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Reactions of Azines. 12. Preparation and Reactions of Triphenyl[2-((phenyl(methoxycarbonyl)methylene)hydrazono)propyl]-phosphonium Bromide

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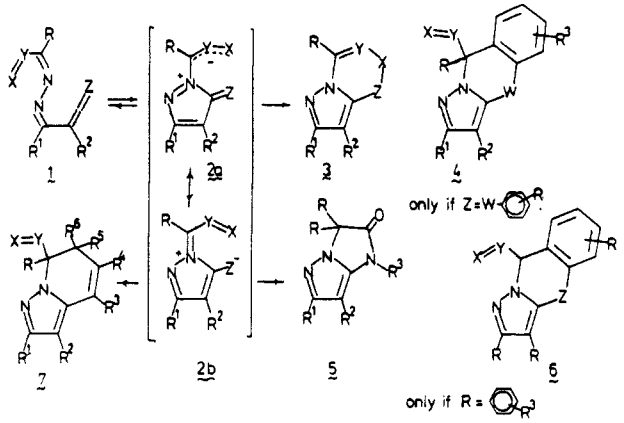
Preparation of triphenyl[2-((phenyl(methoxycarbonyl)methylene)hydrazono)propyl]phosphonium bromide (**13**), triphenyl[1-methyl-2-((phenyl(methoxycarbonyl)methylene)hydrazono)propyl]phosphonium iodide (**15**), and their corresponding ylides **14** and **16** was accomplished. The reaction of **14** with diphenylketene gave 2-methyl-4,9-diphenyl-9-(methoxycarbonyl)-4,9-dihydropyrazolo[1,5-*b*]isoquinoline (**19**/**20**). The reaction of **16** with phenyl isocyanate gave 6,7-dimethyl-3-methoxy-1,3-diphenyl-1*H*-imidazo[1,2-*b*]pyrazol-2(3*H*)-one (**27b**), 2,3-dimethyl-9-(methoxycarbonyl)-9-phenyl-4,9-dihydropyrazolo[5,1-*b*]quinazoline (**30**), and 2,3-dimethyl-9-phenylpyrazolo[5,1-*b*]quinazoline (**31**). Phenylacetoxyketene, on reacting with triphenyl[2-((diphenylmethylene)hydrazono)propyl]phosphorane (**35**), gave 2-methyl-4,9-diphenylpyrazolo[1,5-*b*]isoquinoline (**40**). Carbon disulfide with ylide **16** gave the 2,3-dimethyl-9-(methoxycarbonyl)-9*H*-pyrazolo[5,1-*b*][1,3]benzothiazine (**45**) and desaurine **42** as well as the *trans*-5,10-bis(methoxycarbonyl)-5,10-diphenyldipyrazolo[1,5-*a*:1′,5′-*e*][1,5]diaza-[3,6]dithiocine (**46**). Confirmation of the structures **31**, **42**, and **46** was obtained by crystallographic analyses.

Previously it has been shown that cumulated azines **1** are excellent synthons for a variety of fused pyrazolo heterocycles (**3**–**7**).



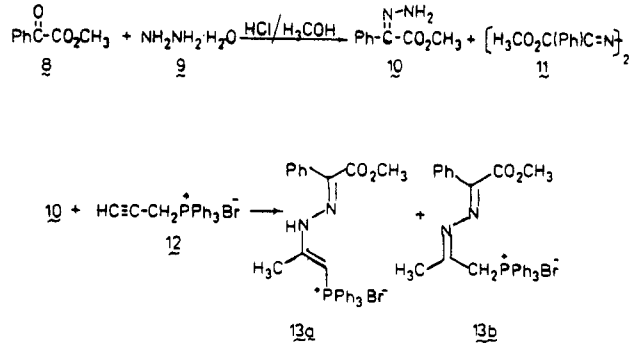
The species produced in high yields from readily available starting materials have been pyrazolo[5,1-*c*]-1,4-oxazines **3** (Y = CR^3, X = O, Z = CR_2^4),[1,2] 4,5-dihydropyrazolo-[1,5-*b*]isoquinolines **4** (W = CR_2^4) or **6** (Z = CR_2^4),[1-3] 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones **5**,[4] 4,9-dihydropyrazolo[5,1-*b*]quinazolines **4** (W = NH) or **6** (Z = NR^4),[4] 4,5-dihydropyrazolo[1,5-*a*]pyridines **3** (Y = CR^3, X = CR^4R^5, Z = CR^6R^7),[5] and 6,7-dihydropyrazolo[1,5-*a*]-pyridines **7**.[5]

The resonance hybrids **2a** ↔ **2b** are the logical intermediates for all of the species (**3**–**7**) reported to date in this reaction series. In the previous work we have never isolated any products attributable to the dimerization of the intermediates **2**. In this paper we report the isolation of a product that is the direct result of such a dimerization.

We also report the preparation of the azine phosphoranes **13** and **16** and their conversion via cumulated azines of type **1** into fused pyrazolo heterocycles similar to those shown by formulas **3**–**7**.

Results and Discussion

On repeating the preparation of methyl α-hydrazonophenylacetate (**10**) from benzoylformate **8** and hydrazine hydrate **9**, described by Neunhoeffer et al.,[6] we obtained the azine **11** as well as the reported **10** in 42% and 17% yields, respectively. Slightly altered reaction conditions, given in the Experimental Section, gave us yields of 17% and 53% of **11** and **10**, respectively. The phosphonium salt **13** was produced (75%) by allowing the hydrazone **10**



(1) Schweizer, E. E.; Evans, S. *J. Org. Chem.* **1978**, *43*, 4328.
(2) Schweizer, E. E.; Lee, K. J. *J. Org. Chem.* **1984**, *49*, 1959.
(3) Schweizer, E. E.; Hsueh, H.; Rheingold, A. L.; Durney, R. L. *J. Org. Chem.* **1983**, *48*, 3889.
(4) Schweizer, E. E.; Lee, K. J. *J. Org. Chem.* **1984**, *49*, 1964.
(5) Schweizer, E. E.; Hayes, J. E.; Hirwe, S. N.; Rheningold, A. L., in press. Reported at the 10th International Congress of Heterocyclic Chemistry, Aug 11–16, 1985, University of Waterloo, Ontario, Canada; Abstracts S12-73.
(6) Neunhoeffer, H.; Neunhoeffer, M.; Litzuis, W. *Liebigs Ann. Chem.* **1969**, *722*, 29.

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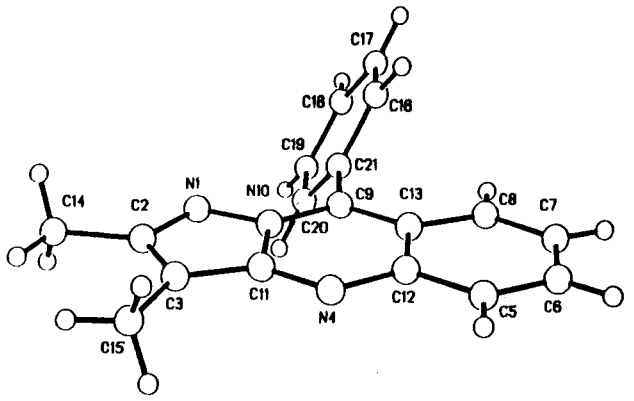
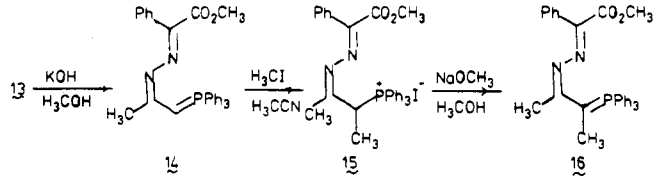


Figure 1. ORTEP diagram of 2,3-dimethyl-9-phenylpyrazolo-[5,1-*b*]quinazoline (**31**).

to react with propargyltriphenylphosphonium bromide (**12**). The reaction of **8** and **9** followed directly by the addition of **12** gave a 64% yield of **13**, whereas the stepwise procedure gave an overall yield of 40% of **13**.

