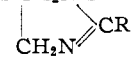
TABLE I

2-ARYLIMIDAZOLINES PREPARED FROM ORTHOESTERS



R	Total hr. heating	Hr. after which solid appeared	Yield, %	M.p. (cor.), °C.	Formula	Nitrogen, % Calcd.	Found
Phenyl	84	...	17[a]	98[c]	$C_9H_{10}N_2$	19.18	18.99
p-Tolyl	48	48	63.5[b]	175–176[d]	$C_{10}H_{12}N_2$	17.50	17.36
m-Tolyl*	96	...	33	97–98.5	$C_{10}H_{12}N_2$	17.50	16.91
p-Ethoxyphenyl*	12	7.5	92	175.5–177.5	$C_{11}H_{14}N_2O$	14.73	14.49
p-Anisyl	42	18	43	109–110[e]	$C_{10}H_{12}N_2O$	15.91	15.68
p-Diphenyl*	112	112	30	177–179	$C_{15}H_{14}N_2$	12.61	12.96
α-Naphthyl	81	...	30	132–134	$C_{12}H_{12}N_2$	14.28	14.21
4-Ethoxynaphthyl*	116	116	16	167–168	$C_{15}H_{16}N_2O$	11.66	11.38

[a] Yield from imidoester was 34.2%; product melted at 101°. [b] Yield from imidoester was 58%; product melted at 178°. [c] A sample of 2-phenylimidazoline prepared from ethyl orthobenzoate mixed with one made from the corresponding imidoester melted at 97°. A mixture of the former with one furnished by S. R. Aspinall made from benzoylethylenediamine and melting at 100.3° melted at 99°. [d] A sample of 2-*p*-tolylimidazoline prepared from the orthoester mixed with one made from the corresponding imidoester melted at 178°. A mixture of the former with one furnished by S. R. Aspinall made from the monoacylethylenediamine and melted at 183° melted at 177–178°. [e] Oxley and Short[6] report melting point to be 140°.

by the length of time required for solid to appear in the reaction mixture.

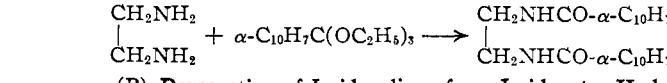
After the removal of the more volatile parts of the reaction mixture by reduced pressure distillation, the product was isolated in most cases by taking up the residue in chloroform or benzene and precipitating the imidazoline with petroleum ether. The solid obtained could then be crystallized from benzene or toluene.

The 2-phenyl- and 2-*p*-tolylimidazolines did not crystallize from a chloroform solution of the reaction mixture upon the addition of petroleum ether but required sublimation at reduced pressure before they could be crystallized. On the other hand, 2-*m*-tolyl-, 2-*p*-anisyl- and 2-α-naphthylimidazolines required no preliminary treatment since the solid reaction mixture was simply recrystallized several times from benzene or toluene.

The products from sealed tube reactions were less discolored, but better yields were obtained from reactions performed under reflux. Among the four unsuccessful attempts to prepare 2-phenylimidazoline was one sealed tube reaction. The fifth and successful attempt was made under reflux.

The imidazolines prepared are soluble in benzene, toluene, chloroform and alcohol, and are insoluble in ether, petroleum ether and water. The hydrochloride of 2-*p*-tolylimidazoline was prepared and found to be soluble in alcohol and water and insoluble in benzene and ether.

A trace of an interesting side product was obtained in the condensation of ethylenediamine with ethyl orthonaphthoate. When the product was recrystallized from benzene some 38 mg. of crystalline benzene-insoluble material melting at 184–185° (cor.) which gave analytical figures[8] for N,N′-ethylenebis-α-naphthamide were removed from the solution. Its presence in the reaction mixture seems to indicate the occurrence to a slight degree of the reaction



(B) **Preparation of Imidazolines from Imidoester Hydrochlorides.**—Imidoester hydrochloride and anhydrous ethylenediamine in the proportion of one mole of imidoester hydrochloride to 1.3 mole of amine were heated in absolute alcohol solution for 7–8 hours over a water-bath maintained between 60–70°. After the evaporation of the alcohol under diminished pressure the crude imidazoline hydrochloride was dissolved in water and the free base was precipitated by the addition of dilute sodium hydroxide solution. The imidazoline was purified by crystallization from benzene or toluene. The products were identified by means of mixed melting points with analyzed samples prepared from orthoesters.

