

An Alternative Preparation of the 2-Dimethylaminomethylene-1,3-bis(dimethylimmonio)propane Salt from Phosphonoacetic Acids and Some Applications in Heterocyclic Synthesis

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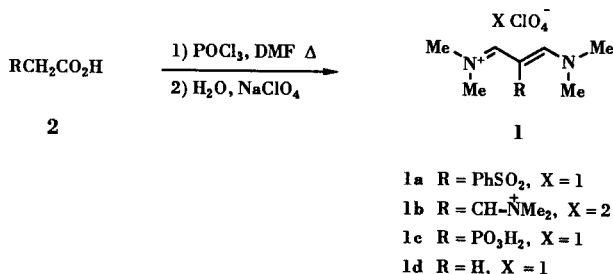
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An alternative preparation of a 2-iminovinamidinium salt from phosphonoacetic acids is described along with its application to the synthesis of 5-formylpyrimidines and masked 4-formylpyrazoles.

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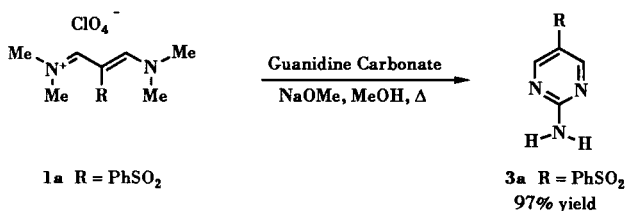
One of our primary research interests [1] in recent years has been to investigate the application of vinamidinium salts [2] in organic synthesis. These substances **1a-d** have the potential to serve as three carbon building blocks and recently we have demonstrated [3] that a 2-phenylsulfonylvinamidinium salt **1a** could be prepared in the standard manner from the appropriately substituted acetic acid (Scheme 1).

Scheme 1



We felt that this was an important transformation since the vinamidinium salt could act as a "carrier" for the phenylsulfonyl group and this could prove useful as either a manipulateable functional group [4] or as an important pharmacophore [5]. The conversion as depicted in Scheme 2 to a pyrimidine is illustrative of this concept.

Scheme 2



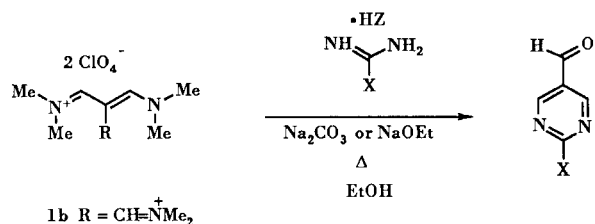
The phosphoryl moiety is also an important functional group [6], and methods for the incorporation of such in heterocyclic systems are not widely available. To this end we decided to examine the use of phosphonoacetic acid as a precursor to a potential phosphonic acid appended vinamidinium salt **1c**.

To our surprise, when the reaction was carried out, the phosphorylated vinamidinium salt **1c** was not obtained, but the 2-dimethylaminomethylene-1,3-bis(dimethylimmonio)propane bisperchlorate (**1b**) was isolated in good yield (59%) as the only product. This compound **1b** has been previously prepared by Arnold and co-workers [7,8] from α -haloacetic acids under similar conditions and in comparable yield. It should also be pointed out that Wudl and co-workers [9] have reported a modification of the original procedure for the preparation of this compound **1b** which involves isolating the product as the tetrafluoroborate salt as opposed to the perchlorate.

We have obtained the 2-iminovinamidinium salt **1b** by Arnold's procedure and this substance is identical in its physical properties to the substance generated from phosphonoacetic acid under Vilsmier-Haack conditions. It is not clear at this time what the mechanism might be for this dephosphonylation process. We have on occasion isolated the 2-unsubstituted vinamidinium salt **1d** from such reaction mixtures in variable yield and it may well be a key intermediate in the process. The phosphonoacetic acid process for the preparation of the 2-iminovinamidinium salt **1b** has distinct advantages over the haloacetic acid method since the reaction is less exothermic and easier to control, and the phosphonoacetic acids (both the diacid and the *O,O*-diethylphosphonylacetic acid can be used) are less of an irritant than the α -haloacids.

