

D. Keith Anderson*, James A. Sikorski, David B. Reitz and Linda T. Pilla

Monsanto Agricultural Products Company, Research Department, 800 N. Lindbergh Blvd.,
St. Louis, Missouri 63167

Received December 3, 1985

The metalation chemistry of several 1-substituted-1*H*-1,2,4-triazoles has been investigated. When various alkyl groups were incorporated in the 1-position, lithiation proceeded exclusively at C-5. The 1-trityl-, 1-methyl-, and 1-benzyl-5-lithio-1,2,4-triazoles were stable at -78° and reacted cleanly with a variety of electrophiles. The 1-benzyl and 1-methyl derivatives were synthetically more versatile and could be successfully utilized to prepare several examples of the previously unknown 1,2,4-triazol-5-yl phosphonates.

J. Heterocyclic Chem., **23**, 1257 (1986).

Introduction.

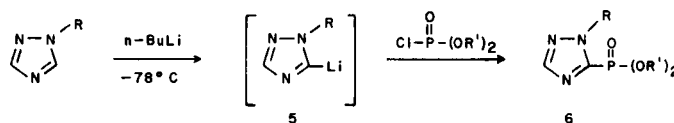
Many heterocyclic ring systems which contain electronegative heteroatoms (*e.g.*, nitrogen, oxygen or sulfur) are known to undergo facile metalation at the sp^2 hybridized carbon that is alpha to the heteroatom (α -lithiation). Alpha lithiation has been synthetically utilized primarily in families of five-membered heterocycles, especially in the thiazole and thiophene ring systems. More recently α -lithiation of hetero-substituted olefins has also gained considerable interest as a synthetic tool [1].

It has been suggested that the initial step of α -lithiations, particularly with π excessive heterocycles, is the precoordination of the lithiating agent with the heteroatom [2], analogous to the precoordination step of ortho lithiations. More recent evidence, as pointed out by Gschwend and Rodriguez [1], suggests, however, that the rate enhancement and regioselectivity of most α -lithiations is due to the inherent higher acidity of the hydrogen at the α -positions rather than precoordination [3].

One heterocyclic system which has received minimal attention for α -lithiation studies is the 1*H*-1,2,4-triazole ring system. Only three reports [4,5,6] of 1,2,4-triazole metalations have appeared. Two of these reports discussed the low temperature lithiation of 1-benzyl-3-phenyl-1*H*-1,2,4-triazole, **1**, with *n*-butyllithium, followed by quenching

with benzophenones or formaldehyde to give the corresponding 1-benzyl-3-phenyl-1*H*-1,2,4-triazol-5-yl carbinols **2** in high yield. The third report described the lithiation of 1-methyl-1*H*-1,2,4-triazole, **3**, as a route to the trimethylstannane **4**. Spectral data were presented for **4** but proof of its regiochemistry was not discussed.

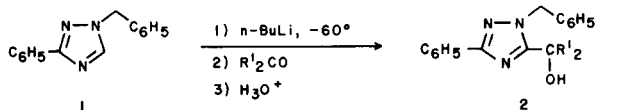
Our interest in this area arose from a desire for a general, direct and efficient route to 1-substituted-1*H*-1,2,4-triazol-5-yl phosphonates **6** which were previously unknown. An electrophilic method which utilized a lithiated triazole **5** and a chlorophosphate quench appeared to be an attractive approach to the synthesis of **6**.



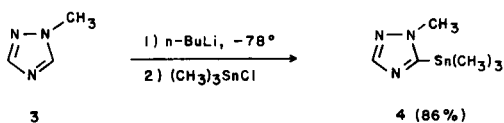
While this approach appears to be very straightforward, several important questions need to be addressed. The metalation reaction must proceed regioselectively to avoid 3- and 5- substituted isomeric mixtures. Literature precedent in other heterocyclic system [7], as well as the previously discussed stannane example [6], suggests that lithiation at C-5 should predominate but the possibility of some lithiation at C-3 had to be considered. The intermediate lithiated triazole **5** must be stable at low temperature to be efficiently trapped by the chlorophosphate or other less reactive electrophiles. In order for this approach to be general, a variety of suitable substituents should be accommodated at the 1-position. These substituents should be compatible with the metalation conditions and should preferably be introduced regioselectively at the 1-position. This report describes the results of our study of the α -lithiation chemistry of 1-substituted-1*H*-1,2,4-triazoles.

