[CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

1,3- and 1,4-Dialkyl-5-iminotetrazoles

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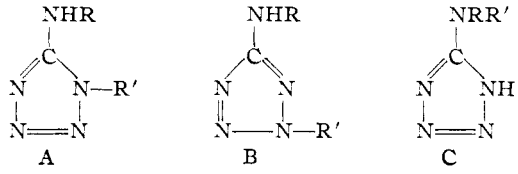
RECEIVED FEBRUARY 8, 1954

The principal product obtained from the alkylation of a 1-alkyl-5-aminotetrazole in non-aqueous systems has been identified as a 1,4-dialkyl-5-iminotetrazole, contrary to earlier structure assignments.[1,2] A small amount of a 1,3-dialkyl-5-iminotetrazole, a cyclic *meso*-ionic compound, is also formed. The alkylation of a 2-alkyl-5-aminotetrazole yields predominantly the 1,3-dialkyl-5-iminotetrazole. These compounds represent a new class of tetrazole derivatives.

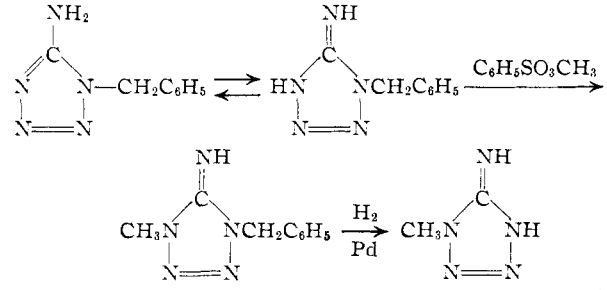
Herbst, Roberts and Harvill[1] studied the monoalkylation of 1-substituted-5-aminotetrazoles, with such reagents as methyl sulfate, methyl benzenesulfonate and benzyl chloride, and concluded without adequate proof that the products were 1-substituted-5-alkylaminotetrazoles. Thiele and Ingle[2] also considered the products which they obtained in the reaction of 5-aminotetrazole with alkyl halides in sealed tubes at elevated temperatures to be 1-alkyl-5-alkylaminotetrazoles. Considerable doubt about the correctness of this structure assignment developed when the general physical and chemical properties of these alkylation products were found to be markedly different than those for 1-substituted-5-alkylaminotetrazoles (A) prepared by unambiguous methods.[3]



A B C

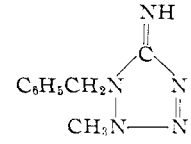
For example, the disubstituted compounds reported by Herbst, *et al.*,[1] are hygroscopic, basic, distillable liquids or low melting solids, which immediately form phenylthiourea derivatives with phenyl isothiocyanate, and which form salts with mineral acids and picrates with picric acid that are stable toward hydrolysis. On the other hand, the authentic 1-substituted-5-alkylaminotetrazoles are solids, are exceedingly weak bases, do not react readily, if at all, with phenyl isothiocyanate[4] and only give salts or picrates under essentially anhydrous conditions. The 2-substituted-5-alkylaminotetrazoles[5] (B) are weaker bases than the alkylation products and react only sluggishly with phenyl isothiocyanate. The 5-dialkylaminotetrazoles[6] (C) are solid acids.

Elimination of these three, isomeric, disubstituted 5-aminotetrazoles as possible structures for the compounds formed in the alkylation of 1-substituted 5-aminotetrazoles forces one to the conclusion that the second or entering alkyl group must also be attached to a ring nitrogen atom. This was conclusively proved by the following experiments which employed the previously reported observation[3,7] that catalytic debenzylation of a benzyl substituted 5-aminotetrazole proceeds without disruption of the tetrazole ring. When 1-methyl-5-aminotetrazole was benzylated with benzyl chloride and the resulting mixture of hydrochlorides was catalytically debenzylated, only 1-methyl-5-aminotetrazole was recovered; this indicates that migration of the methyl group does not occur and that the tetrazole ring is retained during the alkylation. On the other hand, when 1-benzyl-5-aminotetrazole was methylated with methyl benzenesulfonate and the subsequently isolated free bases were catalytically debenzylated, a mixture of 1-methyl-5-aminotetrazole (85.4%) and 2-methyl-5-aminotetrazole (12%) was obtained. Alkylation had occurred, therefore, on the ring at two different positions; the relationship between the methyl and the benzyl groups was obviously 1,4- in the compound which yielded 1-methyl-5-aminotetrazole.

