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# Triazolopyridines. 14.[1]. Substitution Reactions of 7-Amino[1,2,3]Triazolo[1,5-a]Pyridines.

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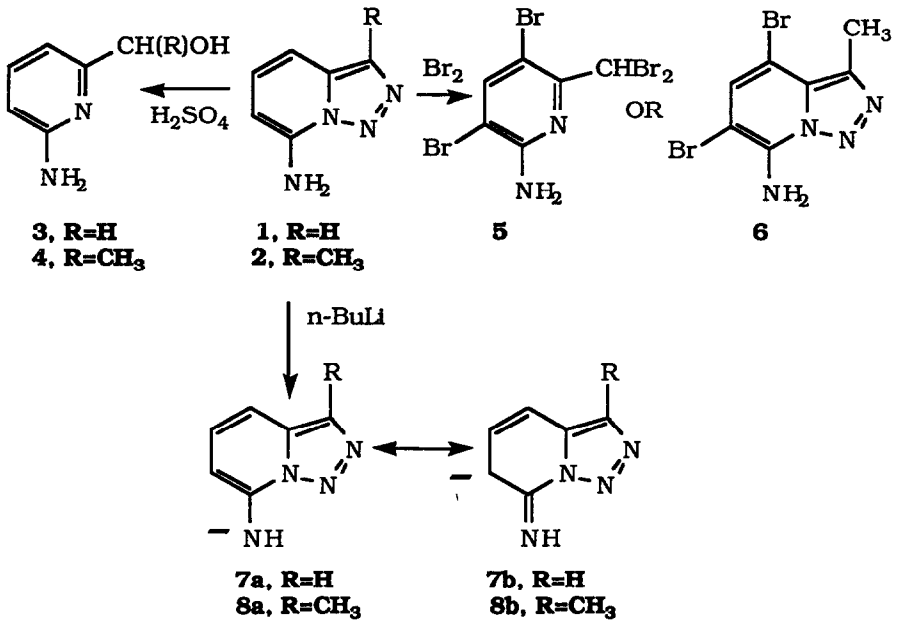
***Abstract*** *Reaction between 7-aminotriazolopyridines* **1** *or* **2** *and sulphuric acid gives hydroxyalkylpyridines* **3** *and* **4** *; bromination gives brominated pyridine* **5** *or triazolopyridine* **6** *The anions from amines* **1** *or* **2** *are ambident, acylating on N but alkylating on N or on C6, in the latter case triazolylalkenylcyanides* **16** *-* **20** *or the 6,6-dialkylated derivative* **19** *are obtained. An X-ray diffraction study has confirmed structure* **19**

We have reported [2] the synthesis of the 7-aminotriazolopyridines **1** and **2**, and their reaction with methyl iodide A more detailed study of the reactions of amines **1** and **2** with electrophiles, and in particular of the unusual reactions with alkylating agents of the anions derived from the amines is described here.

In a reaction characteristic of [1,2,3]-triazolo[1,5-a]pyridine[3], the amines **1** and **2** reacted with hot aqueous sulphuric acid to give hydroxyalkylpyridines **3** and **4** Similarly, the amine **1** reacted with bromine to give the dibromomethylpyridine **5**, in accord with previous observations[3] that 3-substituted triazolopyridines are more stable towards ring opening by halogens, bromination of amine **2** gave the dibromotriazolopyridine **6** as the only isolated product