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(8) *Anal.* Calcd. for $C_{34}H_{30}NO_2$: N, 7.60. Found: N, 8.00.

Mono-alkylation of Sodium 5-Aminotetrazole in Aqueous Medium

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Stolle and co-workers[1] previously prepared 1-methyl-5-aminotetrazole by the alkylation of potassium 5-aminotetrazole with dimethyl sulfate in aqueous solution. They failed, however, to recover the isomeric 2-methyl-5-aminotetrazole which we have now found is formed simultaneously in yields varying from 23 to 32%. Similarly the alkylation of 5-aminotetrazole in basic, aqueous medium with methyl iodide, ethyl iodide, allyl bromide, benzyl chloride, ethylene chlorohydrin or diethyl sulfate always leads to a mixture of isomers substituted in the 1- and 2-positions. Generally the 1-isomers predominate; by way of contrast, the 2-isomers are the principal products when sodium 5-phenyltetrazole[2] and sodium 5-nitrotetrazole are methylated in aqueous acetone.

Alkylation of the 5-amino group apparently occurs only to a very limited extent under the conditions employed in this investigation. For example, 1- and 2-methyl-5-methylaminotetrazole have been isolated in yields amounting to less than one per cent. by careful fractionation of the by-products from experiments with dimethyl sulfate and sodium 5-aminotetrazole; 5-methylamino- or 5-dimethylaminotetrazole have not been identified among the products. This suggests that the dimethylated derivatives result from a further methylation of the 1- and 2-methyl-5-aminotetrazoles. Small quantities of 1,3- and 1,4-dimethyl-5-iminotetrazole[3] also have been isolated as suitable derivatives.

Only one of the ethyl groups in diethyl sulfate appears to be utilized during the alkylation of sodium 5-aminotetrazole in water at 95–100°, whereas both the methyl groups in dimethyl sulfate are effectively used under these conditions. Fur-

(1) R. Stolle, K. Ehrmann, D. Rieder, H. Wille, H. Winter and F. Henke-Stark, *J. prakt. Chem.*, **134**, 282 (1932).

(2) B. Elpern and F. C. Nachod, THIS JOURNAL, **72**, 3379 (1950); R. A. Henry, *ibid.*, **73**, 4470 (1951).

(3) R. A. Henry, W. G. Finnegan and E. Lieber, unpublished results.

thermore, when equimolar quantities of dimethyl sulfate and sodium 5-aminotetrazole react in water, the yield of dimethylated products is not substantially increased and the conversion to monomethylated products is about the same.

2-Methyl-5-aminotetrazole has been prepared in quantitative yield by the catalytic hydrogenation of 2-methyl-5-nitrotetrazole.

Experimental[4]

Methylation of Sodium 5-Aminotetrazole with Dimethyl Sulfate.—Dimethyl sulfate (65.3 g., 0.508 mole) was added with vigorous stirring during 40 minutes to a solution of 103 g. (1.0 mole) of 5-aminotetrazole monohydrate, 41 g. of sodium hydroxide and 200 ml. of water maintained at 92–95°. After the heating had been continued for 55 minutes more, the solution was cooled for 48 hours at 5°. The 1-methyl-5-aminotetrazole which had crystallized was removed by filtration, washed with a small volume of cold water, and air-dried; yield 22.3 g., m.p. 220–223°. The aqueous filtrate was evaporated to dryness and extracted with one 200-ml. and five 50-ml. portions of boiling 95% ethanol; the insoluble residue was largely sodium sulfate and was discarded. When the combined alcoholic extracts had been evaporated to dryness, they were re-extracted with one 200-ml., one 100-ml. and five 50-ml. portions of benzene–absolute ethanol (85-15); the insoluble residue was retained (A). The benzene extracts were combined, concentrated to 200 ml. and cooled overnight at 5°. Coarse aggregates of 2-methyl-5-aminotetrazole contaminated with some of the 1-isomer crystallized and were removed by filtration (the mother liquors were retained (B)); yield 23.8 g. (24.1%); m.p. 95–100°. This isomer can be recrystallized either from benzene (13 ml. per g.) or from chloroform (9 ml. per g.). After several recrystallizations the melting point was raised to 104.5–105.5°.