Results and Discussion.

It was first necessary to determine if carbon-phosphorus bond formation *via* a lithiated triazole is a viable process.

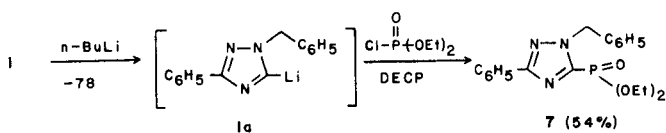


R'	% Yield
C ₆ H ₅ -	92
4-CH ₃ O-C ₆ H ₄ -	94
4-(CH ₃) ₂ N-C ₆ H ₄ -	91
H	78

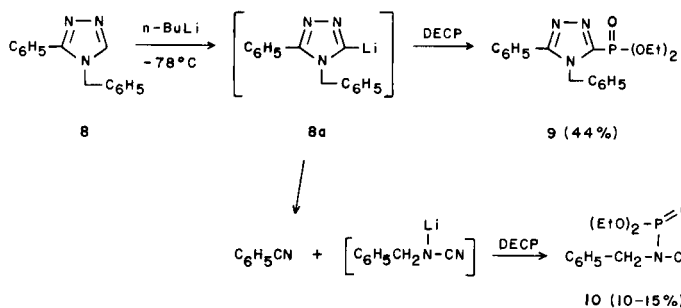


1-Benzyl-3-phenyl-1*H*-1,2,4-triazole, **1** [4,5], was chosen for the initial lithiation studies. This compound has only one available site for α -lithiation thus regiochemical problems were avoided. Treatment of **1** with 1.1 molar equivalents of *n*-butyllithium at -78° in THF gave a dark red solution which turned pale yellow when quenched with a slight excess of diethyl chlorophosphate (DECP).

Work-up gave the desired 1-benzyl-3-phenyl-1,2,4-triazol-5-yl phosphonic acid diethyl ester **7**, in 54% isolated yield. Purification of **7** was accomplished by preparative hplc and the yield is unoptimized. The nmr evaluation of the crude product mixture indicated that the conversion was substantially higher than indicated by this yield with the only detectable by-product being 10-15% unreacted triazole **1**.



The isomeric 3-phenyl-4-benzyl-4*H*-1,2,4-triazole, **8**, reacted similarly to give a 44% yield of 3-phenyl-4-benzyl-4*H*-1,2,4-triazol-5-yl phosphonic acid diethyl ester, **9**. The nmr analysis again indicated that the conversion was better than 70% with 10% recovered **8** and a third minor component (10-15%) as the only impurities in the crude product mixture. The third component was identified as *N*-cyano-*N*-benzylaminophosphonic acid diethyl ester, **10**. Evidently the 5-lithiated intermediate **8a** undergoes some anion mediated ring opening [8] at -78° to produce **10** after quenching with DECP. A similar ring-opening can be envisioned for **1a** but the absence of **10** in the crude product mixture indicates that **1a** is more stable than **8a** at -78° .

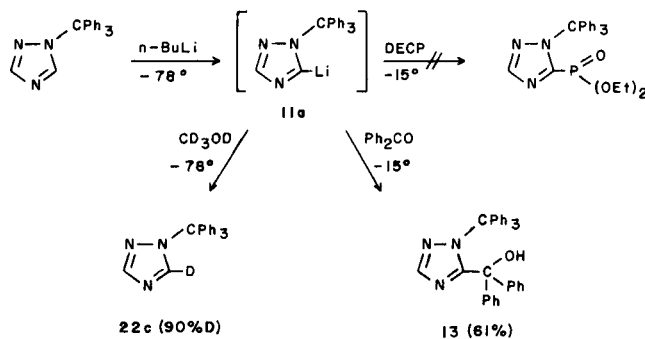


Lithiation Chemistry of Triazole 1-Benzyl Derivatives.