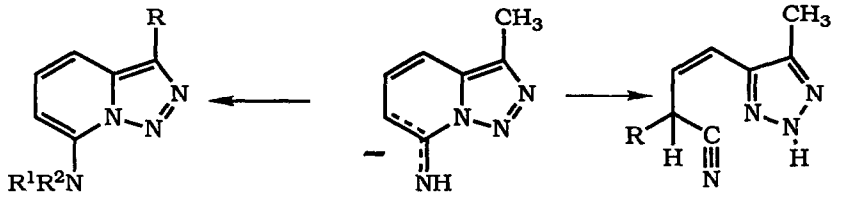



**3, R=H** **1, R=H** **5** **6**
**4, R=$CH_3$** **2, R=$CH_3$**

**7a, R=H** **7b, R=H**
**8a, R=$CH_3$** **8b, R=$CH_3$**

We have observed[2] exclusive methylation on N2 when the amines **1** or **2** were treated with methyl iodide, giving quaternary salts For the preparation of N-substituted amines we treated the amines **1** or **2** with n-butyllithium at -40°C The anions **7** or **8** so formed reacted with benzoyl chloride to give the N-benzoyl derivatives **9** and **10**, and with methyl iodide to give N-methyl derivatives **11** and **12**. From these monomethylated derivatives, by a further treatment with n-butyllithium and methyl iodide the dimethylaminotriazolopyridines **13** and **14** were obtained, although there was no indication of direct formation of these from the original anions **7** or **8** When the anion **8** was treated with ethyl bromide the major product of the reaction had completely different spectral characteristics from those of compounds **11** or **12**, and the subsequently established structures of a series of new alkylation products lead us to propose that the anions are ambident, with limiting structures **7a↔7b**, and **8a↔8b**. Thus, the compound obtained from reaction between anion **8** and ethyl bromide had a $^1H$ nmr spectrum which showed a sequence $CH_3CH_2CH^C\text{-}CH^B{=}CH^A$ (established by a decoupling sequence) with $H^C$ at δ4 52, $H^B$ at δ5 65, and $H^A$ at δ6 32, with a coupling constant $J_{AB}$ of 11 24 Hz Such a sequence could be accommodated by formulae **15** or **16**, although the J value is rather high for the double bond in the six-membered ring of compound **15** The $^{13}C$ nmr spectrum showed a signal for a quaternary carbon at δ121 02, which with an ir band at 2240 $cm^{-1}$ strongly support the structure **16** If we assume that the cyanide carbon is the original C7, alkylation has occurred on C6, confirming the ambident behaviour of the anion of this aromatic amine A signal at δ12 26 (broad, exchangeable) in the spectrum of compound **16** is in the region reported for triazol NH Apart from the cyanide signal only one quaternary carbon signal could be

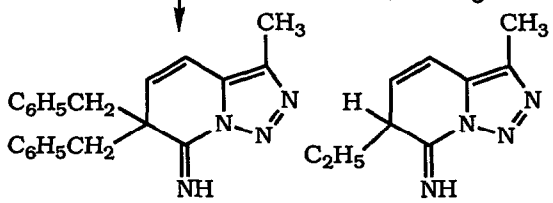
detected (as in the related compound **21**), and we conclude that the predominant tautomer is the 2H-triazole. The alternative 1H tautomer should have quite different shifts for C4 and C5.



**9**, R= $R^1$=H, $R^2$=$C_6H_5CO$
**10**, R=$CH_3$, $R^1$=H, $R^2$=$C_6H_5CO$
**11**, R=$R^1$=H, $R^2$=$CH_3$
**12**, $R^1$=H, R= $R^2$=$CH_3$
**13**, R=H,$R^1$=$R^2$=$CH_3$
**14**, R=$R^1$=$R^2$=$CH_3$
**18**, R=$CH_3$, $R^1$=H, $R^2$=$CH_2C_6H_5$
**20**, R=$CH_3$, $R^1$=H, $R^2$=$CH_2CH_3$

