Reactions of 1-Phenyl-1,2,3-triazolyllithium Compounds; Formation of Ketenimines, Alkynylamines, and Heterocycles from the Ambident (*N*-Phenyl)phenylketenimine Anion

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At room temperature 1,4-diphenyl-1,2,3-triazolyllithium rapidly undergoes fragmentation to nitrogen and lithium (*N*-phenyl)phenylketenimine anion 8c, $(C_6H_5 \cong C = NC_6H_5)^{\ominus}Li^{\oplus}$. Some of the reactions of this ambident anion have been studied. Reaction of 8c with methyl iodide results in *C*-methylation to a mixture of (*N*-phenyl)methylphenylketenimine and 3-methyl-1,3-diphenyl-4-(2'-phenylethylene)-2phenyliminoazetidine. A six-membered heterocyclic compound, 6-anilino-1,3,5-triphenyluracil, results from the reaction between 8c and phenyl isocyanate. With dimethyl sulfate and methyl chloroformate *N*-alkylation and *N*-acylation takes place predominantly, forming *N*-methyl-*N*-phenyl-2-phenylethynylamine and *N*-carbomethoxy-*N*-phenyl-2-phenylethynylamine respectively. Reaction of 8c with methanol and ethanethiol gives an iminoester and an iminothioester respectively.

1-Phenyl-1,2,3-triazolyllithium and 4-methyl-1-phenyl-1,2,3-triazolyllithium undergo fragmentation at somewhat higher temperatures.

Le sel de lithium du diphényl-1,4 triazolyl-1,2,3 se fragmente rapidement à la température de la pièce pour donner de l'azote et le sel de lithium de l'anion 8c, $(C_6H_5-C=C-N-C_6H_5)^{\ominus}Li^{\oplus}$. On a étudié quelques unes des réactions de cet anion ambivalent. La réaction de 8c avec l'iodure de méthyle conduit à une C-méthylation fournissant un mélange de (N-phényl) méthylphényleitinimine et de méthyl-3 diphényl-1,3 (phényléthylène-2)-4 phénylimino-2 azètidine. Un composé hétérocyclique à six chaînons, l'amino-6 triphényl-1,3,5 uracile, se forme par réaction entre 8c et l'izocyanate de phényle. Avec le sulfate de méthyle et le chloroformate de méthyle des réactions de N-alkylation et de N-acylation se produisent de façon prépondérante et conduisent respectivement à la formation du N-méthyl N-phényl phényl-2 éthynylamine et de N-carbométhoxy N-phényl phényl-2 éthynylamine et de carbométhoxy N-phényl phényl-2 éthynylamine. Les réactions de 8c avec le méthanol et l'éthanethiol fournissent respectivement une iminoester et une iminothioester.

Par ailleurs la fragmentation des sels de lithium des phényl-1 triazolyl-1,2,3 et méthyl-4 phényl-1 triazolyl-1,2,3 s'effectuent à des températures un peu plus hautes.

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Lithiation of five-membered heteroaromatics has in several instances provided a useful method for the introduction of ring substituents (1). Certain ring systems however undergo fragmentation with elimination of nitrogen under the influence of base, resulting in alkynylthiolates from 1,2,3-thiadiazoles (2, 3), diphenylacetylene from 4,5-diphenyl-1,2,3-thiadiazole (4), carbodiimides from 1,4-disubstituted tetrazolium salts (5), and phenylcyanamide from the reaction between 5-chloro-1-phenyltetrazole and magnesium or n-butyllithium (6). In the following we report our results on the lithiation of some 1-phenyl-1,2,3-triazoles. This investigation was of interest not only for the syntheses of substituted 1,2,3-triazoles, but also for the possible interesting products resulting from a fragmentation of the triazole ring.