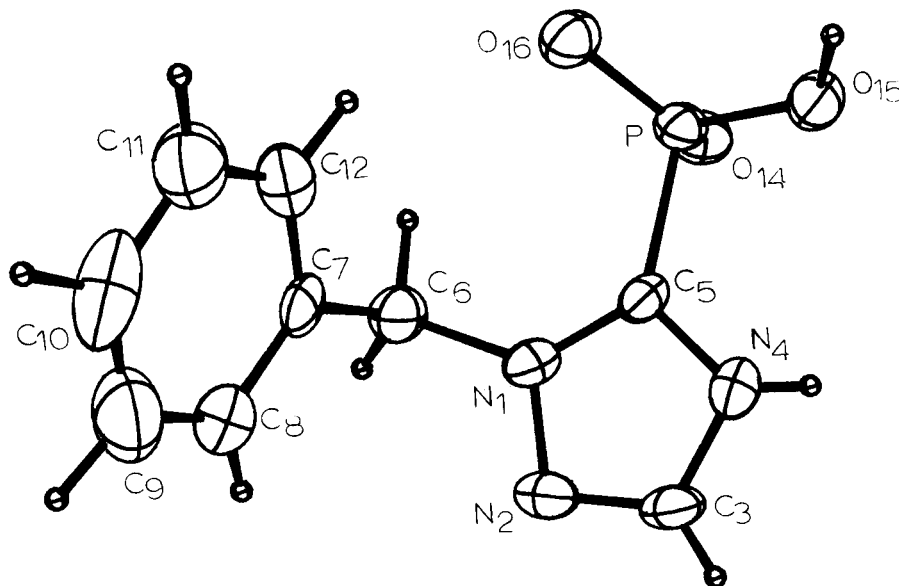
The triphenylmethyl group [9] can be cleaved under a variety of different conditions (acidic, reductive) and should be inert to lithiation at low temperature. 1-Triphenylmethyl-1*H*-1,2,4-triazole, **11**, was prepared and its lithiation chemistry was investigated. Compound **11** was treated with *n*-butyllithium at -78° and quenched with perdeuteriomethanol. The nmr analysis indicated that the

reaction was regiospecific within the limits of ^1H nmr integration. The triazole proton at lower field (8.1 ppm, deuteriochloroform, 60 MHz) was reduced by $\sim 92\%$ while the higher field signal (7.95 ppm) appeared to be unchanged after deuteration. In 1-substituted-1*H*-1,2,4-triazoles the proton at C-5 generally gives a lower field signal than the proton at C-3 [10] indicating that C-5 is most likely the preferred site for lithiation under these conditions. Lithiation studies on other nitrogen heterocycles also suggest that C-5 should undergo α -lithiation more readily than C-3 [7]. However, the small difference in chemical shifts of the C-3 and C-5 protons (0.1 ppm) made the regiochemical assignment quite tentative.

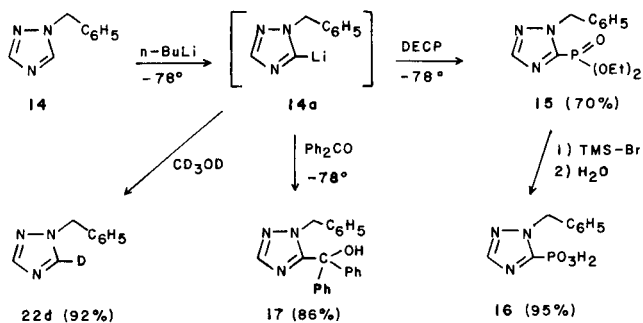
Surprisingly, when the lithiated intermediate **11a** was quenched with DECP none of the desired phosphonate **12** was formed. Warming to -15° and stirring overnight still led only to recovered **11**. The large triphenylmethyl group of **11** evidently shields the lithiated 5-position of **11a**, preventing it from reacting with the bulky chlorophosphate. When **11a** was quenched with benzophenone and warmed to -15° the carbinol **13** was formed and isolated in 61% yield. Since the metalation chemistry of **11** appeared limited by the large steric requirements of the triphenylmethyl group, its chemistry was not investigated further.



