1,4-diethoxycarbonyl-1,4-dimethyl-2-tetrazene gave a 58% yield of 1,4-dimethyltetrazolinone. The small amount of gas which was evolved during the heating period was condensed in an ice bath. The infrared spectrum of the condensate was identical with that of methyl azide.

**1,4-Dibenzyltetrazolinone.**—1,4-Diethoxycarbonyl-1,4-dibenzyl-2-tetrazene (7.68 g, 0.02 mol) was added to 10 g of piperidine and the solution was heated overnight at 100°. After removal of excess piperidine under reduced pressure, the residue was distilled. The first cut, 50–54° (0.5 mm), gave 5.70 g of liquid. The infrared spectrum of the liquid was identical to that of an equal mixture of benzylazide and ethyl N-cyclohexylidenecarbamate. The mixture gave two peaks *via* glpc (Carbowax), with retention times identical to those of authentic samples. The second cut, bp 109–110° (0.2 mm), gave 2.8 g of liquid whose infrared spectrum was identical to that of authentic ethyl N-benzyl carbamate. The solid residue which remained from the distillation was recrystallized twice from ethanol to give 0.2 g (3.8% yield) of white crystals, mp 103–104°; ir (Nujol) strong C=O stretching absorption at 1700 cm$^{-1}$; nmr ($CDCl_3$) 5.08 (s, 4 H) and 7.48 (s, 10 H).

*Anal.* Calcd for $C_{15}H_{14}N_4O$: C, 67.67; H, 5.26; N, 21.05. Found: C, 67.52; H, 5.35; N, 20.87.

Under the same conditions, 1,4-diethoxycarbonyl-1,4-dicyclohexyl-2-tetrazene gave no solid residue upon distillation. Glpc of the distillate gave three peaks in a 1:1:1 ratio whose retention times were identical to those of authentic cyclohexylazide, ethyl N-cyclohexylidenecarbamate, and ethyl N-cyclohexylcarbamate, respectively. The latter precipitated from the distillate on cooling and was found to be identical to an authentic sample. The infrared spectrum of the distillate showed strong azide stretching absorption at 2100 cm$^{-1}$.

**N,N′-Diethoxycarbonyl-*o*-xylyldiamine.**—To a slurry of 50% sodium hydride (4.8 g, 0.1 mol) in 100 ml of freshly distilled diglyme was added dropwise with cooling and stirring a solution of ethyl isopropylidene carbazate (14.4 g, 0.1 mol) in 25 ml of dry diglyme. After gas evolution had ceased, $\alpha,\alpha'$-dibromo-*o*-xylene (13.2 g, 0.05 mol) was added and the mixture was heated at 150° for 24 hr. The solution was cooled and suction filtered, and the solvent was removed under reduced pressure. The residue was taken up in dilute HCl and the solution was treated with liquid bromine until color persisted. The precipitate was collected and recrystallized twice from carbon tetrachloride to give 6.2 g (44.3%) of white crystals, mp 117–118°.

*Anal.* Calcd for $C_{14}H_{20}N_2O_4$: C, 60.00; H, 7.14; N, 10.00. Found: C, 59.91; H, 7.20; N, 10.09.

The product was identical with an authentic sample prepared by adding ethyl chloroformate to *o*-xylyldiamine.

**Photolysis of 1,4-Dimethyltetrazolinone in Ether.**—1,4-Dimethyltetrazolinone (5.7 g, 0.05 mol) was dissolved in 800 ml of freshly distilled diethyl ether. The solution was photolyzed under a blanket of nitrogen with stirring for 48 hr, during which time the 225-m$\mu$ band completely disappeared. A small amount of gummy residue collected on the quartz insert during the photolysis. The solvent was removed under reduced pressure and the liquid residue was distilled, bp 95–98° (0.25 mm), to give 4.10 g (51.2%) of N,N-dimethyl-O-(1-ethoxyethyl)isourea; ir (nujol) imine stretching absorption at 1620 and N-H absorption at 3300 and 1520 cm$^{-1}$; nmr (neat) 6.40 (br, 1 H), 5.49 (q, 1 H), 3.20 (q, 2 H), 2.58 (s, 6 H), 1.04 (d, 3 H), and 0.96 (t, 3 H).

