Triazolopyridines. Part 7.[1] Preparation of Bromo-triazolopyridines and -triazoloisoquinolines

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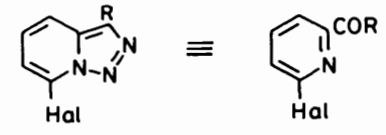
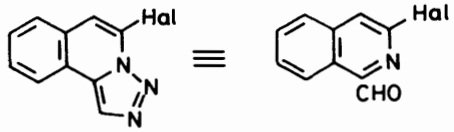
Bromination of the 7-lithiotriazolopyridines (**7**) and (**10**) gave small yields of the 7-bromotriazolopyridines (**8**) and (**11**). Some ring opening was observed with the lithium derivative (**7**); ring opening was a major reaction when bromine reacted with 5-lithiotriazoloisoquinoline (**15**) or with the 7-trimethylsilyltriazolopyridine (**20**). Good yields of 7-bromotriazolopyridines (**8**) and (**18**) and of 5-bromotriazoloisoquinoline (**19**) were obtained from the appropriate lithio derivative and dibromotetrachloroethane. The properties of 5-trimethylsilyltriazoloisoquinoline and its lithium derivative are reported; protodesilylation has been achieved with compounds (**25**)—(**28**).

A considerable widening in the scope of our synthesis of 2,6-disubstituted pyridines[1-4] and of 1,3-disubstituted isoquinolines[5] could be achieved if 7-halogenotriazolopyridines (**1**) or 5-halogenotriazoloisoquinolines (**2**) were readily available. In the former case a 7-bromotriazolopyridine provides a synthon for 6-bromopyridine-2-carbaldehyde. Assuming that the bromine atom could be readily displaced by nucleophiles a range of 6-substituted pyridine-2-carbaldehydes would thus become available which cannot be obtained by nucleophilic attack on the sensitive aldehyde itself. Furthermore, similar reactions on the 5-bromotriazoloisoquinolines would effectively allow nucleophilic substitution at position 3 of isoquinoline, which is not possible on the isoquinoline itself. We report here our efforts to produce such bromotriazolo-pyridines and -isoquinolines, ultimately successful, which have thrown some light on the stability of these compounds towards ring opening and also on the considerable stability of trimethylsilyl groups attached to these heterocycles.



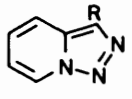
(**1**)



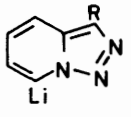
(**2**)

Hal = Halogen

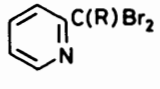
Triazolopyridine (**3**) reacts with bromine very rapidly at low temperatures to give 2-dibromomethylpyridine,[6] and even the 7-lithio derivative (**4**) undergoes substantial ring opening when treated with bromine at −40 °C, leading to 6-bromo-2-dibromomethylpyridine as the major product.[3] Our earlier observation that 3-substituted triazolopyridines were more resistant to bromine [although we have since found that 3-methyltriazolopyridine (**5**) can react to give a high yield of ring-opened product (**6**)] led us to investigate the reaction between the lithio derivative (**7**) and bromine. Much of the reaction mixture appeared polymeric and much triazolopyridine (**5**) was recovered, but there was a small amount (3.5%) of a monobromotriazolopyridine. The n.m.r. spectrum showed it to be the 7-bromo derivative, since the prominent downfield doublet due to 7-H was absent. A second product, formed in slightly higher yield (6%), was the 6-bromo-2-dibromoethylpyridine (**9**). Bromination of 7-lithio-3-(*N*,*N*-diethylcarbamoyl)triazolopyridine (**10**) gave three isomeric monobromotriazolopyridines all in poor yield. The isomer obtained in highest yield (10%) was the 7-bromo derivative (**11**); the other fully characterized isomer showed in the n.m.r. spectrum a downfield doublet (*J* 2 Hz) at δ 8.65 (7-H) indicating that the bromine atom was in position 6—compound (**12**). The third isomer, characterized spectroscopically, was the 4-bromotriazolopyridine (**13**).



