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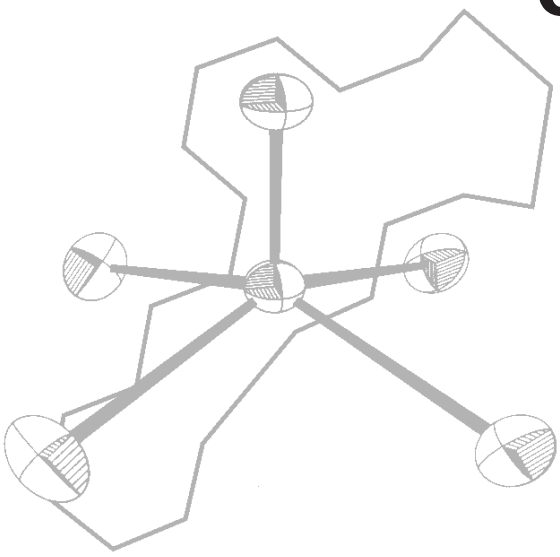

Volume 53, 2000

A journal for the publication of original research
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Aust. J. Chem., 2000, **53**, 619–622

A Synthesis of 1-Hydroxy-5-(2-substituted aryl)tetrazoles by Directed Lithiation

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Dilithiation of 1-hydroxy-5-aryltetrazoles with 2 equiv. of butyllithium in the presence of *N,N,N′N′*-tetramethylethylenediamine enables the introduction of *ortho*-substituents into the aryl ring to form compounds (6a–e). The hydroxy group of 1-hydroxy-5-phenyltetrazole may be masked by alkylation with 9-anthrylmethyl chloride. The masking group is removed with 1,4-diazabicyclo[2.2.2]octane or migrated to N 3 by treatment with trifluoroacetic acid to form the *N*-oxide (10).

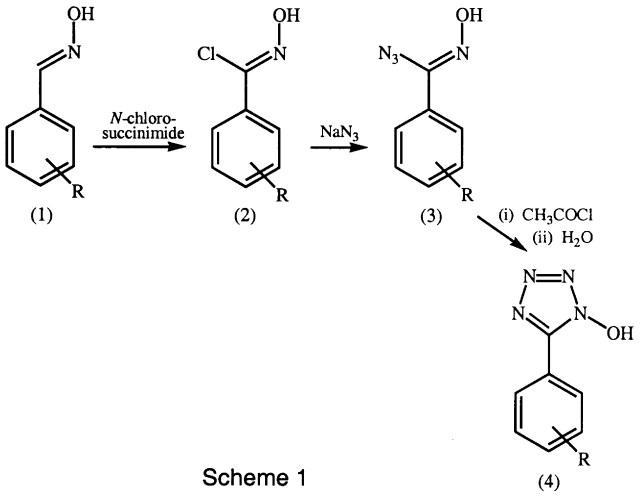
Keywords. 1-Hydroxy-5-aryltetrazoles; lithiation; alkylation; *ortho*-substituent.

Introduction

During a program directed at the discovery of new crop protection chemicals, 1-hydroxytetrazoles were found to provide precursors for a group of highly active herbicides.[1] Subsequent analoging and structure–activity studies suggested that certain 1-hydroxy-5-aryltetrazoles were more likely to provide active compounds, particularly those derivatives where the pendent aryl ring bore a substituent in the 2-position.

In principle, a large number of variations in substitution of the aryl ring are available by adopting the original synthetic pathway devised by Plenkiewicz[2] (Scheme 1, R = H). This procedure utilizes aldoximes (1) as starting materials which in turn are readily obtained from numerous commercially available aryl aldehydes. Chlorination to the hydroximoyl chloride (2) followed by displacement with the azide anion provides azidoximes (3) which can be cyclized to 1-hydroxytetrazoles (4) with acetyl chloride. With some minor modifications to avoid isolation of the hydroximoyl chloride and the potentially hazardous azidoximes, a range of 5-substituted 1-hydroxytetrazoles (4) were obtained without difficulty.