In tetrahydrofuran (THF) the triazoles 1 and 4

were all readily lithiated with *n*-butyllithium at -20 to -60° (Scheme 1). Ring lithiation takes place preferentially at the 5-position as was indicated by the products 2, 3, 6, and 7 obtained by methylation or carboxylation. Whereas the reaction product of 1a with n-butyllithium upon reaction with methyl iodide provided 2 as the only isolable product, 4a and b under these conditions gave high yields of the 5-methyl-1,2,3triazoles 5a and b. Solutions of 5a and b were stable at room temperature but decomposed with gas evolution when heated at 40–50°. A solution of 5c readily decomposed at 20° to a yellow to green solution of the ambident N-phenylketenimine anion 8c, displaying strong absorption at 2140 cm⁻¹ in the i.r. The various reactions performed with 8c are outlined in Scheme 2.

Reaction of 8c with methyl iodide resulted exclusively in *C*-methylation and the formation

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of two products, one being the expected (Nphenyl)methylphenylketenimine¹ (9). The structure of 9 was indicated by the n.m.r. and i.r. spectra, the latter showing strong absorption at 2000 cm⁻¹ in agreement with reported ketenimine absorption (8), and was further proven by conversion to N,2-diphenylpropionamide (10) with dilute acid and to the imino ester 11 by reaction with methanol in the presence of a catalytic amount of sodium methoxide. The empirical formula C30H26N2 of the second product, a pale yellow solid melting at 114-115°, indicated a dimer of 9. The n.m.r. spectrum showed the presence of four phenyl groups and two different C-methyl groups; the i.r. spectrum contained bands at 1730 and 1655 cm^{-1} . The compound hydrolyzed slowly upon heating in a mixture of THF and 3 N hydrochloric acid to aniline and a highly viscous compound, $C_{24}H_{21}NO$. The n.m.r. spectrum of this latter compound showed the presence of three phenyl groups and two C-methyl groups; the i.r. spectrum contained strong bands at 1780 and 1680 cm^{-1} , the former band indicating the presence of a β -lactam carbonyl group (9). These observations point to 3-methyl-1,3-diphenyl-4-(2'-phenylethylene)-2-phenyliminoazetidine (12)

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as being the other alkylation product, hydrolysis of which should lead to 3-methyl-1,3-diphenyl-4-(2'-phenylethylene)-2-azetidinone (13). The formation of 12 can be explained by attack of 8c on the initially formed ketenimine 9 followed by methylation of the intermediate 14 with methyl iodide (Scheme 3). In agreement with this it was found that although the relative amounts of 9 and 12 were little affected by the reaction temperature and the mode of addition of the methyl iodide, it strongly depended on the amount of methyl iodide used. The yields of isolated 9 when a 10, 25, and 100% excess of methyl iodide was employed were 17, 28, and 45% respectively, the yields of isolated 12 being 46, 36, and 19% respectively.

In an attempt to extend the synthesis of azetidine derivatives to compounds derived from the anion 15 (Scheme 3), the reaction between equivalent amounts of 8c and phenyl isocyanate was investigated. However no indication for the formation of 15 was obtained and the only product isolated, after treatment of the reaction mixture with water, was 6-anilino-1,3,5-triphenyl-uracil (16; 37%). The structural assignment of 16 is based on the elemental analyses, the n.m.r. and i.r. spectra, and on its hydrolysis to 1,3,5-triphenylbarbituric acid (17) in a boiling mixture of 6 N hydrochloric acid and acetic acid. Apparently the first addition product of 8c to phenyl isocyanate, rather than cyclizing to 15,

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¹The photochemical decomposition of 1-phenyl-1,2,3triazoles has been reported and also results in the formation of ketenimines, *e.g.* from 4c an 80% yield of diphenylketenimine was obtained (7).



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SCHEME 2

21

-0

C₆H₅

ĊH

13



reacts with a second molecule of phenyl isocyanate followed by cyclization to a uracil derivative.