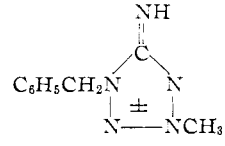


(or tautomeric structures)

Although a logical precursor for the 2-methyl-5-aminotetrazole is 1-benzyl-2-methyl-5-iminotetrazole



the cyclic "*meso*-ionic" compound, 1-benzyl-3-methyl-5-iminotetrazole



is an even more likely choice. Compounds of this type were predicted by Baker, Ollis and Poole[8] as a

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

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

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

(4) There was no evidence of reaction when 1-methyl-5-methylaminotetrazole was heated with an excess of phenyl isothiocyanate at 105° for five hours; the tetrazole derivative was recovered unchanged.

(5) R. A. Henry and W. G. Finnegan, THIS JOURNAL, **76**, 923 (1954).

(6) R. Stolle and F. Henke-Stark, *J. prakt. Chem.*, **124**, 261 (1930); W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1003 (1953).

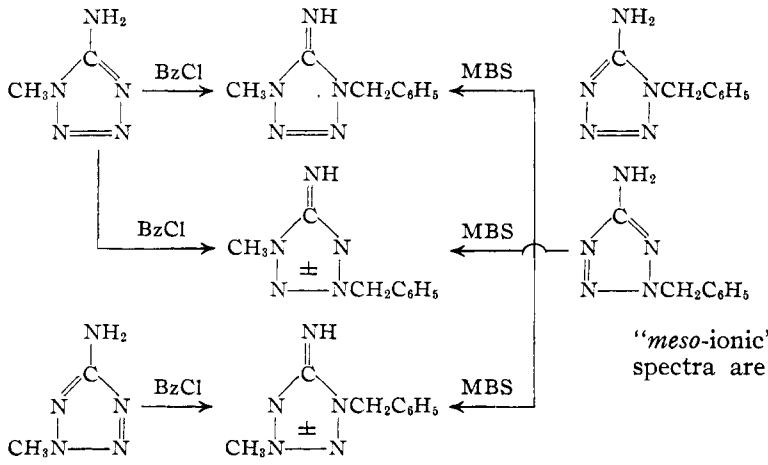
(7) L. Birkofer, *Ber.*, **75B**, 429 (1942).

(8) W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, 307 (1949).

result of their consideration of the sydnones. This conclusion is supported by indirect evidence (see below) and more particularly by analogy with 1,3-dimethyl-5-iminotetrazole whose structure was unambiguously demonstrated[9] by analysis of the X-ray data obtained with two of its salts.

Since the principal product from the monoalkylation of a 2-alkyl-5-aminotetrazole has general physical and chemical properties which are distinctly different than those of the isomeric 2-alkyl-5-alkylaminotetrazole (B), alkylation must have involved primarily a ring nitrogen atom rather than the 5-amino group (a very small amount of alkylation also occurs at this position). Direct evidence for this conclusion was obtained in the following manner: When 2-benzyl-5-aminotetrazole was methylated and the recovered free base was debenzylated, 1-methyl-5-aminotetrazole was the main product isolated. The intermediate free base prepared in this series of reactions is considered by analogy to be 1-methyl-3-benzyl-5-iminotetrazole, rather than the 1-methyl-2-benzyl isomer, since the methylation of 2-methyl-5-aminotetrazole under the same conditions gives 1,3-dimethyl-5-iminotetrazole.[9]

A detailed interrelationship between the various isomeric methyl, benzyl-5-iminotetrazoles has been obtained by separation and comparison of their phenylthiourea or picrate derivatives. This correlation, summarized in the following chart, lends additional support to the structural assignments which have been made.

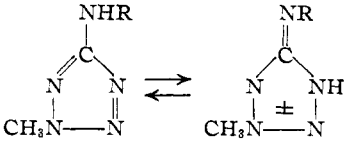


The reaction of 1-methyl-5-aminotetrazole and methyl benzenesulfonate yields two dimethyl-5-iminotetrazoles which can be separated by fractional crystallization of their phenylthiourea derivtives. The minor fraction is a derivative of 1,3-dimethyl-5-iminotetrazole, which is the major compound isolated from the methylation of 2-methyl-5-aminotetrazole. These same dimethyl-5-iminotetrazoles were previously isolated as picrates from the by-products obtained in the methylation of sodium-5-aminotetrazole in aqueous medium.[5]

To date, neither the isolation nor the unequivocal preparation of a 1,2-disubstituted-5-iminotetrazole has been accomplished although such an isomer now appears to be theoretically possible. If the alkylation of a 1-substituted-5-aminotetrazole yields more than the two isomers, the conversion to the third isomer must be very low; similarly, if any 1,2-dialkyl-5-iminotetrazole is formed during the alkylation of a 2-alkyl-5-aminotetrazole, the yield is exceedingly low.

These ring dialkyl-5-iminotetrazoles can be further alkylated.[1] To establish the position of alkylation, 1-methyl-4-benzyl-5-iminotetrazole, recovered from its carefully purified hydrochloride salt, was methylated with methyl benzenesulfonate. Since 1-methyl-5-methylaminotetrazole was recovered when the free base was isolated and catalytically debenzylated, the position of alkylation must have been on the 5-imino group.

