A Short, Asymmetric Synthesis of Natural (−)-Methyl Jasmonate

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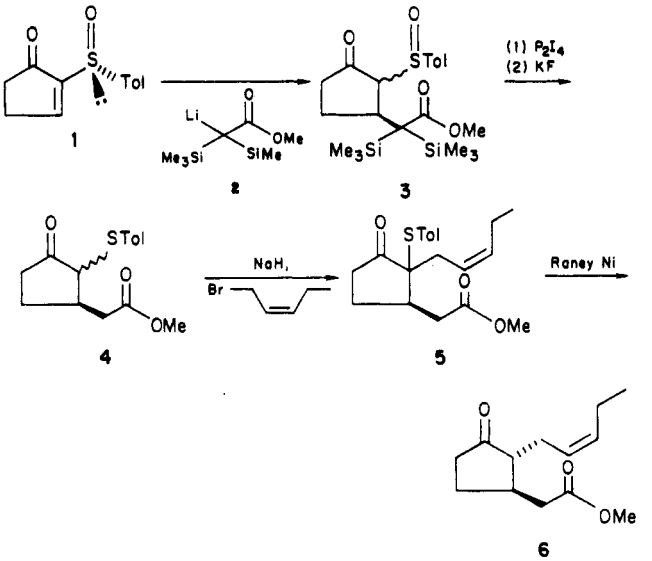
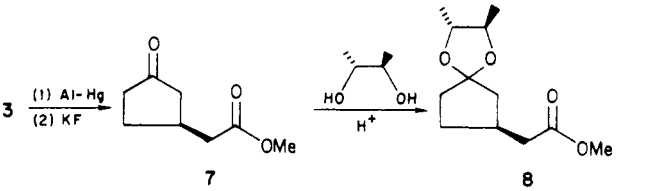
Because of the great commercial value of methyl jasmonate as a very desirable perfume constituent[1] and because of its being an insect sex-attractant pheromone,[2] numerous syntheses of this compound in its *racemic* form have been achieved;[3] only one asymmetric synthesis of (−)-methyl jasmonate has been reported.[4] We report here a very short and highly stereocontrolled total synthesis of (−)-methyl jasmonate in at least 98% enantiomeric purity. The critical asymmetric synthetic step involves carbon–carbon bond formation by conjugate addition of an α-lithioacetate unit to doubly activated, enantiomerically pure, Michael acceptor (*R*)-(−)-2-(*p*-tolylsulfinyl)-2-cyclopentenone.

Conjugate addition of bis α-silylated α-lithioacetate **2**[5] to enantiomerically pure cyclopentenone sulfoxide (*R*)-(−)-**1**[6] at −78 °C in THF proceeded rapidly (<5 min) to produce 2,3-disubstituted cyclopentanone sulfoxide **3** (Scheme I). Sulfoxide deoxygenation with diphosphorus tetraiodide[7] and then desilylation with potassium fluoride[8] produced β-keto sulfide **4** in 54% overall yield from cyclopentenone sulfoxide **1**. Sodium enolate ion formation and then C-alkylation with (*Z*)-2-pentenyl bromide (>98% *Z* by capillary GC)[9] gave 2,2,3-trisubstituted cyclopentanone **5** in 63% yield.[7b] Reductive removal of the sulfinyl group with Raney nickel afforded (−)-methyl jasmonate in 45% yield, $[\alpha]_D$ −93.0° (highest literature value is $[\alpha]_D$ −90.2°),[4] which is of *extremely high enantiomeric purity*.