Even so, it was desirable to increase the number of tetrazoles bearing *ortho*-substituents in the aryl ring beyond the realms accessible from commercial aldehydes. To this end it seemed more efficient to investigate methodology which could enable introduction of a variety of substituents by using a few key 5-aryltetrazole precursors rather than pursue a plethora of *ortho*-substituted aryl aldehydes as individual synthetic targets.



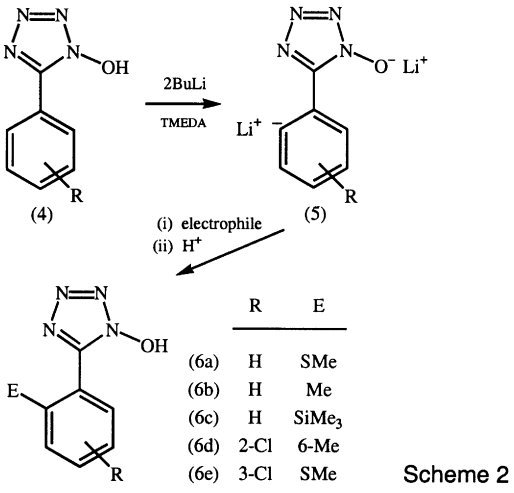
Scheme 1

Results and Discussion

It has been observed that lithiation of aryl-substituted heterocycles often leads to lithiation of the aryl ring at a position adjacent to the location of the heterocyclic ring as a consequence of stabilization of the lithiated product by a proximate heteroatom. Indeed, encouraging results have been obtained following dilithiation of 5-phenyltetrazole[3] as well as with benzoic acids.[4] In addition there was the attractive prospect of obtaining compounds bearing 2,6-disubstitution on the phenyl ring. This structural type was found not to be accessible by the Plenkiewicz procedure as a result of resistance to cyclization by the azidoxime intermediate.

Thus, with the present heterocycle there was the possibility that, following the formation of a lithium salt of the highly acidic hydroxy group, further treatment with butyllithium might abstract an *ortho*-proton from the phenyl substituent. Subsequent reaction with suitable electrophiles should then introduce an *ortho*-substituent (Scheme 2).

Manuscript received 23 May 2000 10.1071/CH00073 0004-9425/00/070619



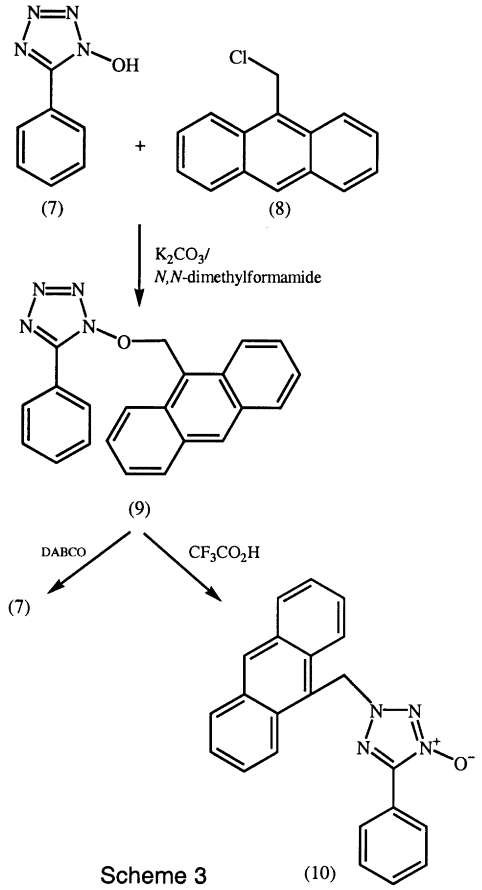
Scheme 2

In the event it was found that treatment of 1-hydroxy-5-phenyltetrazole (4; R = H) with 2 equiv. of *n*-butyllithium in tetrahydrofuran at –77° for 1 h followed by addition of an electrophile and subsequent acidification returned only the starting tetrazole. On the other hand, inclusion of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in the reaction mixture led to formation of coloured solutions during the addition of the second equivalent of butyllithium. These solutions then readily gave 2-substituted products following reaction with dimethyl disulfide (6a), methyl iodide (6b), and trimethylsilyl chloride (6c) respectively. A 2,6-disubstituted product (6d) was prepared without difficulty by methylation of the dianion from 5-(2-chlorophenyl)-1-hydroxytetrazole (4; R = 2-Cl). On the other hand, thioalkylation of the dianion from 5-(3-chlorophenyl-1-hydroxytetrazole (4; R = 3-Cl) with dimethyl disulfide resulted in insertion of the introduced group between the existing substituents[4] to afford (6e).