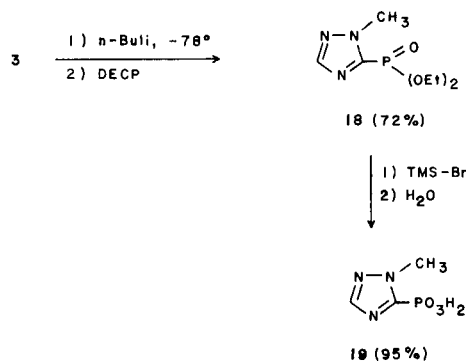
The metalation chemistry of the less sterically hindered 1-benzyl-1*H*-1,2,4-triazole, **14** [11], proved much more productive. Lithiation and deuterium quenching (perdeuteriomethanol) resulted in a 90% reduction of the lower field (8.1 ppm, deuteriochloroform, 60 MHz) triazole proton absorption in the ^1H nmr. The higher field component (8.05 ppm) was unchanged, suggesting that lithiation is again occurring at C-5. When the lithiated intermediate **14a** was quenched with DECP, work-up gave a single phosphonate **15** in 70% yield. Treatment of **15** with trimethylsilyl bromide and subsequent hydrolysis gave the corresponding phosphonic acid **16** in 95% yield. An x-ray crystal structure of **16** (see Figure 1) verified that α -lithiation had occurred at C-5 as suggested by the deuterium

Figure 1. X-Ray Crystal Structure of **16**.

trapping studies. This also verifies that the lower field triazole proton absorption in the ^1H nmr belongs to the C-5 proton. Reaction of **14a** with benzophenone at -78° gave **17** in 86% yield. This latter example illustrates the higher reactivity of **14a** relative to **11a** at low temperature.

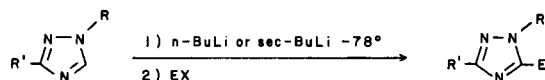


With the regiochemistry of the metalation now clearly established, lithiation/phosphorylation of the 1-methyl derivative **3** was examined. Lithiation of **3** followed by quenching with DECP gave a single phosphonate **18**. Deuteration studies again led to the disappearance of the lower field triazole proton signal (8.3 ppm, deuteriochloroform). This, along with the previously discussed x-ray data indicates that lithiation does occur regioselectively at C-5 of **3**. This is also in agreement with the reported structure of the stannane **4** [6]. Treatment of **18** with excess trimethylsilyl bromide and subsequent hydrolysis gave the phosphonic acid **19**.



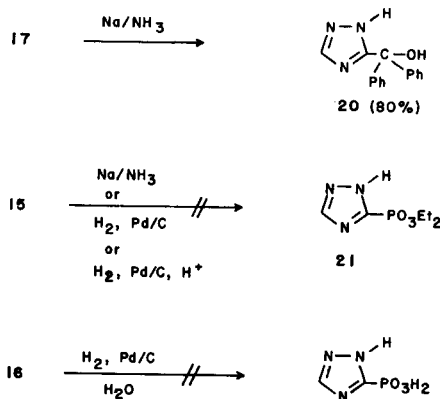
As previously reported by Burgess [4], the *N*-benzyltriazaoles are readily deprotected by treatment with sodium in liquid ammonia. When **17** was treated under these conditions the deprotected triazol-5-yl carbinol **20** was obtained in high yield. As was anticipated, however, when **15** was placed under similar conditions a complicated product mixture was formed and the desired phosphonate **21** was not isolated. The attempted hydrogenolysis of **15** with 10% Pd-C under neutral conditions gave only recovered **15**. This is not surprising since hydrogenolysis of *N*-benzyl-derivatives [16] generally requires acid catalysis. Unfortunately, **15** is not stable under acidic conditions, resulting in carbon-phosphorus bond cleavage. Removal of the benzyl group from **16** also failed due to carbon-phosphorus bond cleavage. To illustrate the versatility of