**8a,b**

**16**, R=$C_2H_5$
**17**, R=$C_6H_5CH_2$
**21**, R=$CH_3$

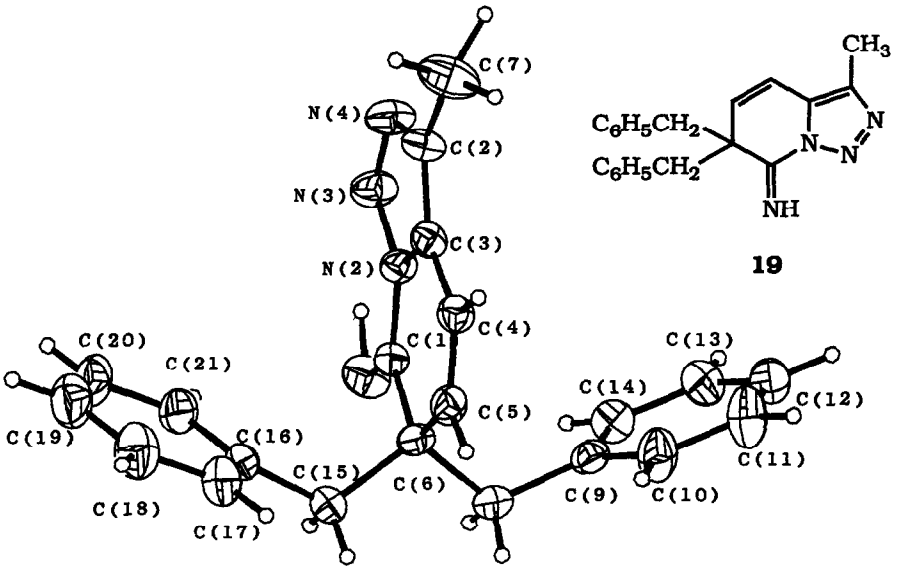


**19** **15**

Treatment of anion **8** with benzyl bromide gave three products, two of which were easily identified by their spectra as the nitrile **17** and the N-benzylamine **18** The third product of molecular formula $C_{21}H_{20}N_4$ was dibenzylated. The nmr spectra were quite different from those of compounds **16** and **17**, no infrared peak was detected around 2200 $cm^{-1}$, and no quaternary signal in the $^{13}C$ nmr spectrum around δ121. The $^1H$ nmr spectrum showed an AB pair of doublets (δ6.02 and 6.27, $J_{AB}$=10 Hz) and the benzylic methylene signals appeared as a pair of doublets, δ3.12 and 3 57 (J=13 2 Hz). The NH signal appeared at δ10.29. The spectral evidence seemed to favour a structure with an intact triazolopyridine ring system and this was confirmed by an X-ray diffraction study, which showed structure **19** . Crystals contain two symmetry independent molecules which differ slightly in the orientation of the benzyl groups A diagram of Molecule A of compound **19** is shown in the Figure and bond lengths and angles in the Table. In the diagram the intact triazolopyridine ring is well shown, as is the C=NH double bond (1 264Å) with the hydrogen oriented towards the N1 of the triazole ring in the expected hydrogen bond We thus have an unambiguous example of C-alkylation in an aromatic amine.

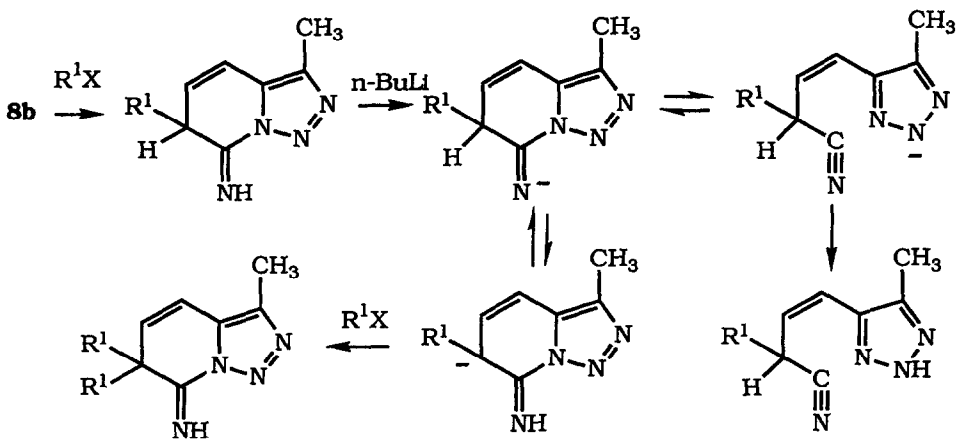
We believe that C-alkylation precedes ring opening (treatment of amine **2** with n-butyllithium without a co-reagent gives unchanged amine on work-up), and the balance of N- against C-alkylation is substantially as predicted by hardness and softness of the electrophile Thus benzoyl chloride attacks only the harder nitrogen atom, while ethyl bromide and benzyl bromide give C-alkylation Variation of the ethylating agent (bromide, iodide, triflate) leads to the isolation of some N-ethyl derivative **20**. The anomaly is observed in methylation, where methyl iodide gives

only N-methylamino derivative **10**, while methyl tosylate gave the C-alkylated and ring-opened product **21**.




Figure; X-Ray diagram of molecule A of compound **19**.

If we assume that C-alkylation precedes the opening of the pyridine ring, and we know that the monobenzylated derivative **17** has undergone ring opening, we must conclude that only in the benzyl halide is the rate of the second alkylation comparable with the rate of ring opening, thus allowing the competitive formation of the 6,6-dibenzyl derivative **19**. The alternative (recyclization of the dialkylated cyanide) seems unlikely, and we have shown that an attempt to benzylate the anion from compound **17** gave no trace of the dibenzyl derivative **19**.