Baker, Ollis and Poole[8] in their investigation of cyclic "*meso*-ionic" compounds reported that sydnones, which contained no other conjugated system showed a well-defined and characteristic absorption band (292 mμ) in their ultraviolet spectra. This was taken to mean that the sydnone ring possessed aromatic character and was a resonance hybrid of a large number of contributing ionic forms. The 1,3-dialkyl-5-iminotetrazoles reveal a characteristic absorption band between 254 and 258 mμ (Fig. 1, Table I), whereas the usual substituted tetrazoles containing no other conjugated system have been reported to show only end absorption.[10] End absorption also characterizes the spectrum for 1-methyl-5-aminotetrazole (Fig. 2). The absorption spectra of 1-benzyl-3-methyl-5-iminotetrazole, whose structure has not been rigorously established, is essentially the same as that for the 1,3-dimethyl compound, whose structure is known. This fact is used as indirect evidence to support the structure assigned to the former compound. Surprisingly, the 2-methyl-5-alkylaminotetrazoles (Fig. 1), which have been considered to possess the tetrazole ring system with normal covalent bonds, appear to exist principally in the "*meso*-ionic" form since their ultraviolet absorption spectra are very similar to those for the 1,3-dialkyl-5-iminotetrazoles (Fig. 1). Introduction of a methyl group into the 5-amino position of either 1- or 2-methyl-5-aminotetrazole effects a bathochromic shift in the absorption maximum.



Experimental[11]

1- and 2-Alkyl-5-aminotetrazoles.—The 1- and 2-methyl-5-aminotetrazoles and 1- and 2-benzyl-5-aminotetrazoles were prepared by the reaction of sodium 5-aminotetrazole with dimethyl sulfate and benzyl chloride, respectively, in aqueous or aqueous alcoholic solutions.[5] 1-Methyl- and 1-benzyl-5-aminotetrazoles may also be prepared by the di-

(9) J. Bryden, R. A. Henry, W. G. Finnegan, R. Boschan, W. S. McEwan and R. W. Van Dolah, THIS JOURNAL, **75**, 4863 (1953).

(10) B. Elpern and F. C. Nachod, *ibid.*, **72**, 3379 (1950); B. Elpern, *ibid.*, **75**, 661 (1953).

(11) The melting points are corrected against known standards.

azotization of 1-methyl- and 1-benzyl-2-aminoguanidines and ring closure of the azides in basic solution.[3]

Methylation of 1-Benzyl-5-aminotetrazole. A. Debenzylation.—1-Benzyl-5-aminotetrazole (43.75 g., 0.25 mole) was methylated with 45 g. (0.26 mole) of unpurified methyl benzenesulfonate, following the procedure of Herbst, *et al.*[1] A total of 23.4 g. (49.6%) of mixed methyl-1-benzyl-5-iminotetrazoles was obtained, together with 8.93 g. (20.4%) of unreacted 1-benzyl-5-aminotetrazole. All of the former fraction in 100 ml. of glacial acetic acid was hydrogenated for 12 hours over 0.2 g. of palladium oxide at an initial pressure of three atmospheres. The theoretical amount of hydrogen was absorbed. The catalyst was removed by filtration and the filtrate was evaporated to dryness at reduced pressure. The residue was dissolved in 200 ml. of boiling chloroform. A less soluble fraction (10.5 g., 85.4%, m.p. 225–226°) was recovered by chilling and concentrating the chloroform solution several times. A mixture melting point with an authentic sample of 1-methyl-5-aminotetrazole was not depressed.

The addition of diethyl ether to the remaining chloroform mother liquors precipitated 1.48 g. (12.0%) of 2-methyl-5-aminotetrazole, m.p. 100–102°. A mixture melting point with an authentic sample of 2-methyl-5-aminotetrazole[5] was not depressed.

B. Phenylthioureas.—The above methylation was repeated with 19.0 g. (0.1085 mole) of recrystallized 1-benzyl-5-aminotetrazole and 19.5 g. (0.113 mole) of redistilled methyl benzenesulfonate. The free bases were isolated by dissolving the reaction product in 50 ml. of water, adding 4.9 g. of 97% sodium hydroxide dissolved in 10 ml. of water, saturating the solution with solid anhydrous sodium carbonate and extracting with several portions of benzene. The benzene solution was dried by azeotropic distillation of the water and finally concentrated to a sirup at reduced pressure. The yield of mixed methyl-1-benzyl-5-iminotetrazoles amounted to 19.35 g. (94.4% yield).