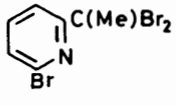
(**3**) R = H
(**5**) R = Me



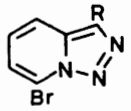
(**4**) R = H
(**7**) R = Me
(**10**) R = $CONEt_2$



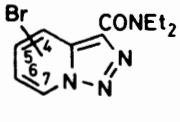
(**6**) R = Me



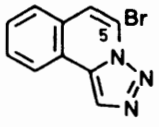
(**9**)



(**8**) R = Me
(**11**) R = $CONEt_2$
(**18**) R = H

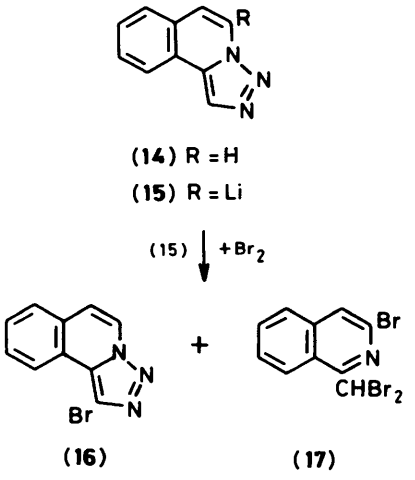


(**12**) 6 - Br
(**13**) 4 - Br



(**19**)

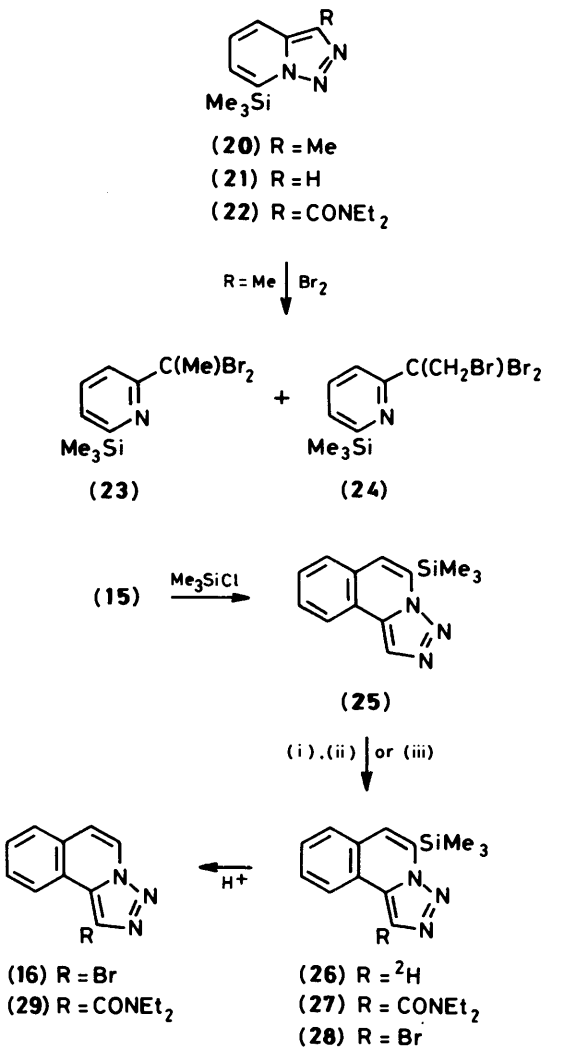
Turning to triazoloisoquinoline (**14**), bromination of its 5-lithio derivative (**15**) at −40 °C gave two products. One product was a bromotriazoloisoquinoline, but was shown to be identical with the known[5] 1-bromo derivative (**16**). The second product, from its analysis and molecular ion isotope pattern, had three bromine atoms. The n.m.r. spectrum was that of an isoquinoline and the product is 3-bromo-1-dibromomethylisoquinoline (**17**). The isolation of this product is notable since direct bromination of triazoloisoquinoline (**14**) gives the 1-bromo derivative (**16**) with no ring opening, and it is becoming obvious that substituents *peri* to nitrogen can destablize the five-membered ring in triazolopyridines, possibly by lone pair–lone pair repulsion.