The methylation of 8c took a different course with dimethyl sulfate, for N-methyl-N-phenyl-2phenylethynylamine (18; 42%) was the only product isolated. Only trace amounts of 9 and 12 were detectable in the n.m.r. and i.r. spectra of the crude reaction product. The product showed strong i.r. absorption at 2230 cm⁻¹ in agreement with reported absorptions of alkynylamines (10). Compound 18, m.p. 47–48°, was further characterized by hydrolysis with dilute acid to (N-methyl-N-phenyl)phenylacetamide (19).

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Acylation of 8c with methyl chloroformate gave N-carbomethoxy-N-phenyl-2-phenylethynylamine (20; 40%) as the main product. The formation of a small amount of the ketenimine 21 was evident from the n.m.r. and i.r. spectra of the crude product, but attempts to isolate this material by chromatography or distillation were unsuccessful. Compound 20 represents a new type of alkynylamine. Whereas 18 undergoes an exothermic reaction with dilute acid, 20 was recovered unchanged from a mixture of THF and 1 N sulfuric acid when left at room temperature for 1 h. With methanolic sodium hydroxide 20 underwent a rapid reaction resulting in the formation of sodium methylcarbonate and methyl (N-phenyl)phenylacetimidate (22), the latter material being identical with that obtained from the reaction between methyl phenylthionacetate and aniline (11).

The iminoester 22 was also obtained when methanol was added to the THF solution of 8c(45%). An 80% yield of the iminothioester 23 was obtained from the reaction between 8c and ethanethiol, indicating that ethanethiolate is a more efficient reactant for the intermediate ketenimine.

The fragmentation of 5*a* to 8*a* produced a dianion as the alkylation of both 8*a* and *b* with dimethyl sulfate gave the same product, *N*-methyl-*N*-phenyl-1-propynylamine (24), in yields of 21 and 31% respectively. The addition of methanol to a solution of 8*a* provided a 47% yield of the iminoester 25 and a 37% recovery of 4*a* (Scheme 4).

Experimental

All melting points and boiling points are uncorrected. The i.r. spectra were recorded on a Perkin-Elmer Model 137 "Infracord" spectrophotometer. The n.m.r. spectra were measured using a Varian Associates Model A-60 spectrometer with tetramethylsilane as a reference. Microanalyses were performed by Dr. F. B. Strauss, Microanalytical Laboratory, Oxford, England.

Substitution Reactions with 1-Phenyl-1,2,3-triazolyllithium Compounds

To a stirred solution (or suspension) of 0.040 mol of either 1-phenyl-1,2,3-triazole (12), 4-methyl-1-phenyl-1,2,3-triazole (13), 5-methyl-1-phenyl-1,2,3-triazole (12), 1,4-diphenyl-1,2,3-triazole (14), or 1,5-diphenyl-1,2,3triazole (14) in 80 ml of anhydrous THF was added dropwise in 15 min, 26 ml of 1.6 M n-butyllithium in *n*-hexane at -20 to -60° (depending on the solubility of the triazole) in a nitrogen atmosphere. When the addition was completed the mixture was stirred and cooled for an additional 0.5-1 h whereafter a solution of methyl iodide (8.5 g, 0.060 mol) in 15 ml of THF was added in one portion. The reaction mixtures were worked up by standard procedures. The following compounds were thus prepared:

5-Ethyl-1-phenyl-1,2,3-triazole (2) (42%), m.p. 79-81°; reported m.p. 79-80° (15). The identity was confirmed by the n.m.r. spectrum and the elemental analyses. The n.m.r. spectrum of the crude product indicated that little (if any) 4,5-dimethyl-1-phenyl-1,2,3-triazole was present. CANADIAN JOURNAL OF CHEMISTRY. VOL. 49, 1971



1,5-Diphenyl-4-methyl-1,2,3-triazole (3) (99%), m.p. 122-124°; n.m.r. (CDCl₃): τ 2.5-3.0 (m, 10H) and 7.58 (s, 3H).