One gram (0.0053 mole) of the product was dissolved in 20 ml. of diethyl ether and treated with 0.72 g. of phenyl isothiocyanate. The 1-benzyl-3-methyl-5-iminotetrazole phenylthiourea (I) (0.22 g., 12.8%) precipitated immediately and was removed by filtration. After recrystallization from 50 ml. of absolute ethanol, the compound melted at 197–198°.

Anal. Calcd. for $C_{16}H_{16}N_6S$: C, 59.23; H, 4.97; N, 25.91; S, 9.88. Found: C, 59.49; H, 5.11; N, 26.00; S, 9.54.

The 1-benzyl-4-methyl-5-iminotetrazole phenylthiourea (II) (1.5 g., 87.2%) formed slowly in the ethereal filtrate and was recovered by evaporation of the solvent. After recrystallization from 30 ml. of absolute ethanol, the compound melted at 123–125°. Herbst, *et al.*,[1] reported 123–124°.

Benzylation of 1-Methyl-5-aminotetrazole.—Following the procedure of Herbst, 1-methyl-5-aminotetrazole (4.95 g., 0.05 mole) and benzyl chloride (6.96 g., 0.055 mole) were heated to and maintained at 155° for 30 minutes after the exothermic reaction ceased.

A. Debenzylation.—The crude hydrochloride was washed thoroughly with diethyl ether to remove unreacted benzyl chloride and treated with a solution of 2.1 g. of sodium hydroxide in 50 ml. of methanol. The methanol solution was evaporated to dryness at reduced pressure and the residue was extracted with three 25-ml. portions of hot chloroform. Evaporation of the chloroform solution yielded 8.4 g. (88.9%) of free base. The latter was dissolved in 150 ml. of glacial acetic acid and hydrogenated over 0.2 g. of palladium oxide at an initial pressure of three atmospheres. Although the theoretical quantity of hydrogen was absorbed in 30 minutes, the hydrogenation was continued for 20 hours. The solution was then heated to 70° and the catalyst was removed by filtration. When the filtrate was evaporated to dryness at reduced pressure, 1-methyl-5-aminotetrazole, m.p. 220–224°, was recovered in theoretical yield, based on the weight of free base.

B. Free Base and Phenylthiourea Derivative.—The above benzylation of 1-methyl-5-aminotetrazole was repeated on a 0.1 mole scale. The crude hydrochloride was recrystallized twice from 150-ml. portions of 87% isopropyl alcohol, yielding 8.02 g. of pure 1-methyl-4-benzyl-5-iminotetrazole hydrochloride, m.p. 216–217° (III); Herbst, *et al.*,[1] reported 217–218° dec. Concentration and cooling of the filtrates yielded an additional 8.48 g. of less pure hydrochloride, m.p. 215–215.5°. Evaporation of the final mother liquors yielded 4.7 g. of soft solid which was not investigated further. The material balance was 94%.

When the 8.48 g. of hydrochloride was treated with a solution of sodium hydroxide, the free base (6.52 g.) (96.5%) was recovered as a mobile oil which slowly crystallized. Recrystallization from ethyl acetate–petroleum ether (1:3), followed by vacuum distillation at 0.1 mm. pressure raised the melting point of the **1-methyl-4-benzyl-5-iminotetrazole** (IV) to 38–40°. This compound is very hygroscopic.

Anal. Calcd. for $C_9H_{11}N_5$: equiv. wt., 189.23. Found: equiv. wt., 190.6.

The phenylthiourea of this compound after recrystallization from 95% ethanol also melted at 123–125°. A mixture melting point with II was not depressed. X-Ray powder patterns were also identical.

C. Picrates.—1-Methyl-4-benzyl-5-iminotetrazole picrate (V) was obtained as rosettes of fine yellow needles, m.p. 107–108°, after three recrystallizations from absolute ethanol.

Anal. Calcd. for $C_{15}H_{14}N_8O_7$: C, 43.06; H, 3.37; N, 26.79. Found: C, 43.26; H, 3.47; N, 27.32.

Methylation of 2-Benzyl-5-aminotetrazole.—2-Benzyl-5-aminotetrazole (6.41 g., 0.037 mole) was methylated with methyl benzenesulfonate as in the previous examples. The free, 1-methyl-3-benzyl-5-iminotetrazole (VI) (6.5 g., 94%) was obtained as an oil by neutralizing an aqueous solution with sodium hydroxide and extracting with benzene.

A. Debenzylation.—Four grams (0.0212 mole) of the free base VI in 25 ml. of glacial acetic acid was catalytically debenzylated over palladium oxide. After the catalyst had been removed the solvent was evaporated under reduced pressure. The residue was freed of acetic acid by several evaporations with absolute ethanol at reduced pressure. The dry residue, 1.9 g. (*ca.* 100%) melted at 222–226°; a mixture melting point with an authentic sample of 1-methyl-5-aminotetrazole was 223–226°.