Anal. Calcd. for $C_2H_5N_5$: C, 24.23; H, 5.09; N, 70.68. Found: C, 24.60; H, 5.04; N, 71.33.

(A).—The dried benzene insoluble fraction was dissolved in 50 ml. of water and cooled overnight at 0°. An additional 27.8 g. of impure 1-methyl-5-aminotetrazole crystallized and was removed by filtration. When the aqueous filtrate was acidified, 5.75 g. (5.6%) of unreacted 5-aminotetrazole hydrate precipitated. The total yield of the 1-isomer was 50.1 g. (50.6%); one recrystallization from water (7 ml. per g.) gave a product melting at 226–228°; Stolle[1] reported 222°. A mixed melting point with a sample made by the cyclization of 1-methyl-2-azidoguanidine[5] was not depressed.

This experiment was repeated several times with slight variations in the time and in the volume of water; the yield of 1-isomer varied from 36–53%, the 2-isomer from 23–32%, and the amount of unreacted 5-aminotetrazole hydrate from 5.4–13.7%. Another experiment, in which one mole of dimethyl sulfate, one mole of 5-aminotetrazole, and two moles of sodium hydroxide were employed, gave a 35% yield of the 1-isomer and a 30% yield of the 2-isomer; recovery of these products was complicated in this case by the large amount of sodium methyl sulfate which was formed.

(B).—The benzene mother liquors were evaporated to leave 6.9 g. of soft solid melting from about 50 to 90°. This mixture was combined with similar fractions from related runs and fractionally crystallized from chloroform.

(B-1).—The least soluble fraction (about 23% on a weight basis) was further fractionated from 95% ethanol to yield 0.1% (molar basis) of 1-methyl-5-aminotetrazole, m.p. 222–227°, and 0.35% (molar basis) of impure 1-methyl-5-methylaminotetrazole, m.p. 165–175°, after recrystallization from dioxane. Further recrystallization from absolute ethanol gave flat needles; m.p. 173–174°; admixture with an authentic sample[5] did not depress the melting point. When additional crops of reasonably pure material could not be obtained, the residue, still in ethanol, was treated with picric acid. Only one acceptably pure picrate was isolated: flat, orange needles, m.p. 211.0–211.5°, after several recrystallizations from water. A mixture melting point with a sample of 1,4-dimethyl-5-iminotetrazole picrate[3] was undepressed.

Anal. Calcd. for $C_9H_{10}N_8O_7$: C, 31.22; H, 2.91; N, 32.37. Found: C, 31.43; H, 3.04; N, 32.42.

This latter picrate is probably identical with the dimethylaminotetrazole picrate prepared by Thiele and Ingle[6] and reported to melt at 203°.

When this separation procedure was repeated on the residues from another experiment, a small amount of picrate, which melted at 168–169° after several recrystallizations from 95% ethanol, was also isolated. This compound proved to be a mixed picrate of 1,3- and 1,4-dimethyl-5-iminotetrazole and was conveniently prepared by dissolving 0.2 g. of each of the separate picrates in 40 ml. of hot 95% ethanol and cooling overnight at 5°.

Anal. Calcd. for $C_9H_{10}N_8O_7$: C, 31.22; H, 2.91; N, 32.37. Found: C, 31.62; H, 2.92; N, 32.72, 32.93.

(B-2).—The next fraction from the chloroform amounted to about 21% on a weight basis and melted at 75–95°. Recrystallization from chloroform raised the melting point to 103–105° with preliminary softening about 95°; this material was 2-methyl-5-aminotetrazole.

(B-3).—The chloroform mother liquors were evaporated, and the residue was separated into diethyl ether soluble and insoluble fractions. The insoluble material was further fractionated from benzene into impure 2-methyl-5-aminotetrazole, m.p. 80–90°, and 1-methyl-5-methylaminotetrazole, m.p. 150–165° (0.38% on molar basis). Repeated recrystallizations of this latter compound from either dioxane or benzene did not improve the melting point, a mixed melting point with an authentic example of 1-methyl-5-methylaminotetrazole, m.p. 172–173°, was 156–165°. The X-ray powder pattern was identical in all major respects with that from a known sample.

(B-4).—The ether soluble material from B-3 was fractionally precipitated with petroleum ether. After a small crop of 2-methyl-5-aminotetrazole had been removed, 9.0 g. (0.63% on molar basis) of a material was obtained which melted at 46–47° with shrinking at 41°; a mixed melting point with a known sample of 2-methyl-5-methylaminotetrazole (see below) also melted at 46–48°.

