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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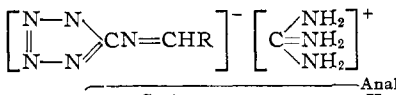
Preparation and Hydrogenation of Azomethines Derived from 5-Aminotetrazole

BY RONALD A. HENRY AND WILLIAM G. FINNEGAN

RECEIVED OCTOBER 13, 1953

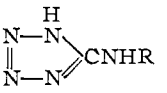
Anhydrous 5-aminotetrazole and aldehydes do not react to any significant extent under the usual conditions employed for the synthesis of azomethines; and there are no prior references to this group of tetrazole derivatives. This difficulty is probably due in part to the fact that 5-amino-

TABLE I



R	Yield, %	M.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
C_6H_5	48	186–188	46.54	46.45	5.21	5.39	48.25	47.43
2,4-$Cl_2C_6H_3$	79	243–244 dec.	35.89	36.20	3.35	3.26	37.21	36.88
4-$NO_2C_6H_4$	75	249–250 dec.	38.99	39.20	4.00	3.97	45.47	45.86
2-HOC_6H_4	74	174.5–175.5	43.54	43.87	4.87	4.91	45.14	44.02

TABLE II



R	Method of preparation	Yield, %	Recrystallization solvent	M.p., °C.	Analyses, % Equiv. wt. Calcd.	Equiv. wt. Found	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
C_2H_5	B	58–71	Acetonitrile	180–181	113.13	113.8	31.85	31.96	6.24	6.25	61.91	61.55
C_7H_{15}	B	74	50% Methanol	164–165	185.28	186.1	...	...	...	...	...	...
C_8H_{17}	B	42	Abs. ethanol	164–165	197.29	198.8	54.79	54.85	9.71	9.45	...	...
C_9H_{19}	B	70	Abs. ethanol	164–165	211.32	213.3	56.84	57.13	10.01	10.06	34.15	34.34
$C_{10}H_{21}$	B	69	50% Isopropyl alcohol	163–164	225.33	223.0	...	...	...	...	...	...
$C_6H_5CH_2$	A	83	Water	183	175.19	176.0	54.84	55.02	5.18	5.11	39.98	39.83
	B	41										
2-$HOC_6H_4CH_2$	A	87	50% Ethanol	177–178	191.19	191.4	50.26	50.84	4.74	4.64	36.63	36.64
	B	71										
4-$HOC_6H_4CH_2$	B	44	Water	184–185	191.19	190.1	50.26	50.35	4.74	4.81	46.63	36.51
2-$ClC_6H_4CH_2$	B	55	50% Ethanol	189–191	209.64	210.6	45.83	46.08	3.84	3.94	16.91[a]	16.92[a]
2,4-$Cl_2C_6H_3CH_2$	A	65	95% Ethanol	198.5–199.5	244.10	244.5	39.36	39.85	2.89	3.10	...	...

[a] Chlorine.

tetrazole is a weak acid ($pK_a \cong 6$), which catalyzes the hydrolysis of any azomethines that might be formed. The azomethines are not directly or readily obtained even under dehydrating conditions. For example, when 5-aminotetrazole is heated with excess benzaldehyde under conditions which permit the continuous removal of the water as an azeotrope, the product appears to be benzal-bis-(5-aminotetrazole). This reluctance to form azomethines apparently also extends to the weakly basic 1-methyl- and 1-phenyl-5-aminotetrazole, which have been reported[1] to condense with benzaldehyde only after prolonged heating; basic catalysis accelerates these latter reactions.[1,2]

In contrast to the behavior of free 5-aminotetrazole, its triethylammonium or guanidinium salt has been found to condense readily with purified aldehydes to give satisfactory yields of the corresponding salts of the azomethines. If the aldehydes contain acidic impurities, the yields are reduced for the same reason mentioned above. Several of the guanidinium salts, which are easy to isolate and purify, are listed in Table I. Some of these salts are initially quite soluble in cold water but they hydrolyze in a few minutes with separation of the aldehyde. A trace of mineral acid causes an immediate decomposition.

Aldehydes which contain a basic group, such as 4-dimethylaminobenzaldehyde, will condense directly with anhydrous 5-aminotetrazole to give an internal salt of the azomethine.