B. Phenylthiourea Derivative.—A portion of the free base VI was condensed with phenyl isothiocyanate in diethyl ether solution. The 1-methyl-3-benzyl-5-iminotetrazole phenylthiourea (VII) precipitated immediately, and was removed by filtration. Several recrystallizations from 95% ethanol gave colorless needles, m.p. 156–157°.

Anal. Calcd. for $C_{16}H_{16}N_6S$: C, 59.23; H, 4.97; N, 25.91; S, 9.88. Found: C, 59.67; H, 5.11; N, 24.6; S, 10.4.

C. Picrate Derivative.—After four recrystallizations from absolute ethanol the picrate VIII of 1-methyl-3-benzyl-5-iminotetrazole was obtained as rosettes of flat needles which melted at 152–153°, resolidified, and remelted at 163–164°.

Anal. Calcd. for $C_{15}H_{14}N_8O_7$: C, 43.06; H, 3.37; N, 26.79. Found: C, 43.64; H, 3.49; N, 27.1.

Benzylation of 2-Methyl-5-aminotetrazole.—2-Methyl-5-aminotetrazole (5.45 g., 0.05 mole) was alkylated with 8.6 g. (0.05 mole) of benzyl bromide as in the benzylation of 1-methyl-5-aminotetrazole. The free 1-benzyl-3-methyl-5-iminotetrazole (IX) was liberated from its hydrobromide by treatment with a solution of sodium hydroxide and extracted with several portions of chloroform. The yield was quantitative. A portion of the free base (IX) was condensed with phenyl isothiocyanate in diethyl ether. **The 1-benzyl-3-methyl-5-iminotetrazole phenylthiourea** was removed by filtration and recrystallized from 95% ethanol (200 ml./g.) as pale yellow plates, m.p. 196–197°. A mixture melting point with the 1-benzyl-3-methyl-5-iminotetrazole phenylthiourea (I) isolated as a by-product in the methylation of 1-benzyl-5-aminotetrazole was not depressed. The X-ray powder patterns were also identical. **The hydrochloride of 1-benzyl-3-methyl-5-iminotetrazole** melted at 180–181° dec. after two recrystallizations from isopropyl alcohol–diethyl ether.

Anal. Calcd. for $C_9H_{12}N_5Cl$: N, 31.03. Found: N, 30.92.

Methylation of 1-Methyl-5-aminotetrazole.—Four grams of 1-methyl-5-aminotetrazole was methylated with 7.2 g. of methyl benzenesulfonate according to the procedure of Herbst, *et al.*[1] After the methylation mixture had been re-

fluxed for 30 minutes with a solution consisting of 0.85 g. of sodium in 75 ml. of methanol, the solution was evaporated to dryness. The residue was dissolved in 25 ml. of water and adjusted to *p*H 5 with concentrated hydrochloric acid. When this solution was cooled at 0° for 30 hours, large clear prisms crystallized; 3.2 g., m.p. 215–218°. Recrystallization from 15 ml. of water raised the melting point to 217–218°.

Anal. Calcd. for $C_3H_7N_5 \cdot C_6H_5SO_3H$: C, 39.84; H, 4.83; N, 25.82. Found: C, 39.96; H, 25.98.

The aqueous filtrate, remaining after the above salt had been removed, was saturated with anhydrous potassium carbonate and extracted with eight 25-ml. portions of benzene. The benzene solution was dried over potassium carbonate and then evaporated to yield 2.76 g. of soft solid. This product was redissolved in 20 ml. of benzene and allowed to stand at room temperature for several hours. The supernatant liquid was then decanted from a small quantity of oily material and cooled to 0°. Hard spherulites crystallized slowly. The mother liquors were retained (A). The yield was 1.3 g., m.p. 85–95°. Two recrystallizations from benzene, followed by a vacuum sublimation, raised the melting point to 108.5–109.5°. The analyses and properties are in agreement with those expected for **1,4-dimethyl-5-iminotetrazole**. The pK_b, as determined by potentiometric titration in water, was 5.32.

Anal. Calcd. for $C_3H_7N_5$: C, 31.85; H, 6.24; N, 61.91; equiv. wt., 113.14.

Found: C, 32.02, 31.78; H, 6.29, 6.18; N, 62.38; equiv. wt., 116.0.

The phenylthiourea which formed immediately in cold benzene solution melted at 210.5–211.5° after several recrystallizations from benzene. A mixture melting point with the phenylthiourea of 1,3-dimethyl-5-iminotetrazole was 185–186°.

Anal. Calcd. for $C_{10}H_{12}N_6S$: C, 48.36; H, 4.87; N, 33.85. Found: C, 48.62; H, 4.75; N, 33.97.