In a repeat experiment, the ether soluble fraction, on treatment with phenyl isothiocyanate, yielded a thiourea which melted at 204–207°. Recrystallization from 95% ethanol gave large, flat plates; m.p. 210.5–211.5°. A mixture melting point with the phenylthiourea of 1,4-dimethyl-5-iminotetrazole[3] was undepressed.

Anal. Calcd. for $C_{10}H_{12}N_6S$: C, 48.37; H, 4.87; N, 33.85. Found: C, 48.84, 48.73; H, 4.83, 5.01; N, 33.90.

Methylation of Sodium 5-Aminotetrazole with Methyl Iodide.—Methyl iodide (14.2 g., 0.1 mole) in 160 ml. of acetone was added to a solution of 8.5 g. (0.1 mole) of anhydrous 5-aminotetrazole, 4.0 g. (0.1 mole) of sodium hydroxide and 40 ml. of water. The initially heterogeneous mixture became homogeneous during the three-hour reflux period. The solution was evaporated to dryness under reduced pressure and the residue extracted with five 50-ml. portions of hot benzene; the insoluble material was retained. The benzene extracts were combined, cooled to room temperature, treated with 85 ml. of ligroin, filtered and cooled overnight at 0°. The first crop of product weighed 0.8 g. after drying and melted at 100–105°; by concentrating the mother liquors to 100 ml. and recooling, 0.85 g. more of product, m.p. 95–100°, was obtained. The total recovery of crude **2-methyl-5-aminotetrazole** amounted to 16.8%. One recrystallization from benzene raised the melting point to 104–105°.

The benzene-insoluble material was dissolved in 25 ml. of hot water and cooled at 5° for several days. The solid material was removed by filtration, washed with a small volume of cold water, and dried; yield 4.0 g. (40.4%), m.p. 210–220°. Recrystallization from water gave a product which was identical in all respects with the 1-methyl-5-aminotetrazole prepared in the previous experiments.

1- and 2-Methyl-5-nitrotetrazole.—A solution consisting of 18.0 g. of sodium 5-nitrotetrazole tetrahydrate,[7] 40 ml. of water, 160 ml. of acetone and 20 g. of methyl iodide was re-

(4) The melting points were determined in capillary tubes and are corrected.

(5) W. G. Finnegan, R. A. Henry and E. Lieber, *J. Org. Chem.*, **18**, 779 (1953).

(6) J. Thiele and H. Ingle, *Ann.*, **287**, 233 (1895).

(7) E. von Herz, U. S. Patent 2,066,954 (January 5, 1937).

fluxed for 3.5 hours. After two hours 6 g. more of methyl iodide was added to replace any losses due to volatility. The orange-red solution was evaporated on the steam-bath until free of acetone. The oil which separated was extracted with 200 ml. of benzene and the aqueous phase was re-extracted with 75 ml. more of benzene. The combined benzene extracts were washed first with 75 ml. of cold 2% sodium hydroxide solution saturated with sodium chloride, then with two 25-ml. portions of cold, saturated salt solution, and finally dried over anhydrous sodium sulfate. Evaporation of the benzene left 8.73 g. (78.6%) of a mixture of 1- and 2-methyl-5-nitrotetrazole. By redissolving the mixture in 100 ml. of benzene, adding 30 ml. of petroleum ether, and cooling at 0° for 48 hours, there was recovered 5.85 g. of 2-methyl-5-nitrotetrazole, m.p. 85–86°. The addition of 125 ml. of petroleum ether to the mother liquors and further cooling at 0° gave only 0.5 g. more of the 2-isomer. Recrystallization from benzene–petroleum ether did not alter the melting point.

Anal. Calcd. for $C_2H_3N_5O_2$: C, 18.61; H, 2.34; N, 54.25. Found: C, 19.03; H, 2.40; N, 54.57.

When the benzene–petroleum ether mother liquors were evaporated, there was left an oil which slowly solidified. Crystallization from a minimum volume of diethyl ether gave diamond shaped plates of 1-methyl-5-nitrotetrazole, m.p. 57.5–58°.

Anal. Calcd. for $C_2H_3N_5O_2$: C, 18.61; H, 2.34; N, 54.25. Found: C, 18.90; H, 2.33; N, 54.62.