*Anal.* Calcd for $C_7H_{16}N_2O_2$: C, 52.50; H, 10.00; N, 17.50. Found: C, 52.34; H, 9.98; N, 17.72.

A sample of the distillate, when treated with 2,4-dinitrophenylhydrazine reagent, gave a precipitate, mp 147° (from ethanol), which was identical with an authentic sample of the 2,4-dinitrophenylhydrazone of acetaldehyde.

**N,N′-Dimethyl-O-benzylisourea.**—To a slurry of 50% sodium hydride (12.0 g, 0.25 mol) in 150 ml of dry diglyme was added *sym*-dimethylurea (22.0 g, 0.25 mol). The slurry was refluxed for 1 hr, after which time gas evolution ceased. Benzyl chloride (31.5 g, 0.25 mol) was added and the solution was refluxed for 1 hr, cooled, and suction filtered. The solvent was removed from the filtrate under reduced pressure and the liquid residue was distilled, giving 22.25 g (50.0%) of product, bp 120° (0.3 mm); ir (neat) imine stretching absorption at 1650 cm$^{-1}$; nmr ($CCl_4$) 7.20 (s, 5 H), 6.10 (br, 1 H), 4.25 (s, 2 H), and 2.58 (s, 6 H).

*Anal.* Calcd for $C_{10}H_{14}N_2O$: C, 67.41; H, 7.86; N, 15.72. Found: C, 67.34; H, 7.81; N, 15.81;

**Photolysis of 1,4-Dimethyltetrazolinone in 2-Propanol.**—1,4-Dimethyltetrazolinone (5.7 g, 0.05 mol) was dissolved in 800 ml of freshly distilled isopropyl alcohol. The solution was photolyzed under a blanket of nitrogen for 2 hr, during which time the 225-m$\mu$ band completely disappeared. The solvent was removed under reduced pressure. The residue was distilled, bp 70° (15 mm), giving 46.8 g (81.0%) of pinacol. The residue from the distillation solidified on cooling and was recrystallized from acetonitrile to give 4.0 g (91%) of *sym*-dimethylurea. Both products were identified by comparison with authentic samples.

**Registry No.**—1-Ethoxycarbonyl-1-benzyl-2-isopropylidenehydrazine, 20628-48-2; 1,4-dimethyltetrazolinone, 13576-20-0; 1,4-dibenzyltetrazolinone, 20628-50-6; N,N′-diethoxycarbonyl-*o*-xylyldiamine, 20628-51-7; N,N-dimethyl-*o*-(1-ethoxyethyl)isourea, 20688-52-8; N,N′-dimethyl-*o*-benzylisourea, 20628-53-9.

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# Permanganate Oxidation of Tetrasubstituted 2-Tetrazenes[1]

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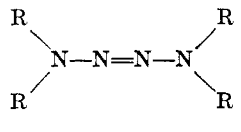
Tetraalkyl-2-tetrazenes, derivatives of the unsaturated hydronitrogen $N_4H_4$, are oxidized by potassium permanganate in acetone solution to 2-tetrazenes containing a carbonyl group $\alpha$ to a terminal nitrogen of the 2-tetrazene. Further oxidation results in the formation of symmetrically substituted 1,4-diacyl-1,4-dialkyl-2-tetrazenes, confirmed independently by oxidation of an appropriate hydrazine. The oxidation reaction extends to a cyclic derivative containing methylene groups $\alpha$ to the terminal nitrogen. Oxidation of tetrabenzyl- and 1,4-dimethyl-1,4-diphenyl-2-tetrazenes gives 2-tetrazenes containing only a single carbonyl group. Although heat, light, or acid may readily rupture the 2-tetrazene linkage to give nitrogen and other fragments, the permanganate oxidation is an example of a reaction in which the four-membered nitrogen chain remains intact. This stability is attributed to sp$^2$ hybridization of the terminal nitrogen atoms in the cation radical of the 2-tetrazene; a mechanism involving this species is proposed for the permanganate oxidation. The new hydronitrogen derivative, 1-nitroso-1,4,4-trimethyl-2-tetrazene, is a product of the oxidation of tetramethyl-2-tetrazene with dinitrogen trior tetroxide.