Encouraged by our isolation of small amounts of 7-bromotriazolopyridines we sought a brominating agent which was less reactive in electrophilic ring opening. Treatment of 7-lithio-3-methyltriazolopyridine (**7**) with *N*-bromosuccinimide gave no bromination. Addition of 1,2-dibromo-1,1,2,2-tetrachloroethane (DBTCE) to a solution of the lithio derivative (**7**) in tetrahydrofuran gave the 7-bromo derivative (**8**) in 25% yield; change of solvent to toluene increased the yields to 70—80%. Similar reactions using 7-lithiotriazolopyridine (**4**) and 5-lithiotriazoloisoquinoline (**15**) gave the bromo compounds (**18**) (60—70%) and (**19**) (65%) respectively.

In a parallel approach to the 7-bromotriazolopyridines we have studied the preparation and properties of the trimethylsilyl derivatives (**20**)—(**22**), and (**25**). Trimethylsilyl groups are reported[7] to react with bromine to give aryl bromides, but we have discovered that trimethylsilyl substituents adjacent to bridgehead nitrogen in triazolopyridines are very stable except to the most extreme conditions of electrophilic substitution. The trimethylsilyl derivatives were obtained in good yield from the appropriate lithio derivative and trimethylsilyl chloride. When the 3-methyltriazolopyridine (**20**) was treated with bromine in carbon tetrachloride a gas was evolved. Two products were obtained, one in trace quantities. The major product was shown by microanalysis and mass spectroscopy to be a dibromopyridine; n.m.r. signals at δ 0.3 (9 H) and at 3.0 (3 H), and aromatic absorption at δ 7.4, 7.6, and 8.0 established the structure as 2-(1,1-dibromoethyl)-6-trimethylsilylpyridine (**23**). Treatment of this compound with bromine in hot carbon tetrachloride gave partial conversion into the trace product from the original reaction. Spectroscopic evidence leads us to formulate the second product as 2-(1,1,2-tribromoethyl)-6-trimethylsilylpyridine (**24**).

The apparent stability of the trimethylsilyl group in compound (**20**) inhibited further work on compounds (**21**) and



Reagents: for compound (**26**), i, LDA, ^2H_2O; ii, for compound (**27**), i, LDA, Et_2NCOCl; iii, for compound (**28**), Br_2

(**22**). However, we have investigated the reactions of 5-trimethylsilyltriazoloisoquinoline more extensively, viewing the trimethylsilyl substituent as an excellent blocking group. When compound (**25**) was lithiated and the lithio derivative quenched with deuterium oxide, [1-^{2}H]triazoloisoquinoline (**26**) was obtained, easily identified by the loss of the 1-H singlet from the n.m.r. spectrum. Treatment of the lithium derivative with *N*,*N*-diethylcarbamoyl chloride gave the 1-(*N*,*N*-diethylcarbamoyl)-triazoloisoquinoline (**27**). Direct bromination of compound (**25**) gave the 1-bromo derivative (**28**). As expected, removal of the trimethylsilyl groups from compounds (**25**), (**27**), and (**28**) was difficult. Hot glacial acetic acid failed to remove the trimethylsilyl group from compounds (**27**) or (**28**). When a carbon tetrachloride solution of 5-trimethylsilyltriazoloisoquinoline was treated with 98% sulphuric acid the n.m.r. spectrum of the protonated form was obtained, with a downfield shift of 1-H of 0.6 p.p.m. as the most obvious change. When the solution was warmed to 60 °C, the spectrum changed over 10 min, with the development of a doublet at δ 8.55 due to 5-H in the protonated triazoloisoquinoline; the free base (**14**) could be isolated in virtually quantitative yield. Similar treatment (80 °C, 2 h) of the amidotrimethylsilyl derivative (**27**) gave 1-(*N*,*N*-diethylcarbamoyl)triazoloisoquinoline (**29**), characterized by analysis and by its n.m.r. spectrum. The bromotrimethylsilyl derivative

(**28**) was protodesilylated in 98% sulphuric acid (1 h) to give the known 1-bromotriazoloisoquinoline (**16**) in virtually quantitative yield. Although the conditions for removal of the trimethylsilyl group from a triazoloisoquinoline appear harsh, we have not observed appreciable ring opening, nor have other substituent groups been affected, so that the trimethylsilyl group must be considered satisfactory for blocking position 5 in triazoloisoquinoline. We have observed similar protodesilylation of 3-methyl-7-trimethylsilyltriazolopyridine (**20**), using 98% sulphuric acid (52 h at 35 °C).