Table I
Reaction of Lithiated 1,2,4-Triazoles with Electrophiles [a]



Substrate	Electrophile	Product	E	R	R'	Yield (%) [b]
1	DECP	7	-P(O)(OEt) ₂	-CH ₂ Ph	-Ph	54
1	PhS-SPh	22a	-SPh	-CH ₂ Ph	-Ph	50
1	<i>t</i> -BuSiMe ₂ Cl	22b	-SiMe ₂ <i>t</i> -Bu	-CH ₂ Ph	-Ph	50
3	DECP	18	-P(O)(OEt) ₂	-CH ₃	-H	72
11	CD ₃ OD	22c	-D	-CPh ₃	-H	95 [c]
11	Ph ₂ CO	13	-C(OH)Ph ₂	-CH ₂ Ph	-H	86
14	CD ₃ OD	22d	-D	-CH ₂ Ph	-H	95 [c]
14	Ph ₂ CO	17	-C(OH)Ph ₂	-CH ₂ Ph	-H	86
14	DECP	15	-P(O)(OEt) ₂	-CH ₂ Ph	-H	70
14	<i>t</i> -BuSiMe ₂ Cl	22e	-SiMe ₂ <i>t</i> -Bu	-CH ₂ Ph	-H	68
14	CH ₃ I	22f	-CH ₃	-CH ₂ Ph	-H	77
14	Cl ₃ CCl ₃	22a	-Cl	-CH ₂ Ph	-H	80
14	CH ₃ COCl	22h	-CO ₂ CH ₃	-CH ₂ Ph	-H	71

[a] See Experimental for details. [b] Yields are unoptimized and are for isolated and purified material unless otherwise notes. [c] Isolated yield of material with >90% deuterium incorporation.



electrophilic substitution of lithiated 1,2,4-triazoles several other electrophiles were examined. The results of these studies are shown in Table 1.

Conclusion.

We have demonstrated a lithiation procedure that leads to regioselective electrophilic substitution of the 5-position of various 1-alkyl-1,2,4-triazoles. The procedure appears to be fairly general with respect to choice of electrophile and allowed for the first synthesis of several 1-substituted-1,2,4-triazol-5-yl phosphonates. Steric hindrance reduced the reactivity of the 1-trityl derivative, which would not react with some bulky electrophiles. The 1-benzyl and 1-methyl triazoles have greater synthetic versatility and did not suffer from similar problems.

EXPERIMENTAL

General.

Melting points were determined on a Thomas-Hoover or a Laboratory Devices Mel-Temp apparatus and are uncorrected. Boiling points, taken from distillations are also uncorrected. Proton NMR spectra were recorded on a Varian EM-360L (60 MHz) or XL-300 (300 MHz) spectrometer and all chemical shifts are reported in ppm downfield from an internal TMS standard. The ¹³C nmr spectra were recorded on a Varian XL-300 spectrometer and chemical shifts are reported in ppm relative to TMS. The ³¹P nmr spectra were recorded on a JEOL FX-100 spectrometer and chemical shifts are reported in ppm relative to an external co-axial standard of 85% phosphoric acid. High pressure liquid chromatography (hplc) separations were performed on a Waters Associates Prep 500A LC System (PLC-500) instrument using silica gel columns. Chromatotron purification refers to chromatography on Harrison Research's model 7924 Chromatotron using silica gel (4 mm) plates. *n*-Butyllithium and *sec*-butyllithium were obtained from Alfa Products. Anhydrous THF was obtained from Aldrich and used without further drying. All other solvents were Fisher reagent grade. The x-ray structure was solved by Dr. Huey-Sheng Shieh of Monsanto Corporate Research Laboratories. Microanalyses were performed by Atlantic Microlabs, Inc. or by Galbraith Laboratories, Inc.

1-Benzyl-3-phenyl-5-(1,2,4-triazolyl)phosphonic Acid, Diethyl Ester [7].