Anal. Calcd. for C₁₅H₁₃N₃: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.63; H, 5.70; N, 17.67.

5-Methyl-1-phenyl-1,2,3-triazole (6a) (94%), m.p. 63-65°; reported m.p. 64° (12). The material was identical with an authentic sample.

4,5-Dimethyl-1-phenyl-1,2,3-triazole (6b) (81%), m.p. $87-88^{\circ}$; reported m.p. 98° (16). The structure was confirmed by the n.m.r. spectrum and elemental analyses.

1,4-Diphenyl-5-methyl-1,2,3-triazole (6c) (78%), m.p. 156–159° ($C_6H_6 - n-C_6H_{14}$); n.m.r. (CDCl₃): τ 2.1–2.8 (m, 5H), 2.52 (s, 5H) and 7.59 (s, 3H).

Anal. Calcd. for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.56; H, 5.46; N, 17.72.

1,4-Diphenyl-1,2,3-triazole-5-carboxylic Acid (7)

This compound was prepared in 62% yield by pouring the 1,4-diphenyl-1,2,3-triazolyllithium solution on solid carbon dioxide, followed by acidification of an aqueous solution of the salt; m.p. $169-170^{\circ}$ (dec.); reported m.p. 177.5° (17). The structure was confirmed by an elemental analysis.

Lithium (N-Phenyl)phenylketenimine Anion (8c)

To a stirred suspension of 1,4-diphenyl-1,2,3-triazole (8.8 g, 0.040 mol) in 80 ml of anhydrous THF was added dropwise in 10–15 min 26 ml of 1.6 M n-butyllithium in n-hexane at -20 to -40° in a nitrogen atmosphere. The mixture was cooled for an additional 15 min (a white precipitate had formed) and was then allowed to warm up. At approximately 10° gas evolution became noticeable. At room temperature the gas evolution became rapid and was complete within one hour to give a yellow to green solution, the i.r. spectrum of which contained a very intense absorption at 2140 cm⁻¹.

Reaction of 8c with Methyl Iodide

The above prepared solution of 8c was cooled to -60° and a solution of methyl iodide (11.4 g, 0.080 mol) in 20 ml of THF was added in one portion. After the mixture had reached room temperature the solvent was removed, the residue was dissolved in 75 ml of ether and this solution was washed with two 25 ml portions of water. The ether solution was dried and the solvent removed giving 8.1 g of liquid residue, the n.m.r. spectrum of which indicated that it consisted only of the ketenimine 9 (61%) and the dimer 12 (39%). A solution of the residue in 50 ml of *n*-hexane was cooled to give 1.6 g (19%) of crystalline 12, m.p. 109–111°. The material could be recrystallized from methanol to pale yellow crystals, m.p. 114–115°; v_{max} (Nujol) 1730, 1655, and 1590 cm⁻¹; n.m.r. (CDCl₃): τ 2.6–3.7 (multiplet, 20H), 8.16 (s, 3H), and 8.31 (s, 3H).

Anal. Calcd. for $C_{30}H_{26}N_2$ (mol. wt. 414.5): C, 86.92; H, 6.32; N, 6.76. Found (409 (Rast)): C, 86.92; H, 6.26; N, 7.18.

The hexane filtrate was concentrated and the residue distilled *in vacuo* to give 3.7 g (45%) of 9 as a yellow liquid, b.p. 128-129° (0.5 mm), which crystallized upon cooling and could be recrystallized from a small amount of methanol to long yellow needles, m.p. $35-37^\circ$; v_{max} (Nujol) 2000 cm⁻¹; n.m.r. (CDCl₃): τ 2.6-2.9 (m, 10H) and 7.92 (s, 3H).

Anal. Calcd. for C₁₅H₁₃N: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.96; H, 6.45; N, 7.00.

The crude reaction product could also be distilled directly, in which case the dimer 12 could be isolated by recrystallization of the distillation residue from methanol.