When 6.82 g. (0.0529 mole) of 2-methyl-5-nitrotetrazole was hydrogenated in 100 ml. of methanol over Adams platinum catalyst, there was recovered 5.15 g. (98.5%) of crude 2-methyl-5-aminotetrazole, m.p. 96–102°. One recrystallization from 250 ml. of benzene–liquoin (4:1) yielded 3.6 g. of needles, m.p. 105.5–106.5°.

A similar hydrogenation of 0.28 g. (0.00217 mole) of 1-methyl-5-nitrotetrazole yielded 0.20 g. (93%) of very crude 1-methyl-5-aminotetrazole, m.p. 80–160°. One recrystallization from 40 ml. of benzene–ethanol (5:1) yielded small white needles, m.p. 226°. A mixture melting point with an authentic sample of 1-methyl-5-aminotetrazole was 228–229°.

1-Methyl-5-benzalaminotetrazole.—A solution consisting of 9.9 g. (0.1 mole) of 1-methyl-5-aminotetrazole, 12.0 g. (0.113 mole) of benzaldehyde, 4 drops of piperidine and 75 ml. of toluene was refluxed for 6 hours while the liberated water was removed continuously as the azeotrope. After the toluene solution had been cooled to 5°, the product was removed by filtration, washed with a small volume of cold toluene, and dried. The yield was 18.0 g. (96.2%). After recrystallization from toluene (18 ml. per g.) the melting point was 159.5–160.5°; Stolle[1] reported 157°.

Anal. Calcd. for $C_9H_9N_5$: C, 57.74; H, 4.85; N, 37.41. Found: C, 58.06; H, 4.92; N, 37.24.

1-Methyl-5-benzylaminotetrazole.—Hydrogenation of 9.35 g. of the preceding compound in 100 ml. of absolute methanol over Adams platinum catalyst gave 9.4 g. of a compound melting about 130°. One recrystallization from 15% aqueous ethanol (70 ml. per g.) yielded white needles, melting 131.5–132.5°. A mixture melting point with a sample of 1-methyl-5-benzylaminotetrazole, made by another method[6] and melting sharply at 99°, was 111–114°. Apparently the two compounds are not polymorphic forms; but the reason for the difference is not evident.

Anal. Calcd. for $C_9H_{11}N_5$: C, 57.12; H, 5.86; N, 37.02. Found: C, 57.49; H, 5.90; N, 36.96.

2-Methyl-5-acetamidotetrazole.—2-Methyl-5-aminotetrazole (9.9 g., 0.1 mole) was suspended in 100 ml. of chloroform, 9.4 g. (0.12 mole) of acetyl chloride was added, and the solution was refluxed for four hours. The solution was cooled to 0° and the precipitated 2-methyl-5-acetamidotetrazole was removed by filtration, washed on the filter with chloroform and dried; yield 7.07 g. (50.2%), m.p. 153–154°. One recrystallization from acetonitrile (5 ml. per g.) gave thick prisms, m.p. 153–154°.

Anal. Calcd. for $C_4H_7ON_5$: C, 34.03; H, 5.00; N, 49.63. Found: C, 34.41; H, 4.99; N, 49.36.

Phenylthiourea of 2-Methyl-5-aminotetrazole.—A mixture of 0.55 g. of 2-methyl-5-aminotetrazole and 2 ml. of phenyl isothiocyanate was heated at 140–150° for five minutes, cooled to room temperature, and slurried with 20–25 ml. of ligroin. The solid product was removed by filtration and washed with ligroin until free of excess isothiocyanate. The yield was 0.8 g. After two recrystallizations from 95% ethanol, the thiourea melted at 186.5–187.5° dec.

Anal. Calcd. for $C_9H_{10}N_6S$: C, 46.14; H, 4.30; N, 35.87. Found: C, 45.75; H, 4.28; N, 35.80.

There was no appreciable amount of reaction when equivalent quantities of phenyl isothiocyanate and 2-methyl-5-aminotetrazole were refluxed in benzene solution.

2-Methyl-5-benzalaminotetrazole.—This compound was prepared from 2-methyl-5-aminotetrazole by the same procedure described above for the 1-isomer; however, in this case only four hours were required to collect the theoretical amount of water. The yield from 0.2-mole quantities of reactants was 29.0 g. (77.5%). Recrystallization from benzene gave long needles which melted at 99.5–100.5°.