It was expected that instances would occur where conversion was incomplete and the product would consist of two or more highly polar tetrazoles which could prove difficult to separate. It seemed prudent, therefore, to investigate the feasibility of forming some less polar derivative amenable to chromatographic purification yet susceptible to facile cleavage to restore the parent tetrazole. For such a purpose, *O*-alkylated derivatives seemed potentially useful. With ease of subsequent cleavage in mind, the possibility of employing a 9-anthrylmethyl group was considered since derivatives of this type have been previously advocated[5] for the protection of carboxylic acids, phenols and some other classes of compounds. They have been shown to be easily cleaved by the sodium salt of methyl mercaptan in *N*,*N*-dimethylformamide at room temperature or, in some instances, by trifluoroacetic acid in methylene chloride.[5]

Alkylation of 1-hydroxy-5-phenyltetrazole (7) with 9-anthrylmethylchloride (8) in *N*,*N*-dimethylformamide in the presence of potassium carbonate readily gave the crystalline ether (9) in 90% yield (Scheme 3).

Conditions for efficient recovery of the tetrazole from this derivative proved more difficult to establish than expected. In our hands, treatment of (9) with sodium methyl mercaptide in *N*,*N*-dimethylformamide produced irksome mixtures as did



Scheme 3

several alternatives.[5] In due course it was found that the model compound could be cleaved efficiently by brief heating with an excess of 1,4-diazabicyclo[2.2.2]octane (DABCO) in acetonitrile. Apparently under these conditions DABCO is readily quaternized by transfer of the 9-anthrylmethyl group to give a water-soluble quaternary salt together with the DABCO salt of the 1-hydroxy-5-phenyltetrazole from which the tetrazole (70% yield) was easily liberated by acidification.

Surprisingly, treatment of (9) with trifluoroacetic acid[5] induced rapid transformation to an isomeric product (10) in high yield. Evidently the acid causes protonation of the oxygen atom and this is followed by dissociation into the starting hydroxytetrazole together with the anthrylmethyl cation. Recombination occurs to a significant extent at nitrogen to give a product stable to trifluoroacetic acid. After several cycles, much of the substituent is redistributed to form a thermodynamically favoured *N*-oxide product (10) (60%). In addition, some 1-hydroxy-5-phenyltetrazole (7) (16%) is generated, possibly as a consequence of a minor pathway whereby the carbenium ion is trapped by the weakly nucleophilic trifluoroacetate anion. The observed shift of the methylene carbon in its ^{13}C n.m.r. spectrum from δ 75.6 in the *O*-alkylated material (9) to δ 50.9 in the *N*-oxide (10) is consistent with this interpretation. Thermal migration of substituents from oxygen to nitrogen in 1-alkoxy-5-aryltetrazoles to form 3-alkyl-5-aryltetrazole 1-oxides has been observed previously,[6] apparently arising by an intermolecular transfer mechanism.

Experimental

Melting points were determined on a Reichert Kofler hot-stage micro-melting point apparatus and are uncorrected. Microanalyses were performed by Campbell Microanalytical Laboratory, University of Otago, New Zealand. Infrared spectra were recorded on a Perkin–Elmer 842 spectrophotometer (cm^{-1}) and refer to paraffin mulls. ^1H and ^{13}C n.m.r. spectra were recorded at 200 and 50.3 MHz, respectively, on a Bruker AC-200 spectrometer. Chemical shifts (δ) are measured in ppm with tetramethylsilane as an internal standard. Radial thin-layer chromatography was performed on a Harrison Research Chromatron (7924T) by using 4 mm thick silica plates (silica gel 60 PF_{254}, Merck No. 7749). All reactions involving organometallic reagents and intermediates were performed under an atmosphere of argon. The butyllithium solution was standardized by using 2,5-dimethoxybenzyl alcohol as an indicator[7] and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was distilled from potassium hydroxide. Tetrahydrofuran was freshly distilled from sodium/benzophenone under argon immediately prior to use. All other commercially available reagents were used without further purification. Light petroleum refers to the fraction with a b.p. of 40–60°.