The triphenyl[2-((phenyl(methoxycarbonyl)-methylene)hydrazono)propyl]phosphonium bromide (**13**) obtained was shown to exist in one enamine form **13a** and two imine forms **13b** in ratios of 45% and 37 + 18% by ^{1}H NMR and 41% and 34 + 25% by ^{31}P NMR. The ^{1}H NMR of **13** showed three doublets: one for the vinyl proton (at C-4) of the enamine form **13a** at δ 4.57 (J_{PH} = 15.4 Hz) and two for the C-4 methylene protons of the imine forms **13b** at δ 5.46 (J_{PH} = 13.2 Hz) and δ 5.63 (J_{PH} = 17.4 Hz). These chemical shifts are in agreement with the assignments previously reported for enamine and imine triphenylphosphonium salts.[7] The ^{13}C NMR also showed three doublets: one for **13a** at δ 67.5 (J_{CP} = 105.6 Hz) and two for **13b** at δ 33.7 (J_{CP} = 55.2 Hz) and δ 28.0 (J_{CP} = 46.4 Hz), which again agreed with assignments previously made.[8] The ^{31}P NMR at δ 22.2 for enamine form **13a** and δ 15.6 and 16.6 contradicts the chemical shifts purported for enamines and imines earlier.[7]

The phosphorane **14**, corresponding to the salt **13**, was prepared (85%) readily with methanolic KOH at −5 °C.

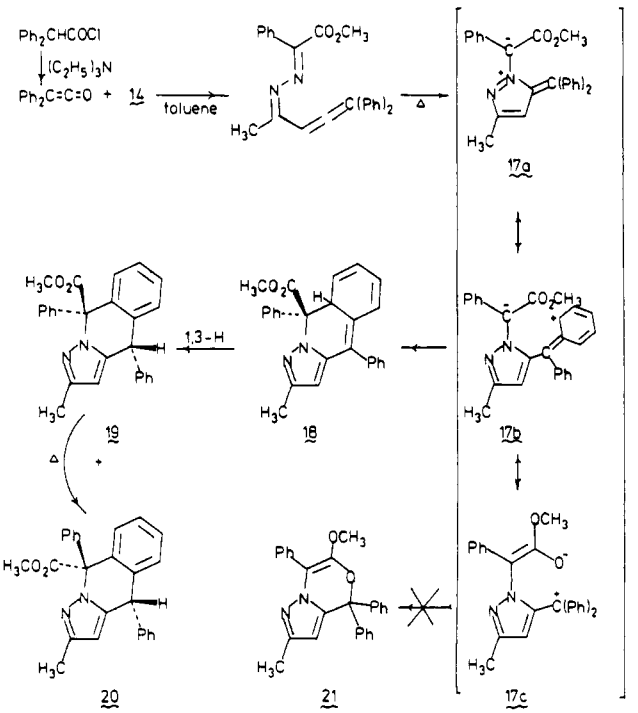


The ^{1}H, ^{13}C, and ^{31}P NMR showed the presence of two isomers (in a ratio of 8:2). The ^{1}H NMR showed the methoxyl group at δ 3.76 and 2.96. Compound **10** has its methoxyl group at δ 3.72, in the normal range (δ 3.62–3.79) for methoxycarbonyl groups.[9] This suggests that the methoxyl protons at 2.96 ppm have extra shielding due to the ring current effects of the phenyl groups of the triphenylphosphorane moiety, where these groups are cisoid to each other as shown in **14** (this is the major isomer).

The phosphorane **14** was methylated with methyl iodide (83% yield) to give only the imine form **15**. The ^{1}H NMR showed the C4-methyl at 1.73 doublet of doublets. The ^{14}C NMR shows the C4-methine at δ 37.3 (J_{CP} = 51.9 Hz); no vinyl carbons were found (δ 57.7–102.4).[8] The single ^{31}P NMR signal at δ 29.2 is in agreement with the previous work.[7]

The phosphorane **16** was produced (in 86% yield) by treating the salt **15** with methanolic sodium methoxide.

The reaction of the phosphorane **14** with diphenylketene in toluene for 1 h at room temperature gave triphenylphosphine oxide and the *E*/*Z* isomers of 2-methyl-4,9-diphenyl-9-(methoxycarbonyl)-4,9-dihydropyrazolo[1,5-*b*]isoquinoline (**19**/**20**) in a ratio of 3:7.



A similar reaction followed by 4 h of heating under reflux gave triphenylphosphine oxide and the more stable *Z* isomer **20**. Presumption of the *Z* orientation of the more stable isomer **20** was based on the smaller conformational free energy of the methoxycarbonyl group vs. the phenyl group[10] and the orientation found by X-ray crystallographic analysis of the stable isomer of 2-methyl-4,9-diphenyl-4,9-dihydropyrazolo[1,5-*b*]isoquinoline.[3]

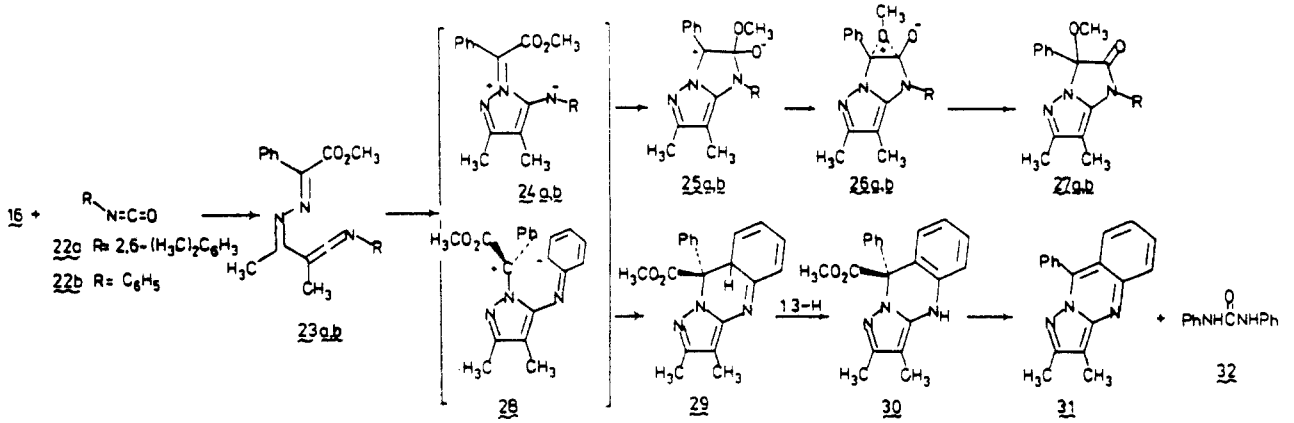
As we had anticipated, on the basis of previous work done in these laboratories with triphenyl[2-(((ethoxycarbonyl)methylene)hydrazono)propylidene]phosphorane and diphenylketene,[1] none of the corresponding pyrazolo[5,1-*c*]-1,4-oxazine (**31**) was formed.

The reaction of the phosphorane **16** with 2,6-dimethylphenyl isocyanate (**22a**) gave triphenylphosphine oxide and 6,7-dimethyl-3-methoxy-3-phenyl-1-(2,6-dimethylphenyl)-1*H*-imidazo[1,2-*b*]pyrazol-2(3*H*)-one (**27a**) (86%).