Scheme I



To evaluate more accurately the level of asymmetric induction in the key carbon–carbon bond-forming step (i.e., **1** → **3**, Scheme I) and, therefore, to determine the enantiomeric purity of our synthetic (−)-methyl jasmonate more reliably than by optical rotation,[10] β-keto sulfoxide **3** was reductively cleaved with aluminum–amalgam and then desilylated with potassium fluoride to produce 3-oxocyclopentaneacetic acid methyl ester **7**, $[\alpha]^{18}_D$ −119.4°.[11] Ketalization of this cyclopentanone gave ketal **8** (eq 1).[12]



(1)

A control experiment showed that independently prepared *racemic* cyclopentanone **7** underwent ketalization with (*R*,*R*)-(−)-2,3-butanediol to give a 1:1 mixture of diastereomeric ketals **8** and epi-**8**. By ^{13}C NMR analysis, ketal **8** prepared via eq 1 was determined to be at least 98% diastereomerically pure, which indicates that our synthetic (−)-methyl jasmonate is at least 98% enantiomerically pure.

All of the following variations of Scheme I using *tert*-butyl or methyl α-lithioacetate in place of α-silylacetate **2** gave less satisfactory, non-chelate-model[13] asymmetric inductions: (1) use of zinc dibromide to preform a chelate with β-keto sulfoxide **1**,[13] (2) use of titanium ester enolates,[14] (3) use of the enantiomerically pure *p-anisyl* sulfoxide corresponding to *p*-tolyl sulfoxide **1**,[15] and (4) use

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(2) Nishida, R.; Baker, T. C.; Roeloffs, W. L.; Acree, T. E. "Abstracts of Papers", 186th Antional Meeting of the American Chemical Society, Washington, DC, Aug 28–Sept. 2, 1983; American Chemical Society: Washington, DC, 1983; AGFD 100.

(3) (a) Oppolzer, W.; Guo, M.; Baettig, K. *Helv. Chim. Acta* **1983**, *66*, 2140. (b) Kita, Y.; Segawa, J.; Haruta, J.; Yasuda, H.; Tamura, Y. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1099. (c) Matsuda, I.; Murata, S.; Izumi, Y. *J. Org. Chem.* **1980**, *45*, 237. (d) Naf, F.; Decorzant, R. *Helv. Chim. Acta.* **1978**, *61*, 2524. (e) Gerlach, H.; Kunzler, P. *Helv. Chim. Acta.* **1978**, *61*, 2503. (f) Dubs, P.; Stussi, R. *Helv. Chim. Acta.* **1978**, *61*, 990. (g) Kondo, K.; Sugimoto, K.; Tunemoto, D.; Takahatake, Y. *Tetrahedron Lett.* **1978**, 907. (h) Monteiro, H. J. *J. Org. Chem.* **1977**, *42*, 2324. (i) Torii, S.; Tanaka, H.; Kobayashi, Y. *J. Org. Chem.* **1977**, *42*, 3473. (j) Greene, A. E.; Crabbe, P. *Tetrahedron Lett.* **1976**, 4867. (k) Torii, S.; Tanaka, H.; Mandai, T. *J. Org. Chem.* **1975**, *40*, 2221. (l) Torii, S.; Tanaka, H. *J. Org. Chem.* **1975**, *40*, 462. (m) Meyers, A. I.; Nazarenko, N. *J. Org. Chem.* **1973**, *38*, 175. (n) Ducos, P.; Rouessac, F. *Tetrahedron* **1973**, *29*, 3233. (o) Buchi, G.; Egger, B. *J. Org. Chem.* **1971**, *36*, 2021. (p) Sisido, K.; Kurozumi, S.; Utimoto, K. *J. Org. Chem.* **1969**, *34*, 2661. (q) Demole, E.; Stoll, M. *Helv. Chim. Acta.* **1962**, *45*, 692.

(4) Quinkert, G.; Adam, F.; Durner, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 856. Cf.: Posner, G. H.; Asirvatham, E.; Ali, S. *J. Chem. Soc., Chem. Commun.* **1985**, 542.

(5) Methyl bis(trimethylsilyl)acetate was prepared from methyl acetate and trimethylsilyl trifluoromethanesulfonate according to: Simchen, G.; Emde, H. *Synthesis* **1977**, 867.