With this unique vinamidinium salt **1b** in hand we thought that we would examine some applications in heterocyclic synthesis. When this compound **1b** was reacted with guanidine bicarbonate in ethanol and base, a very good yield of the 2-amino-5-formylpyrimidine was isolated after an aqueous work up (Table 1). Such a transformation has significant value in the preparation of regioselectively functionalized heterocycles since during the reaction or the isolation step a dimethylimino group is transformed to an aldehyde. Such regioselectively formylated pyrimidines are not easily accessible and are not widely represented in the literature [10]. This process is very general and a variety of amidines have been examined and are represented in Table 1.

Table 1



Compound	X	Z	% Yield [a]
4a	3-NO ₂ Ph	Cl	93 (75)
4b	NMe ₂	HSO ₂	(65)
4c	NHEt	Cl	(70)
4d	OMe	HSO ₄	95 (80)
4e	Me	Cl	100 (20)
4f [b]	SMe	HSO ₄	(100)
4g	Ph	Cl	(84)
4h	NH ₂	HCO ₃	(93)

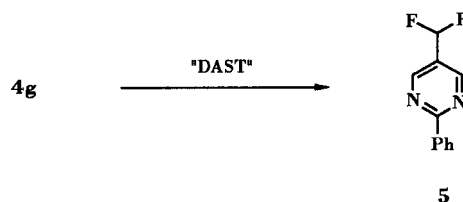
[a] Yields in parenthesis are after recrystallization. [b] No base was used in this reaction.

All of the examples reported in Table 1 worked well with the exception of the 2-methylthiopyrimidine-5-carboxaldehyde (**4f**). When this reaction was carried out in the standard manner with base, the 2-*N,N*-dimethylaminopyrimidine-5-carboxaldehyde (**4b**) was isolated unexpectedly. This presumably happens because dimethylamine is released in the reaction of the vinamidinium salt under basic conditions and displaces the thiomethyl group. When this reaction is run in the absence of base, the desired 2-thiomethyl-5-formylpyrimidine (**4f**) is produced in high yield since the dimethylamine is present as the salt and cannot react. This theory was tested by reacting the 2-thiomethyl-5-formylpyrimidine (**4f**) with dimethylamine under the standard reaction conditions which provided the 2-*N,N*-dimethylaminopyrimidine-5-carboxaldehyde (**4b**) as the only product.

To demonstrate the utility of these formylated pyrimi-

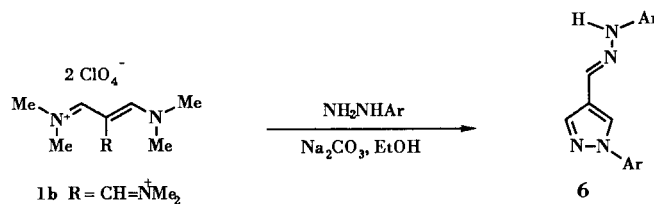
dines we have converted the 2-phenylpyrimidine-5-carboxaldehyde (**4g**) to the corresponding gem-difluoro analog **5** in good yield (Scheme 3) using the DAST reagent (diethylaminosulfur trifluoride) [11]. Therefore, the aldehyde group becomes a convenient vehicle for functional group interconversion.

Scheme 3



The next reaction that we chose to evaluate was the condensation of the 2-iminovinamidinium salt **1b** with mono-substituted hydrazines. This selection was made since the hydrazine represents a 1,2-dinucleophile and the anticipated product would be a regioselectively formylated pyrazole (Table 2). Such a reaction may also be important due to the wide range of biological activities demonstrated [12] by functionalized pyrazoles. The results of this study are reported in Table 2.

Table 2



Compound	Ar	% Yield [a]
6a	4-MePh	68 (57)
6b	4-ClPh	92 (74)
6c	4-MePh	69 (58)
6d	4-BrPh	95 (84)
6e	4-MePhSO ₂	100
6f	Ph	88 (53)

[a] Yields in parenthesis are after recrystallization.

