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.

Acknowledgment. We thank the NIH (Grant GM-30052) and McCormick & Co., Inc., for financial support and Firmenich, Inc., for a generous gift of (±)-methyl jasmonate. Purchase of a 400-MHz NMR spectrometer was made possible by the NIH (Grant 1 S10 RR01934) and the the NSF (Grant PCM 83-03776). We also thank Professor T. Acree (Geneva, NY) and Dr. G. Cassani (Novara, Italy) and Dr. J. Salaun (Orsay, France) for a preprint and some helpful comments, respectively.

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

Edward E. Schweizer,* John E. Hayes, and Erin McDonald Hanawalt

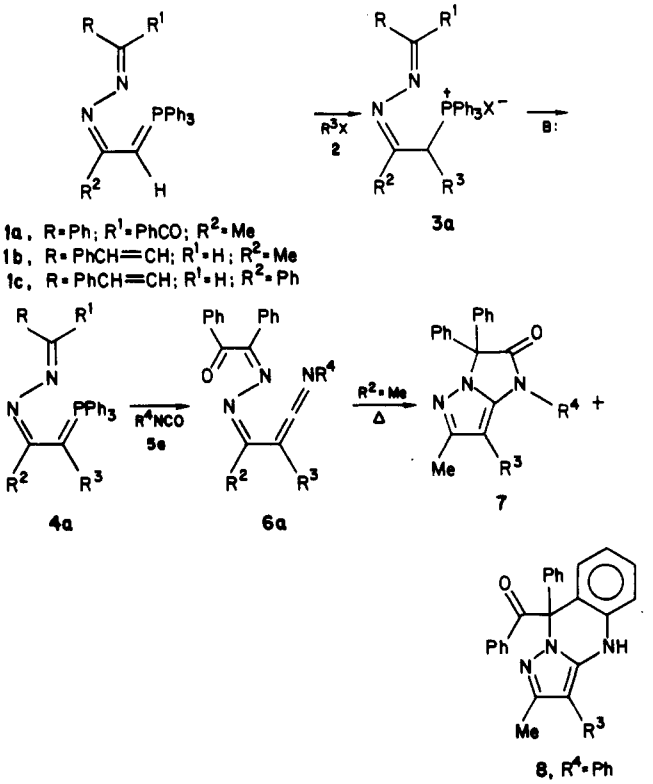
Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received October 18, 1984

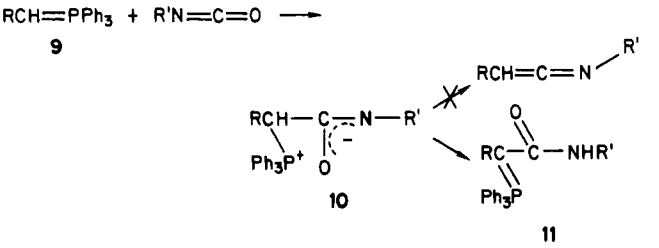
The thermal rearrangements of 1-oxo-3,4,8-triaza-2,4,6,7-octatetraenes **6** have been shown[1] to provide an excellent synthesis of 2,3-dihydro-1*H*-imidazo[1,2-*b*]-pyrazol-2-ones **7** and 4,9-dihydropyrazolo[5,1-*b*]-quinazolines **8** (Scheme I). The preparations of the ketimine–azines **6** could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