A solution of 1 [4] (10 g, 43 mmol) in 200 ml of anhydrous THF was cooled to -78° under nitrogen and treated with *n*-butyllithium (19.5 ml of a 2.3 M solution in hexane, 45 mmol) over a 15 minute period. The dark red solution was stirred for 1.5 hours at -78°, then treated with diethylchlorophosphate (7.5 g, 43 mmol) via a syringe. After 30 minutes at -78° the solution (now a pale yellow) was allowed to warm to room temperature and stir overnight. The reaction was quenched with water and concentrated *in vacuo*. Work-up yielded a thick oil which was purified by hplc with 60/40 ethyl acetate/cyclohexane. This gave 7 as a clear oil weighing 8.6 g (54%), *n*_D²⁵ = 1.560; ¹H nmr (deuteriochloroform): 7.9-8.2 (2H, m), 7.1-7.6 (8H, m), 5.4 (2H, s), 4.1 (4H, pentaplet, J = 7

Hz), 1.3 (6H, t, $J = 7$ Hz); ^{31}P nmr (deuteriochloroform): (decoupled) 0.0 (s).

Anal. Calcd. for $\text{C}_{19}\text{H}_{22}\text{N}_3\text{O}_3\text{P}_1$: C, 61.45; H, 5.97; N, 11.31; P, 8.34. Found: C, 61.50; H, 5.95; N, 11.34; P, 8.49.

The following triazoles were prepared using the same general procedure as described for 7.

3-Phenyl-4-benzyl-5-(1,2,4-triazolyl)phosphonic Acid, Diethyl Ester, (9).

This compound was obtained in a yield of 44% (14 g) from **8** after chromatography (60/40 ethyl acetate/cyclohexane on silica); ^1H nmr (deuteriochloroform): 7.4 (5H, s), 6.7-7.5 (5H, m), 5.5 (2H, s), 4.1 (4H, pentuplet, $J = 7$ Hz) 1.3 (6H, t, $J = 7$ Hz); ^{31}P nmr (deuteriochloroform): (decoupled) -0.4 (s).

Anal. Calcd. for $\text{C}_{19}\text{H}_{22}\text{N}_3\text{O}_3\text{P}_1$: C, 61.45; H, 5.97; N, 11.31; P, 8.34. Found: C, 61.06; H, 6.19; N, 11.27; P, 8.41.

Chromatography also yielded 2.7 g (12%) of **10** as a tan oil; ^1H nmr (deuteriochloroform): 7.4 (5H, s), 4.4 (2H, d, $J = 9$ Hz), 4.1 (4H, d of q, $J = 7$ Hz, $J = 7$ Hz, appears as pentuplet), 1.3 (6H, t, $J = 7$ Hz); ^{31}P nmr (deuteriochloroform): (decoupled) -0.85 (s); ir (film): 2230 cm^{-1} (strong and sharp).

Anal. Calcd. for $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_3\text{P}_1$: C, 53.73; H, 6.39. Found: C, 53.85; H, 6.32.

5-(α -Hydroxy- α , α -diphenylmethyl)-1-triphenylmethyl-1*H*-1,2,4-triazole (13).

This compound was obtained in a yield of 61% (60 g) from **11** after chromatography (20/80 toluene/methylene chloride on silica), mp 173-174°; ^1H nmr (deuteriochloroform): 7.96 (1H, s), 6.95-7.30 (25H, bs), 2.00 (1H, s).

Anal. Calcd. for $\text{C}_{38}\text{H}_{27}\text{H}_3\text{O}$: C, 82.73; H, 5.51; N, 8.52. Found: C, 82.89; H, 5.65; N, 8.49.

1-Benzyl-5-(1,2,4-triazolyl)phosphonic Acid, Diethyl Ester (15).

This compound was obtained in a yield of 70% (83 g) from **14** [11] after chromatography (60/40 ethyl acetate/cyclohexane on silica), $n_D^{25} = 1.517$; ^1H nmr (deuteriochloroform): 7.95 (1H, s), 7.0-7.4 (5H, m), 5.65 (2H, s), 4.05 (4H, pentatuplet, $J = 8$ Hz), 1.20 (6H, t, $J = 8$ Hz); ^{31}P NMR (deuteriochloroform); nmr (deuteriochloroform): 0.4 (s).