When phenyl isocyanate **22b** was employed, both 1*H*-imidazo[1,2-*b*]pyrazol-2(3*H*)-one (**27b**) (30%) and 2,3-dimethyl 9-methoxycarbonl)-9-phenyl-4,9-dihydropyrazolo-[5,1-*b*]quinazoline (**30**) (40%) as well as the unexpected[4] 2,3-dimethyl-9-phenylpyrazolo[5,1-*b*]quinazoline (**31**) (5%) and diphenylurea **32** (5%) were found (Scheme I). The structures **27** and **30** were identified by comparison of their spectral data with that found for similar compounds isolated in previously reported work.[4] The structure of **31** was determined by X-ray crystallography, and an ORTEP diagram is shown in Figure 1. Compound **30** could be readily converted into **31** (97%) by heating under reflux

(7) Schweizer, E. E.; Goff, S. D.; Murray, W. P. *J. Org. Chem.* **1977**, *42*, 200.
(8) Albright, T. A.; DeVoe, S. V.; Freeman, W. J.; Schweizer, E. E. *J. Org. Chem.* **1975**, *40*, 1650.
(9) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 220.
(10) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry A*, 2nd ed.; Plenum: New York, 1985; p 118.

Scheme I



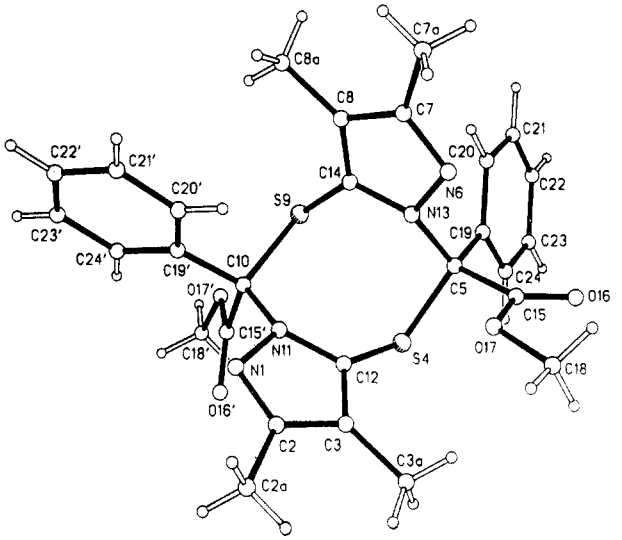
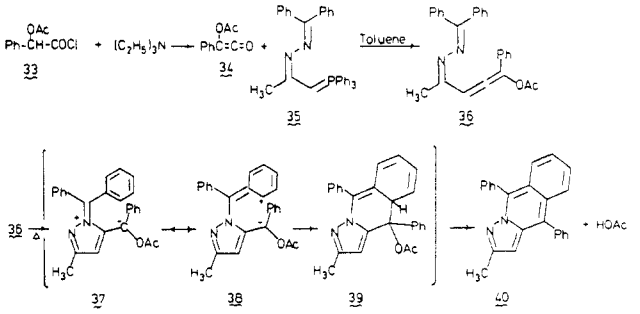


Figure 2. ORTEP diagram of *trans*-5,10-bis(methoxycarbonyl)-5,10-diphenyldipyrazolo[1,5-*a*:1′,5′-*e*][1,5]diaza[3,6]dithiocine (**46a**).

with potassium hydroxide in a toluene/methanol (20:1) mixture.

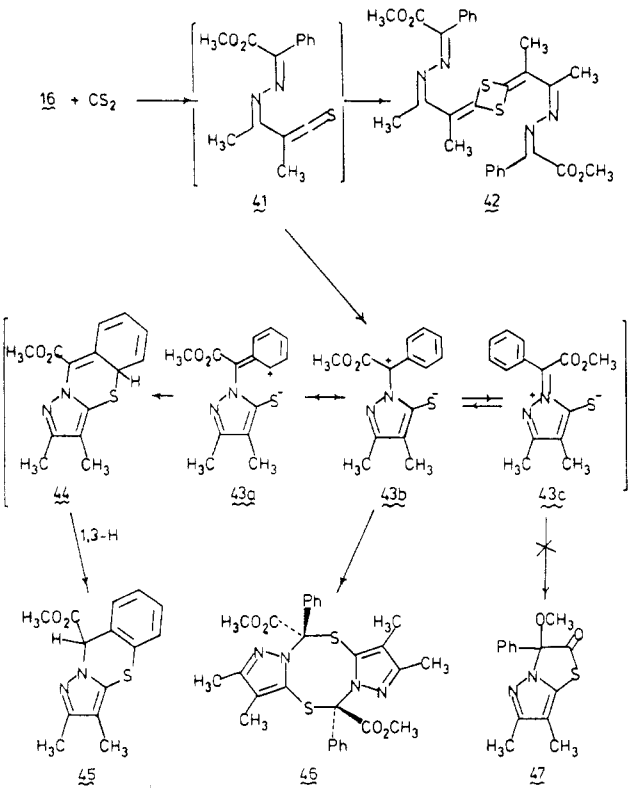
A compound similar to the fully unsaturated **31**, but with a carbon in the 4 position, may be prepared by allowing *O*-acetylmandelic acid chloride (**33**) to react in the presence of triethylamine with triphenyl[2-((diphenylmethylene)-hydrazono)propyl]phosphorane (**35**).[3] The product, 2-



methyl-4,9-diphenylpyrazolo[1,5-*b*]isoquinoline (**40**), was isolated in 76% yield. The analytical data are consistent with the structure proposed.

Staudinger and co-workers[11] first reported that the reaction of phosphoranes with carbon disulfides gave products whose unisolable intermediates were thioketenes. Although many reactions of phosphoranes and carbon disulfide have given saltlike intermediates,[12] there have been a few reports of products that directly implicate unstable thioketene intermediates.[12c,d,13] Some products from the reactions of cumulated azines **1** (where Z = S), produced from the reactions of azine phosphoranes (similar to **16**) with carbon disulfide, have been briefly reported.[5]

On allowing the azine ylide **16** to react with carbon disulfide, in a sealed tube at 140 °C for 1.5 h, triphenylphosphine sulfide (79%) and three products were isolated and identified as follows.



(a) 2,3-Dimethyl-9-phenyl-9*H*-pyrazolo[5,1-*b*][1,3]-benzothiazine (**46**) was found in 5% yield. All analytical data agree with this structural assignment.

We recognize that the mechanistic sequence depicted (**41** → **43** → **44** → **45**) may actually involve a one-step [4

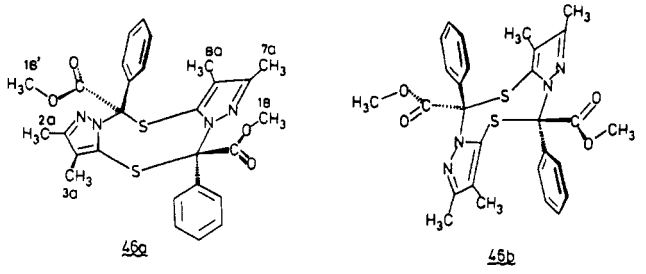
(11) Staudinger, H.; Rathsam, G.; Kjelsberg, F. *Helv. Chim. Acta* **1920**, *3*, 853.

(12) (a) Kunze, U.; Merkel, R.; Winter, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 290, 291. (b) Bestmann, H. J.; Engler, R.; Hartung, H.; Roth, K. *Ber.* **1979**, *112*, 28. (c) Bombieri, G.; Forselli, E.; Chiacchio, U.; Fiandaca, P.; Purrello, G.; Foresti, E.; Graziani, R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1404. (d) Purrello, G.; Fiandaca, P. *J. Chem. Soc., Perkin Trans. 1* **1976**, 692. (e) Pappas, J. J.; Gancher, E. *J. Org. Chem.* **1966**, *31*, 3877.

(13) Schönberg, A.; Frese, E.; Brosowski, K. H. *Ber.* **1962**, *95*, 3077.

+ 2]-electrocyclization of the thioketene azine **41** to form **44** followed by the 1,3-hydride shift to give **45**. Similarly, [4 + 2]-electrocyclization steps may be involved in the direct formation of **18**, **29**, and **39** from the corresponding cumulated azine.