N,2-Diphenylpropionamide (10)

A mixture of (N-phenyl)methylphenylketenimine (0.35 g, 0.0017 mol), 1 N aqueous sulfuric acid (10 ml), and THF (10 ml) was briefly heated at 50°. The product isolated was recrystallized from benzene -n-hexane to give 0.31 g (82%) of white crystals, m.p. $135-136^{\circ}$; reported m.p. $133-134^{\circ}$ (18). The n.m.r. and i.r. spectra and the elemental analyses were also in agreement with the assigned structure.

Methyl N,2-Diphenylpropionimidate (11)

A mixture of ketenimine 9 (1.24 g, 0.006 mol), sodium methoxide (0.10 g), and methanol (25 ml) was left at room temperature for 1 h, by which time the yellow color had disappeared. From the reaction mixture was isolated 1.3 g (77%) of pale yellow product, b.p. $110-112^{\circ}$ (0.1 mm); v_{max} (neat) 1655 cm^{-1} ; n.m.r. (CCl₄): $\tau 2.87$ (s, 5H), 2.5–3.5 (m, 5H), 6.20 (q, 1H), 6.25 (s, 3H), and 8.59 (d, 3H).

Anal. Calcd. for C₁₆H₁₇NO: C, 80.32; H, 7.16; N, 5.85. Found: C, 80.18; H, 7.09; N, 6.10.

Hydrolysis of 12

A mixture of 12 (1.0 g), THF (30 ml), and 3 N hydrochloric acid (30 ml) was heated under reflux for 5 h. The mixture was cooled and extracted with two 50 ml portions of ether. The aqueous solution was made alkaline and extracted with ether to give 0.25 g of a liquid residue,

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the i.r. spectrum of which was superimposable with that of aniline. The ether solution was dried, the solvent removed, and the residue distilled *in vacuo* to give 0.52 g (63%) of a very viscous liquid, distilling at approximately 190° (0.1 mm) with slight decomposition. An analytical sample was obtained by chromatography on silica gel and elution with benzene; v_{max} (neat) 1780 and 1680 cm⁻¹; n.m.r. (CDCl₃): τ 2.3–3.3 (m, 15H), 8.01 (s, 3H), and 8.06 (s, 3H).

Anal. Calcd. for $C_{24}H_{21}NO$ (13): C, 84.93; H, 6.24; N, 4.13. Found: C, 84.82; H, 6.43; N, 3.99.

6-Anilino-1,3,5-triphenyluracil (16)

A solution of phenyl isocyanate (2.4 g, 0.020 mol) in 10 ml of THF was added in one portion to a stirred solution of 8c in THF, prepared from 4.4 g (0.020 mol) of 1,4-diphenyl-1,2,3-triazole, at -60° . The cooling bath was removed and when the temperature of the reaction mixture had reached -20° , 20 ml of water was added followed by some ethyl acetate. The organic layer was washed with water, dried, and concentrated. The residue was treated with 40 ml of ether and cooled, resulting in the formation of a white solid precipitate (2.0 g). A small amount of starting material 4c could be removed by treating this solid with cold methylene chloride which dissolved 16 but not 4c. The product thus obtained amounted to 1.6 g (37%), m.p. 230-234°. The m.p. could be raised to 242-243° by recrystallization from a 1:4 mixture of chloroform and carbon tetrachloride; v_{max} (CHCl₃) 3400, 1700, and 1640 cm⁻¹; n.m.r. (CDCl₃): complex phenyl absorption at τ 2.5-3.6 and a singlet at 4.37 with an integrated area ratio of approximately 20:1. Anal. Calcd. for C₂₈H₂₁N₃O₂ (mol. wt. 431.5): C

Anal. Calcd. for $C_{28}H_{21}N_3O_2$ (mol. wf. 431.5): C, 77.93; H, 4.91; N, 9.74. Found (432 (osmometric)): C, 77.47; H, 4.96; N, 9.61.