SCHEME

## EXPERIMENTAL

Mps were measured on a heated stage, and are uncorrected. Nmr spectra were determined for $CDCl_3$ solutions, unless otherwise stated. Separation of products by chromatography was done by Chromatotron, using 2 mm silica coating, solvents for elution were ethyl acetate and 60-80° petrol, in proportions given thus (1:5)

*Reaction of Amines* ***1*** *and* ***2*** *with sulphuric acid.* A solution of the amine (0 6 to 0.8 mmol) in 10% sulphuric acid (5 $cm^3$) was boiled (2h), cooled, and basified using aqueous $NaHCO_3$. Extraction with dichloromethane, drying of the solution ($Na_2SO_4$), and evaporation gave a solid Recrystallisation of compound **3** from benzene/dichloromethane gave a colourless solid, m.p. 93-94°C (35%). (Found· C, 57 97; H, 6.45, N, 22 25. $C_6H_8N_2O$ requires C, 58.06, H, 6 45, N, 22 58% δ($^1$H, $d_6$-acetone) 3 73 (2H, brs, $NH_2$), 4.47 (2H, s), 5.53 (1H, brs, OH), 6.42 (1H, dd, J=8 3 and 1 4 Hz, H3), 6 64 (1H, dd, J=7.3 and 0.7 Hz, H5), and 7.38 (1H, m, H4). m/z 124 (60.5%, $M^+$), 123 (46%, $M^+$-1), 95 (100%) Recrystallisation of compound **4** from benzene/dichloromethane gave colourless crystals, m.p. 112°C. (Found C, 61 13; H, 7 31; N, 20 02 $C_7H_{10}N_2O$ requires C, 60 87, N, 7 25; N, 20.29%). δ1 4 (3H, d, C**H**$_3$CH), 3 6 (1H, brs, OH), 4 53 (2H, brs, NH), 4.65 (1H, q, **CH**$CH_3$), 6 37 (1H, d, J 8 Hz, H3), 6.58 (1H, d, J 7 5 Hz, H5), 7.4 (1H, m, H4) m/z 138 (36%, $M^+$), 123 (100%, M-$CH_3$), 95 (55%).

*Reaction of Amines* ***1*** *and* ***2*** *with Bromine.* A solution of bromine (5% in $CCl_4$, 1 meq ) was added with stirring at room temperature to a solution of the amine (1 meq.) in dichloromethane. A yellow solid formed and shown to be product. The filtrate, on evaporation, gave more crude product **5** or **6** , purified by recrystallisation. From amine **1** was isolated 2-amino-3,5-dibromo-6-dibromomethylpyridine, (**5**), m.p 208° (from $CHCl_3$)(25-30 %) (Found: C, 17 47, H, 0 91; N, 6.65 $C_6H_4Br_4N_2$ requires C, 16.98; H, 0 95, N, 6.6%). δ($^1$H) 5 2 (2H, brs, $NH_2$), 6 8 (1H, s, $CHBr_2$), 7.7 (1H, s, H4). m/z 426(7.8%), 424(11 7%), 422(7 7%), (visible $M^+$ isotope peaks), 347(35 3%), 345(99 2%), 343(100%), 341(33.5%) (M-79, isotope peaks), 265(25%), 263(25%), 185(19%), 183(18 6%) From amine **2** was isolated 7-amino-4,6-dibromo-3-methyltriazolopyridine (**6**), m p. 210-212°C (From methanol)( 26%) (Found C, 27.56, H, 1 58, N, 17 83 $C_7H_6Br_2N_4$ requires C, 27.48, H, 1 97; N, 18.31%) δ($^1$H, $d_6$-DMSO) 2 69 (3H, s), 7 43 (2H, brs, $NH_2$), 7 66 (1H, s, H5) m/z 308(8.8%), 306(17.2%), 304(7 6%)($M^+$ isotopes), 280(44%), 278(77%), 276(38%), 199(54%), 197(48%), 118(100%)

*Benzoylation of Amines* ***1*** *and* ***2*** The amine (1.42 mmol) was dissolved in tetrahydrofuran (15 $cm^3$) and treated with stirring under nitrogen at -40°C with n-butyllithium (1 1 $cm^3$, 1.63 M in hexane). After 3 5 h at -40°C benzoyl chloride (1 5 mmol) was added, and the mixture allowed to warm to room temperature and

kept overnight. The crude benzoyl derivatives were purified by Chromatotron (3 7), and then recrystallised from benzene or cyclohexane/benzene.