Anal. Calcd. for $C_9H_9N_5$: C, 57.74; H, 4.85. Found: C, 58.08; H, 5.17.

2-Methyl-5-benzylaminotetrazole.—The above compound in absolute ethanol was quantitatively hydrogenated over Adams platinum catalyst. After recrystallization from Skellysolve C, the compound melted at 86–87°.

Anal. Calcd. for $C_9H_{11}N_5$: C, 57.12; H, 5.86; N, 37.02. Found: C, 57.35; H, 6.12; N, 36.65.

1- and 2-Methyl-5-methylaminotetrazoles.—5-Benzylmethylaminotetrazole[5] (20.9 g., 0.11 mole) was added in small portions with continuous stirring to a cold solution of 0.133 mole of diazomethane in 200 ml. of diethyl ether. Nitrogen was evolved and a clear homogeneous solution was obtained. The ether was removed by distillation, and the oily residue dissolved in 75 ml. of glacial acetic acid. Palladium oxide (0.2 g.) was added, and the solution was hydrogenated for 20 hours at an initial pressure of 50 p.s.i.; about 0.1 mole of hydrogen absorbed. The catalyst was then removed by filtration and the filtrate was evaporated to dryness at reduced pressure on a steam-bath. When the semi-solid residue was extracted three times with 50-ml. portions of boiling benzene, 3.56 g. of 1-methyl-5-methylaminotetrazole remained undissolved. The combined benzene extracts were cooled overnight to yield an additional 1.12 g. of 1-methyl-5-methylaminotetrazole. The total yield amounted to 37.6%. After several recrystallizations from benzene, the melting point was 173–175°. A mixed melting point with an authentic sample, prepared by ring closure of 1,2-dimethyl-3-azidoguanidine,[6] was not depressed.

The benzene filtrate was evaporated to dryness to yield 7.73 g. (62.2%) of 2-methyl-5-methylaminotetrazole. The melting point, after recrystallization from diethyl ether–petroleum ether (1:2) was 48–49°.

Anal. Calcd. for $C_3H_7N_5$: N, 61.91. Found: N, 62.04.

The **picrate of 2-methyl-5-methylaminotetrazole** recrystallized from absolute ethanol as needles, m.p. 84–85°.

Anal. Calcd. for $C_9H_{10}N_8O_7$: C, 31.22; H, 2.91; N, 32.37. Found: C, 31.79; H, 2.88; N, 31.87.

Ethylation of Sodium 5-Aminotetrazole with Diethyl Sulfate.—Diethyl sulfate (79.0 g., 0.5 mole) was added with stirring during 1.5 hours to a solution of 103 g. (0.5 mole) of 5-aminotetrazole monohydrate, 41 g. of sodium hydroxide and 300 ml. of water maintained at 90–95°. The solution was next refluxed for four hours. After the slightly acidic solution had been readjusted to *p*H 7.5, it was evaporated to dryness under reduced pressure. The residue was extracted with one 200- and four 100-ml. portions of boiling benzene (the insoluble fraction was retained), the combined extracts were concentrated to 300 ml. and chilled to 5°. The small crop of 1-ethyl-5-aminotetrazole (2.9 g., m.p. 134–140°), which separated was removed, and the mother liquors were evaporated to leave 29.6 g. (26.2%) of the liquid 2-ethyl-5-aminotetrazole. After this isomer had been distilled, b.p. 94° at 1.0 mm., it melted about 20°.

Anal. Calcd. for $C_3H_7N_5$: C, 31.85; H, 6.24; N, 61.91. Found: C, 32.01; H, 6.06; N, 62.23.

When the benzene-insoluble material was dried, dissolved in 50 ml. of water and cooled for several days at 0°, there was obtained 17.3 g. (15.3%) more of crude 1-ethyl-5-aminotetrazole, m.p. 130–140°. The two crops of this isomer (17.7%) were combined and recrystallized from a minimum volume of water, m.p. 148°. Herbst, Roberts and Harvill[8]

(8) R. M. Herbst, C. W. Roberts and E. J. Harvill, *J. Org. Chem.*, **16**, 139 (1951).

reported 148–148.5°. A mixture melting point with a sample of 1-ethyl-5-aminotetrazole made by cyclizing 1-ethyl-2-azidoguanidine[5] was the same.