1,3,5-Triphenylbarbituric Acid (17)

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A mixture of 16 (1.0 g, 2.3 mmol), acetic acid (30 ml), and 6 N hydrochloric acid (15 ml) was heated under reflux for 1.5 h, then diluted with 15 ml of water and cooled. The solid precipitate was collected by filtration, washed with water, dried, and recrystallized from ethyl acetate – n-hexane to give 0.5 g (63%) of fine white needles, m.p. 262–263°; reported m.p. 261–262° (19). The i.r. spectrum (in CHCl₃) contained no absorption at 3100–3600 cm⁻¹, but showed a strong carbonyl band at 1690 cm with a shoulder at 1710 cm⁻¹; the n.m.r. spectrum (in DMSO-d₆) contained singlets at τ 2.55 and 4.62 (broad) with an integrated area ratio of approximately 15:1.

Anal. Calcd. for $C_{22}H_{16}N_2O_3$ (mol. wt. 356); C, 74.14; H, 4.53; N, 7.86. Found (380 (Rast)): C, 73.95; H, 4.55; N, 7.96.

N-Methyl-N-phenyl-2-phenylethynylamine (18)

To the previously described solution of **8***c* (prepared from 0.040 mol of 4*c*) in THF, cooled at -60° , was added in one portion a solution of dimethyl sulfate (5.05 g, 0.040 mol) in 20 ml of THF. The mixture was worked-up as before to give 7.5 g of crude reaction product which upon distillation *in vacuo* provided 3.5 g (42%) of pale yellow liquid, b.p. 134–136° (0.1 mm), which crystallized from *n*-hexane to colorless crystals, m.p. 47–48°; v_{max} (Nujol) 2230 and 1595 cm⁻¹; n.m.r. (CDCl₃): τ 2.5–3.2 (m, 10H) and 6.73 (s, 3H).

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.67; H, 6.46; N, 6.86.

Treatment of a solution of the product in THF with 1 N aqueous sulfuric acid resulted in an exothermic reaction to give a quantitative amount of (*N*-methyl-*N*-phenyl)phenylacetamide, identical with an authentic sample prepared from phenylacetyl chloride and *N*-methylaniline.

N-Carbomethoxy-N-phenyl-2-phenylethynylamine (20)

To a solution of 8c in THF, prepared from 4.42 g (0.020 mol) of 1,4-diphenyl-1,2,3-triazole, was added, at -60° , a solution of methyl chloroformate (2.3 g, 0.024 mol) in 10 ml of THF in one portion. After the usual work-up, 5.4 g of crude product was obtained. The i.r. spectrum contained bands at 2250 and 2020 cm⁻¹ of approximately equal intensity and a strong band at 1740 cm⁻¹ with a shoulder at 1710 cm⁻¹, indicating the presence of both 20 and 21. The amount of the ketenimine was small as was also indicated by the n.m.r. spectrum. The crude product was extracted with n-hexane $(5 \times 50 \text{ ml})$ to remove some hexane-insoluble resinous material. The residue (3.3 g) obtained by removal of the hexane was chromatographed on silica gel in an attempt to separate 20 and 21. Although no separation was effected, the material eluted with a 1:4 mixture of ether and benzene contained only a trace of the ketenimine as most of this compound had decomposed on the column. The eluted product (2.8 g) was distilled in vacuo to give 2.0 g (40%) of pale yellow viscous liquid, b.p. $150-152^{\circ}$ (0.1 mm); v_{max} (neat) 2250 and 1740 cm⁻¹; n.m.r. (CCl₄): 7 2.3-3.0 (multiplet, 10H) and 6.16 (s, 3H).

Anal. Calcd. for $C_{16}H_{13}NO_2$: C, 76.49; H, 5.21; N, 5.58. Found: C, 76.22; H, 5.38; N, 5.75.