These salts of the azomethines are smoothly and rapidly hydrogenated in alcoholic solution over Adams platinum catalyst to salts of 5-alkylaminotetrazoles. The free 5-alkylaminotetrazoles (Table II) are recovered from these salts by acidification. This method constitutes a much simpler approach to the unambiguous synthesis of 5-alkylaminotetrazoles than the previously reported procedures,[3] especially since the salt of the azomethine can be prepared in absolute ethanol or methanol and hydrogenated immediately without isolation or purification. These 5-alkylaminotetrazoles are of interest because of the ease with which they can be rearranged to the isomeric 1-alkyl-5-aminotetrazoles.[3,4]

Experimental[5]

Guanidinium 5-Arylidene-(or 5-alkylidene)-aminotetrazole. General Procedure.—To 14.4 g. (0.1 mole) of guanidinium 5-aminotetrazole,[6] dissolved in 75 ml. of hot absolute ethanol, was added 0.1 mole of redistilled or recrystallized aldehyde. In a few cases the product began to separate almost immediately and was removed by filtration after the solution had been cooled to 5° for several hours; these products were recrystallized from absolute ethanol. In other cases, where the salt of the azomethine was more soluble, the crystallization was assisted by cooling and the addition of anhydrous diethyl ether; such salts were recrystallized from absolute ethanol–diethyl ether. The results are summarized in Table I.

5-(4-Dimethylaminobenzal)-aminotetrazole.—A solution of 8.5 g. (0.1 mole) of anhydrous 5-aminotetrazole, 14.9 g. (0.1 mole) of 4-dimethylaminobenzaldehyde and 100 ml. of absolute ethanol was digested on the steam-bath for one hour. The orange-yellow plates were removed by filtration (after the mixture had been cooled to 5°) and washed with small portions of cold ethanol. The yield was 12.7 g. (58.8%); m.p. 210° dec. After one recrystallization from absolute ethanol (50 ml. per gram) the melting point was 210.5–211°.

Anal. Calcd. for $C_{10}H_{12}N_6$: C, 55.54; H, 5.60; N, 38.87. Found: C, 55.84; H, 5.96; N, 39.01.

(1) R. Stolle, *et al.*, *J. prakt. Chem.*, **134**, 282 (1932).

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

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

(4) R. A. Henry, W. G. Finnegan and E. Lieber, THIS JOURNAL, **76**, 88 (1954).

(5) The melting points are corrected.

(6) R. A. Henry, THIS JOURNAL, **74**, 6303 (1952).

5-Alkylaminotetrazoles. (A).—The guanidinium salt of the azomethine (0.05 mole) was dissolved in 100 ml. of absolute methanol or ethanol, by heating if necessary, and hydrogenated over 0.05 g. of Adams platinum catalyst at an initial pressure of 50 p.s.i. until the theoretical amount of hydrogen was absorbed. After the catalyst had been removed, the alcohol was evaporated and the residue dissolved in 100 ml. of hot water. The solution was then adjusted to *p*H 3–3.5 with concentrated hydrochloric acid, and cooled at 0° for several hours. The precipitated 5-alkylaminotetrazole was removed by filtration, washed with a small volume of cold water, and dried. The products were recrystallized from the solvents reported in Table II.

(B).—To a solution of 8.5 g. (0.1 mole) of anhydrous 5-aminotetrazole and 10.1 g. (0.1 mole) of anhydrous triethylamine in 50 ml. of absolute methanol was added 0.1 mole of the freshly distilled or neutral aldehyde. There was an immediate exothermic reaction due to the formation of the azomethine. This solution was hydrogenated and processed in the same manner as outlined under A. Because the formation of the azomethine was not quantitative under these conditions, the crude product frequently had to be washed several times with diethyl ether or ligroin to remove unreacted aldehyde or the alcohol resulting from its reduction.

Benzal-bis-(5-aminotetrazole).—Anhydrous 5-aminotetrazole (4.3 g., 0.05 mole) and 15 ml. of benzaldehyde, were heated to and maintained at 140–150° until a homogeneous solution was obtained and the evolution of water had ceased (about 15 minutes). When the solution had been cooled to room temperature, the product was removed by filtration and washed with benzene. The yield of dried material was 5.5 g., m.p. 160–165° when plunged into a hot bath. A sample for analysis was prepared by rapid recrystallization from benzaldehyde and was washed immediately with a large volume of petroleum ether until free of benzaldehyde; m.p. 190–192° dec. When plunged into a hot bath, the compound melts at 166–168°, resolidifies, then remelts at 187–188° (depends on heating rate). This compound hydrolyzes very readily. The analyses indicate a contamination with unreacted 5-aminotetrazole.

Anal. Calcd. for $C_9H_{10}N_{10}$: C, 41.85; H, 3.90; N, 54.24; equiv. wt., 129.13. Found: C, 40.06; H, 3.92; N, 55.89; equiv. wt., 133.9.