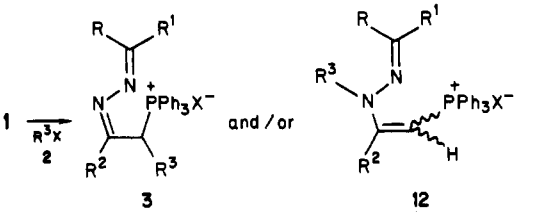
Scheme I



Scheme II



Scheme III



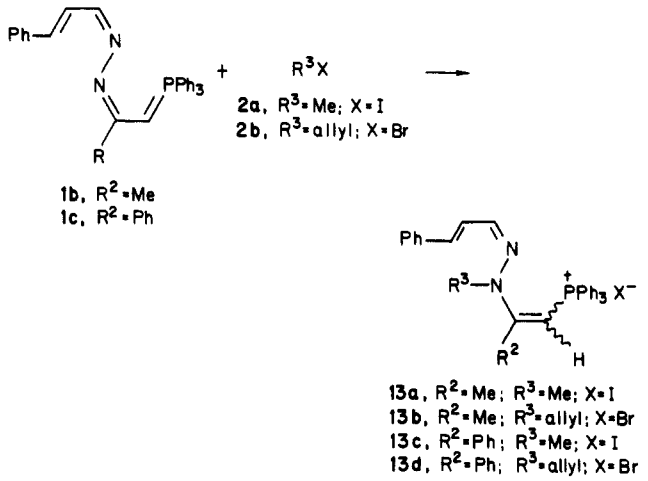
We have shown that ylides **1a** (where R = Ph, R^1 = PhCO) are readily alkylated to give the desired salts **3** which may be employed to prepare the ylides **4** which have no α-protons.[4]

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-

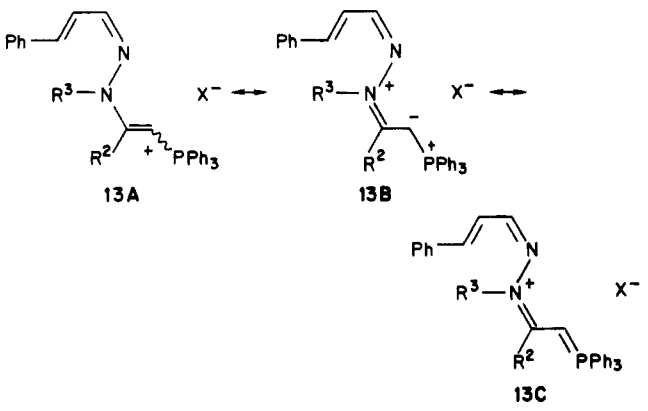
(1) Schweizer, E. E.; Lee, K. J. *J. Org. Chem.* **1984**, *49*, 1964.
(2) Staudinger, H.; Meyer, J. *Chem. Ber.* **1920**, *53*, 72.
(3) Trippett, S.; Walker, D. M. *J. Chem. Soc.* **1959**, 3874.
(4) Schweizer, E. E.; Lee, K. J. *J. Org. Chem.* **1982**, *47*, 2768.
(5) Schweizer, E. E.; Lee, K. J. *J. Org. Chem.* **1984**, *49*, 1959 and references cited therein.

0022-3263/85/1950-2591$01.50/0

Scheme IV



Scheme V



clusively N-alkylated products **12**, not the hoped for C-alkylated products[6] **3** (Scheme III). This reaction, the N-alkylation instead of C-alkylation, is a reaction that we have encountered in the past when attempting to alkylate α,β-unsaturated phosphonium ylides with nitrogen atoms attached to the β-position from the phosphonium moiety.[7]

Two of the ylides (**1b** and **1c**) which were alkylated showed only N-alkylation.[6b] The reaction of **1b,c** with methyl iodide or allyl bromide gave only **13** (Scheme IV).

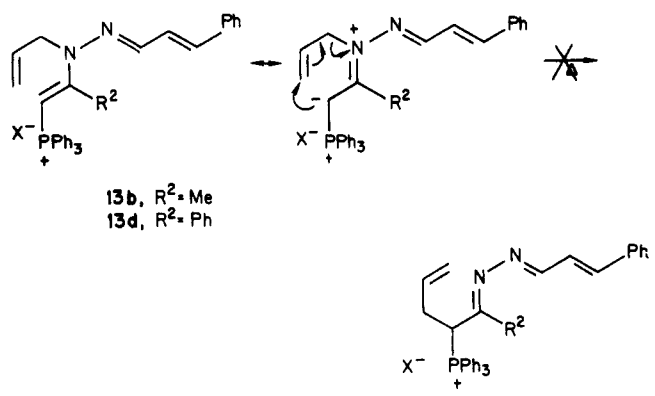
It has been shown in our laboratories[8] that when vinylphosphonium salts (i.e., **13**) have electron-donating substituents on the β-carbon atom from the phosphonium moiety the contribution of the resonance from **13B** is significant (Scheme V). This led us to believe that thermolysis of the allyl-substituted phosphonium salts **13b** and **13d** might lead us to the desired C-alkylated products **14** (**3**) by a hetero-Cope[9] rearrangement as shown in Scheme VI.