The picrate of 1,4-dimethyl-5-iminotetrazole obtained from either the purified free base or the benzenesulfonate crystallized from 95% ethanol as fine needles, m.p. 211.5–212.5 dec. This picrate is identical with one obtained from a by-product formed during the methylation of sodium 5-aminotetrazole in aqueous medium.[5] This is probably the same as the dimethylaminotetrazole picrate prepared by Thiele and Ingle[2] and reported to melt at 203°.

Anal. Calcd. for $C_9H_{10}N_8O_7$: C, 31.58; H, 2.95; N, 32.74. Found: C, 31.43; H, 3.04; N, 32.42.

The hydrochloride of 1,4-dimethyl-5-iminotetrazole was obtained as long, thin needles, m.p. 242–244° dec., after three recrystallizations from 90% isopropyl alcohol.

Anal. Calcd. for $C_3H_8N_5Cl$: C, 24.09; H, 5.39; N, 46.82. Found: C, 24.16; H, 5.13; N, 46.86.

The hydrobromide decomposed at 190–191° after several recrystallizations from absolute ethanol.

Anal. Calcd. for $C_3H_8N_5Br$: C, 18.57; H, 4.15; N, 36.10. Found: C, 18.6, 18.5; H, 3.91, 3.87; N, 35.96.

(A) The benzene mother liquors were evaporated and the residue dissolved in 100 ml. of diethyl ether. When a slight excess of phenyl isothiocyanate was added, a yellowish-white precipitate formed immediately and was removed by filtration as rapidly as possible. This fraction, without further purification, melted at 194–195° (fast heating); a mixture melting point with an authentic sample of 1,3-dimethyl-5-iminotetrazole phenylthiourea was not depressed. An X-ray powder pattern was identical with that from the authentic sample and was distinctly different than the one for 1,4-dimethyl-5-iminotetrazole phenylthiourea.

When the ethereal mother liquors were allowed to stand, a second phenylthiourea, m.p. 200–202°, precipitated more slowly. Since a mixture melting point with 1,3-dimethyl-5-iminotetrazole phenylthiourea was about 180°, this crop was presumed to be largely the impure 1,4-isomer and was not further investigated.

Methylation of 2-Methyl-5-aminotetrazole.—2-Methyl-5-aminotetrazole[5] (19.8 g., 0.2 mole) was methylated with 37.8 g. (0.22 mole) of methyl benzenesulfonate according to the procedure of Herbst, *et al.*[1] The thick viscous product was dissolved in 100 ml. of boiling methanol and a solution of 4.6 g. of sodium in 100 ml. of methanol was added. The resulting mixture was boiled for 30 minutes and then evaporated to dryness at reduced pressure. The residue was extracted with three 100-ml. portions of boiling chloroform. The soft solid obtained by evaporating the chloroform solution was dissolved in 25 ml. of water and acidified with 20 ml. of concentrated hydrochloric acid. Evaporation of the aqueous solution yielded a gummy solid which was extracted first with four 100-ml. portions of boiling chloroform, then with two 100-ml. portions of cold 98% isopropyl alcohol. The yield of dried **1,3-dimethyl-5-iminotetrazole hydrochloride**, m.p. 202–205°, was 13.0 g. (43.5%). Recrystallization from 90% isopropyl alcohol gave long needles or coarse prisms, m.p. 208–209°.

Anal. Calcd. for $C_3H_8N_5Cl$: C, 24.09; H, 5.39; N, 46.82; Cl, 23.70. Found: C, 24.16; H, 5.24; N, 47.08; Cl, 23.90.

The hydrochloride, 13.0 g., m.p. 202–205°, was dissolved in 100 ml. of boiling methanol and a solution of 3.5 g. of 97% sodium hydroxide in 100 ml. of methanol was added. The resulting mixture was evaporated to dryness at reduced pressure and the residue was extracted with three 50-ml. portions of boiling chloroform. Evaporation of the chloroform solution at reduced pressure left 9.8 g. of free base, as a yellow oil which solidified on standing. The free base was distilled to yield 7.9 g. (35% based on the 2-methyl-5-aminotetrazole) of **1,3-dimethyl-5-iminotetrazole**, b.p. 88° at 1 mm., m.p. 41–43°. The pK_b was approximately 2.5.

Anal. Calcd. for $C_3H_7N_5$: C, 31.85; H, 6.24; N, 61.91; equiv. wt., 113.13. Found: C, 31.83; H, 5.87; N, 62.23; equiv. wt., 116.6.

This compound is exceedingly hygroscopic and readily absorbs carbon dioxide from the air.

The picrate of 1,3-dimethyl-5-iminotetrazole melted at 186–187° after three recrystallizations from absolute ethanol. An admixture with the picrate of 1,4-dimethyl-5-iminotetrazole melted about 168–170°.