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Kinetics of the Alkaline Decomposition of 1,3-Dinitro-1,3-diazacyclopentane

BY WALTER H. JONES

RECEIVED AUGUST 24, 1953

As part of an investigation, which has been indefinitely interrupted, of the alkaline decomposition of secondary nitramines, we here report the kinetics of the reaction of 1,3-dinitro-1,3-diazacyclopentane (hereinafter referred to as DDC) with methoxide ion in absolute methanol solution. This compound, prepared recently by Goodman,[1] is a simpler analog of cyclotrimethylenetrinitramine (hereinafter called RDX), which has been studied in a previous communication,[2] and it was hoped that the mechanism proposed there would be substantiated. Also, further investigation of this type of elimination reaction may be of theoretical interest.[3]

It was found that in absolute methanol DDC reacts with methoxide ion to provide quantitatively one mole of nitrite while consuming two moles of base. The rate of this reaction was investigated by determination of residual alkali and by analysis for nitrite. The kinetics were exceptionally clean throughout the course of the reaction (to about 90%), and experimentally identical rate constants were obtained by the two analytical procedures in terms of the mechanism

$$\mathrm{DDC} + (\bar{\mathrm{O}}\mathrm{CH_3}) \xrightarrow{k} \mathrm{A} + \mathrm{CH_3OH} + (\mathrm{N}\bar{\mathrm{O}}_2)$$

$$\mathrm{A} + (\bar{\mathrm{O}}\mathrm{CH_3}) \xrightarrow{\text{fast}} \bar{\mathrm{B}} + \mathrm{CH_3OH}$$

The kinetic results are summarized in Table I. A tenfold range of initial concentration ratios was employed, and no trend in rate constant was noted.

A plot of log (k/T) against $(1/T)$[4] gave a good straight line, and from the slope and intercept and their standard deviations[5] the activation quantities[6] $\Delta H^{\ddagger} = 29.51 \pm 0.04$ kcal./mole, $\Delta S^{\ddagger} = 17.10 \pm 0.11$ e.u. were obtained. These may be compared with the values of $\Delta H^{\ddagger} = 27.85 \pm 0.40$, $\Delta S^{\ddagger} = 23.6 \pm 1.3$ e.u. found for RDX.[2] At the common temperature employed, 44.93°, the RDX k_1 value was 4.08 ± 0.07 l. (mole min.)$^{-1}$. Hence, even allowing for a statistical factor of three in favor of RDX because of the greater number of acidic hydrogens available for attack, the RDX rate still exceeded that of DDC by 118 times and the difference was not predominantly in either the enthalpy or entropy of activation. If the initial reaction in both cases were an E2 elimination of nitrite, it might be speculated that the difference was due to an electrical effect of the additional nitramine group present in RDX or to greater ring strain associated with the transition state for DDC. Preliminary studies on the related open-chain compounds 2,4-dinitro-2,4-diazapentane and 5,7-dinitro-5,7-diazaundecane[7] indicated that these materials reacted considerably more slowly than the ring compounds. Dimethylnitramine showed no decomposition under the same conditions.

TABLE I

DDC KINETIC DATA

Temp., °C.	N^a	k^b
58.14 ± 0.05	4	0.0780 ± 0.0029
58.14 ± .05	5[c]	.0748 ± .0027
44.93 ± .01	4	.0115 ± .0001
72.86 ± .05	3	.543 ± .006
30.15 ± .02	2	.00131, 0.00128

[a] Number of rate runs. [b] Units: l. (mole min.)$^{-1}$. ± values are standard deviations of the mean. [c] $(\bar{\mathrm{O}}\mathrm{CH_3})$ analysis; all others nitrite determinations.

Although we were unable to isolate and identify the reaction products (see Experimental), we may note that by analogy with the mechanism proposed for the RDX decomposition the intermediate A might be formulated as 1,3-diaza-3-nitrocyclopentene-1 (the alternative, 1,4-diaza-4-nitrocyclopentene-1, would require attack on the least acidic hy-

(1) L. Goodman, THIS JOURNAL, **75**, 3019 (1954).

(2) W. H. Jones, *ibid.*, **76**, 829 (1954).

(3) W. H. Jones, *Science*, **118**, 387 (1953).

(4) According to the equation $k = (kT/h)e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$; S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(5) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 42.

(6) In obtaining these quantities, the 30.15° data were not used, although they gave good straight-line agreement with the others, because it was only practical to study the first few per cent. of reaction at this temperature.

(7) Samples of these materials were kindly provided by Leon Goodman, to whom we wish to express our thanks.