Results and Discussion

After thermolysis none of the desired salts **14** were obtained. The volatilized material showed only pyrazoles **16**/**17** and the residue exhibited none of the ^1H, ^{13}C, or ^{31}P NMR peaks characteristic of salts of structure **14**.[4]

We propose that these cyclizations occur via an initial diaza-Cope[9] rearrangement with loss of triphenylphosphine

Scheme VI



Scheme VII

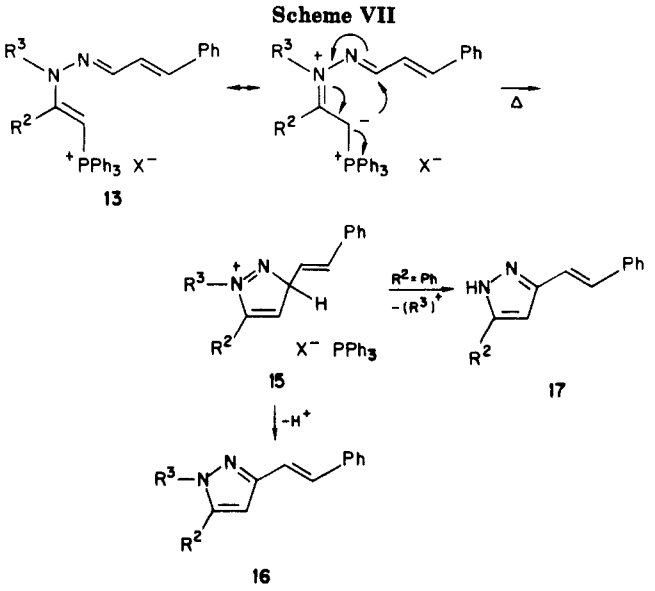
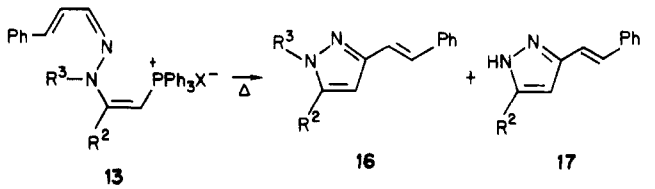


Table I. Cyclization Reactions of β-N-Substituted Vinylphosphonium Salts



reactant	R^2	R^3	X	procedure	products (yield, %)
				A	**16a** (5)
13a	Me	Me	I	B	**16a** (36)
				C	**16a** (47)
				A	**16b** (13)
13b	Me	allyl	Br	B	**16b** (30)
				C	**16b** (20),[a] (67)[b]
				A	**16c** (20) + **17** (16)
13c	Ph	Me	I	B	**16c** (25) + **17** (63)
				C	**16c** (34)[a] + **17** (25)[a]
				A	**16d** (45) + **17** (29)
13d	Ph	allyl	Br	B	**16d** (53) + **17** (33)
				C	**16d** (3)[a] + **17** (46)[a]

[a] Where salts **13b** and $PhCO_2Na$ were stirred together before fusion. [b] Where salts **13b** and $PhCO_2Na$ were ground together before fusion.

(**13** → **15**) followed by aromatization of the pyrazole moiety by proton abstraction (**15** → **16**) or followed by dealkylation and 1,3-hydride shift (**15** → **17**) (see Scheme VII).

Initially the thermolyses were undertaken in sealed glass jars at high temperature (procedure A). The yields of

(6) (a) Boring, J. C. M.S. Thesis, University of Delaware, Newark, DE, June, 1984. (b) Schweizer, E. E.; Hayes, J. E., unpublished results.
(7) Schweizer, E. E.; Kim, C. S. *J. Org. Chem.* **1971**, *36*, 4033.
(8) Albright, T. A.; DeVoe, S. V.; Freeman, W. J.; Schweizer, E. E. *J. Org. Chem.* **1975**, *40*, 1650.
(9) Blechert, S. *Tetrahedron Lett.* **1984**, *25* 1547 and references cited therein.