1-Hydroxy-5-phenyltetrazole (4; R = H)

1-Hydroxy-5-phenyltetrazole (4; R = H) was prepared as described,[2] m.p. 154–156° (lit.[2] 151–152°). ^1H n.m.r. δ ($(CD_3)_2SO$) 7.3, m, 3H, ArH; 8.05, m, 2H, ArH. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 122.6, 127.4, 129.1, 131.3, 145.7.

5-(2-Chlorophenyl)-1-hydroxytetrazole (4; R = 2-Cl)

To a solution of 2-chlorobenzaldoxime (7.8 g, 0.05 mol) in acetonitrile (40 ml) containing 5 drops of concentrated hydrochloric acid was added *N*-chlorosuccinimide (7.3 g, 0.055 mol) in portions (*c*. 1 g) at a rate which allowed a transient blue-green colour to fade before each subsequent addition. Following the final addition, the solution was allowed to stand for 30 min, and then diluted with water (80 ml) and extracted with benzene (2×40 ml). The combined benzene extracts containing the hydroxamoyl chloride were subsequently used to prepare a solution of the azidoxime without any further purification.

A solution of sodium azide (6.5 g, 0.1 mol) in water (33 ml) was added in a thin stream with stirring to the benzene solution of the hydroxamoyl chloride (obtained as described above) cooled in an ice bath. The mixture was then stirred at room temperature for 48 h. The aqueous layer was then separated and the organic phase was washed with water (2×100 ml). The extract was dried over sodium sulfate and used in the cyclization without undue delay. Drying the solution over anhydrous magnesium sulfate sometimes led, after a brief delay, to commencement of a brisk effervescence with decomposition of the azidoxime. A similar phenomenon was on rare occasions observed during drying with anhydrous sodium sulfate, but only after a much longer delay.

The benzene solution containing crude azidoxime (obtained as described above) was added in a thin stream to an excess of acetyl chloride (20 ml) in benzene (20 ml) cooled in ice; the mixture was allowed to warm over 2 h to room temperature and then allowed to stand for 48 h. The mixture was partially evaporated (to about 30 ml), cautiously diluted with water (10 ml) and stirred for 10 min and then simmered for 2 h. The cooled mixture was diluted with water (100 ml) and extracted with diethyl ether (100 ml). The ether extract was washed with water and then extracted with two portions of saturated sodium bicarbonate (100 ml each). The combined sodium bicarbonate extracts were acidified to pH 1 by the addition of concentrated hydrochloric acid and the precipitate was collected by filtration and washed on the filter with water to give the *tetrazole* (4; R = 2-Cl) (5.3 g, 54%) as colourless needles, m.p. 187–190°. A portion was recrystallized from ethyl acetate to give colourless prisms, m.p. 189–192° (Found: C, 43.0; H, 2.3; N, 28.5. $C_7H_5ClN_4O$ requires C, 42.8; H, 2.6; N, 28.5 %). ^1H n.m.r. δ ($(CD_3)_2SO$) 7.83–7.45, m . ^{13}C n.m.r. δ ($(CD_3)_2SO$) 122.4, 2×C; 127.5; 130.0; 132.1; 133.0; 145.5.

5-(3-Chlorophenyl)-1-hydroxytetrazole (4; R = 3-Cl)

The *tetrazole* (4; R = 3-Cl) was obtained (51% yield) by a similar procedure as above from 3-chlorobenzaldehyde. Colourless prisms were obtained from ethyl acetate/light petroleum, m.p. 122–124° (Found: C, 42.6; H, 2.4; N, 28.3. $C_7H_5ClN_4O$ requires C, 42.8; H, 2.6; N, 28.5%). ^1H n.m.r. δ ($(CD_3)_2SO$) 7.42–7.61, m, 2ArH; 7.94–8.08, m, 2ArH. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 125.2, 125.4, 126.2, 130.4, 130.8, 133.5, 143.6.