(6) (a) Hulce, M.; Mallamo, J. P.; Frye, L. L.; Kogan, T. P.; Posner, G. H. *Org. Synth.*, in press. (b) Posner, G. H.; Mallamo, J. P.; Hulce, M.; Frye, L. L. *J. Am. Chem. Soc.* **1982**, *104*, 4180. (c) Aldrich Chemical Co. now sells both (*R*)-(+)- and (*S*)-(−)-menthyl 4-toluenesulfinates; (+)-methyl jasmonate, therefore, is available via our Scheme I starting with (*S*)-(+)-**1**.

(7) (a) Krief, A.; Denis, J. N. *Tetrahedron Lett.* **1979**, 3995. (b) Attempts to pentenylate the β-keto sulfoxide corresponding to sulfide **4** using sodium hydride and (*Z*)-2-pentenyl bromide lead to substantial O-alkylation.

(8) Matsuda, I.; Murata, S.; Izumi, Y. *J. Org. Chem.* **1980**, *45*, 237.

(9) Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, 4339.

(10) For a good discussion of the drawbacks of using optical rotation as a measure of enantiomeric purity, see: Rosen, T.; Watanabe, M.; Heathcock, C. H. *J. Org. Chem.* **1984**, *49*, 3657.

(11) The $[\alpha]_D$ value of this compound has been revised significantly over the years even though the original (low) value was obtained via (apparently incomplete) resolution: $[\alpha]_D$ −27° (Hill, R. K.; Edwards, A. G. *Tetrahedron* **1965**, *21*, 1501); $[\alpha]_D$ −121.0° (Shingu, K.; Takaoka, Y.; Kuritani, H. *J. Org. Chem.* **1979**, *44*, 452).

(12) Hiemstra, H.; Wynberg, H. *Tetrahedron Lett.* **1977**, 2183.

(13) Posner, G. H. In "Asymmetric Synthesis"; Morrison, J., Ed.; Academic Press: New York, 1983; Vol. 2, p 225.

(14) Mukaiyama, T. *Org. React.* **1982**, *28*, 203.

(15) Posner, G. H.; Frye, L. L.; Hulce, M. *Tetrahedron* **1984**, *40*, 1401.

0022-3263/85/1950-2589$01.50/0

of 2,5-dimethyltetrahydrofuran in place of THF as solvent.[16]

Scheme I represents not only an expeditious and highly asymmetric synthesis of natural (−)-methyl jasmonate but also an effective chelate-model[13] conjugate addition of an ester enolate ion[17] to a nonracemic, chiral, doubly activated Michael acceptor to form a *1,5-dicarbonyl* adduct in very high enantiomeric purity. This methodology complements our use of enantiomerically pure 2-(arylsulfinyl)-2-cycloalkenones for asymmetric synthesis of cycloalkanones substituted at the 3-position by *hydrocarbon* groups.[13,18] We are now applying this type of asymmetric Michael addition to synthesis of other valuable synthetic intermediates and natural products.

Experimental Section

All solvents were distilled before use. Infrared spectra were recorded on a Perkin-Elmer 599B spectrometer and were calibrated with the 1601-cm^{-1} polystyrene absorption as reference. ^1H NMR spectra were obtained by using a Varian CFT-20 or a Varian XL-400 spectrometer operating at 80 and 400 MHz, respectively. Chemical shifts are reported in ppm downfield from a Me_4Si internal standard. ^{13}C NMR spectra were recorded with the Varian XL-400 spectrometer operating at 100 MHz. Specific rotations were determined with a Perkin-Elmer 141 variable-wavelength polarimeter using thermostated 1-dm quartz-window cells of 1-mL capacity. Concentrations (*c*) for specific rotations are reported in units of g/100 mL. Mass spectra were performed by the Middle Atlantic Regional Mass Spectrometry Facility, The Johns Hopkins University, Baltimore, MD. Gas–liquid phase chromatography (GLPC) was performed on a Hewlett-Packard 5890 capillary gas chromatograph with a carrier-gas (He) flow rate of 15 mL/min. Column chromatography was performed with silica gel 60 and reagent grade solvents. HPLC was performed with a Waters liquid chromatograph equipped with a differential refractometer detector. A Partisil 10-M9/50-cm column was used with 10% ethyl acetate in hexane (4 mL/min) as solvent.