(b) The second product, isolated in 14% yield, was found by mass spectral analyses to be a dimer of **43**. On examining the ^1H NMR of the dimerized product, **46**, we identified six methyl absorptions: a pair δ 3.681 and 3.698, in the methoxycarbonyl region, and two pairs δ 1.697, 2.026 and 1.935, 2.001, corresponding to the area where the pyrazole methyls are usually found. As we were unable to decide conclusively on the structure, an X-ray analysis of a single crystal[14] was determined, an ORTEP diagram of which is shown in Figure 2. The conformation for the 1,5-diaza-3,6-dithiocine in Figure 2 shows a molecule devoid of symmetry (i.e., C_1, **46a**). In Me_2SO-d_6 solution, at 20 °C, the molecule must retain the asymmetry in evidence in Figure 2 (**46a**). When the solution is heated, the eth-



46a **46b**

oxycarbonyl methyls (C18 and C18′) coalesce at 32 °C, whereas the coalescence temperatures for the pyrazole methyls (C2a, C7a and C3a, C8a) occur at 48 and 78 °C, respectively.

The rate constant k for the conformational interconversion at the coalescence temperature was calculated[15] from the equation $k = \pi\Delta\nu 2^{1/2}$, which was shown to allow one to adequately determine $\Delta G^{\ddagger}$, which would be equivalent to the free energy of activation for the conformational interconversion.[16] Using the Eyring equation, $\ln (k/T) = (\Delta H^{\ddagger}/R)(1/T) + \ln (\Delta S^{\ddagger}k/Rh)$, where R is the gas constant (kcal/mol), h is Planck's constant (erg s), k is Boltzmann's constant in (erg/deg), T is the coalescence temperature (K), and plotting $1/T$ vs. $\ln k/T$, we calculated the slope to be −6366.567, with a standard deviation of 623.1668 (9.8%). These data give an inversion barrier of 12.3 ± 1.2 kcal/mol for the conformational inversion and are consistent with an enantiomerization process via a C_i (centrosymmetric) transition state (**46b**).

(c) The third product, found in 9% yield, was identified as the symmetrical 2,4-dialkylidene-1,3-dithietane **42**.[17] Thioketenes generally dimerize into the dithietane structures, called desaurine,[18-20] which are stable, high-melting, yellow compounds. The product found was yellow, which we initially though pointed to the structure **41**. However, the precise mass was that of **42**. The compound was very insoluble in a variety of solvents; however, we managed to obtain a proton NMR: three singlets, δ 1.95 (6 H), 2.30 (6H), and 4.00 (6 H), and an aromatic multiplet δ 7.18–7.79 (10 H). The imine C–CH_3 protons of azines have been

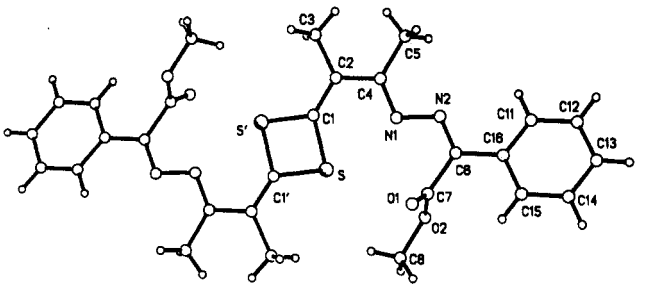


Figure 3. ORTEP diagram of desaurine (**42**).

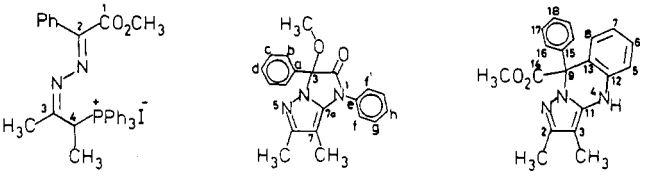
shown[21] to appear between δ 2.19 and 2.45 with the range between δ 2.31 and 2.38 predominating. The desaurine structure **42** is supported by an X-ray diffraction study (see Figure 3).

Thus we have, for the first time, identified dimeric products from the reactions of cumulated azines. Further examination of the reactions of azine phosphoranes is in progress.

Experimental Section

General. Dry nitrogen was routinely used as the reaction atmosphere in all reactions. All glassware was baked at 100–120 °C for a minimum of 2 h before being used. Melting points were obtained with a Thomas-Hoover Unimelt capillary apparatus and were uncorrected.

The ^1H, ^{13}C, and ^{31}P NMR spectra of approximately 10% (w/v) solution in $CDCl_3$ or Me_2SO-d_6 were obtained on a Burker Spectrospin Model WM 250 or AM 250 or on a Nicolet QE 300. Chemical shifts are reported in parts per million (δ scale) employing tetramethylsilane as an internal standard. In reporting the NMR data, we have employed the following abbreviations: coupling constant in hertz (J), singlet (s), double (d), doublet of doublet (dd), and multiplet (m). The numbering system used to depict the NMR is shown below.



Precise mass spectra were recorded by using a Du Pont 21-492B instrument with a resolution of 3300 or 5000. All precise masses found were within 0.003 mass units of the calculated values. IR spectra were recorded on a Unicap SP 100 infrared spectrophotometer and calibrated by comparison with a standard polystyrene film sample.

Methanol and toluene were dried and distilled from sodium metal. Acetonitrile was dried over calcium hydride, followed by its distillation over P_2O_5. Baker silica gel (60–200 mesh) and EM7747 silica gel for column chromatography[25] were used throughout for product separation. Eastman Chromagram (silica gel with a fluorescent indicator on polyethylene) precoated sheets were employed in thin-layer chromatographic (TLC) operations.

Propargyltriphenylphosphonium bromide (**12**) was prepared by the procedure of Eiter and Oediger.[22] Diphenylacetyl chloride was prepared from the acid with thionyl chloride under refluxing in toluene.[23] Methyl benzoylformate (**8**), hydrazine monohydrate (**9**), diphenylacetic acid, phenyl isocyanate, 2,6-dimethylphenyl isocyanate, and *O*-acetylmandelic acid chloride (**33**) were purchased from Aldrich Chemical Co. The isocyanates were purified by distillation prior to use.

Preparation of Methyl α-Hydrazonophenylacetate (10) and Methyl α-Phenyl-α-((phenyl(methoxycarbonyl)-methylene)hydrazono)acetate (11). To a solution of aqueous

(14) Numbering for this discussion is that shown on the ORTEP diagram, shown in Figure 2, and formula **46**.
(15) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.
(16) Kost, D.; Carlson, E. H9; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656.
(17) The end groups may be reversed.
(18) Yates, P.; Moore, D. R. *J. Am. Chem. Soc.* **1958**, *80*, 5577.
(19) Dickoré, K.; Wegler, R. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 970.
(20) Behringer, H.; Meinetsberger, E. *Tetrahedron Lett.* **1973**, 1915.
(21) Schweizer, E. E.; Hirwe, S. N. *J. Org. Chem.* **1982**, *47*, 1652.
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(23) Taylor, E. C.; McKillop, A.; Hawks, G. H. *Org. Synth.* **1972**, *52*, 36.

hydrazine monohydrate **9** (85%) (2.65 g, 0.045 mol) and 150 mL of methanol in a 300-mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer was added 22.5 mL of 2 N HCl with stirring. Methyl benzoylformate **8** (4.92 g, 0.030 mol) was then added. The reaction mixture was stirred at room temperature for 4 days. The resulting mixture as a yellow solution was concentrated on a rotary evaporator and then chromatographed on a silica gel column, eluting with ethyl acetate/hexanes (1:1). This yielded the following two compounds in the order of elution.

a. Compound 11 (0.83 g, 17%) as yellow crystals: recrystallization from methanol yielded a yellow analytical sample; mp 142–143 °C; ^{1}H NMR ($CDCl_3$) δ 3.98 (s, 6 H, $2CH_3O$), 7.38–7.79 (m, 10 H, $2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 52.2 (OCH_3), 128.1 and 128.9 (C ortho and C meta), 131.7 (C ipso), 132.2 (C para), 162.4 (–N=C–), 165.7 (–C(=O)O); exact mass calcd for $C_{18}H_{16}N_2O_4$ 324.111, found 324.112.

b. Methyl α-hydrazonophenylacetate (10) (2.81 g, 53%) as colorless crystals: mp 66–68.5 °C (lit.[26] mp 70–71 °C); ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3 H, OCh_3), 6.51 (s, 2 H, NH_2), 7.26–7.45 (m, 5 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 51.5 (–OCH_3), 128.3 (C ortho), 128.56 (C meta), 128.62 (C para), 129.3 (C ipso), 135.7 (–C=N), 164.4 (–C(=O)O); exact mass calcd for $C_9H_{10}N_2O_2$ 178.074, found 178.074.