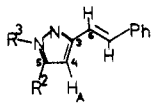


Figure 1.

pyrazoles were generally low when employing this procedure (Table I). Since HBr or HI is liberated, on formation or pyrazoles **16**, and it is known that pyrazoles are acid sensitive,[10] the thermolyses were undertaken under low-pressure conditions in the hopes of removing the pyrazole species as they were formed (procedure B). Some increase of yield occured (Table I).

Further attempts at enhancing the yield involved the use of a stirred mixture of the phosphonium salts and equimolar amounts of sodium benzoate. A further increase of one of the yields was experienced (Table I).

In one further experiment, the phosphonium salt **13c** and sodium benzoate were ground together instead of just mixed together, and there was a significant increase in yield over the comparable vacuum procedure (B).

Overall there are some generalities which were evident. Where R^2 (in **13**) was methyl only pyrazole **16** was found. Where R^2 (in **13**) was phenyl both pyrazoles **16** and **17** were formed. In all of the experiments tried, where the R^3 groups were the same, the overall yields of the two phenyl-substituted pyrazoles obtained (**16** + **17**, R^2 = Ph) were greater than the comparable yields of methyl-substituted pyrazoles (**16**, R^2 = Me).

Spectral Characteristics. Compound **17** shows the following ^{1}H NMR data as referred to in Figure 1: ^{1}H NMR δ 6.72 (s, 1 H, H_A), 7.0–7.7 (m, 12 H, Ar and vinyl H). Compounds **16** exhibit ^{1}H NMR in the following regions: δ 6.22–6.47 (s, 1 H, H_A), 2.18–2.24 (s, 3 H, where $R^2 = CH_3$), 3.67–3.74 (s, 3 H, where $R^3 = CH_3$), 4.56–4.60 (br s, 2 H, CH_2 where R^3 = allyl), 5.04–5.16 (d, 1 H, J = 10, (*E*)-H_2C=CH— where R^3 = allyl), 4.96 (d, 1 H, J = 17, (*Z*)-H_2C=C— where R^3 = allyl), 5.90–5.91 (m, 1 H, H_2C=C*H*— where R^3 = allyl), 7.0–7.7 (m, 12 H, —C*H*=C*H*C_6H_5).

The ^{13}C NMR for compound **17** is as follows (see Figure 1): ^{13}C NMR δ 149.2 (C3), 100.3 (C4), 147.0 (C5), 117.7 (C6).

For compounds **16** the ^{13}C NMR appears in the following regions: ^{13}C NMR δ 148.8–149.6 (C3), 102.7–103.4 (C4), 139.5–144.0 (C5), 120.4–121.3 (C6), 10.9–11.1 ($R^2 = CH_3$), 36.0–36.7 ($R^3 = CH_3$) and 51.7–51.8 ($R^3 = CH_2CH$=CH_2), 117.0–117.1 ($R^3 = CH_2CH$=CH_2).

Experimental Section

General Methods. Dry nitrogen was routinely used as the atmosphere in all reactions. All glassware was baked at 110–120 °C for at least 1 h before use. Melting points are uncorrected and were obtained with a Thomas-Hoover apparatus. The ^{1}H, ^{13}C, and ^{31}P NMR of approximately 10% (w/v) solutions in $CDCl_3$ were obtained on a Bruker Spectrospin Model AM 250 or WM 250. Chemical shifts are reported in parts per million (δ scale) vs. tetramethylsilane (phosphoric acid for ^{31}P NMR) as an internal standard. The following abbreviations have been used in reporting NMR data: coupling constant in hertz (J); singlet (s); doublet (d); doublet of doublets (dd); triplet (t); quartet (q); and multiplet (m). Precise mass spectra were recorded on a Du Pont 21-492B instrument with a resolution of 3300 or 5000. Acetonitrile was dried over calcium hydride and distilled over P_2O_5. Eastman Chromagram (silica gel with fluorescent indicator on polyethylene) precoated sheets were used in thin-layer chromatography. Baker silica gel (60–200 mesh) and EM 774 silica gel for column chromatography were used for product separation.[11]