Conjugate Addition of Enolate 2 to Cyclopentenone (*R*)-(−)-1. A flame-dried 10-mL round-bottomed flask was charged with 1 mL of dry THF and 173 μL (1.05 mmol) of *N*-isopropylcyclohexylamine and cooled to −78 °C. After 10 min, 645 μL of 1.55 M *n*-butyllithium (1.00 mmol) was added, and the reaction mixture was stirred 30 min at −78 °C under nitrogen atmosphere. Methyl bis(trimethylsilyl)acetate[5] (218.4 mg, 1.00 mmol) was added, and, after 10 min, a −78 °C solution of 110 mg (0.50 mmol) of (*R*)-(−)-1 in 3.5 mL of THF was added dropwise over 10 min via precooled cannula. After addition, the pale yellow solution was stirred for 15 min at −78 °C. Then the reaction mixture was quenched by adding a saturated solution of sodium hydrogen phosphate and warmed to room temperature. The contents in the flask were extracted with ether (2 × 10 mL), and the combined ether layers were washed with water and dried over anhydrous $MgSO_4$. Solvent evaporation gave 370 mg of a yellow oil, which was directly used in the next step without further purification.

Preparation of β-Keto Sulfide 4. To a stirred suspension of 712 mg (1.25 mmol) of diphosphorus tetraiodide (Aldrich) in dry methylene chloride (2.5 mL) was added 1.41 g of the crude conjugate adduct (prepared from 2.5 mmol of (*R*)-(−)-1 and 2) in 2.5 mL of dry methylene chloride in one portion at room temperature under nitrogen atmosphere. Crystalline, orange diphosphorus tetraiodide dissolved immediately, and the solution turned reddish-brown. After 10 min, the reaction mixture was quenched by adding water. The organic layer was separated, washed with an aqueous solution of sodium thiosulfate, and dried over $MgSO_4$. Solvent evaporation gave 1.095 g of yellow oil, which was purified by column chromatography (eluting solvent, 1:9 ether–hexane) to give 622 mg [60% overall yield from (*R*)-(−)-1] of the sulfide. Protodesilylation of this sulfide was carried out in a 20% aqueous methanol solution (7 mL) with potassium fluoride (340 mg, 5.89 mmol) stirred at room temperature for 3 h. The resultant reaction mixture was concentrated under reduced pressure, and the residue was extracted with methylene chloride (3 × 10 mL). The combined extracts were washed with water and dried over $MgSO_4$. Filtration and solvent evaporation gave 375 mg of pale yellow oil, which was purified by column chromatography (eluting solvent, 1:9 ethyl acetate–hexane) to give 368 mg (90%) of β-keto sulfide **4**: IR ($CHCl_3$) 1750–1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05–2.55 (m, 10 H), 3.05 (d, 1 H, *J* = 10.1 Hz), 3.70 (s, 3 H, OCH_3), 7.04–7.44 (q, 4 H, Ar).

C-Alkylation of β-Keto Sulfide 4. Sodium hydride (40 mg, 0.83 mmol, 50% dispersion in mineral oil) was added to a solution of 4 (210 mg, 0.755 mmol) in dry glyme (1.5 mL) which was kept in an ice bath at 0 °C with stirring under an argon atmosphere. After the evolution of hydrogen stopped (~25 min), 170 mg (1.134 mmol) of (*Z*)-1-bromo-2-pentene[9] was added and the reaction mixture left stirring for 3 h at 0 °C and 12 h at room temperature. The dark brown reaction mixture was cooled to 0 °C, quenched with saturated ammonium chloride, and extracted with ether (2 × 10 mL). The ether extracts were combined, washed successively with brine, 5% sodium hydroxide, and brine, and then dried over $MgSO_4$. Filtration and solvent evaporation gave 250 mg of a yellow oil, which was purified by column chromatography (eluting solvent, 5:95 ethyl acetate–hexane) to give 165 mg (63%) of **5**: IR (neat) 3060, 1740, 1600, 1175, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H, *J* = 7.3 Hz), 1.85–2.85 (m, 14 H), 3.71 (s, 3 H, OCH_3), 5.0–5.55 (m, 2 H), 7.0–7.25 (m, 4 H, Ar); mass spectrum, *m/e* (relative intensity) 346 (M^+, 60), 315 (30), 278 (75), 223 (55), 217 (85), 124 (80), 83 (100).