The aqueous mother liquors were acidified after the 1-isomer had been removed; there was recovered 35.3 g. (anhydrous basis, 41.6%) of unreacted 5-aminotetrazole. In a repeat experiment 39.7% of the starting 5-aminotetrazole was recovered; this is taken to mean that only one of the ethyl groups in the diethyl sulfate is easily or readily available for alkylation under these conditions.

Ethylation of Sodium 5-Aminotetrazole with Ethyl Iodide.—A procedure similar to that described for the methylation of sodium 5-aminotetrazole with methyl iodide was employed with the following differences: 0.5 molar quantities of reactants were used in a proportionately larger volume of solvent, the reflux time was 20 hours and the *p*H was readjusted to 7.5–8 before the solution was concentrated to dryness. The yield of impure, liquid 2-ethyl-5-aminotetrazole obtained when the benzene extract was evaporated was 21.6 g. (38.2%). Because of large losses due to the appreciable solubility of 1-ethyl-5-aminotetrazole in water, only 8.2 g. of crude 1-isomer was recovered, m.p. 143–147°. Recrystallization from a minimum volume of water raised the melting point to 147–148°.

1- and 2-Allyl-5-aminotetrazole.—5-Aminotetrazole monohydrate (103 g., 1.0 mole) and sodium hydroxide (40 g., 1.0 mole) were dissolved in 150 ml. of water; the *p*H of the solution was adjusted to the phenolphthalein end-point. Allyl bromide (121 g., 1.0 mole) in 600 ml. of acetone was added and the heterogeneous system refluxed for 22 hours. The mixture never became completely homogeneous. The *p*H of the solution was readjusted to the phenolphthalein end-point prior to the removal of the acetone under reduced pressure. Both a solid and an oil separated from the aqueous phase. By cooling the mixture overnight at 5° the gummy product could be removed by filtration and was extracted with three 50-ml. portions of benzene–ligroin (2:1). There remained 62.9 g. (dry basis) of crude 1-allyl-5-aminotetrazole, m.p. 90–110°; the benzene–ligroin washings were retained. The aqueous filtrate was evaporated to dryness under reduced pressure and extracted with two 150-ml. and two 75-ml. portions of benzene–absolute ethanol (2:1) (from the insoluble residue after solution in 150 ml. of water and acidification, there was recovered 18.5 g. (18%) of unreacted 5-aminotetrazole hydrate). The extracts were concentrated to 200 ml., cooled and 3 g. more of 1-allyl-5-aminotetrazole removed by filtration. These benzene mother liquors were combined with the benzene–ligroin extracts, dried over anhydrous sodium sulfate, and the solvent removed to leave a viscous oil, consisting largely of 2-allyl-5-aminotetrazole. The yield of distilled compound, 110–112° at *ca.* 1 mm., was 25.8 g. (20.6%). After recrystallization from diethyl ether, containing about 10% petroleum ether, the compound melted at 67°.

Anal. Calcd. for $C_4H_7N_5$: C, 38.39; H, 5.64; N, 55.97. Found: C, 38.89; H, 5.98; N, 55.03.

When the 65.9 g. of the crude 1-isomer was recrystallized from 100 ml. of water, there was recovered 37.7 g. (30.1%), m.p. 127–129°. This compound can also be recrystallized from ethyl acetate. This material was identical with a sample of 1-allyl-5-aminotetrazole prepared by the cyclization of 1-allyl-2-azidoguanidine.[5]

1-(2,3-Dibromopropyl)-5-aminotetrazole.—Three grams of recrystallized 1-allyl-5-aminotetrazole was dissolved in 75 ml. of absolute methanol and treated dropwise with 3.9 g. of bromine. After the solution had stood for one hour at room temperature, the methanol was removed by a current of air. The solid residue was stirred for one hour with 25 ml. of water, containing 0.5 g. of sodium bisulfite, filtered and washed with cold water. The yield of dried product was 5.1 g. (75%); recrystallization from 120 ml. of 50% ethanol gave rosettes of white, dendritic crystals, m.p. 161–162°.

Anal. Calcd. for $C_4H_7N_5Br_2$: C, 16.86; H, 2.48; Br, 56.09. Found: C, 16.30; H, 2.38; Br, 56.96.