Instead of obtaining the expected 1-aryl-4-formylpyrazoles by such a reaction, the corresponding hydrazones were obtained in good yield. Although the reaction stoichiometry for the conversion of the vinamidinium salt to the hydrazine was 1:1, a 1:2 adduct was obtained. Attempts to obtain the 1:1 adduct were not successful and the reaction was optimized in favor of the 1:2 adduct. Wudl has reported [13] a single example of the 2-iminovinamidinium salt **1b** reacting with hydroxylamine in which case a similar 1:2 adduct (an oximinooxazole) is obtained. These examples may well suggest that a bis adduct is

formed rapidly in a first step which is followed by ring closure. Regardless of the mechanistic pathway, the overall process represents an efficient and simple synthesis of regioselectively functionalized pyrazoles.

In summary, an alternative procedure has been described to prepare a 2-iminovinamidinium salt. This substance has been shown to be a useful vehicle for the incorporation of a formyl or masked formyl group into selected heterocycles. There is little doubt that other interesting and useful reactions of this unusual vinamidinium salt will be uncovered.

EXPERIMENTAL

The following procedures are typical of the experimental conditions used for the preparation and the reaction of the vinamidinium salt. Infrared spectra were obtained on a Perkin-Elmer Model 1420 instrument as either nujol mulls or potassium bromide pellets. High field nmr spectra were obtained in deuteriochloroform or dimethylsulfoxide- d_6 with a Varian Gemini 200 spectrometer. All melting points are uncorrected.

Preparation of 2-Dimethylaminomethylene-1,3-bis(dimethylimmonio)propane Bisperchlorate (**1b**) from Phosphonoacetic Acid.

A 500 ml, three-necked flask was equipped with a condenser, magnetic stirring, thermometer, mineral oil bubbler and a nitrogen atmosphere. Phosphorous oxychloride (49.3 g, 0.321 mole) and *N,N*-dimethylformamide (46.9 g, 0.643 mole) were added to the flask along with 15.0 g (0.107 mole) of phosphonoacetic acid. This mixture was heated at 110-120° until gas evolution ceased (approximately 2 hours). The reaction mixture was cooled to room temperature and carefully poured into a cold solution of 32.3 g of perchloric acid in 150 ml of methanol. The cold solution was allowed to stand for a few minutes and the resulting solid was removed by filtration and dried at room temperature *in vacuo* to yield 24.1 g (59% yield) of tan solid which had mp 222-223° (lit [7] 217-226°); pmr (dimethyl sulfoxide- d_6): δ 3.33 (s, 9H, N-CH₃), 3.50 (s, 9H, N-CH₃) and 8.40 (s, 3H, CH); cmr (dimethyl sulfoxide- d_6): δ 43.11, 48.83, 91.12 and 164.94; ir (nujol): ν 1620 cm⁻¹. The analogous reaction with the *O,O*-diethylphosphonoacetic acid works equally well.

Isolation of the Unsubstituted Vinamidinium Salt **1d**.

Phosphonoacetic acid (0.7 g, 0.005 mole) was added to a solution prepared by adding oxalyl chloride (1.46 g, 0.02 mole) to dimethylformamide (1.46 g, 0.02 mole) in chloroform (8 ml). The mixture was heated to 50° until the evolution of gas ceased (4 hours). The solvent was removed *in vacuo* and the residue was treated with methanol (10 ml) followed by perchloric acid (0.5 ml, 70%) in methanol (2 ml). Some impure vinamidinium salt **1b** was removed by filtration and another portion of perchloric acid (0.5 ml) was added to the mother liquor and after cooling to -50° the unsubstituted vinamidinium salt **1d** separated as a crystalline material. After recrystallization from ethanol, 150 mg (12% yield) of the unsubstituted vinamidinium salt **1d** was obtained which exhibited a mp of 119-120° (lit [14] mp 120°) and was spectroscopically (nmr, ir and uv) identical to the reported values. The reaction of the *O,O*-dimethylphosphonoacetic acid proceeds in

analogous fashion.

2-(3-Nitrophenyl)pyrimidine-5-carboxaldehyde (**4a**).