Preparation of Triphenyl[2-((phenyl(methoxycarbonyl)methylene)hydrazono)propyl]phosphonium Bromide (13). A slurry of 1.20 g (0.0067 mol) of hydrazone **10** and 2.40 g (0.0063 mol) of propargyl salt **12** in 15 mL of methylene chloride in a 100-mL three-necked flask fitted with a reflux condenser, a $CaCl_2$ drying tube, and an N_2 inlet was heated under reflux with stirring (4 h). The resulting orange mixture was added dropwise to 60 mL of boiling benzene (15 min). This mixture was allowed to cool to room temperature and filtered. The residue was recrystallized from acetonitrile to give light yellow crystals (2.66 g). Evaporation of the filtrate gave another 0.17 g of the light yellow solid product. The total combined yield of **13** was 75%: mp 213–214 °C. Thin-layer chromatography showed on spot (solvent employed was EtOAc/MeOH, 5:1). The NMR showed that three isomers, **13a**, **13b** and **13b′**, were present.

13a: ^{1}H NMR ($CDCl_3$) δ 2.66 (s, 3 H, C3-CH_3), 3.79 (s, 3 H, OCH_3), 4.57 (d, J_{HP} = 15.4 Hz, 1 H, =CHP), 7.31–7.95 (m, 20 H, Ar), 11.87 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 23.5 (C3-CH_3), 53.4 (OCH_3), 67.5 (d, J_{CP} = 105.6 Hz, C4), 122.0 (d, J_{CP} = 95.9 Hz, C5), 157.6 (C2), 160.6 (d, J_{CP} = 2.9 Hz, C3), 163.1 (C1); ^{31}P NMR δ 22.2.

13b: ^{1}H NMR ($CDCl_3$) δ 2.44 (d, J_{HP} = 1.0 Hz, 3 H, C3-CH_3), 3.37 (s, 3 H, OCH_3), 5.46 (d, J_{HP} = 13.2 Hz, 2 H, CH_2P), 7.31–7.95 (m, 20 H, Ar); ^{13}C NMR ($CDCl_3$) δ 20.5 (d, J_{CP} = 7.5 Hz, C3-CH_3), 33.7 (d, J_{CP} = 55.2 Hz, C4), 52.1 (OCH_3), 119.3 (d, J_{CP} = 88.5 Hz, C5), 162.8 (C2), 163.9 (d, J_{CP} = 8.6 Hz, C3), 165.2 (C1); ^{13}P NMR δ 15.6.

13b′: ^{1}H NMR ($CDCl_3$) δ 2.21 (d, J_{HP} = 2.6 Hz, 3 H, C3-CH_3), 3.88 (s, 3 H, OCH_3), 5.63 (d, J_{HP} = 17.4 Hz, 2 H, CH_2P), 7.31–7.95 (m, 20 H, Ar); ^{13}C NMR ($CDCl_3$) δ 26.0 (C3-CH_3), 28.0 (d, J_{CP} = 46.4 Hz, C4), 53.9 (OCH_3), 124.0 (d, J_{CP} = 91.5 Hz, C5), 160.8 (C2), 161.8 (d, J_{CP} = 7.0 Hz, C3), 163.4 (C1); ^{31}P NMR ($CDCl_3$) δ 16.6.

The ratio of **13a:13b:13b′** is 45:37:18 and 41:34:25 based on the C4-H of the ^{1}H NMR and ^{31}P NMR, respectively.

Direct Preparation of Propargyl Salt 13 from Benzoylformate 8. To a solution of 32.83 g (0.200 mol) of methyl benzoylformate (**8**), 20 mL of glacial acetic acid and 750 mL of methanol in a 100-mL round-bottom flask fitted with a reflux condenser was added 12.96 g (0.220 mol) of 85% hydrazine monohydrate **9**. The mixture was stirred with a magnetic stirrer at room temperature for 9 h. The solution was concentrated on a rotary evaporator to 50 mL, followed by extractions with ether (5 × 30 mL). The ether extract was concentrated on a rotary evaporator to 50 mL and dried over $CaCl_2$.

After filtration, the dried ethereal solution was added to a slurry of 76.25 g (0.200 mol) of propargyl salt **12** and 180 mL of methylene chloride in a three-necked, 250-mL, round-bottom flask fitted with a reflux condenser carrying a $CaCl_2$ drying tube and an N_2 inlet. The reaction mixture was heated under reflux with stirring for 29 h, during which time a precipitate appeared. Filtration of the reaction mixture and then washing of the filter cake with methylene chloride (2 × 10 mL) gave a crude product as a light yellow solid. Reprecipitation of the crude product from methylene chloride/ethyl acetate (1:3) afforded 71.82 g (65%) of the mixture of isomers **13a**, **13b**, and **13b′** as a light yellow powder: mp 206–207 °C. Thin-layer chromatography showed one spot (solvent employed was EtOAc/MeOH, 5:1). Further reprecipitation of the product gave the same melting point, as reported in the previous experiment. The NMR is essentially the same as the one described in the previous experiment. The difference is to be found in the ratios of the three isomers, **13a:13b:13b′** = 34:37:29.[24]

Anal. Calcd for $C_{30}H_{28}N_2O_2PBr$: C, 64.41; H, 5.05; Br, 14.38. Found: C, 64.86; H, 5.38; Br, 13.99.

Preparation of Triphenyl[2-((phenyl(methoxycarbonyl)methylene)hydrazono)propylidene]phosphorane (14). In a 50-mL round-bottom flask was dissolved 1.35 g (0.021 mol) of potassium hydroxide in 25 mL of absolute methanol. The solution was cooled to –5 °C (ice–acetone). Phosphonium salt **13** (5.60 g, 0.010 mol) was added into the precooled solution with stirring. The reaction mixture, as yellow slurry, was stirred at –5 °C for 30 min. Filtration of the reaction mixture afforded a yellow-orange solid. To the solid was added 10 mL of methylene chloride, and the resulting mixture was stirred for 10 min. The insoluble side product, KBr (1.00 g) as a white solid, was filtered off. To the yellow-orange filtrate was added hexane dropwise until crystals appeared (15 mL). After filtration followed by removal of solvent in vacuo, ylide **14** (4.07 g, 85%) as yellow-orange crystals was obtained: mp 173–174 °C. The NMR showed that two isomers were present.

14a: ^{1}H NMR ($CDCl_3$) δ 2.73 (d, J_{PH} = 1.7 Hz, 3 H, C3-CH_3), 2.96 (s, 3H, OCH_3), 3.07 (d, J_{PH} = 24.5, 1 H, CHP), 6.99–7.11 (m, 20 H, Ar); ^{13}C NMR ($CDCl_3$) δ 19.2 (d, J_{CP} = 16.6 Hz, C3-CH_3), 47.2 (d, J_{CP} = 109.9 Hz, C4), 50.7 (OCH_3), 142.9 (C2), 169.1 (C1), 173.1 (C3); ^{31}P NMR ($CDCl_3$) δ 13.8.

14b: ^{1}H NMR ($CDCl_3$) δ 2.24 (d, J_{PH} = 1.9 Hz, 3 H, C3-CH_3), 2.69 (d, J_{PH} = 23.4 Hz, 1 H, CHP), 3.76 (s, 3 H, OCH_3), 6.99–7.11 (m, 20 H, Ar); ^{13}C NMR ($CDCl_3$) δ 26.2 (d, J_{CP} = 20.6 Hz, C3-CH_3), 41.5 (d, J_{CP} = 120.8 Hz, C4), 51.3 (OCH_3), 147.4 (C2), 168.3 (C1), 173.7 (C3); ^{31}P NMR ($CDCl_3$) δ 14.6.