1- and 2-Benzyl-5-aminotetrazole.—A solution of 103 g. (1.0 mole) of 5-aminotetrazole monohydrate, 40 g. of sodium hydroxide, 130 g. (1.03 mole) of benzyl chloride, 200 ml. of water and 400 ml. of 95% ethanol was refluxed for 8 hours, evaporated to 200 ml. and cooled at 5° for five hours. The separated, oily solid was removed by filtration and washed with 100 ml. of cold water. The dried mixture of isomers was conveniently separated into a sparingly soluble fraction (89.2 g., 51%, m.p. 180–185°) and a very soluble fraction (83.1 g., 48%, m.p. 70–80°) by extraction with four 200-ml. portions of benzene. One recrystallization of the former fraction from isopropyl alcohol raised the melting point to 187–189°; a mixture melting point with an authentic sample of 1-benzyl-5-aminotetrazole was not depressed. Three wasteful recrystallizations of the latter fraction (impure 2-benzyl-5-aminotetrazole) from isopropyl alcohol gave rosettes of long, flat needles, m.p. 84.5–85°.

Anal. Calcd. for $C_8H_9N_5$: C, 54.84; H, 5.18; N, 39.98. Found: C, 55.1; H, 4.8; N, 40.2.

1-Benzyl-5-benzalaminotetrazole was made in 81% yield by a procedure similar to that outlined above for the preparation of 1-methyl-5-benzalaminotetrazole. After one recrystallization from benzene and one from absolute ethanol the compound melted at 133.5-134.5°.

Anal. Calcd. for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98. Found: C, 68.20; H, 5.27.

Hydrogenation of the above compound in absolute ethanol over Adams platinum oxide catalyst gave **1-benzyl-5-benzylaminotetrazole**, m.p. 170–171° after recrystallization from ethanol.

Anal. Calcd. for $C_{15}H_{15}N_5$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.94; H, 5.38; N, 27.03, 26.70.

2-Benzyl-5-benzalaminotetrazole, prepared in 72% yield, melted at 106.5–107.5° after one recrystallization from toluene and one from absolute ethanol (needles).

Anal. Calcd. for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98; N, 26.60. Found: C, 68.40; H, 5.08; N, 26.60.

2-Benzyl-5-benzylaminotetrazole melted at 64–65° after recrystallization from a toluene–petroleum ether mixture (large, clear prisms).

Anal. Calcd. for $C_{15}H_{15}N_5$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.85; H, 5.63; N, 26.42.

1- and 2-(2-Hydroxyethyl)-5-aminotetrazole.—A solution consisting of one mole of sodium 5-aminotetrazole, 88.6 g. (1.1 moles) of 2-chloroethanol, and 200 ml. of water, was refluxed for 6 hours and then evaporated to dryness at reduced pressure on a steam-bath. The residue was extracted twice with 100-ml. portions of boiling acetone and twice with 100-ml. portions of boiling 95% ethanol. When the combined extracts were evaporated, 132 g. of semi-solid product, contaminated with a small amount of sodium chloride, was obtained. 1-(2-Hydroxyethyl)-5-aminotetrazole (37.0 g., 28.7%) was isolated from the mixture of isomers by redissolving the latter in 200 ml. of boiling 95% ethanol, filtering and cooling the solution overnight at 5°. After two additional recrystallizations from 95% ethanol (15 ml./g.) the melting point was 160–161°.

Anal. Calcd. for $C_3H_7N_5O$: C, 27.90; H, 5.47; N, 54.24. Found: C, 27.97; H, 5.30; N, 54.09.

When the alcoholic filtrate was evaporated, crude 2-(2-hydroxyethyl)-5-aminotetrazole (92 g., 71%) was recovered as an oil, which solidified on long standing. Two recrystallizations from ethyl acetate yielded colorless needles, m.p. 87.5–89.5°.

Anal. Calcd. for $C_3H_7N_5O$: C, 27.90; H, 5.47; N, 54.24. Found: C, 28.24; H, 5.41; N, 53.65.

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Preparation and Hydrogenation of Azomethines Derived from 5-Aminotetrazole

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Anhydrous 5-aminotetrazole and aldehydes do not react to any significant extent under the usual conditions employed for the synthesis of azomethines; and there are no prior references to this group of tetrazole derivatives. This difficulty is probably due in part to the fact that 5-amino-