5-(4-Chlorophenyl)-1-hydroxytetrazole (4; R = 4-Cl)

The *tetrazole* (4; R = 4-Cl) was obtained by a similar procedure as above (57% yield) from 4-chlorobenzaldehyde. Colourless needles were obtained from ethyl acetate, m.p. 207–208° (Found: C, 42.9; H, 2.4; N, 28.3%. $C_7H_5ClN_4O$ requires C, 42.8; H, 2.6; N, 28.5 %) ^1H n.m.r. δ ($(CD_3)_2SO$) 7.61, d, *J* 8.8 Hz; 8.20, d, *J* 8.8 Hz. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 123.0; 128.1, 2×C; 128.7, 2×C; 134.7; 143.0.

1-Hydroxy-5-(2-methylphenyl)tetrazole (6b)

The *tetrazole* (4; R = 2-Me) was prepared (41% yield) in a similar manner from 2-methylbenzaldehyde. Fawn plates were obtained from benzene, m.p. 122–124° (Found: C, 54.2; H, 4.8; N, 31.6 . $C_8H_8N_4O$ requires C, 54.5; H, 4.6; N, 31.8 %). ^1H n.m.r. δ ($(CD_3)_2SO$) 2.31, s, Me; 7.25–7.66, m, 4ArH. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 19.5, 122.2, 126.0, 129.8, 130.7, 131.0, 137.7, 146.9.

1-Hydroxy-5-(2-methylsulfanylphenyl)tetrazole (6a)

To a stirred solution of 1-hydroxy-5-phenyltetrazole (4; R = H) (1.0 g, 6.2 mmol) in dry tetrahydrofuran (100 ml) cooled to –77° in a dry ice/acetone bath was added TMEDA (2.0 ml, 13.3 mmol) followed by *n*-butyllithium (6.5 ml, 13.6 mmol, 2.1 M solution in hexane) added dropwise. After stirring for a further 1 h at –77°; the reaction mixture was allowed to slowly warm to between –20 to –30° and held at this temperature for a further 20 min after the addition of dimethyl disulfide (1.2 ml, 13.6 mmol). The reaction mixture was quenched with dilute hydrochloric acid and water (50 ml) was then added. The resulting solution was then adjusted to pH 7 by the addition of solid $NaHCO_3$. After the organic and aqueous phases were separated, the organic phase was extracted with saturated $NaHCO_3$ (20 ml). The aqueous phase and extract were combined and acidified with concentrated hydrochloric acid and extracted with ether (2×40 ml). The combined ether extracts were washed with water (3×40 ml), dried ($MgSO_4$), and evaporated under vacuum to give a colourless oil which crystallized slowly on standing (1.1 g, 85%). Recrystallization from methanol/water gave the *product* (6a) as colourless needles, m.p. 118–120° (Found: C, 45.8; H, 3.7; N, 26.8; S, 15.3. $C_8H_8N_4OS$ requires C, 46.1; H, 3.9; N, 26.9; S, 15.4%). ^1H n.m.r. δ ($(CD_3)_2SO$) 2.45, s, Me; 7.24–7.40, m, 1ArH; 7.50–7.77, m, 3ArH. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 15.5, 121.4, 124.9, 126.6, 130.4, 131.7, 139.8, 146.1.

1-Hydroxy-5-(2-methylphenyl)tetrazole (6b) by Methylation

Following the same procedure as outlined for (6a), 1-hydroxy-5-phenyltetrazole (4; R = H) (1.0 g, 6.2 mmol) in dry tetrahydrofuran (100 ml) was treated with *n*-butyllithium (6.5 ml, 13.6 mmol, 2.1 M solution in hexane) in the presence of TMEDA (2.0 ml, 13.3 mmol). Methyl iodide (0.5 ml, 7.4 mmol) was added in place of dimethyl disulfide. The crude product (918 mg, 83%) was obtained as a pale yellow solid on acidification and extraction of the basic aqueous phase with ether. The product was recrystallized from benzene to give colourless needles (m.p. 121–123°) identical (m.p., mixture m.p. and ^1H n.m.r.) with material prepared by total synthesis.