Into a 200 ml, three-necked flask equipped with a condenser, magnetic stirring and a nitrogen atmosphere was placed 0.157 g (0.00393 mole) of a 60% by weight dispersion of sodium hydride. The sodium hydride was washed with hexane, and the hexane was removed *via* cannula. Ethanol (70 ml) was added to the reaction vessel, and after stirring for several minutes, 3-nitrobenzamidinium hydrochloride (0.264 g, 0.00133 mole) and vinamidinium salt (0.5 g, 0.00131 mole) **1b** were added, respectively. The reaction mixture was refluxed for 2 hours, and the solvent was removed *in vacuo*. The residue was partitioned between water (50 ml) and chloroform (3 x 50 ml) and, after drying the chloroform extracts over anhydrous magnesium sulfate, they were concentrated *in vacuo* to yield a solid. The solid was purified by recrystallization from ethanol-water to produce 0.283 g (93% yield) of the pyrimidine **4a** which had mp 144-147°; pmr (dimethyl sulfoxide- d_6): δ 7.90 (t, J = 6.4 Hz, 1H, CH), 8.48 (d, J = 6.4 Hz, 1H, CH), 8.90 (d, J = 6.4 Hz, 1H, CH), 9.20 (s, 1H, CH), 9.45 (s, 2H, CH), and 10.20 (s, 1H, CH); cmr (dimethyl sulfoxide- d_6): δ 123.2, 126.7, 127.8, 131.2, 134.8, 138.1, 148.8, 159.4, 164.5 and 191.3; ir (potassium bromide): ν 1702, 1527 and 1352 cm⁻¹; ms: (m/e) 229 (M⁺).

Anal. Calcd. for C₁₁H₇N₃O₃: C, 57.64; H, 3.08; N, 18.34. Found: C, 57.99; H, 3.25; N, 18.35.

2-*N,N*-Dimethylaminopyrimidine-5-carboxaldehyde (**4b**) from 2-Methylthiopyrimidine-5-carboxaldehyde (**4f**).

Into a 50 ml flask equipped with a condenser, magnetic stirring and a nitrogen atmosphere was placed 0.05 g (0.000325 mole) of 2-methylthiopyrimidine-5-carboxaldehyde (**4f**). Ethanol was added along with 0.04 g (0.000256 mole) of sodium carbonate and 0.06 g (0.000735 mole) of dimethylamine hydrochloride. The mixture was refluxed for several hours, and the solvent was removed *in vacuo* and the residue was partitioned between water (50 ml) and chloroform (3 x 50 ml). After drying the chloroform extracts over anhydrous magnesium sulfate and concentration *in vacuo*, a solid was obtained. Recrystallization from ethanol-water gave 0.0490 g (100% yield) of the pyrimidine **4b** which had mp 267-268° dec; pmr (deuteriochloroform): δ 3.30 (s, 6H, N(CH₃)₂), 8.72 (s, 2H, CH), and 9.78 (s, 1H, CH); cmr (deuteriochloroform): δ 37.7, 119.6, 161.0, 163.5, and 188.6; ir (potassium bromide): ν 1688 cm⁻¹; ms: (m/e) 151 (M⁺).

Anal. Calcd. for C₇H₇N₃O: C, 55.61; H, 6.01; N, 27.80. Found: C, 55.90; H, 5.81; N, 27.68.

2-Aminopyrimidine-5-carboxaldehyde (**4h**).

This compound had mp 190-195°; pmr (dimethyl sulfoxide- d_6): δ 7.88 (broad s, 2H, NH₂), 8.72 (s, 2H, CH), and 9.72 (s, 1H, CH); cmr (dimethyl sulfoxide- d_6): δ 120.3, 161.4, 165.5, and 189.1; ir (nujol): ν 3296, 3150 and 1695 cm⁻¹; ms: (m/e) 123 (M⁺).

Anal. Calcd. for C₅H₅N₃O: C, 48.77; H, 4.10. Found: C, 48.38; H, 4.08.

2-Methylthiopyrimidine-5-carboxaldehyde (**4f**).

This compound had mp 79-83° (lit [10] 84°); pmr (deuteriochloroform): δ 2.62 (s, 3H, CH₃), 8.90 (s, 2H, CH) and 10.0 (s, 1H, CH); cmr (deuteriochloroform): δ 37.8, 119.6, 161.0, 163.6, and 188.7; ir (nujol): ν 1688 cm⁻¹; ms: (m/e) 154 (M⁺).