*7-Benzamido-3-methyltriazolopyridine,* ***10***, (30%) had m.p. 131-132°C. (Found· C, 66.96; H, 4.65; N, 22.16. $C_{14}H_{12}N_4O$ requires C, 66.66; H, 4 79, N, 22.21%) $\nu_{max}$ ($CHCl_3$) 3380, 1710, 1600 $cm^{-1}$. $\delta(^1H)$ 2 64 (3H, s), 7 20-7.45 (2H, m), 7.50-7.70 (3H, m), 7 90-8.10 (3H, m), 9.92 (1H, brs, NH) $\delta(^{13}C)$ 10.49 (q), 101.43 (d, C4), 111 04 (d, C6), 125 75 (d, C5), 127 43 (d, C3',5'), 128.36 (s, C3a), 129.07 (d, C2',6'), 132.00 (s, C3), 132.21 (s, Cl'), 132.95 (d, C4'), 135.42 (s, C7), 164.94 (s, C=0). m/z 224 (20%, $M^+$-$N_2$), 105 (100%, $PhCO^+$).

*7-Benzamidotriazolopyridine,* ***9***, (34%) had m.p. 187-188°. $\delta(^1H)$ 6 93 (1H, d, J=9 5 Hz, H6), 7 26-7 55 (7H, m), 7 99 (1H, s, H3), and 8.35 (1H, brs, NH). m/z 238 (36.6%, $M^+$), 209 (25%, $M^+$-$N_2H$), 105 (100%, $PhCO^+$), 77 (50%, $C_6H_5^+$)

*General Procedure for Alkylation of Amines* ***1*** *and* ***2*** A solution of the amine (2 24 mmol) in THF (10 $cm^3$), was treated with n-butyllithium (1 5 cm3, 1 63 M in hexane) at -40° under nitrogen After 3 5 h. an excess of the alkylating agent was added, and the reaction mixture allowed to come to room temperature overnight Treatment with a saturated solution of ammonium chloride in ammonia (s g. 0 880), separation, drying of the organic layer ($MgSO_4$), and evaporation gave crude residue, purified on a Chromatotron eluting with mixtures of ethyl acetate 60-80° petrol, (usually 1.1) Final purification was by recrystallization

*7-Methylaminotriazolopyridine,* ***11***, had m p 116-117°C (cyclohexane) (62% yield) (Found C, 56.41, H, 5.4, N, 37 87 $C_7H_8N_4$ requires C, 56 76, H, 5 4, N, 37 84%) $\nu_{max}$ ($CHCl_3$) 3386 $cm^{-1}$. $\delta(^1H)$ 2 0 (3H, d, J=5 Hz), 5 70-5 90 (1H, dd, J=6 Hz, H6), 6.00 (1H, brs, NH), 7 00-7.20 (2H, m), 7 90 (1H, s, H3) $\delta(^{13}C)$ 29 02 (q), 88 82 (d, C6), 103 27 (d, C4), 125 09 (d, C3), 127 49 (d, C5), 132 5 (s, C3a), 143 31 (s, C7)

*3-Methyl-7-methylaminotriazolopyridine,* ***12***, had m p. 134-135°C (cyclohexane) (63 9%) (Found· C, 59 53, H, 6 02, N, 34 55 $C_8H_{10}N_4$ requires C, 59 25, H, 6 21, N, 34 54%) $\nu_{max}$ ($CHCl_3$) 3410 $cm^{-1}$ $\delta(^1H)$, 2.59 (3H, s, C-$CH_3$), 3 11 (3H, d, J=5 4 Hz, NH**$CH_3$**), 5 90 (1H, d, J=7 33 Hz, H6), 6 10 (1H, brs, NH), 6 95 (1H, dd, J=8 79 and 0 98 Hz, H4), 7 14-7 20 (1H, m, H5) $\delta(^{13}C)$ 10 56 (q, $CH_3$), 29 22 (q, $NCH_3$), 88 77 (d, C6), 103 18 (d, C4), 126 31 (d, C5), 132 34 (s, C3), 133 92 (s, C3a), 141 92 (s, C7) m/z 162 (21%, $M^+$), 134 (32 5%, $M^+$-28), 133 (100%, $M^+$-29), 119 (42%), 105 (41%), 92 (47%)