Anal. Calcd. for $C_9H_{10}N_8O_7$: C, 31.58; H, 2.95; N, 32.74. Found: C, 31.41, 31.85; H, 2.72, 2.89; N, 33.02, 32.95.

The hydrobromide decomposed at 188.5–189° after recrystallization from 98% isopropyl alcohol.

The nitrate was recrystallized three times from absolute ethanol; m.p. 153.5–154.5°.

Anal. Calcd. for $C_3H_8N_6O_3$: C, 20.45; H, 4.58; N, 47.72. Found: C, 20.6; H, 4.7; N, 48.1.

The phenylthiourea precipitated when phenyl isothiocyanate was added to a benzene solution of the free base; after recrystallization from ethanol the compound was obtained as thin white plates, m.p. 192–193° dec.

Anal. Calcd. for $C_{10}H_{12}N_6S$: C, 48.36; H, 4.87; N, 33.85. Found: C, 48.47, 48.59; H, 4.87, 5.01; N, 33.79.

If the impure free base recovered from a methylation experiment was recrystallized directly from benzene, rather than purified by conversion to the hydrochloride, a compound melting at 85–90° was obtained. Several recrystallizations from methylene chloride–petroleum ether raised the melting point to 88–91°. Vacuum sublimation further raised the melting point to 94–95°. A mixture melting point with 2-methyl-5-aminotetrazole was 75–85°, a mixture melting point with 1,4-dimethyl-5-iminotetrazole was 80–95°. Reaction with phenyl isothiocyanate in benzene solution yielded the phenylthiourea of 1,3-dimethyl-5-iminotetrazole; 2-methyl-5-aminotetrazole was recovered from the benzene mother liquors. The compound[12] was identified as a 1:1 complex of 1,3-dimethyl-5-iminotetrazole and 2-methyl-5-aminotetrazole; this complex is also hygroscopic and absorbs carbon dioxide.

Anal. Calcd. for $C_5H_{12}N_{10}$: C, 28.29; H, 5.70; N, 66.01; equiv. wt., 212.25. Found: C, 28.0; H, 5.02; N, 65.50, 66.78; equiv. wt., 214.4, 213.6.

The infrared spectrum was identical with that of a sample made by melting an equimolar mixture of the two components, and is not strictly the sum of the spectra of the individual components, but shows several new and distinctive absorption peaks.

When the benzene mother liquors from the original recrystallization of the impure free base were treated with phenyl isothiocyanate, the phenylthiourea of 1,3-dimethyl-

(12) This compound was erroneously reported in reference 8 as the free 1,3-dimethyl-5-iminotetrazole.

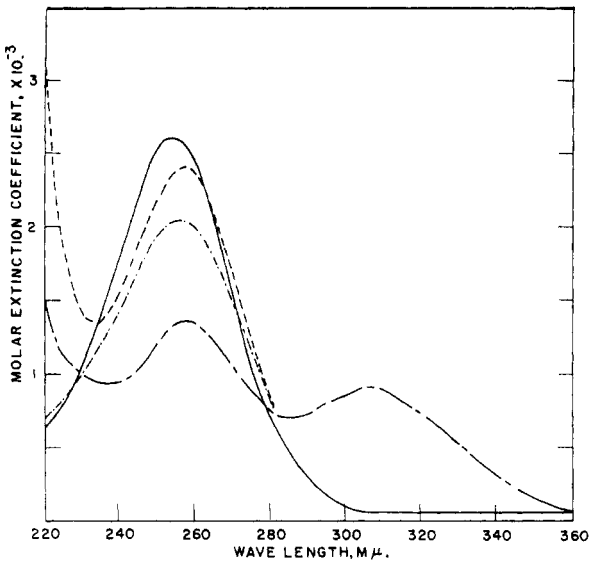


Fig. 1.—Absorption spectra for 1,3-disubstituted-5-iminotetrazoles and related compounds: ————, 1,3-dimethyl-5-iminotetrazole hydrochloride in water and in 1×10^{-3} *N* hydrochloric acid; — — — —, 1,3-dimethyl-5-iminotetrazole hydrochloride in 4×10^{-3} *N* sodium hydroxide; —·—·, 2-methyl-5-methylaminotetrazole in water; – – – –, 2-methyl-5-benzylaminotetrazole in water.