The ratio of **14a:14b** is 80:20, from the ^{31}P NMR: exact mass calcd for $C_{29}H_{27}N_2O_2P$ 478.181, found 478.183.

Preparation of Triphenyl[1-methyl-2-((phenyl(methoxycarbonyl)methylene)hydrazono)propyl]phosphonium Iodide (15). To a 100-mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser carrying a $CaCl_2$ drying tube were added 2.39 g (0.005 mol) of ylide **14**, 1.43 g (0.01 mol) of methyl iodide, and 25 mL of acetonitrile. The mixture, as an orange solution, was heated under reflux with stirring for 30 min, during which time a solid precipitated. Thin-layer chromatography with EtOAc/hexanes (1:1) as solvent showed no starting material present in the reaction mixture. The mixture was allowed to cool to room temperature and then filtered. The filtrate was concentrated on a rotary evaporator to about 10 mL. Ether (15 mL) was added gradually, and yellow-orange crystals appeared. The material, isolated by filtration, was recrystallized from acetonitrile/ether (1:1). Product **15** (2.38 g, 83%) as a light yellow powder was obtained: mp 191–195 °C; ^{1}H NMR ($CDCl_3$) δ 1.73 (dd, J_{HH} = 7.1 Hz, J_{HP} = 18.5 Hz, 3 H, C4-CH_3), 2.44 (s, 3 H, C3-CH_3), 3.28 (s, 3 H, OCH_3), 6.24 (m, 1 H, C4-H), 7.43–7.97 (m, 20 H, Ar); ^{13}C NMR ($CDCl_3$) 15.0 (C4-CH_3), 19.4 (C3-CH_3), 37.3 (d, J_{CP} = 51.9 Hz, C4), 52.2 (OCH_3), 118.6 (d, J_{CP} = 85.8 Hz, C5), 155.1 (C2), 164.7 (C1), 165.7 (d, J_{CP} = 6.6 Hz, C3); ^{31}P NMR ($CDCl_3$) δ 29.2.

Anal. Calcd for $C_{31}H_{30}N_2O_2PI$: C, 60.01; H, 4.87; I, 20.45. Found: C, 60.25; H, 5.06; I, 20.60.

Preparation of Triphenyl[1-methyl-2-((phenyl(methoxycarbonyl)methylene)hydrazono)propylidene]phosphorane (16). In a 50-mL round-bottom flask was dissolved 0.13 g (0.006 mol) of sodium metal in 15 mL of absolute methanol. This solution was cooled to –5 °C (ice–acetone), and 1.86 g (0.003 mol) of phosphonium salt **15** was added with stirring. The resulting mixture, as a slurry, was stirred at 0 °C for 30 min, during which

(24) Ratio based on ^{31}P NMR spectrum of the mixture.
(25) Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.
(26) Davis, T. L.; Blanchard, K. C. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, p 453.

time the color of the slurry changed from yellow-orange to orange. Filtration of the slurry gave an orange solid. Purification of the crude product by precipitation from methylene chloride/hexanes (1:1) afforded 1.26 g (86%) of compound **16** as an orange powder: mp 192–195 °C; ^{1}H NMR ($CDCl_3$) δ 1.65 (d, J_{PH} = 15.7 Hz, 3 H, C4-CH_3), 2.46 (s, 3 H, C3-CH_3), 2.71 (s, 3 H, OCH_3), 7.42–7.60 (m, 20 H, Ar); ^{13}C NMR ($CDCl_3$) δ 14.3 (C4-CH_3), 14.5 (d, J_{CP} = 11.8 Hz, C3-CH_3), 50.3 (OCH_3), 53.0 (d, J_{CP} = 108.9 Hz, C4), 138.7 (C2), 168.8 (C1), 172.8 (C3); ^{31}P NMR ($CDCl_3$) δ 18.2; exact mass calcd for $C_{31}H_{29}N_2O_2P$ 492.197, found 492.196.

Preparation of (*E*)- and (*Z*)-2-Methyl-4,9-diphenyl-9-(methoxycarbonyl)-4,9-dihydropyrazolo[1,5-*b*]isoquinolines (19 and 20). a. A solution of diphenylacetyl chloride (0.740 g, 0.0032 mol) in 5 mL of toluene was added dropwise with stirring at room temperature during 10 min to a solution of ylide **16** (1.200 g, 0.0041 mol) and triethylamine (0.410 g, 0.0041 mol) in 30 mL of toluene. The resulting orange reaction mixture was stirred at room temperature for 1 h, during which time a white precipitate appeared. The white precipitate, which was identified as Et_3N·HCl, was filtered off. After removal of the solvent in vacuo (t_{max} < 35 °C), the crude product was chromatographed on a 35- × 350-mm silica gel column with methylene chloride as eluent. The products, triphenylphosphine oxide and then **19** and **20** (0.550 g, 56%), the latter two in a ratio of 72% to 28%, respectively, by ^{1}H NMR, were obtained as light tan solids: mp 187–194 °C. TLC with methylene chloride as solvent showed one spot. ^{1}H NMR ($CDCl_3$): **20** (72%) δ 2.19 (s, 3 H, C2-CH_3), 3.75 (s, 3 H, OCH_3), 5.18 (s, 1 H, C4-H), 5.70 (s, 1 H, C3-H), 7.13–7.32 (m, 16 H, Ar); **19** (28%) δ 2.17 (s, 3 H, C2-CH_3), 3.73 (s, 3 H, OCH_3), 5.37 (s, 1 H, C4-H), 5.74 (s, 1 H, C3-H); ^{13}C NMR ($CDCl_3$) δ 13.9 (C2-CH_3), 44.0 (C4), 53.1 (OCH_3), 72.7 (C9), 103.5 (C3), 149.1 (C2), 170.7 (-C(=O)-).

Anal. Calcd for $C_{26}H_{22}N_2O_2$: C, 79.16; H, 5.62. Found: C, 78.96; H, 5.80.

b. The reaction was carried out the same as in (a), except for one step: After the reaction mixture was stirred at room temperature for 1 h, it was heated under reflux for 4 h prior to its separation. Pure product **20** (0.590 g, 60%) was obtained. The ^{1}H NMR showed only one compound, and the chemical shifts identified with the major component (**20**) in (a). Recrystallization of **20** from methyl chloride afforded a pure sample as colorless crystals: mp 200–201 °C; exact mass calcd for $C_{26}H_{22}N_2O_2$ 394.168, found 394.168.

Preparation of 6,7-Dimethyl-3-methoxy-3-phenyl-1-(2,6-dimethylphenyl)-1*H*-imidazo[1,2-*b*]pyrazol-2(3*H*)-one (27a). A solution of 1.48 g (0.003 mol) of ylide **16** and 0.59 g (0.004 mol) of 2,6-dimethylphenyl isocyanate (**22a**) in 30 mL of toluene was heated under reflux with stirring for 16 h. Thin-layer chromatography (solvent: EtOAc/hexanes, 1:6) showed that there were two major and two trace products in the reaction mixture. After removal of solvent in vacuo, the crude product was chromatographed on a silica gel column with EtOAc/hexanes (1:6) as eluent. One of the major products, collected as the first fraction, was identified as triphenylphosphine oxide. The trace products were not identified. Collection of the other major product, as the third fraction, and recrystallization from ether/petroleum ether gave 0.930 g (86%) of compound **27a** as white crystals: mp 128.5–130 °C; ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 3 H, C7-CH_3), 1.99 (s, 3 H, C6-CH_3), 2.25 (s, 3 H, Ar-substituted CH_3), 2.29 (s, 3 H, Ar-substituted CH_3), 7.08–7.35 (m, 8 H, Ar); ^{13}C NMR ($CDCl_3$ δ 5.6 (C7-CH_3), 12.8 (C6-CH_3), 17.6 (C2-CH_3), 18.2 (C6-CH_3), 52.9 (OCH_3), 91.6 (C3), 94.6 (C7), 126.5 (Cb), 128.6 and 128.7 (Cc and Cg), 129.4 and 129.6 (Cd and Ch), 130.4 + 135.8 + 136.9 (ipso Ce + Cf + Cf'), 136.5 (ipso Ca), 141.4 (C6), 153.8 (C7a), 170.0 (C2); exact mass calcd for $C_{22}H_{23}N_3O_2$ 361.180, found 361.180.