Anal. Calcd. for $\text{C}_{13}\text{H}_{18}\text{N}_3\text{O}_3\text{P}_1$: C, 52.88; H, 6.14; N, 14.23; P, 10.49. Found: C, 52.87; H, 6.19; N, 14.20; P, 10.56.

1-Benzyl-5-(α -hydroxy- α , α -diphenylmethyl)-1*H*-1,2,4-Triazole (17).

This compound was obtained in a yield of 88% (63 g) from **14** [11] after recrystallization from toluene, mp 174-175°; ^1H nmr (deuteriochloroform): 7.60 (1H, s), 6.90-7.50 (15H, m), 5.10 (2H, s), 4.25 (1H, s).

Anal. Calcd. for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}$: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.50; H, 5.78; N, 12.24.

1-Methyl-5-(1,2,4-triazolyl)phosphonic Acid Diethyl Ester (18).

This compound was obtained in a yield of 72% (9.5 g) from **3** [6] after distillation (90°, 0.3 mm); ^1H nmr (deuteriochloroform): 8.8 (1H, s), 4.5 (4H, pentuplet, $J = 8$ Hz), 4.4 (3H, s, overlapped by pentuplet), 1.4 (6H, t, $J = 8$ Hz); ^{31}P nmr (deuteriochloroform): (decoupled) -0.015 (s).

Anal. Calcd. for $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_3\text{P}$: C, 38.36; H, 6.44; N, 19.17. Found: C, 38.38; H, 6.52; N, 19.17.

1-Benzyl-3-phenyl-5-phenylthio-1*H*-1,2,4-triazole (22a).

This compound was obtained in a yield of 50% (7.3 g) from **1** [4] after recrystallization from methylene chloride/ether, mp 79-82°; ^1H nmr (deuteriochloroform): 7.9-8.2 (2H, m), 7.0-7.4 (13H, m), 5.3 (2H, s).

Anal. Calcd. for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{S}_1$: C, 73.44; H, 4.99; S, 9.34. Found: C, 73.49; H, 5.04; S, 9.48.

1-Benzyl-3-phenyl-5-*t*-butyldimethylsilyl-1*H*-1,2,4-triazole (22b).

This compound was obtained in a yield of 50% (7.1 g) from **1** [4] after chromatography (5/95, ethyl acetate/cyclohexane), mp 87.5-88.5°; ^1H nmr (deuteriochloroform): 8.0-8.3 (2H, m), 6.9-7.5 (8H, m), 5.5 (2H, s), 1.0 (9H, s), 0.3 (6H, s).

Anal. Calcd. for $\text{C}_{22}\text{H}_{27}\text{N}_3\text{Si}$: C, 72.16; H, 7.79; N, 12.02. Found: C, 71.96; H, 7.82; N, 11.98.

1-Benzyl-5-*t*-butyldimethylsilyl-1*H*-1,2,4-triazole (22e).

This compound was obtained in a yield of 68% (91 g) from **14** [11] as an orange oil after chromatography (5/95 ethyl acetate/cyclohexane on silica); ^1H nmr (deuteriochloroform): 7.9 (2H, s), 6.8-7.3 (5H, m), 5.4 (2H, s), 0.9 (9H, s), 0.3 (6H, s).

Anal. Calcd. for $\text{C}_{15}\text{H}_{23}\text{N}_3\text{Si}$: C, 65.88; H, 8.48; N, 15.37. Found: C, 65.75; H, 8.54; N, 15.35.

1-Benzyl-5-methyl-1*H*-1,2,4-triazole (22f).

This compound was obtained in a yield of 77% (8.2 g) from **14** [11] after distillation; ^1H nmr (deuteriochloroform): 7.9 (1H, s), 7.1-7.5 (5H, m), 5.3 (2H, s), 2.4 (3H, s).

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{N}_3$: C, 69.34; H, 6.40. Found: C, 69.03; H, 6.56.

1-Benzyl-5-chloro-1*H*-1,2,4-triazole (22g).

