylpropionic acid and thionyl chloride, was added to the ethoxymagnesium salt of diethyl malonate [Mg, 2.59 g (0.103 mol); EtOH, 2.5 mL; CCl_4, 0.1 mL; diethyl malonate, 16 g (0.1 mol), prepared according to Dolphin et al.[16]] and gave 23.4 g (80%) of the title compound as a liquid: bp 145–152 °C (~0.3 mmHg); ^1H NMR δ (K = keto and E = enol tautomers) 1.26 (K + E, m, 6 H, OCH_2CH_3), 2.73–2.98 (K + E, m, 4 H, $PhCH_2CH_2CO$), 4.22 (K + E, m, 4 H, OCH_2CH_3), 4.45 (K, s, 0.5 H, methine H), 7.15–7.30 (m, 5 H, aromatic), 13.5 (E, s, 0.5 H, OH). Keto–enol ratio approximately 1:1, ^{13}C NMR δ 198.0 (K, C=O), 181.8 [E, C(OH)=], 140.4, 140.3 (K or E, ipso carbon of phenyl), 128.4 (meta), 128.2 (ortho), 126.1 (para), 99.9 [E, $=C(CO_2Et)_2$], 61.3 [K, $CH(CO_2Et)_2$], 60.8 (K, OCH_2CH_3), 43.4 (K, $PhCH_2CH_2$), 35.6 (E, $PhCH_2CH_2$), 35.2 (E, $PhCH_2C_2$), 29.3 (K, $PhCH_2CH_2$), 13.8 and 13.9 (K or E, OCH_2CH_3).

Precise mass calcd for $C_{16}H_{20}O_5$: 292.131. Found: 292.132.

Preparation of Ethyl 3-Oxo-5-phenylpentanoate. The title compound (10.8 g, 73%) was prepared from 20 g (0.0684 mol) of diethyl 3-phenylpropionylmalonate according to Dolphin et al.:[16] bp 112–118 °C (~0.3 mmHg); ^1H NMR δ 1.20 (t, J = 7 Hz, 3 H, OCH_2CH_3), 2.83 (m, 4 H, $PhCH_2CH_2CO$), 3.36 (s, 2 H, $COCH_2CO_2$), 4.11 (q, J = 7.3 Hz, 2 H, OCH_2CH_3), 7.12–7.13 (m, 5 H, aromatic), 12.22 (E, br s, OH). Keto–enol ratio approximately 27:1; ^{13}C NMR δ 201.7 (C=O), 166.9 ($CO_2CH_2CH_3$), 140.4 (ipso carbon of phenyl), 128.3 (meta), 128.1 (ortho), 126.0 (para), 61.1 (OCH_2CH_3), 49.2 ($COCH_2CO_2$), 44.2 ($PhCH_2CH_2CO$), 29.5 ($PhCH_2CH_2CO$), 13.9 (OCH_2CH_3).

Precise mass calcd for $C_{13}H_{16}O_3$: 220.110. Found: 220.111.

Preparation of 3,4-Diphenyl-6-(2-phenylethyl)-pyridazine-5-carboxylic Acid (17). To 75 mL of benzene were added 4.62 g (0.021 mol) of ethyl 3-oxo-5-phenylpentanoate, 4.5 g (0.02 mol) of benzil monohydrazone, and a catalytic amount (20 mg) of *p*-toluenesulfonic acid. A Dean–Stark water collector, condenser, and $CaCl_2$ drying tube were attached and the mixture was heated at reflux until the theoretical amount of water had collected (~2 h). The benzene was removed in vacuo, the residual golden oil was dissolved in 75 mL of hot EtOH, and 0.2 g of potassium hydroxide was added. A deep-red color developed, which faded on gentle boiling for 1 h to a pale yellow; 30 mL of water and 2.6 g (0.04 mol) of potassium hydroxide were added to the reaction mixture, and it was refluxed overnight. The bulk of the ethanol was removed in vacuo, and the residue was acidified to pH ~2 with 50% HCl and thoroughly extracted with methylene chloride. After the extracts were dried (anhydrous $MgSO_4$) and the solvent was removed in vacuo, the combined CH_2Cl_2 extracts yielded 5.3 g (70%) of **17** as a white solid. Recrystallization from ethanol afforded a colorless analytical sample: mp 215–216 °C; ^1H NMR ($CDCl_3$ + Me_2SO-d_6) δ 3.23 (m, 2 H, CH_2CH_2Ph), 3.35 (m, 2 H, CH_2CH_2Ph), 7.17–7.30 (m, 15 H, aromatic), 10.2 (br s, 1 H, COOH); ^{13}C NMR ($CDCl_3$ + Me_2SO-d_6) δ 156.5, 154.0 (C1,