Experimental

M.p.s were performed on a Kofler heated stage and are uncorrected. N.m.r. spectra were determined for solutions in $CDCl_3$ and i.r. spectra for KBr discs unless otherwise stated. Purification was by column on silica or alumina (activity IV), on p.l.c. plates (silica PF_{254}) or on Chromatotron discs (2 mm silica). Lithiations were performed under an argon atmosphere.

Bromination of 7-Lithio-3-methyltriazolopyridine (**7**).—(*a*) Bromine (2.11 g, 13.23 mmol) was added dropwise to a solution of the lithio derivative (**7**) (12.06 mmol) prepared from LDA and 3-methyltriazolopyridine [2] at −40 °C. The mixture was allowed to come to room temperature overnight and then treated with water. Separation of the organic layer was followed by successive extractions of the aqueous layer by dichloromethane, chloroform, and ethyl acetate. The combined organic layers were dried ($MgSO_4$) and the solvents evaporated to give an oil (2.2 g) which was purified on a Chromatotron eluting with light petroleum (b.p. 60—80 °C) with increasing amounts of ethyl acetate. First eluted was 6-bromo-2-(1,1-dibromoethyl)pyridine (**9**), m.p. 36—38 °C (light petroleum) (0.18 g, 6%); δ 2.9 (3 H, s), 7.35 (1 H, dd), 7.5 (1 H, t), and 8.0 (1 H, dd, *J* 8 and 2 Hz). The second product eluted in very small yield was tentatively identified as 6-bromo-2-(1,1,2-tribromoethyl)pyridine, δ 4.7 (2 H, s), 7.3—7.7 (2 H, m), and 7.8—8.0 (1 H, m). The third product was *7-bromo-3-methyltriazolopyridine* (**8**) (0.07 g, 3.5%), m.p. 103—105 °C [from light petroleum (b.p. 60—80 °C)] (Found: C, 39.95; H, 2.7; N, 19.55. $C_7H_6BrN_3$ requires C, 39.6; H, 2.85; N, 19.8%); *m/z* 211, 213 (M^+); δ 2.6 (3 H, s), 6.8—7.2 (2 H, m), and 7.5 (1 H, dd, *J* 8 and 3 Hz, 4-H). After starting material (**5**) (0.3 g) had been eluted, methanol eluted black tar (1 g).

(*b*) A solution of 3-methyltriazolopyridine (**5**) (6.5 g) in anhydrous toluene was added to butyl-lithium (2.3M in hexane; 23 ml) in toluene (50 ml) at −40 °C and the solution kept at this temperature (2.5 h). Addition of a solution of dibromotetrachloroethane (DBTCE) (sublimed, 17 g) in toluene (50 ml) discharged the red colour and the mixture was allowed to come to room temperature. Addition of a saturated solution of ammonium chloride in aqueous ammonia (*d* 0.88; 50 ml) was followed by separation of the toluene layer and extraction of the aqueous layer by further toluene. The combined toluene solutions, after drying, were evaporated to give a brown solid (14 g). Chromatography on alumina (400 g) eluting with ethyl acetate–light petroleum (b.p. 60—80 °C) (1:9) gave DBTCE (3 g). Increasing the proportion of ethyl acetate to 50% allowed elution of the bromotriazolopyridine (**8**) (7.3 g, 70%). In some runs 80% yield could be achieved.