Methyl (N-Phenyl)phenylacetimidate (22)

(a) From 8c

Methanol (10 ml) was added in one portion to a solution of 8c, prepared from 2.21 g (0.010 mol) of 1,4-diphenyl-1,2,3-triazole, in THF at -60° . The reaction mixture was worked-up in the usual manner to give 1.0 g (45°_{\circ}) of yellow oil, b.p. 114–115° (0.5 mm), the i.r. spectrum of which was superimposable with that of the product obtained from aniline and methyl phenylthion-acetate (11).

(b) From 20

Methanolic sodium hydroxide (1.3 ml of 3 N) was added to a solution of 20 (0.64 g, 0.0025 mol) in 3 ml of methanol. After 15 min at room temperature the mixture was diluted with ether and cooled. A white solid (0.09 g) precipitated, the i.r. spectrum of which was identical with that of sodium methylcarbonate. The ether solution was washed with water and dried. Removal of the solvent gave 0.53 g (95%) of liquid residue, identical with the material obtained under method *a*. Distillation *in vacuo* gave 0.38 g of colorless liquid, b.p. 110–112° (0.3 mm).

Ethyl (N-Phenyl)phenylthioacetimidate (23)

A solution of ethanethiol (3.1 g, 0.050 mol) in 10 ml of THF was added in one portion to a solution of 8c, prepared from 4.42 g (0.020 mol) of 1,4-diphenyl-1,2,3-triazole, in THF at -60° , followed by the usual work-up. After distillation there was obtained 4.1 g (80%) of yellow oil, b.p. 125–127° (0.05 mm); v_{max} (neat) 1610 and

1595 cm⁻¹; n.m.r. (CCl₄): τ 2.5–3.5 (multiplet, 10H), 6.38 (s, 2H), 7.06 (q, 2H), and 8.75 (t, 3H).

Anal. Calcd. for C₁₆H₁₇NS: C, 75.25; H, 6.71; N, 5.49; S, 12.56. Found: C, 75.47; H, 6.83; N, 5.43; S, 12.28.

Methyl N-Phenylacetimidate (25)

To a stirred solution of 1-phenyl-1,2,3-triazole (4.35 g, 0.030 mol) in 45 ml of THF was added, in 15 min, 19 ml of a 1.6 M solution of n-butyllithium in n-hexane, at -60° in a nitrogen atmosphere. The reaction mixture was heated at 40-45° for 30 min when the gas evolution was complete. The darkly colored mixture was cooled to -60° and 10 ml of methanol was added. After work-up there was obtained 4.0 g of crude product, from which 1.6 g (37%) of starting material, m.p. 55-56°, was recovered by the addition of *n*-hexane. The remaining material was distilled in vacuo to give 1.3 g (47%, based on unrecovered starting material) of product, b.p. 64-65° (3 mm); reported b.p. 81-82° (12 mm) (20). The n.m.r. and i.r. spectra and the elemental analyses were in agreement with the assigned structure.

N-Methyl-N-phenyl-1-propynylamine (24)

A solution of 5b, prepared from 4-methyl-1-phenyl-1,2,3-triazole (3.20 g, 0.020 mol) in the usual manner, in THF was heated at 40-50° for 2 h in a nitrogen atmosphere. The darkly colored solution was cooled to -60° and a solution of dimethyl sulfate (2.52 g, 0.020 mol) in 10 ml of THF was added in one portion. From the reaction mixture was isolated 0.9 g (31%) of product, b.p. 60–62° (0.2 mm); v_{max} (neat) 2250 and 1595 cm⁻¹; n.m.r. (CDCl₃): τ 2.5–3.3 (m, 5H), 6.83 (s, 3H), and 8.00 (s, 3H). Reported b.p. 96° (6 mm) (21). The material was readily hydrolyzed with dilute acid to N-methyl-Nphenylpropionamide, m.p. 57-58°; reported m.p. 58° (21).

Compound 24 was also obtained, in 21% yield, when the reaction was repeated with 1-phenyl-1,2,3-triazole.

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