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C4 or reversed), 132.6 (C2), 124.4 (C3), 34.1 (C5), 33.2 (C6), 139.3 (C7), 134.9 (ipso carbon of C1 phenyl), 132.7 (ipso carbon of C2 phenyl), 165.6 (COOH).

Precise mass calcd for $C_{25}H_{20}N_2O_2$: 380.152. Found: 380.151.

Decarboxylation of 17. Preparation of the Authentic Sample of 3,4-Diphenyl-6-(2-phenylethyl)pyridazine (16). In a 10-mL round-bottom flask fitted with a $CaCl_2$ drying tube was placed 1.0 g (0.0026 mol) of **17**. The flask was immersed in an oil bath held at 225 °C for 30 min. As the sample melted, gas was evolved. The crude residue was dissolved in ether and crystallized by standing at room temperature. The resulting light yellow solid was recrystallized from ether–petroleum ether to yield **17** (0.86 g, 98%) as an analytical sample: mp 114.5–115.5 °C; ^{1}H NMR δ 3.19 (m, 2 H, CH_2CH_2Ph), 3.37 (m, 2 H, CH_2CH_2Ph), 7.09–7.44 (m, 16 H, aromatic); ^{13}C NMR δ 158.0 (C1), 136.9 (C2), 126.2 (C3), 161.2 (C4), 37.7 (C5), 35.6 (C6), 140.9 (C7), 138.8 (ipso carbon of C1 phenyl), 137.0 (ipso carbon of C2 phenyl).

Precise mass calcd for $C_{24}H_{20}N_2$: 336.163. Found: 336.164.

Preparation of (*E*)-2-(3-Methyl-5-phenyl-1*H*-pyrazol-1-yl)-1,2-diphenyl-1-(benzoyloxy)ethene (24). In a 100-mL flask fitted with $CaCl_2$ tube, 0.16 g (0.005 mol) of dry methanol was added to 0.42 g (57% assay, 0.010 mol) of NaH in 10 mL of ether. When hydrogen evolution ceased, the solution was cooled to −20 °C, and 1.76 g (0.005 mol) of pyrazole **23**[2a] was added (reaction mixture changed to a deep-yellow color). When gas evolution had ceased, 1.48 g (0.0105 mol) of benzoyl chloride was added and stirred for 2 h at ambident temperature. The reaction mixture was filtered, and the filtrate was concentrate to dryness in vacuo to yield 1.5 g (65.7%) of **24** as a white solid: mp 148–149 °C; IR (KBr) 1745, 1600, 1495, 1450 cm^{-1}; ^{1}H NMR δ 2.34 (s, 3 H, C3 CH_3), 6.11 (s, 1 H, C4 H), 6.66 (d, J = 7.7 Hz, 2 H, aromatic), 6.95–7.60 (m, 16 H, aromatic), 8.00 (d, J = 7.7 Hz, 2 H, aromatic ortho to C=O); ^{13}C NMR δ 164.7 (C1 OCOPh), 150.2 (C1), 77.4 (C2), 146.6 (C3), 106.6 (C4), 145.9 (C5), 13.7 (C3 CH_3).

Precise mass calcd for $C_{31}H_{24}N_2O_2$: 456.184. Found: 456.186.