(−)-Methyl Jasmonate (6). To 90 mg (0.260 mmol) of **5** in 5 mL of acetone was added 800 mg of W-2 Raney Ni, and stirring was continued at room temperature under nitrogen atmosphere for 3 h. The Raney Ni was filtered off, and the filtrate, on solvent evaporation, gave 40 mg of a pale yellow liquid, which showed three peaks (retention times 8.02, 8.27, and 8.76 min in a 20:65:15 ratio, respectively) on glass capillary GC. Each compound was isolated by preparative HPLC. The first compound (13% yield) appeared by ^1H NMR to be extremely similar to methyl jasmonate, but it had a strong IR absorption at 975 cm^{-1}, characteristic of a trans-disubstituted carbon–carbon double bond. We tentatively assign this material to be methyl isojasmonate having a *trans*-pentenyl side chain: $[\alpha]^{20}_{\lambda}$ −89.0° (589), −93.76° (578), −111.36 (546), −246.48° (436), −610.35° (365) (*c* 1.71, CH_3OH). The second compound (**6**, 45%) was identical by ^1H NMR at 400 MHz, by IR, and by glass capillary GC (including coinjections) with authentic (±)-methyl jasmonate: IR ($CHCl_3$) 1740–1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (t, 3 H, *J* = 7.4 Hz), 1.65–2.75 (m, 12 H), 3.68 (s, 3 H, OCH_3), 5.20–5.28 (m, 1 H), 5.40–5.48 (m, 1 H); $[\alpha]^{20}_{\lambda}$ −93.0° (589), −99.0° (578), −117.5° (546), −256.5° (436), −634.1° (365) (*c* 0.2, CH_3OH). The corresponding literature values[4] are as follows: $[\alpha]^{20}_{\lambda}$ −90.2° (589), −95.8° (578), −113.4° (546), −252.3° (436), −623.7° (365) (CH_3OH). The third compound (10% yield) appeared to be methyl epijasmonate. It had the same capillary GC retention time as authentic (±)-methyl epijasmonate, and equilibration (EtOH–NaOAc) converted this material to a 92:8 mixture of methyl jasmonate–methyl epijasmonate.

Preparation of Methyl 3-Oxocyclopentaneacetate (7). The conjugate adduct **3** (prepared from 110 mg, 0.50 mmol, of (*R*)-(−)-1) was dissolved in 10 mL of aqueous THF solution (9:1 THF–H_2O) and cooled to −15 °C. Aluminum–amalgam (5.0 mmol)[19] was added, and the reaction mixture was slowly warmed to room

(16) Posner, G. H.; Frye, L. L. *Isr. J. Chem.* **1984**, *24*, 88.

(17) (a) For the first example of an enolate ion asymmetric conjugate addition to a vinylic sulfoxide, see: Tsuchihashi, G.; Mitamura, S.; Inoue, S.; Ogura, K. *Tetrahedron Lett.* **1973**, 323. (b) For a related example of an asymmetric Michael addition of an ester enolate, see: Oppolzer, W.; Pitteloud, R.; Bernardinelli, G.; Baettig, K. *Tetrahedron Lett.* **1983**, *24*, 4975. (c) In contrast to a literature report on the failure of *methyl* α-lithioacetate to undergo carbon–carbon coupling reactions (Cregge, R. J.; Herrmann, J. L.; Lee, C. S.; Richman, J. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2425), we have succeeded in using *methyl* α-lithioacetate for conjugate addition to cyclopentenone sulfoxide (*S*)-(+)-1 at −78 °C; which proceeds in good chemical yield with 45–50% asymmetric induction to give (−)-7 via eq 1.