Anal. Calcd. for C₆H₆N₂OS: C, 46.73; H, 3.93; N, 18.17. Found: C, 46.45; H, 4.16; N, 18.16.

2-Methylpyrimidine-5-carboxaldehyde (**4e**).

This compound had mp 68-69°; pmr (deuteriochloroform): δ 2.85 (s, 3H, CH₃), 9.10 (s, 2H, CH), and 10.10 (s, 1H, CH); cmr (deuteriochloroform): δ 26.8, 126.7, 150.8, 179.7, and 189.6; ir (nujol): ν 1704 cm⁻¹; ms: (m/e) 122 (M⁺).

Anal. Calcd. for C₆H₆N₂O: C, 59.00; H, 4.96; N, 22.94. Found: C, 58.91; H, 5.01; N, 22.81.

2-Phenylpyrimidine-5-carboxaldehyde (**4g**).

This compound had mp 121-123°; pmr (dimethyl sulfoxide-d₆): δ 7.58 (m, 3H, CH), 8.48 (d, J = 6 Hz, 2H, CH), 9.31 (s, 2H, CH), and 10.15 (s, 1H, CH); cmr (dimethyl sulfoxide-d₆): δ 127.1, 129.0, 129.3, 132.5, 136.4, 159.2, 166.6, and 191.4; ir (nujol): ν 1701 cm⁻¹; ms: (m/e) 184 (M⁺).

Anal. Calcd. for C₁₁H₈N₂O: C, 71.72; H, 4.39; N, 15.21. Found: C, 71.58; H, 4.52; N, 15.29.

2-Ethylaminopyrimidine-5-carboxaldehyde (**4c**).

This compound had mp 131-133°; pmr (deuteriochloroform): δ 1.23 (t, J = 6.5 Hz, 3H, CH₃), 3.53 (pent, J = 6.5 Hz, 2H, CH₂), 8.68 (s, 1H, CH), 8.73 (s, 1H, CH) and 9.90 (s, 1H, CH); cmr (deuteriochloroform): δ 14.8, 36.9, 121.1, 160.9, 162.1, 164.2 and 188.5; ir (nujol): ν 3225 and 1691 cm⁻¹; ms: (m/e) 151 (M⁺).

Anal. Calcd. for C₈H₉N₃O: C, 55.61; H, 6.01; N, 27.80. Found: C, 55.33; H, 6.06; N, 27.76.

2-Methoxypyrimidine-5-carboxaldehyde (**4d**).

This compound had mp 89-90°; pmr (dimethyl sulfoxide-d₆): δ 4.01 (s, 3H, CH₃), 9.10 (s, 2H, CH) and 10.01 (s, 1H, CH); cmr (dimethyl sulfoxide-d₆): δ 55.7, 124.8, 162.2, 167.4, and 190.3; ir (nujol): ν 1701 cm⁻¹; ms: (m/e) 138 (M⁺).

Anal. Calcd. for C₈H₈N₂O₂: C, 52.16; H, 4.39; N, 20.28. Found: C, 52.25; H, 4.42; N, 20.20.

Preparation of 2-Phenyl-5-difluoromethylpyrimidine (**5**).

Into a 25 ml, round-bottomed flask was placed 2-phenylpyrimidine-5-carboxaldehyde (**4g**) (0.50 g, 0.00272 mole) and 10 ml of 1,1,1-trichloroethane. A condenser, was installed along with magnetic stirring, and the apparatus was flushed with nitrogen. Diethylaminosulfur trifluoride (0.44 g, 0.00273 mole) was added slowly and the resulting mixture was refluxed for 30 minutes. After cooling to room temperature, the mixture was extracted with water (2 x 25 ml) and dried over anhydrous magnesium sulfate. Concentration of the organic extracts *in vacuo* gave a residue which was recrystallized from an ethanol-water mixture to yield 0.44 g (61%) of a light-yellow solid **5** which exhibited mp 95-97°; pmr (deuteriochloroform): δ 6.80 (t, J = 55 Hz, 1H, CHF₂), 7.50 (m, 3H, aromatic CH), 8.45 (m, 2H, aromatic CH), and 8.91 (s, 2H, heteroaromatic CH); cmr (deuteriochloroform): δ 113.0 (t, J = 240 Hz), 125.9 (t, J = 24.9 Hz), 129.1, 129.2, 132.1, 137.1, 155.5 (t, J = 6 Hz) and 167.0; ir (nujol) no observable C=O; ms: (m/e) 206 (M⁺).