Reduction of (*Z*)- and (*E*)-2-(3-Methyl-5-phenyl-1*H*-pyrazol-1-yl)-1,2-diphenyl-1-(benzoyloxy)ethene (22 and 24). In each of two 100-mL flasks was dissolved 0.7 g (0.00153 mol) of O-benzoylated pyrazole **22** and **24** in 30 mL of ether. These solutions were cooled with an ice bath, and 0.04 g (0.00105 mol) of $LiAlH_4$ was added with stirring. The reaction mixture stirred at room temperature for 1 h and worked up with standard procedure to yield quantitatively the same known pyrazole, **23** (by ^{1}H NMR, ^{13}C NMR, IR and mmp with authentic sample[2a]) in both cases: mp 105–106.5 °C; IR (KBr) 1700, 1595, 1580, 1555, 1500 cm^{-1}; ^{1}H NMR δ 2.20 (s, 3 H, C3 CH_3), 6.15 (s, 1 H, C4 H), 6.64 (s, 1 H, C2 H), 7.22–7.42 (m, 13 H, aromatic), 7.57–7.61 (m, 2 H, aromatic ortho to C=O); ^{13}C NMR δ 192.7 (C1), 66.9 (C2), 149.0 (C3), 106.8 (C4), 145.0 (C5), 13.6 (C3 CH_3).

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Registry No. 1, 63570-24-1; **11a**, 81724-88-1; **11b**, 81724-89-2; **11c**, 81724-90-5; **12**, 81724-91-6; **13a**, 81724-92-7; **13b**, 81724-93-8; **13c**, 81724-94-9; **13d**, 81724-95-0; **13e**, 81724-96-1; **14**, 81724-97-2; **15**, 81724-98-3; **16**, 81724-99-4; **17**, 81725-00-0; **22**, 81725-01-1; **23**, 63570-09-2; **24**, 81725-02-2; diethyl 3-phenylpropionyl malonate, 62984-12-7; ethyl 3-oxo-5-phenylpentanoate, 17071-29-3; benzil monohydrazone, 5344-88-7; methyl iodide, 74-88-4; allyl bromide, 106-95-6; benzyl chloride, 100-44-7; benzoyl chloride, 98-88-4; ethyl chloroformate, 541-41-3.

Photodehalogenation of the Monochloro- and Monofluoroanisoles

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Evidence is presented for a plurality of mechanisms in the photoreduction and photonucleophilic substitution of the monochloroanisoles in alcohol solvents. 4-Chloroanisole appears to react partly via a radical anion and partly by radicals, while the reactions of 3-chloroanisole are more consistent with aryl cations and aryl radicals. The intermediates in the reaction of 2-chloroanisole, which gives no photosubstitution, are as yet not identified but are probably not radical anions. In the case of 4-chloroanisole, substitution and reduction may proceed from different states. Preliminary results on the fluoroanisoles show the 2-F isomer giving both reduction and substitution and the 3- and 4-F isomers only substitution.

Irradiation of aryl halides produces products of reductive dehalogenation (eq 1), nucleophilic substitution (eq 2), and

$$\mathrm{ArX} \xrightarrow[\mathrm{SH}]{h\nu} \mathrm{ArH} + \mathrm{HX} \qquad (1)$$

$$\mathrm{ArX} \xrightarrow[\mathrm{Y:^-}]{h\nu} \mathrm{ArY} + \mathrm{X^-} \qquad (2)$$

inter- and intramolecular arylations. There has been little consensus on the mechanism of these reactions. In the photoreduction, triplet excited states,[1] singlet eximers and charge-transfer complexes,[2] radical pairs,[3] radical anions, and radical cations[2a,4] have all been suggested intermediates. The photonucleophilic substitution of aryl halides was first reported by Pinhey and Rigby,[5] who proposed a Meisenheimer type of intermediate but did not exclude an aryl cation. Subsequently, others have proposed reaction via aryl radical cations,[2a,6] radical anions,[2b,7] and

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