(18) (a) Posner, G. H.; Hulce, M. *Tetrahedron Lett.* **1984**, *25*, 379. (b) Posner, G. H.; Kogan, T. P.; Hulce, M. *Tetrahedron Lett.* **1984**, *25*, 383. (c) Posner, G. H.; Kogan, T. P.; Haines, S. R.; Frye, L. L. *Tetrahedron Lett.* **1984**, *25*, 2627.

(19) Corey, E. J.; Chaykovsky, M. J. *J. Am. Chem. Soc.* **1964**, *86*, 1939.

temperature and stirred overnight. Anhydrous $MgSO_4$ was added to the gray slurry, and the organic layer was filtered off. Evaporation of the solvent under reduced pressure gave a pale yellow liquid, which was purified by column chromatography (eluting solvent, 1:9 ether–hexane) to give 70 mg (46% from (*R*)-(−)-1) of desulfurized keto ester: ^1H NMR ($CDCl_3$) δ 0.17 (s, 18 H), 2.05–2.75 (m, 7 H), 3.63 (s, 3 H, OCH_3). Protodesilylation of this keto ester was carried out in 20% aqueous methanol solution (7 mL) with potassium fluoride (54 mg, 0.93 mmol) for 3 h at room temperature. Usual workup gave 35 mg (95%) of **7**: IR ($CHCl_3$) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4–2.8 (m, 9 H), 3.70 (s, 3 H, OCH_3); mass spectrum, *m/e* 156 (M^+). Kugelrohr distillation gave 30 mg of a colorless liquid, $[\alpha]^{18}_D$ −119.4° (*c* 0.89, $CHCl_3$) [lit. $[\alpha]^{18}_D$ −121.0° (*c* 1.47, $CHCl_3$)].[11]

Preparation of Ketal 8. Methyl 3-oxocyclopentaneacetate **7** (30 mg, 0.19 mmol) was dissolved in 15 mL of benzene with 35 mg (0.38 mmol) of (*R,R*)-(−)-2,3-butanediol (Aldrich) and a catalytic amount of *p*-toluenesulfonic acid in a 25-mL round-bottomed flask fitted with a Dean–Stark trap. The ketone was ketalized by heating to reflux for 48 h and removing the water generated by azeotropic distillation. The reaction mixture was cooled to room temperature, the benzene was removed under vacuum, and the residue was dissolved in 20 mL of pentane. The pentane was washed with saturated $NaHCO_3$ and aqueous $NaHSO_3$ (5%) and dried over $MgSO_4$. Filtration and evaporation of the pentane gave an oil, which was purified by column chromatography (eluting solvent, 1:9 ether–hexane) to give 22 mg (50%) of the desired ketal **8**. No starting ketone **7** was detectable. Relative integration of the diastereotopic carbon resonances at 30.218 and at 30.157 ppm in the ^{13}C NMR spectrum indicated >98% diastereomeric excess. For comparison the diastereomeric ketals of (±)-**8** were prepared and showed a 1.07:1.00 ratio of resonances at 30.061 and at 29.667 ppm.

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Reactions of Phosphorus Compounds. 41. Thermal Rearrangement of Hydrazono Vinylphosphonium Salts to Pyrazoles