Reaction of Triphenyl[1-methyl-2-((phenyl(methoxycarbonyl)methylene)hydrazono)propyl]phosphorane (16) with Phenyl Isocyanate (22b). Preparation of Compounds 27b, 30, and 31. A solution of 1.480 g (0.003 mol) of ylide **16** and 0.480 g (0.004 mol) of phenyl isocyanate (**22b**) in 30 mL of toluene was heated under reflux with stirring for 16 h. Thin-layer chromatography (EtOAc/hexanes, 1:6) showed the presence of five spots. The resulting reaction mixture was concentrated on a rotary evaporator to dryness. This crude product was then triturated with methanol, which gave a white solid residue. Washing of the residue with 3 × 2 mL of methanol afforded 0.28 g of compound **30** (mp 257.5–260 °C). The combined liquid residue, after removal of solvent in vacuo, was chromatographed on a silica gel column with EtOAc/hexanes 1:10) as eluent. This yielded the following five compounds in the order of elution:

a. Compound **31** was obtained after recrystallization from ether/petroleum ether as brown-red needle-like crystals (0.040 g, 5%): mp 231–233 °C; ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 3 H, C3-CH_3), 2.53 (s, 3 H, C2-CH_3), 7.14–7.95 (m, 9 H, Ar); ^{13}C NMR ($CDCl_3$) δ 7.4 (C3-CH_3), 13.5 (C2-CH_3), 99.8 (C3), 114.9 (C13), 123.8, 126.2, 128.3, 128.8, 129.5 (C ipso), 130.5, 131.1, 144.1 (C2), 147.1 (C12), 147.9 (C11), 157.5 (C9); exact mass calcd for $C_{18}H_{15}N_3$ 273.127, found 273.126.

b. Compound **27b**, after recrystallization from ether/petroleum ether, was obtained as white crystals (0.300 g, 30%): mp 86–70 °C; ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 3 H, C7-CH_3), 2.77 (s, 3 H, C6-CH_3), 3.43 (s, 3 H, OCH_3), 7.25–7.49 (m, 10 H, Ar); ^{13}C NMR ($CDCl_3$) δ 7.3 (C7-CH_3) 12.6 (C6-CH_3), 52.5 (OCH_3), 90.9 (C3), 94.8 (C7), 125.5 or 126.6 (Cb or Cf), 128.2 or 128.4 (Cd or Ch), 129.3 (Cc and Cg), 123.8 (Ce), 135.4 (Ca), 141.8 (C6), 153.9 (C7a), 170.6 (C2); exact mass calcd for $C_{20}H_{19}N_3O_2$ 333.148, found 333.148.

c. Diphenylurea (**32**), after recrystallization from ether/petroleum ether, was found as white needle-like crystals (0.019 g, 5%): mp 242–244 °C (lit.[26] mp 235 °C); ^{1}H NMR (Me_2SO-d_6) δ 6.96 (t, J_{HH} = 7.3 Hz, 2 H, para), 7.27 (t, J_{HH} = 7.5 Hz, 4 H, meta), 7.45 (d, J_{HH} = 7.51 Hz, 4 H, ortho), 8.65 (s, 2 H, -NH-); ^{13}C NMR (Me_2SO-d_6) δ 118.1 (C para), 121.7 (C meta), 128.7 (C ortho), 139.6 (C ipso), 152.5 (-C(=O)-); exact mass calcd for $C_{13}H_{12}N_2O$ 212.095, found 212.094.

d. Compound **30** was found as a white solid (0.120 g), which when combined with the initial 0.280 g of **30**, which was obtained earlier (combined yield 40%), and then recrystallized from methanol (gave an analytical pure sample as white crystals: mp 268–269 °C; ^{1}H NMR (Me_2SO-d_6) δ 1.91 (s, 3 H, C3-CH_3), 1.96 (s, 3 H, C2-CH_3), 3.64 (s, 3 H, OCH_3), 9.55 (s, 1 H, -NH-), 7.22–7.29 (m, 4 H, C5-H, C6-H, C7-H, C8-H), 6.82–7.10 (m, 5 H, Ar); ^{13}C NMR (Me_2SO-d_6) δ 6.5 (C3-CH_3), 12.0 (C2-CH_3), 48.6 (OCH_3), 70.6 (C9), 91.7 (C3), 118.1 (13), 114.6 and 119.7 and 127.4 and 127.9 and 128.4 and 129.0 (aromatic), 136.2 and 137.7 (C12 and C15), 140.9 (C2), 147.3 (C11), 170.3 (C14); IR (KBr) 3100, 1745, 1635, 1594 cm^{-1}; exact mass calcd for $C_{20}H_{19}N_3O_2$ 333.148, found 333.149.

e. Triphenylphosphine oxide, after recrystallization from EtOAc/hexanes, was obtained as white crystals (0.380 g, 46%): mp 156–158 °C (lit.[27] mp 156–157 °C).

Preparation of 2,3-Dimethyl-9-phenylpyrazolo[5,1-*b*]-quinazoline (31) by Decarboxylation of 30. In a 50-mL round-bottom flask fitted with a reflux condenser carrying a $CaCl_2$ drying tube was dissolved 11 mg (0.17 mmol) of KOH in 1 mL of methanol. Compound **30** (50 mg, 0.15 mmol) and 20 mL of toluene were then added. This solution was stirred at room temperature until all solid dissolved. The resulting colorless solution was then heated at 130 °C with stirring for 2 h, during which time the color of the solution changed to brown-red. The reaction was terminated, even though TLC showed that the starting material (**30**) had not been converted completely. After removal of solvent on a rotary evaporator, the reaction mixture was chromatographed (solvent employed was EtOAc/hexanes, 1:2). The first fraction collected from column chromatography was a brown-red solid. Recrystallization from ether afforded 31 mg (76%) of compound **31** (identified by NMR spectra) as brown-red needle-like crystals. The unconverted starting material (**30**) as the second fraction was collected and recrystallized from EtOAc, which gave 11 mg (22%) of white solid. Thus conversion, based on recovered staring material, was 97%. Analytical data were identicial with the compound reported earlier.

Preparation of 2-Methyl-4,9-diphenylpyrazolo[1,5-*b*]isoquinoline (40). A solution of *O*-acetylmandelic acid chloride (1.28 g, 6 mmol) (**3**) in 5 mL of toluene was added dropwise over a period of 0.5 h, at room temperature with stirring, to a solution of the phosphorane (1.98 g, 4 mmol) **35**[3] and triethylamine (0.81 g, 8 mmol) in 45 mL of toluene. After all of the acid chloride had been introduced, the solution was heated under reflux for 10 h. Analysis

(27) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Boca Raton, FL, 1984; p C-450.

by TLC showed on bright green fluorescent spot in addition to triphenylphosphine oxide. The mixture was cooled to room temperature and concentrated in vacuo. The residue was chromatographed with petroleum ether/ethyl acetate (80:20) as eluent. This yielded, after evaporation of the solvent, the pyrazole **40** (1.02 g, 76%) as an orange solid. Recrystallization from ethyl acetate afforded an analytically pure sample of **40**: mp 205–206 °C; ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 3 H, C2-CH_3), 6.31 (s, 1 H, C3-H), 7.02–7.21 (m, 4 H, Ar), 7.47–7.69 (m, 10 H, Ar); ^{13}C NMR ($CDCl_3$) δ 14.7 (CH_3), 94.4 (C3), 119.8, 123.9 (C5[a]), 124.4 (C6[a]), 125.8 (C7[a]), 126.1 (C8[a]), 127.8, 128.0 (C17[b]), 128.7 (C16[c]), 128.8 (C20[c]), 129.1, 129.3 (C21[b]), 130.4 (C15[d]), 130.9 (C19[d]), 132.3, 135.8, 136.7, 141.6 (C11), 153.9 (C2) (superscript letters may be interconvertible within the set); exact mass calcd for $C_{24}H_{18}N_2$ 334.141, found 334.144.