Bromination of 3-(N,N-Diethylcarbamoyl)-7-lithiotriazolopyridine (**10**).—A solution of bromine (3.84 g, 24 mmol) in ether (50 ml) was added at −40 °C to a solution of the lithio derivative (**10**) [from the amide (4.48 g) and LDA (45 mmol) in ether (60 ml), previously stirred at −40 °C for 6 h]. The mixture was left overnight to reach room temperature and then worked up with ammonium chloride in aqueous ammonia as described above. Crude product (5.82 g) was purified on an alumina column eluting with light petroleum (b.p. 60—80 °C) with increasing amounts of ethyl acetate. Four compounds were obtained described in order of elution. (i) *6-Bromo-3-diethylcarbamoyltriazolopyridine* (**12**), m.p. 136—138 °C (from ether) (0.2 g, 5%) (Found: C, 44.15; H, 4.05; N, 18.5. $C_{11}H_{13}BrN_4O$ requires C, 44.45; H, 4.35; N, 18.85%); δ 1.3 (6 H, dt), 3.3—4.2 (4 H, 2 q), 7.3 (1 H, dd, *J* 8 and 2 Hz, 5-H), 8.15 (1 H, d, *J* 8 Hz, 4-H), and 8.65 (1 H, d, *J* 2 Hz, 7-H). (ii) *7-Bromo-3-diethylcarbamoyltriazolopyridine* (**11**) (0.4 g, 10%), m.p. 95 °C [light petroleum (b.p. 60—80 °C)] (Found: C, 44.35; H, 4.15; N, 18.9%); δ 1.3 (6 H, t), 3.6 (2 H, br q), 4.0 (2 H, br q), 7.15—7.35 (2 H, m), and 8.35 (1 H, dd, *J* 6 and 1 Hz, 4-H). (iii) 3-(*N,N*-Diethylcarbamoyl)triazolopyridine (1.5 g). (iv) A mixture, repurified on alumina, to give 4-bromo-3-diethylcarbamoyltriazolopyridine (**13**) as an oil; δ 1.25 (6 H, br t), 3.25 (2 H, q), 3.6 (2 H, q), 6.8 (1 H, t, *J* 6 Hz, 6-H), 7.45 (1 H, d, *J* 6 Hz, 5-H), and 8.6 (1 H, d, *J* 6 Hz, 7-H).

Bromination of 5-Lithiotriazoloisoquinoline (**15**).—(*a*) A solution of the triazoloisoquinoline (**15**) (4.7 mmol) in ether (200 ml) was added at −70 °C to LDA [from di-isopropylamine (0.5 g) and butyl-lithium (1.6M; 3 ml)]. Stirring was continued at −20 °C (1 h) and then bromine (1.8 g) in ether (30 ml) was added and the solution allowed to come to room temperature overnight. Saturated aqueous potassium carbonate was added and the ether layer separated; the aqueous layer was then washed with ether and the combined extracts and ether layer were dried (Na_2SO_4), and evaporated. The residue was purified on a column of silica, eluant dichloromethane. First eluted was *3-bromo-1-dibromomethylisoquinoline* (**17**) (0.4 g, 22%), m.p. 136—138 °C [light petroleum (b.p. 40—60 °C)] (Found: C, 31.95; H, 1.5; N, 3.65. $C_{10}H_6Br_3N$ requires C, 31.55; H, 1.55; N, 3.7%); δ 7.05 (1 H, s), 7.5—7.8 (3 H, m), 7.85 (1 H, s), and 8.4—8.8 (1 H, m). Second eluted was 1-bromotriazoloisoquinoline (**16**) (0.3 g), m.p. 136 °C (cyclohexane), identical with a sample prepared by direct bromination of triazoloisoquinoline.[5] (*b*) A solution of triazoloisoquinoline (**14**) (1 g) in anhydrous toluene (40 ml) was converted into the 5-lithio derivative (**15**) as described for 3-methyltriazolopyridine (method b). Addition of DBTCE (1.9 g) and work-up as described gave a crude product (1.65 g) which was recrystallized from carbon tetrachloride to give *5-bromotriazoloisoquinoline* (**19**) (0.95 g, 65%), m.p. 161—162 °C (Found: C, 48.0; H, 2.45; N, 16.9. $C_{10}H_5BrN_3$ requires C, 48.4; H, 2.4; N, 16.9%); δ 7.3 (1 H, s, 6-H), 7.4—7.6 (3 H, m), 7.7—8.05 (1 H, m), and 8.35 (1 H, s, 1-H).