*7-Dimethylaminotriazolopyridine,* ***13***, prepared from compound **11** was unstable to chromatography, and gave inconsistent analyses (yield of crude product >90%), but

was characterised by nmr spectra. $\delta(^1H)$ 2.90 (6H, s, $N(CH_3)_2$), 5.90 (1H, m, H6), 6 90 (2H, m, H4 and H5), 7.7 (1H, s, H3). $\delta(^{13}C)$ 40.72 ($NCH_3$), 98.27 (d, C6), 108 06 (d, C4), 124 31 (d, C3), 126.32 (d, C5), 131.44 (s, C3a), 136.95 (s, C7).

*7-Dimethylamino-3-methyltriazolopyridine*, **14**, was a yellow oil (52% yield). (Found. C, 61.06; H, 7.10; N, 31.32. $C_9H_{12}N_4$ requires C, 61.35, H, 6 86, N, 31.79%). $\delta(^1H)$ 2.50 (3H, s), 3.05 (6H, s, $N(CH_3)_2$), 6.08-6.11 (1H, dd, J=6 84 and 1 46 Hz, H6), 7.02-7.13 (2H, m, H4 and H5). $\delta(^{13}C)$ 9.40 (q, $CH_3$), 40.25 (q, $N(CH_3)_2$) 97.78 (d, C6), 107.65 (d, C4), 124.23 (d, C5), 132 41 (s, C3), 132 64 (s, C3a), 144 50 (s, C7). m/z 176 ($M^+$, 54.7%), 148 ($M^+$-$N_2$, 24 3%), 147(100%, $M^+$ -$N_2H$), 133 (77%)

*3-Cyano-1-(5-methyl[1,2,3]-triazol-4-ylpent-1-ene*, **16**, had m p. 107-108°C (cyclohexane), (51 7%). (Found· C, 61.50; H, 7 12; N, 31.83 $C_9H_{12}N_4$ requires C, 61.35; H, 6 86; N, 31 79%) $\nu_{max}$ ($CHCl_3$) 2240 $cm^{-1}$ $\delta(^1H)$ 1 05 (3H, t, $CH_3CH_2$), 1 74 (2H, m, H4), 2 29 (3H, s, $CH_3$), 4 52 (1H, m, H3), 5.61-5 69 (1H, m, H2), 6 32 (1H, dd, J=11 24 and 0.98 Hz, H1), 12.26 (1H, brs, NH). $\delta(^{13}C)$ 9 23 (q, $CH_3$), 11.35 (q, $CH_3$), 26 32 (t, C4), 32 01 (d, C3), 118 75 (d, Cl), 121.02 (s, CN), 127 33 (d, C2), 141.03 (s, C4' and C5') m/z 176 ($M^+$, 33%), 148 ($M^+$-$N_2$, 57%), 147 ($M^+$-$N_2H$, 79%), 133 (100%)

*3-Cyano-4-phenyl-1-(5-methyl[1,2,3]triazol-4-yl)but-1-ene*, **17**, was a low melting solid (28 6%) (Found: C, 70.83; H, 5.89; N, 23 28. $C_{14}H_{14}N_4$ requires C, 70 57; H, 5 92, N, 23.51%). $\nu_{max}$ ($CHCl_3$) 3440, 2240 $cm^{-1}$. $\delta(^1H)$ 2.30 (3H, s), 3 01-3.06 (2H, m, H4), 4.91 (1H, m, H3), 5.68-5 75 (1H, m, H2), 6.36 (1H, dd, J=10.98 and 0 97 Hz, H1), 7.22-7.32 (5H, m, $C_6H_5$), 12 30 (1H, brs, NH). $\delta(^{13}C)$, 9.16 (q, $CH_3$), 32.80 (d, C3), 38 61 (t, C4), 118 90 (d, C1), 120.68 (s, CN) 126.68 (d, C-para), 127.20 (d, C2), 128 54 (d, C-meta), 129.22 (d, C-ortho), 136.59 (s), 140 91 (s, C4' and C5'). m/z 238 ($M^+$, 9.8%), 210 ($M^+$-$N_2$, 26%), 209 ($M^+$-$N_2H$, 32%), 92 (23 5%), 91 ($C_6H_5CH_2^+$, 100%).