1-Hydroxy-5-(2-trimethylsilylphenyl)tetrazole (6c)

Following the same procedure as outlined above, the hydroxytetrazole (4; R = H) (1.0 g, 6.2 mmol) in dry tetrahydrofuran (100 ml) was treated with *n*-butyllithium (6.5 ml, 13.6 mmol, 2.1 M solution in hexane) in the presence of TMEDA (2.0 ml, 13.3 mmol) followed by chlorotrimethylsilane (1.2 ml, 9.3 mmol). The reaction mixture was quenched with water (20 ml) and extracted with ether (30 ml). The

aqueous phase was cooled in an ice bath, acidified with concentrated hydrochloric acid, and extracted with ether (2×30 ml). The combined ether extracts were washed with water (4×30 ml), dried ($MgSO_4$) and evaporated under vacuum to give the crude product as a colourless solid (0.89 g, 62%), m.p. 156–160°. Recrystallization of a sample from methanol/water gave the *tetrazole* (6c) as colourless prisms, m.p. 158.5–160.0° (Found: C, 51.1; H, 5.9; N, 23.9. $C_{10}H_{14}N_4OSi$ requires C, 51.3; H, 6.0; N, 23.9%). ^{1}H n.m.r. δ ($(CD_3)_2SO$) 0.03, 9H, $SiMe_3$; 7.42–7.59 and 7.63–7.73, m, 3H. ^{13}C n.m.r. δ ($(CD_3)_2SO$) –0.5, 128.0, 129.0, 129.8, 130.0, 135.0, 140.9, 148.3.

5-(2-Chloro-6-methylphenyl)-1-hydroxytetrazole (6d)

Following the same procedure as outlined for (6a), the hydroxytetrazole (4; R = 2-Cl) (2.0 g, 10.2 mmol) in dry tetrahydrofuran (150 ml) was treated with *n*-butyllithium (10.7 ml, 22.4 mmol, 2.1 M solution in hexane) in the presence of TMEDA (3.4 ml, 22.4 mmol) followed by methyl iodide (0.8 ml, 12.8 mmol). The crude product (1.8 g) was obtained as a pale yellow solid on acidification and extraction of the basic aqueous phase with ether. The corresponding organic phase did not contain any *O*-alkylated hydroxytetrazole, as judged by the absence of any signal attributable to a methoxy group in the proton magnetic resonance spectrum. Recrystallization from aqueous methanol gave the *product* (6d) as colourless prisms (1.4 g, 68%), m.p. 233–235° (dec.) (Found: C, 45.5; H, 3.1; N 26.4. $C_8H_7ClN_4O$ requires C, 45.6; H, 3.4; N, 26.6%). ^{1}H n.m.r. δ ($(CD_3)_2SO$) 2.06, s, Me; 7.4–7.8, m, 3ArH. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 19.3, 122.1, 126.6, 128.5, 131.9, 133.8, 140.6, 144.8.

5-(3-Chloro-(2-methylsulfanylphenyl)-1-hydroxytetrazole (6e)

Following the same procedure as outlined above, the 1-hydroxytetrazole (4; R = 3-Cl) (1.5 g, 7.7 mmol) in dry tetrahydrofuran (120 ml) was treated with *n*-butyllithium (8.8 ml, 16.8 mmol, 2.1 M solution in hexane) in the presence of TMEDA (2.5 ml, 16.8 mmol), followed by dimethyl disulfide (1.5 ml, 16.8 mmol). The crude product (1.5 g, 80%) was obtained as a pale yellow oil which crystallized slowly on standing. *5-(3-Chloro-1-hydroxy-(2-methylsulfanylphenyl)tetrazole* (6e) was obtained as colourless needles from ether/benzene, m.p. 163–164° (Found: C, 39.5; H, 3.1; N, 23.1; S, 12.9. $C_8H_7ClN_4OS$ requires C, 39.6; H, 2.9; N, 23.1; S, 13.2%). ^{1}H n.m.r. δ ($(CD_3)_2SO$) 2.39, s, SMe; 7.60, t, *J* 7.7 Hz, H 5; 7.62, dd, *J* 1.8, and 7.7 Hz, H 4; 7.87, dd, *J* 1.8 and 7.7 Hz, H 6. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 18.4, 129.9, 130.0, 130.3, 132.8, 135.3, 139.6, 146.9.