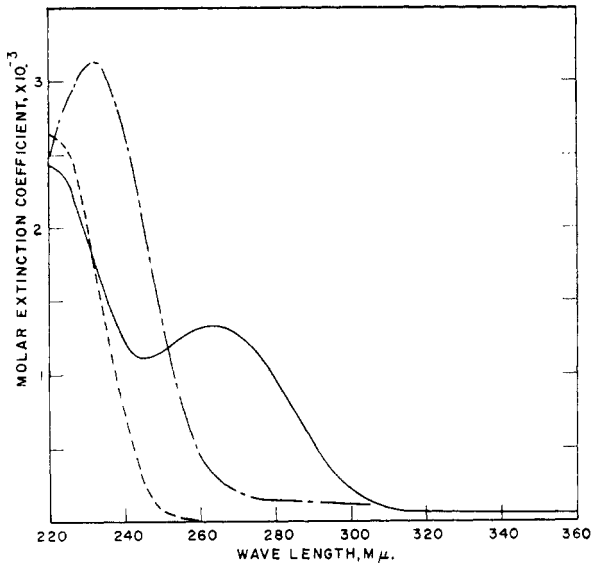
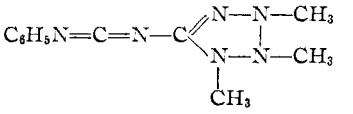


Fig. 2.—Absorption spectra for 1,4-disubstituted-5-iminotetrazoles and related compounds in water: ————, 1,4-dimethyl-5-iminotetrazole hydrochloride: — — —, 1-methyl-5-methylaminotetrazole; – – – –, 1-methyl-5-aminotetrazole.

5-iminotetrazole precipitated and was removed by filtration. The addition of an excess of petroleum ether to the filtrate yielded a very small amount of another product. This product recrystallized from benzene–ligroin (1 to 3) as bright yellow prisms, m.p. 127–128°. The analyses are in agreement with those calculated for



Anal. Calcd. for $C_{11}H_{14}N_6$: C, 57.37; H, 6.13; N, 36.50. Found: C, 57.69; H, 5.93; N, 36.38.

Some methylation apparently also occurred on the 5-amino group since, in one experiment on a larger scale, the **phenylthiourea of 2-methyl-5-methylaminotetrazole**, was isolated in addition to the previous compound. The recovery corresponded to a yield of 2.5%. The same thiourea, m.p. 123–124° after recrystallization from 60% ethanol, was prepared by heating 2-methyl-5-aminotetrazole[5] with a slight excess of phenyl isothiocyanate at 105° for several hours.

Methylation of 1-Methyl-4-benzyl-5-iminotetrazole.—The methylation of 1-methyl-4-benzyl-5-iminotetrazole with methyl benzenesulfonate was accomplished by the procedure of Herbst, *et al.*[1]

The yield of unpurified free base, which was isolated from the reaction product by treatment with aqueous sodium hydroxide, followed by benzene extraction, amounted to 9.76 g. (96.1%). This product did not react with phenyl isothiocyanate. All of the free base was dissolved in 50 ml. of glacial acetic acid and debenzylated over palladium oxide. The hydrogenation was essentially complete in 10 minutes. After the catalyst was removed, the filtrate was evaporated to dryness. The residue of soft solid, after water and acetic acid had been removed by several evaporations with absolute ethanol at reduced pressure, weighed 5.4 g. (100%). After several recrystallizations from ethyl acetate, this material melted at 174–176°. A mixture melting point with an authentic sample of 1-methyl-5-methylaminotetrazole[3] was not depressed; X-ray powder patterns were also identical.

Absorption Spectra.—The ultraviolet absorption spectra were determined in aqueous systems using a Beckman spectrophotometer model DU. Pertinent results are summarized in Figs. 1 and 2, and Table I.

TABLE I

ULTRAVIOLET ABSORPTION DATA

Compound	Solvent	λ_{max}, mμ	ε
1,3-Dimethyl-5-iminotetrazole-HCl	Water	254	2630
1,3-Dimethyl-5-iminotetrazole-HCl	1×10^{-3} *N* HCl	254	2670
1,3-Dimethyl-5-iminotetrazole-HCl	4×10^{-3} *N* NaOH	258	1350
1,3-Dimethyl-5-iminotetrazole-HCl	4×10^{-3} *N* NaOH	305	910
1,3-Dimethyl-5-iminotetrazole-HBr	Water	256	2270
1,3-Dimethyl-5-iminotetrazole-HBr	95% ethanol	259	1900
1-Benzyl-3-methyl-5-iminotetrazole-HCl	Water	258	2740
2-Methyl-5-aminotetrazole	Water	241	2340
2-Methyl-5-methylaminotetrazole	Water	256	2040
2-Methyl-5-methylaminotetrazole	1×10^{-3} *N* HCl	256	1980
2-Methyl-5-benzylaminotetrazole	Water	258	2410
2-Methyl-5-benzylaminotetrazole	1×10^{-3} *N* HCl	258	2330
1,4-Dimethyl-5-iminotetrazole-HCl	Water	265	1340
1-Methyl-5-methylaminotetrazole	Water	232	3140

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