*6,6-Dibenzyl-7-imino-3-methyltriazolopyridine* **19**, had m p 94-95° (from cyclohexane) (12.6%). (Found: C, 76.97; H, 6 19; N, 17.09 $C_{21}H_{20}N_4$ requires C, 76 81, H, 6 13, N, 17.06%). $\nu_{max}$ ($CHCl_3$) 3300, 1660 $cm^{-1}$. $\delta(^1H)$ 2 09 (3H, s), 3 12 and 3 57 (each 2H, d, J=13 2 Hz, benzyl $CH_2$), 6 02 (1H, d, J=10 Hz, H4), 6 27 (1H, d, J=10 Hz, H5), 7.13 (10H, 2 x $C_6H_5$), and 10.29 (1H, brs, C=N**H**). $\delta(^{13}C)$ 9 41 (q, $CH_3$), 47 30 (t, $CH_2$), 52.22 (s, C6), 112.03 (d, C4), 126 82 (d, para-C), 127 83 (d, meta-C), 127.98 (d, C5), 130 08 (d, Ortho-C), 135 09 (s, C3), 135 50 (s, benzene C1), 139.06 (s, C3a), 157 84 (s, C=NH).

*3-Cyano-1-(5-methyl[1,2,3]triazol-4-yl)but-1-ene*, **21**, was obtained using methyltosylate as alkylating agent on amine anion **8**. Consistent analyses were not obtained because of a slight amount of a persistent impurity, but the compound was characterised by passage through a Hewlett-Packard GC/MS, with a mass spectral pattern on the single major peak. m/z 162 ($M^+$, 47%), 134 ($M^+$-$N_2$, 100%), 133 ($M^+$-$N_2H$, 44%), 119 ($M^+$-($N_2$ + $CH_3$), 57%), 106 ($M^+$-$CH_3CHN_2$, 55%). $\nu_{max}$ ($CHCl_3$) 2240 $cm^{-1}$. δ(1H) 1.50 (3H, d, $CH_3CH$), 2.36 (3H, s), 4.69-4.81 (1H, m, H3), 5 68-5.76 ($^1$H, m, H2), 6.34 (1H, dd, J=11.08 and 1.01 Hz, H1), 13.14 (1H, brs, NH) δ($^{13}$C) 9.05 (q, $CH_3$), 18.56 (q, $CH_3$), 24.89 (d, C3), 118 29 (d, H1), 122.02 (s, CN), 128.16 (d, C2), 140.70 (s, C3 and C3a)

*7-Benzylamino-3-methyltriazolopyridine*, **18**, was characterised by nmr spectra only δ($^1$H) 2.61 (3H,s), 4 51 (2H, d, $NCH_2$), 5.92 (1H, d, J=7 33 Hz, H6), 6 44 (1H, brs, NH), 6 98 (1H, d, J=8 79 Hz, H4), 7.10-7 46 (1H, m, H5), 7 25-7 38 (5H, m). δ($^{13}$C), 10.54 (q, $CH_3$), 46.88 (t, $CH_2$), 90.02 (d, C6), 103 82 (d, C4), 126 28 (d, C5), 127.25 (d, C-para), 128.89 (d, C-meta), 129 31 (d, C-ortho), 132.45 (s, C3), 134 15 (s, C3a), 137.06 (s, Cl-phenyl), 140.74 (s, C7).

*7-Ethylamino-3-methyltriazolopyridine*, **20**, characterised only by nmr spectroscopy δ($^1$H) 1.39 (3H, t), 2.57 (3H, s), 3.38-3 46 (2H, m), 5 81 (1H, brs, NH), 5 9 (1H, d, J=7.32 Hz, H6), 6.94 (1H, dd, J=8.54 and O.98 Hz, H4), 7.12-7 23 (1H, m, H5) δ($^{13}$C) 10 55 (q, $CH_3$), 14 33 (q, $CH_3$), 37 44 (t, $CH_2$), 88 98 (d, C6), 103 16 (d, C4), 126.23 (d, C5), 132.36 (s, C3), 133 98 (s, C3a), 140 84 (s, C7)