1-(Anthracen-9-ylmethoxy)-5-phenyltetrazole (9)

Anthracen-9-ylmethyl chloride (460 mg, 2.0 mmol) was added to a solution of 5-phenyl-1-hydroxytetrazole (300 mg, 1.9 mmol) dissolved in *N,N*-dimethylformamide (5 ml) containing potassium carbonate (643 mg, 4.6 mmol) and the mixture was stirred overnight at room temperature. The next day the mixture was diluted with water (5 ml), stirred for 20 min and the product was collected by filtration and washed with water on the filter to afford yellow needles (631 mg, 90%) showing only one spot by t.l.c. The *compound* (9) was recrystallized from dichloromethane/cyclohexane to give pale yellow needles, m.p. 144–146° (Found: C, 74.8; H, 4.7; N, 15.6. $C_{22}H_{16}N_4O$ requires C, 75.0; H, 4.6; N, 15.9%). ^{1}H n.m.r. δ ($CDCl_3$) 6.42, s, CH_2; 7.09, m, 2H; 7.25, m, 2H; 7.49, m, 5H; 7.91, m, 2H; 8.13, m, 2H; 8.42, s, 1H. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 75.6, OCH_2; 120.0–133.0, aromatic C.

Cleavage of (9) by 1,4-Diazabicyclo[2.2.2]octane

To a solution of the ether (9) (0.5 g, 1.4 mmol) in acetonitrile (10 ml) was added 1,4-diazabicyclo[2.2.2]octane (0.5 g, 4.5 mmol) and the whole was simmered for 25 min. After this time, t.l.c. showed an absence of starting material and a drop of the solution added to water gave a clear solution. The solvent was removed by evaporation, the residue was stirred with hydrochloric acid (5 N, 10 ml) and extracted with ether. Evaporation of the organic phase gave a pale yellow, crystalline residue which was stirred with water (5 ml) and sodium bicarbonate. A small amount of yellow flocculent material was filtered off and the aqueous filtrate was acidified with concentrated hydrochloric acid to precipitate 1-hydroxy-5-phenyltetrazole as colourless needles (168 mg, 70%) identical (m.p., mixture m.p.) with authentic material.

3-(Anthracen-9-ylmethyl)-5-phenyltetrazole 1-Oxide (10)

Trifluoroacetic acid (2 ml) was added dropwise to a solution of the 9-anthrylmethyl ether (9) (600 mg, 1.7 mmol) in dichloromethane (10 ml) maintained at 0°. After 10 min the volatile components were removed by evaporation and the residue was taken up in benzene (20 ml) and the solution was extracted with aqueous sodium bicarbonate. Acidification of the aqueous extract with concentrated hydrochloric acid followed by extraction with ether gave a small quantity (44 mg, 16%) of tetrazole after evaporation of the ethereal solution. On standing for several hours, the original benzene solution deposited a yellow solid which was collected by filtration to give the *product* (10) (360 mg, 60%). Recrystallization from dichloromethane/methanol gave yellow plates, m.p. 176–178° (Found: C, 74.7; H, 4.8; N, 15.7. $C_{22}H_{16}N_4O$ requires C, 75.0; H, 4.7; N, 15.9%). ^{1}H n.m.r. δ ($CDCl_3$) 6.58, CH_2; 7.32–7.70, m, 7H, ArH; 8.08, m, 2H; 8.33, m, 2H; 8.53, m, 2H; 8.58, s, 1H. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 50.9, NCH_2; 122.0–131.0, aromatic C.

Acknowledgments

We thank E. I. DuPont de Nemours and Co., Agricultural Products Department, for the evaluation of herbicidal activity. We are also indebted to Mr Ian Willing for the determination of n.m.r. spectra.

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