7-Bromotriazolopyridine (**18**).—Using a procedure identical with that described for 3-methyltriazolopyridine (method b), *7-bromotriazolopyridine* (**18**), m.p. 95—95.5 °C (from cyclohexane) was obtained in 60—70% yield (Found: C, 36.2; H, 1.95; N, 21.25. $C_6H_4BrN_3$ requires C, 36.5; H, 2.0; N, 21.2%); δ 7.0—7.2 (2 H, overlapping d, *J* 7 and 6 Hz, 4- and 6-H), 7.55—7.65 (1 H, dd, *J* 7 and 6 Hz, 5-H), and 8.1 (1 H, s, 3-H).

3-Methyl-7-trimethylsilyltriazolopyridine (**20**).—A solution of 7-lithio-3-methyltriazolopyridine (**7**) [from 6 g of compound (**5**)] prepared as described above at −40 °C, was allowed to come to room temperature and trimethylsilyl chloride (5 g) was added; the mixture was stirred overnight and then decomposed with water and worked up in the usual way. The product (a red oil, 8 g) was almost pure product (**20**). Final purification by Chromatotron [eluant: ethyl acetate–light petroleum (b.p. 60—80 °C), 1:9] gave the pure *trimethylsilyl derivative* (**20**) (5.6 g, 60%), b.p. 120 °C/0.04 mmHg (bulb tube) (Found: C, 58.35; H, 7.6; N, 20.3. $C_{10}H_{15}N_3Si$ requires C, 58.5; H, 7.35; N, 20.45%); δ 0.5 (9 H, s), 2.55 (3 H, s), 6.9—7.2 (2 H, m), and 7.5 (1 H, dd, *J* 7 and 1 Hz, 4-H).

3-(N,N-*Diethylcarbamoyl*)-7-*trimethylsilyltriazolopyridine* (**22**).—Prepared as described for compound (**20**), from 3-(*N,N*-diethylcarbamoyl)triazolopyridine,[4] the *trimethylsilyl derivative* (**22**) had m.p. 79—80 °C (Found: C, 58.25; H, 7.75; N, 19.35. $C_{14}H_{22}N_4OSi$ requires C, 57.9; H, 7.65; N, 19.3%).

Reaction of 3-*Methyl*-7-*trimethylsilyltriazolopyridine* (**20**) *with Bromine*.—(*a*) A solution of bromine in carbon tetrachloride (5%; 6 ml) was added dropwise to a stirred solution of compound (**20**) in dichloromethane (10 ml) at room temperature. Vigorous evolution of gas was noted. After 3 h at room temperature the solvent was removed to give a crude residue (1.3 g). Separation on a Chromatotron (eluant light petroluem) gave first a trace of compound (**24**) [see (*b*)], then 2-(1,1-*dibromoethyl*)-6-*trimethylsilylpyridine* (**23**) (0.7 g, 50% on unrecovered starting material) (Found: C, 33.75; H, 4.45; N, 4.0. $C_{10}H_{15}Br_2NSi$ requires C, 35.6; H, 4.45; N, 4.15%); δ 0.3 (9 H, s), 3.0 (3 H, s), 7.4 (1 H, dd, *J* 8 and 2 Hz), 7.6 (1 H, t, *J* 8 Hz, 4-H), 8.0 (1 H, dd, *J* 8 and 2 Hz). Further elution with light petroleum–ethyl acetate (19:1) gave starting material (**20**) (0.17 g).