*Crystal Data for Compound 19*. The formula was $C_{21}H_{20}O_4$ and $M_r$ 328.47, monoclinic, a=17.604(2), b=8.4886(6), c=24 628(2) A, β=98.90(2)°, space group $P2_1/c$, Z=8. The crystal used was a small block, dimensions 0 4x0.3x0 2$mm^3$. Unit cell and intensity data were obtained using a FAST TV area detector diffractometer, following previously described procedures[4]. The total data collected were 11977 which merged to give 5315 unique ($R_{int}$=0 059) but only 1989 observed ($F_o$>3σ($F_o$)). The structure was solved by direct methods and refined by least squares (two blocks). All non-hydrogen atoms were refined anisotropically, hydrogens were included in idealised positions except for that on N(1) which was experimentally located and refined The phenyl rings were refined as idealised hexagons Unit weights were used. Atomic coordinates and displacement factor coefficients have been deposited at the Cambridge Crystallographic Data Centre

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Table: Bond Lengths and Bond Angles in Compound 19

| Bond Lengths(A°) | Molecule 1 | Molecule 2 |
|---|---|---|
| C(1)-N(1) | 1 264(8) | 1.259(9) |
| N(3)-N(2) | 1 351(7) | 1 356(7) |
| C(1)-N(2) | 1.413(8) | 1 411(8) |
| C(3)-N(2) | 1 356(8) | 1 361(8) |
| N(4)-N(3) | 1 315(8) | 1 316(9) |
| C(2)-N(4) | 1 358(9) | 1 374(10) |
| C(6)-C(1) | 1 534(9) | 1.524(10) |
| C(3)-C(2) | 1 359(9) | 1.356(8) |
| C(7)-C(2) | 1 501(10) | 1 490(10) |
| C(4)-C(3) | 1.449(8) | 1 434(8) |
| C(5)-C(4) | 1 317(8) | 1 321(10) |
| C(6)-C(5) | 1.505(9) | 1 512(11) |
| C(8)-C(6) | 1.569(8) | 1 563(10) |
| C(15)-C(6) | 1 557(9) | 1 571(11) |
| C(9)-C(8) | 1.521(9) | 1.506(10) |
| C(16)-C(15) | 1 511(8) | 1.521(10) |
| H(1)-N(1) | 1 148(5) | 1 190(6) |

| Bond Angles(deg ) | | |
|---|---|---|
| C(1)-N(2)-N(3) | 121 9(5) | 121.5(6) |
| C(3)-N(2)-N(3) | 110 8(5) | 111.0(5) |
| C(3)-N(2)-C(1) | 127 3(5) | 127.3(5) |
| N(4)-N(3)-N(2) | 106.2(5) | 106.1(6) |
| C(2)-N(4)-N(3) | 109 9(5) | 109.7(6) |
| N(2)-C(1)-N(1) | 122.9(6) | 123.7(6) |
| C(6)-C(1)-N(1) | 122 1(6) | 122 1(6) |
| C(6)-C(1)-N(2) | 115 0(5) | 114 1(6) |
| C(3)-C(2)-N(4) | 108.1(6) | 108 1(6) |
| C(7)-C(2)-N(4) | 121 0(6) | 121 9(6) |
| C(7)-C(2)-C(3) | 130 8(5) | 130 0(7) |
| C(2)-C(3)-N(2) | 105.0(6) | 105 0(6) |
| C(4)-C(3)-N(2) | 118.3(6) | 119 1(6) |
| C(4)-C(3)-C(2) | 136 7(5) | 135.9(6) |
| C(5)-C(4)-C(3) | 120.2(6) | 119 5(6) |
| C(6)-C(5)-C(4) | 124.6(6) | 124.4(6) |
| C(5)-C(6)-C(1) | 114 5(5) | 114 9(5) |
| C(8)-C(6)-C(1) | 108 0(5) | 108 8(6) |
| C(8)-C(6)-C(5) | 109 9(5) | 108 5(6) |
| C(15)-C(6)-C(1) | 109.5(5) | 107 5(6) |
| C(15)-C(6)-C(5) | 109 5(5) | 110 7(6) |
| C(15)-C(6)-C(8) | 105 0(5) | 106.0(5) |
| C(9)-C(8)-C(6) | 116 4(5) | 115 9(5) |
| C(10)-C(9)-C(8) | 119.9(4) | 119.8(5) |
| C(14)-C(9)-C(8) | 120 0(5) | 120.1(6) |
| C(16)-C(15)-C(6) | 116 2(5) | 115.5(6) |
| C(17)-C(16)-C(15) | 120 1(5) | 122 6(6) |
| C(21)-C(16)-C(15) | 119 5(4) | 117.3(6) |
| C(1)-N(1)-H(1) | 116.0(5) | 103 4(5) |

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