Anal. Calcd. for C₁₁H₈N₂F₂: C, 64.07; H, 3.92; N, 13.59. Found: C, 63.98; H, 4.00; N, 13.25.

1-Phenyl-4-pyrazolecarboxaldehyde Phenylhydrazone (**6f**).

Into a 250 ml, three-necked flask equipped with a condenser, magnetic stirring and a nitrogen atmosphere was placed 0.38 g (0.0036 mole) of sodium carbonate and 60 ml of absolute ethanol. This was followed by the addition of 0.38 g (0.0026 mole) of phenylhydrazine hydrochloride and 0.50 g (0.0013 mole) of the vin-

amidinium salt **1b**. The solution was stirred for 24 hours at room temperature, the solvent was removed *in vacuo* and water was added to the solid residue. The mixture was filtered and the resulting solid was recrystallized from ethanol-water and vacuum dried to give 0.29 g (85% yield) of solid which exhibited mp 168-172°; pmr (dimethyl sulfoxide-d₆): δ 6.70 (t, J = 7.8 Hz, 1H, CH), 7.03 (d, J = 7.8 Hz, 2H, CH), 7.20 (t, J = 7.8 Hz, 2H, CH), 7.30 (t, J = 7.8 Hz, 1H, CH), 7.50 (t, J = 7.8 Hz, 2H, CH), 7.85 (m, 3H, CH), 8.04 (s, 1H, CH), 8.72 (s, 1H, CH), and 10.12 (s, 1H, NH); cmr (dimethyl sulfoxide-d₆): δ 112.02, 118.47, 118.57, 121.65, 125.69, 126.61, 129.34, 129.56, 129.87, 139.04, 139.76, and 145.84; ir (nujol): ν 3230 and 1598 cm⁻¹; ms: (m/e) 262 (M⁺).

Anal. Calcd. for C₁₆H₁₄N₄: C, 73.26; H, 5.31; N, 21.36. Found: C, 73.02; H, 5.32; N, 21.34.

1-(4'-Methylphenyl)-4-pyrazolecarboxaldehyde 4'-Methylphenylhydrazone (**6a**).

This compound had mp 194-196°; pmr (dimethyl sulfoxide-d₆): δ 2.20 (s, 3H, CH₃), 2.35 (s, 3H, CH₃), 6.92 (d, J = 7.8 Hz, 2H, CH), 7.00 (d, J = 7.8 Hz, 2H, CH), 7.31 (d, J = 7.8 Hz, 2H, CH), 7.76 (d, J = 7.8 Hz, 2H, CH), 7.80 (s, 1H, CH), 8.00 (s, 1H, CH), 8.18 (s, 1H, CH), and 10.02 (s, 1H, NH); cmr (dimethyl sulfoxide-d₆): δ 20.22, 20.43, 112.05, 118.40, 121.53, 121.53, 127.02, 129.02, 129.76, 130.23, 135.92, 137.60, 138.69, and 143.64; ir (nujol): ν 3330 and 1654 cm⁻¹; ms: (m/e) 290 (M⁺).

Anal. Calcd. for C₁₈H₁₈N₄: C, 74.46; H, 6.25; N, 19.3. Found: C, 74.15; H, 6.34; N, 19.35.

1-(4'-Chlorophenyl)-4-pyrazolecarboxaldehyde 4'-Chlorophenylhydrazone (**6b**).