(*b*) To a solution of compound (**23**) (0.23 g) in carbon tetrachloride was added dropwise a solution of bromine in carbon tetrachloride (5%; 1.5 ml), and then the mixture was boiled (2 h). A precipitate was filtered off; evaporation of the filtrate gave 2-(1,1,2-tribromoethyl)-6-trimethylsilylpyridine (**24**) (43% yield); δ 0.4 (9 H, s), 4.9 (2 H, s), 7.25 (1 H, dd, *J* 8 and 2 Hz), 7.6 (1 H, t, *J* 8 Hz), 7.95 (1 H, dd, *J* 8 and 2 Hz). The *precipitate*, treated with water and extracted with dichloromethane, gave compound (**23**).

1-(N,N-*Diethylcarbamoyl*)-5-*trimethylsilyltriazoloisoquinoline* (**27**).—A solution of the trimethylsilyl derivative (**25**)[5] (1.24 g) in anhydrous ether (70 ml) was added at 0 °C to LDA [from butyl-lithium (1.6M in hexane; 4.5 ml) and diisopropylamine (0.5 g) prepared at −70 °C]; during the addition a violet colour developed. A solution of *N,N*-diethylcarbamoyl chloride (0.69 g) in ether (10 ml) was added after which the mixture was allowed to come to room temperature and stirred (48 h). Hydrolysis with ammonium chloride–ammonia, separation, drying of the organic layer and combined ethereal extracts, and evaporation gave crude product (1.62 g). Purification on a silica column, eluting with chloroform with increasing amounts of ethyl acetate gave first starting material (**25**) (0.21 g) and then the *carbamoyltrimethylsilyltriazoloisoquinone* (**27**) (0.74 g, 46%), m.p. 114—116 °C [light petroleum (b.p. 40—60 °C)] (Found: C, 63.45; H, 7.25; N, 16.4. $C_{18}H_{24}N_4OSi$ requires C, 63.5; H, 7.25; N, 16.4%); δ 0.5 (9 H, s), 1.0—1.5 (6 H, t), 3.3—3.8 (4 H, q), 7.2 (1 H, s, 6-H), 7.4—7.7 (3 H, m), and 8.5—8.7 (1 H, m); $\nu_{max.}$ 1 620 and 1 630 cm^{-1}.

1-*Bromo*-5-*trimethylsilyltriazoloisoquinoline* (**28**).—A solution of bromine (0.38 g) in carbon tetrachloride (5 ml) was added at room temperature to a stirred solution of compound (**25**)[5] (0.2 g) in carbon tetrachloride (5 ml). Stirring was continued for 20 min during which a solid separated. The filtrate was evaporated to give almost pure *bromotrimethylsilyltriazoloisoquinoline* (**28**) (0.14 g), m.p. 129—130 °C (light petroleum) (Found: C, 48.7; H, 4.4; N, 13.1. $C_{13}H_{14}BrN_3Si$ requires C, 48.75; H, 4.35; N, 13.1%); δ 0.5 (9 H, s), 7.1 (1 H, s, 6-H), 7.3—7.6 (3 H, m), 8.4—8.8 (1 H, m). The solid was treated with water and extracted with dichloromethane; evaporation of the extract after drying gave a further product (**28**) (0.12 g); total yield 0.26 g (95%).

1-(N,N-*Diethylcarbamoyl*)*triazoloisoquinoline* (**29**).—An n.m.r. solution of the trimethylsilyl derivative (**27**) in CCl_4 was treated with 1 drop of 98% H_2SO_4 and the spectrum determined. The solution was then heated at 80 °C; over 2 h the signal at δ 0.39 was replaced by one at δ 0.5. The solution was cooled, poured into aqueous sodium hydrogen carbonate, and the organic product isolated, giving the *amide* (**29**) in virtually quantitative yield, m.p. 101—103 °C (light petroleum) (Found: C, 66.8; H, 6.0; N, 20.55. $C_{15}H_{16}N_4O$ requires C, 67.15; H, 5.95; N, 20.9%); δ 1.35 (6 H, t), 3.55 (4 H, q), 7.05 (1 H, d, *J* 8 Hz, 6-H), 7.2—7.6 (3 H, m), 8.25 (1 H, d, *J* 8 Hz, 5-H), and 8.7—8.9 (1 H, m, 10-H).

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