Formation of Desaurine (42), 2,3-Dimethyl-9-phenyl-9*H*-pyrazolo[5,1-*b*][1,3]benzothiazine (45), and *trans*-5,10-Bis(methoxycarbonyl)-5,10-diphenyldipyrazolo[1,5-*a*:1′,5′-*e*][1,5]diaza[3,6]dithiocine (46). Phosphorane **16** (1.480 g, 3 mmol) and 20 mL of carbon disulfide (~0.3 mol) were placed in a thick-wall glass tube, capped, and heated in an oil bath at 140 °C with stirring for 1.5 h. The reaction mixture color changed from orange-red to dark brown. After removal of the excess CS_2 on a rotary evaporator, the reaction mixture was dissolved in 15 mL of methylene chloride and filtered, which gave 0.072 g (9%) of **42** as orange powder (mp 205–209 °C). The filtrate, after removal of the solvent, was chromatographed on a silica gel column, eluting with EtOAc/hexanes. Products **45** and **46** along with triphenylphosphine sulfide were collected. Recrystallization of **45** and **46** from EtOAc afforded analytical samples:

a. Compound **42** (0.072 g, 9%) as orange powder after recrystallization from $CHCl_3$: mp 213–214 °C; ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 6 H, C4-CH_3), 2.30 (s, 6 H, C3-CH_3), 4.00 (s, 6 H, OCH_3), 7.41–7.79 (m, 10 H, Ar); ^{13}C NMR ($CDCl_3$) δ 14.9 (C3- and C4-CH_3), 52.6 (OCH_3), 119.1 (C4), 127.3 (C ortho), 128.7 (C meta), 131.0 (C para), 132.5 (C ipso), 168.5 (-C(=O)-), others not distinguishable from background due to low solubility of sample; exact mass calcd for $C_{28}H_{28}N_4O_4S_2$ 548.155, found 548.155.

b. Compound **45** (0.041 g, 5%) as colorless crystals: mp 162–164.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 3 H, C3-CH_3), 22.2 (s, 3 H, C2-CH_3), 3.68 (s, 3 H, OCH_3), 6.19 (s, 1 H, C9-H), 7.27–7.51 (m, 4 H, Ar); ^{13}C NMR ($CDCl_3$) δ 8.0 (C3-CH_3), 12.0 (C2-CH_3), 53.1 (OCH_3), 63.7 (C9), 111.3 (C3), 126.7 and 127.1 and 129.0 and 192.9 (C5 and C6 and C7 and C8), 128.0 (C13), 128.8 and 128.9 (C11 and C12), 149.0 (C2), 168.4 (C=O); exact mass calcd for $C_{14}H_{14}N_2O_2S$ 274.078, found 274.077.

c. Compound **46a** (0.102 g, 14%) as colorless crystals: mp 206–207 °C; ^{1}H NMR (Me_2SO-d_6) at 20 °C δ 1.94 (s, 3 H, C2-CH_3), 1.70 (s, 3 H, C3-CH_3), 2.00 (s, 3 H, C7-CH_3), 2.03 (s, 3 H, C8-CH_3), 3.68 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 6.81–7.36 (m, 10 H, Ar); $\Delta\delta$ (C2-CH_3, C7-CH_3) = 24.0 Hz, $\Delta\delta$ (C3-CH_3, C8-CH_3) = 118.5 Hz, $\Delta\delta$(OCH_3, OCH_3) = 6.4 Hz; ^{13}C NMR ($CDCl_3$) 147.8, 148.1 (C2 and C7), 111.1, 111.3 (C3 and C8), 139.3, 137.3 (C3a and C8a), 167.6, 168.8 (C13, C13′), 53.6, 53.7 (C16, C16′), 9.0, 9.3 (C3-CH_3), C8-CH_3), 12.2, 12.3 (C2-CH_3, C7-CH_3), 127.0, 126.4 (Ar ipso C17, C17′); exact mass calcd for $C_{28}H_{28}N_4O_4S_2$ 548.155, found 548.154.

d. 46b at 80 °C: 1.87 (br s, 6 H, C3 + C8), 1.97 (s, 6 H, C2 + C7), 3.70 (s, 6 H, 2OCH_3), 7.00–7.35 (m, 10 H, Ar).

Crystallographic Structural Determinations of 31, 42, and 46. All structures were obtained at ambient temperatures (22–24 °C) with a Nicolet R3m diffractometer. All software is contained in the SHELXTL software package (Nicolet Corp., Madison, WI). For **31**, $C_{18}H_{15}N_3$, orthorhombic, $Pn2_1a$ (nonstandard setting of $Pna2_1$) a = 7.116 (2), b = 10.701 (3), c = 18.542 (5) Å, v = 1412.0 (6) Å^3, Z = 4, D(calcd) = 1.285 g cm^{-3}, μ(Mo Kα) = 1.2 cm^{-1}. Of 1236 reflections collected ($4° \leq 2\theta \leq 48°$), 1068 unique reflections with $F_o \geq 2.5\sigma(F_o)$ were considered observed. For **42**, $C_{28}H_{28}N_4O_4S_2$, monoclinic, $C2/c$, a = 12.584 (3), b = 8.704 (3), c = 24.709 (10) Å, β = 91.06 (3)°, V = 2706 (2) Å^3, Z = 4, D(calcd) = 1.35 g cm^{-3}, μ(Mo Kα) = 2.3 cm^{-1}. Of 2614 reflections collected ($4° \leq 2\theta \leq 50°$), 1847 unique reflections with $F_o \geq 3.0(F_o)$ were considered observed (R_{int} = 1.5%). For **46**, $C_{28}H_{28}N_4O_2S_2$, triclinic, $P\bar{1}$, a = 9.349 (3), b = 11.031 (4), c = 14.613 (5) Å, α = 96.98 (3)°, β = 94.86 (3)°, γ = 114.33 (3)°, V = 1347.7 (8) Å^3, Z = 2, D(calcd) = 1.273 g cm^{-3}, μ(Mo Kα) = 2.3 cm^{-1}. Of 3702 reflections collected ($4° \leq 2\theta \leq 45°$), 2718 unique reflections with $F_o \geq 3\sigma(F_o)$ were considered observed (R_{int} = 1.5%). No absorption corrections were applied. Solutions were by direct methods and difference Fourier syntheses. Anisotropic refinement of all non-hydrogen atoms and an idealized treatment of hydrogen-atom contributions led to these final parameters: **31**, $R(F)$ = 4.11%, $R(F)_w$ = 4.52%, GOF = 1.20, N_o/N_v = 6.0, $\Delta\rho$(max) = 0.20 e Å^{-3}; **42** $R(F)$ = 5.18%, $R(F)_w$ = 6.65%, GOF = 1.36, N_o/N_v = 11.5, $\Delta\rho$(max) = 0.38 e Å^{-3}; **46**, $R(F)$ = 6.34%, $R(F)_w$ = 7.16%, GOF = 1.44, N_o/N_v = 7.9, $\Delta\rho$(max) = 0.49 e Å^{-3}. Tables of atomic coordinates, bond distances and angles, and anisotropic temperature coefficients are available as supplementary material.

Supplementary Material Available: Atomic coordinates, bond distances and angles, and anisotropic temperature coefficients for compounds **31**, **42**, and **46** (16 pages). Ordering information is given on any current masthead page.