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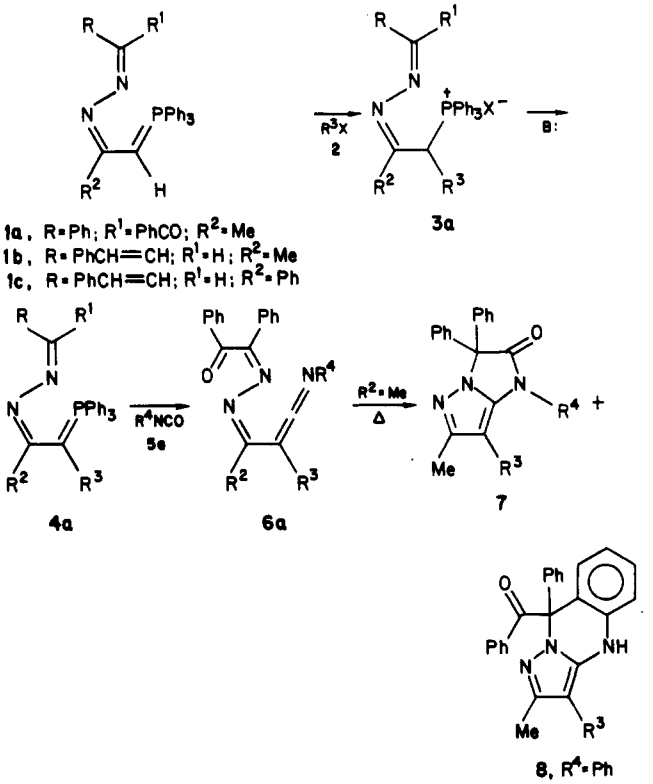
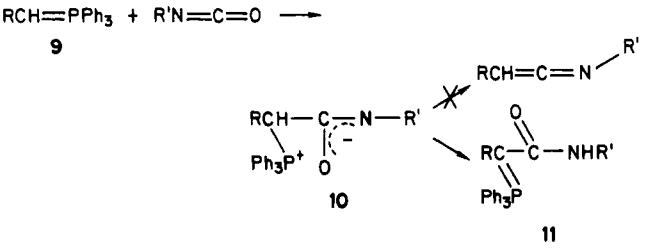
The thermal rearrangements of 1-oxo-3,4,8-triaza-2,4,6,7-octatetraenes **6** have been shown[1] to provide an excellent synthesis of 2,3-dihydro-1*H*-imidazo[1,2-*b*]-pyrazol-2-ones **7** and 4,9-dihydropyrazolo[5,1-*b*]-quinazolines **8** (Scheme I). The preparations of the ketimine–azines **6** could be accomplished readily by the reactions of the ylides **4** with isocyanates **5**.

The ylide **4** contains no α-proton to the triphenylphosphonium moiety. This is a necessary condition for the preparation of ketimines from ylides and isocyanates.[2] The reactions of isocyanates with ylides **9** with α-protons (of type **1**, Scheme I) give betamines **10** which do not decompose[3] to ketimines but transfer a proton to give stable phosphoranes **11** (Scheme II).

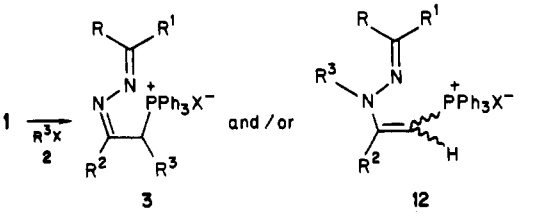
Scheme I



Scheme II



Scheme III



We have shown that ylides **1a** (where R = Ph, R^1 = PhCO) are readily alkylated to give the desired salts **3** which may be employed to prepare the ylides **4** which have no α-protons.[4]

We have examined the reactions of a number of allene azines which may be prepared readily by allowing the unsubstituted ylide **1** to react with ketenes.[5] We wish to extend these reactions to the isocyanates with comparable alkylated ylides **4**. However, we have found that many ylides **1** when alkylated with a variety of alkylating agents, under a variety of conditions, gave predominantly or ex-

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(3) Trippett, S.; Walker, D. M. *J. Chem. Soc.* **1959**, 3874.
(4) Schweizer, E. E.; Lee, K. J. *J. Org. Chem.* **1982**, *47*, 2768.
(5) Schweizer, E. E.; Lee, K. J. *J. Org. Chem.* **1984**, *49*, 1959 and references cited therein.

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