This compound was obtained in a yield of 80% (9.8 g) from **14** [11] as a colorless liquid after distillation (90°, 0.3 mm); ^1H nmr (deuteriochloroform): 7.8 (1H, s); 7.3 (5H, s), 5.3 (2H, s).

Anal. Calcd. for $\text{C}_9\text{H}_8\text{ClN}_3$: C, 55.83; H, 4.16; N, 21.70. Found: C, 55.87; H, 4.19; N, 21.61.

1-Benzyl-5-carbomethoxy-1*H*-1,2,4-triazole (22h).

This compound was obtained in a yield of 71% (4.9 g) from **14** [11] as a white solid after distillation (110°, 0.3 mm), mp 40-42°; ^1H nmr (deuteriochloroform): 8.0 (1H, s), 7.3 (5H, s), 5.8 (2H, s), 4.0 (3H, s).

Anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2$: C, 60.82; H, 5.10; N, 19.34. Found: C, 60.78; H, 5.16; N, 19.35.

1-Benzyl-1*H*-1,2,4-triazol-5-yl Phosphonate (1b).

A solution of **15** (7.5 g, 25 mmoles) in trimethylsilyl bromide [13] (19.4 g, 127 mmoles) was stirred at room temperature under nitrogen for 48 hours. The excess TMS bromide was removed *in vacuo*, the residue was dissolved in THF, and treated with 0.9 ml of water. After stirring overnight the precipitate was filtered, washed with THF and dried *in vacuo*. This gave 5.8 g (95%) of **16** as a white solid, mp 205-206°. This material is readily recrystallized from hot water; ^1H nmr (DMSO- d_6): 8.6 (1H, s), 7.4 (5H, s), 5.7 (2H, s); ^{31}P nmr (DMSO- d_6): (decoupled) -5.3 (s).

Anal. Calcd. for $\text{C}_9\text{H}_{10}\text{N}_3\text{O}_3\text{P}_1$: C, 45.20; H, 4.21; P, 12.95. Found: C, 45.07; H, 4.37; P, 12.92.

1-Methyl-1*H*-1,2,4-triazol-5-yl Phosphonate (19).

A solution of **18** (4.0 g, 18.3 mmoles) in trimethylsilyl bromide [17] (16.8 g, 110 mmoles) was stirred at 40° under a nitrogen atmosphere for 24 hours. The excess TMS-bromide was removed *in vacuo* with careful exclusion of water. The residue was dissolved in THF (50 ml), and treated with 1.0 ml of water. A white precipitate immediately formed and was filtered and dried, to yield 2.8 g (95%) of **19**. No further purification was necessary. ^1H nmr (DMSO- d_6): 8.0 (1H, s), 4.0 (3H, s), 1.5 (2H, broad s) ^{31}P nmr (DMSO): (decoupled) -7.3 (s).

Anal. Calcd. for $\text{C}_5\text{H}_6\text{N}_3\text{O}_3\text{P}$: C, 22.39; H, 3.88; N, 25.27. Found: C, 22.15; H, 3.68; N, 25.03.

5-(α -Hydroxy- α , α -diphenylmethyl)-1*H*-1,2,4-triazole (20).

Following Burgess' procedure [4], a suspension of **17** (37.5 g, 110 mmoles) in liquid ammonia was reduced with sodium (7.0 g, 300 mmoles). The triazole did not go completely into solution and the heterogeneous mixture turned several different colors, *i.e.*, yellow to red to blue, with the addition of small pieces of sodium. A homogeneous solution was obtained after the addition was complete. After 2.5 hours the reaction was carefully quenched with ammonium chloride (18.2 g, 340 mmoles), and the ammonia was allowed to evaporate. The residue (23.5 g) was recrystallized from dimethylformamide/water to give 22.1 g (80%) of colorless **20**, mp 226-227°C; ^1H nmr (DMSO- d_6): 8.20 (1H, s), 6.70-8.40 (11H, m), 5.70 (1H, s).

Anal. Calcd. for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.85; H, 5.33; N, 16.83.

Supplementary Material Available.

Tables of atomic positional parameters, thermal parameters, etc. are available for **16** (4 pages) from the authors.

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