This compound had mp 168-170°; pmr (dimethyl sulfoxide-d₆): δ 7.05 (d, J = 8 Hz, 2H, CH), 7.10 (d, J = 8 Hz, 2H, CH), 7.25 (d, J = 8 Hz, 2H, CH), 7.93 (d, J = 8 Hz, 2H, CH), 7.96 (s, 1H, CH), 8.10 (s, 1H, CH), 8.82 (s, 1H, CH) and 10.32 (s, 1H, NH); cmr (dimethyl sulfoxide-d₆): δ 113.46, 120.14, 121.74, 121.85, 126.05, 129.13, 129.80, 130.27, 130.75, 138.57, 139.49, and 144.73; ir (nujol): ν 3330 and 1601 cm⁻¹; ms: (m/e) 330, 332 (M⁺).

Anal. Calcd. for C₁₆H₁₂Cl₂N₄: C, 58.02; H, 3.66. Found: C, 57.78; H, 3.37.

1-(4'-Methoxyphenyl)-4-pyrazolecarboxaldehyde 4'-Methoxyphenylhydrazone (**6c**).

This compound had mp 175-177°; pmr (dimethyl sulfoxide-d₆): δ 3.70 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), 6.84 (d, J = 8.5 Hz, 2H, CH), 7.00 (d, J = 8.5 Hz, 2H, CH), 7.09 (d, J = 8.5 Hz, 2H, CH), 7.79 (d, J = 8.5 Hz, 2H, CH), 7.81 (s, 1H, CH), 7.98 (s, 1H, CH), 8.60 (s, 1H, CH), and 9.88 (s, 1H, NH); cmr (dimethyl sulfoxide-d₆): δ 55.40, 55.54, 79.35, 113.06, 114.88, 120.05, 121.44, 125.20, 128.75, 133.50, 138.40, 140.07, 152.70, and 158.06; ir (nujol): ν 3325 cm⁻¹; ms: (m/e) 322 (M⁺).

Anal. Calcd. for C₁₈H₁₈N₄O₂: C, 67.05; H, 5.64; N, 17.38. Found: C, 66.83; H, 5.34; N, 17.00.

1-(4'-Bromophenyl)-4-pyrazolecarboxaldehyde 4'-Bromophenylhydrazone (**6d**).

This compound had mp 176-177°; pmr (dimethyl sulfoxide-d₆): δ 7.00 (d, J = 9.1 Hz, 2H, CH), 7.36 (d, J = 9.1 Hz, 2H, CH), 7.70 (d, J = 9.1 Hz, 2H, CH), 7.85 (m, 3H, CH), 8.10 (s, 1H, CH), 8.80 (s, 1H, CH), and 10.35 (s, 1H, NH); cmr (dimethyl sulfoxide-d₆): δ 109.33, 113.97, 118.92, 120.44, 121.73, 126.04, 130.34, 131.96, 132.72, 138.95, 139.54 and 145.07; ir (nujol): ν 3330 and 1596

cm⁻¹; ms: (m/e) 418 and 420 (M⁺).

Anal. Calcd. for C₁₆H₁₂Br₂N₄: C, 45.74; H, 2.88; N, 13.34.
Found: C, 45.79; H, 2.60; N, 13.28.

1-(4'-Methylphenylsulfonyl)-4-pyrazolecarboxaldehyde 4'-Methylphenylsulfonylhydrazone (**6e**).

This compound had mp 164-166°; pmr (dimethyl sulfoxide-d₆): δ 2.34 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 7.39 (d, J = 7.2 Hz, 2H, CH), 7.48 (d, J = 7.2 Hz, 2H, CH), 7.73 (d, J = 7.2 Hz, 2H, CH), 7.83 (s, 1H, CH), 7.87 (d, J = 7.2 Hz, 2H, CH), 8.08 (s, 1H, CH) and 8.70 (s, 1H, CH); cmr (dimethyl sulfoxide-d₆): δ 20.98, 21.17, 120.89, 127.49, 128.14, 129.96, 130.79, 132.23, 133.20, 136.38, 138.76, 143.12, 143.80, and 146.92; ir (nujol): ν 3179 and 1621 cm⁻¹; ms: (m/e) 418 (M⁺).

Anal. Calcd. for C₁₈H₁₈N₄O₄S₂: C, 51.66; H, 4.34; N, 13.39.
Found: C, 51.70; H, 4.71; N, 12.99.

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