The following compounds were prepared by known methods: (2-methyl-7-phenyl-3,4-diaza-2,3,6-heptatrienylidene)triphenylphosphorane[6] (**3a**) and (2,7-diphenyl-3,4-diaza-2,4,6-heptatrienylidene)triphenylphosphorane[6] (**3b**).

Pyrolysis of Salts. Procedure A. The salts **13** (1.5–2.0 g) were placed in a 250-mL thick-walled glass bottle[12] under nitrogen. The bottle was sealed and placed in a 240 °C oil bath just until all of the salt had melted. The bottle was then cooled to room temperature and the residue was separated by column chromatography to isolate the pyrazoles **16** and **17** which were shown to be pure by TLC. Pyrazole **17** was recrystallized from ethanol, mp 154 °C. All of the pyrazoles **16** were oils. The precise mass of all of the compounds **16** and **17** were within ± 0.003 of theory.

Pyrolysis of Salts. Procedure B. The salts **13** (0.5 g) were placed in a distillation flask equipped with a magnetic stirrer. The salt was rinsed down from the sides of the flask with methylene chloride. The flask was connected to a vacuum pump equipped with a cold trap, and the methylene chloride was removed. The pressure was reduced to 0.5 mmHg, and the flask was heated in a hot oil bath (200 °C) until the salt was completely melted. After cooling, the residue inside the flask was separated by column chromatography to isolate the pyrazoles **16** and **17**.

Pyrolysis of Salts. Procedure C. The salts **16** (0.5 g) and equimolar amounts of sodium benzoate were placed in a distillation flask equipped with a magnetic stirrer. The reaction was undertaken in the same manner as described for the previous procedure.

In the reaction with **13b**, the reaction was also undertaken after intimately mixing **13b** and the sodium benzoate by grinding to a fine powder with a mortar and pestel.

Registry No. **13a**, 96688-86-7; **13b**, 96688-87-8; **13c**, 96688-88-9; **13d**, 96688-89-0; **16a**, 96688-90-3; **16b**, 96688-91-4; **16c**, 96688-92-5; **16d**, 96688-93-6; **17**, 96688-94-7.

(10) Paquette, L. A. "Principles of Modern Heterocyclic Chemistry"; W.A. Benjamin, Inc.; New York, 1968; p 195.

(11) Chromatographic technique used was that of Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.

(12) This thick-walled glass bottles used in procedure A were Kimble Glass Co. centrifuge bottles (Cat. No. 14700).

Chemistry of Sulfenic Acids. 6.[1,2] Structure of Simple Sulfenic Acids Generated by Flash Vacuum Pyrolysis

Franklin A. Davis* and Robert L. Billmers

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

Received December 13, 1984

The importance of transient sulfenic acid (RSOH) intermediates in organic and bioorganic sulfur reactions is now well recognized.[3] In principle, two tautomeric structures, **1a** and **1b**, can be considered for sulfenic acids.

R-S-O-H RS(O)H

1a **1b**

Despite the fact that these species have been of interest for more than three-quarters of a century their structure remains unclear. The reason for this is that in the rare case where stable sulfenic acids have been isolated they

(1) Part 5: Davis, F. A.; Awad, S. B.; Jenkins, R. H.; Billmers, R. L.; Jenkins, L. A. *J. Org. Chem.* **1983**, *48*, 3071.

(2) These results were taken from: Billmers, R. L. Ph.D. Thesis Drexel University, 1984.

(3) (a) For reviews on the chemistry of sulfenic acids, see: Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65. Hogg, D. R. *Compr. Org. Chem.* **1979**, *4*, 261. (b) For leading references to the biological reactions of sulfenic acids, see: Davis, F. A.; Billmers, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 7016.

0022-3263/85/1950-2593$01.50/0