Tetrasubstituted 2-tetrazenes are derivatives of a hydro nitrogen containing a chain of four nitrogen atoms.[2] The most fully explored reaction of this type of compound involves loss of molecular nitrogen from the nitrogen chain. Thus, pyrolysis or photolysis of the free base yield nitrogen and disubstituted amino radicals



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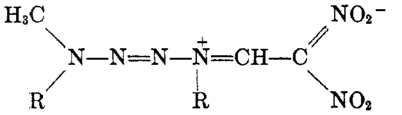
(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley & Sons, Inc., New York, N. Y., 1951, pp 3–6.

which may subsequently combine, disproportionate, or abstract hydrogen,[3] or add to an appropriate substrate.[4] Alternatively, decomposition of the conjugate acid of the 2-tetrazene in aqueous solution quantitatively gives nitrogen gas along with other fragments.[5] The reported energy of activation for this aqueous decomposition of tetramethyl-2-tetrazene, 27.1 kcal/mol, is quite similar to 34.6 kcal/mol, obtained from pyrolysis of the neat material.[4]

Several reactions have been reported where nitrogen gas is not evolved and the nitrogen chain of a tetrasubstituted 2-tetrazene remains intact. Fischer[6] found that iodine added to 1,4-dimethyl-1,4-diphenyl-2-tetrazene gives a solid product with the empirical formula $C_{14}H_{16}N_4I_4$. Compounds of this type are generally unstable and can decompose spontaneously. Wieland and Reisenegger[7] added dinitrogen tetroxide to fully substituted 2-tetrazenes containing at least two phenyl groups and obtained the corresponding di-*p*-nitro derivative of the 2-tetrazene. More recently, the reaction of tetraalkyl-2-tetrazenes with tetranitromethane to give dipolar ions of trialkyl-(β,β-dinitrovinyl)-2-tetrazenes (I) has been described.[8] This reaction, to our knowledge, is the first reported in which an alkyl group of a 2-tetrazene was modified without cleavage of the four-membered nitrogen chain. Treatment of the dipolar ion of trimethyl-(β,β-dinitrovinyl)-2-tetrazene (I, R = $CH_3$) with bromine and then an aqueous solution of potassium hydroxide formed a small amount of material identified as 1-formyl-1,4,4-trimethyl-2-tetrazene in a yield never exceeding 2%. The present paper describes an alternative synthesis for this class of acyl derivatives and considers some aspects of the question concerning the stability of nitrogen chains during oxidative reactions.



I

## Experimental Section

Microanalytical work summarized in Table I was performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Ultraviolet spectra from absolute ethyl alcohol solutions (Table I) were recorded with a Cary Model 11 MS spectrophotometer. Infrared spectra of the materials in potassium bromide disks were measured with a Perkin-Elmer Model 137 spectrophotometer; the carbonyl stretching frequency, usually the most intense absorption, and several other principal absorptions (Table I) are reported in order of decreasing intensity. Proton magnetic resonance spectra (Table II) were recorded with a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained using Hitachi Perkin-Elmer RMU-6E or Bendix Model 12 spectrometers. General methods for the preparation of the tetraalkyl-2-tetrazenes were reported previously.[5] Melting points for the compounds described in the following sections are uncorrected.

**1-Formyl-1,4,4-trimethyl-2-tetrazene.**—A solution of tetramethyl-2-tetrazene (1.16 g) in 200 ml of acetone was cooled to −78°; potassium permanganate (2.12 g) and calcium sulfate (*ca.* 3 g) were added. The mixture was allowed to warm to room temperature; stirring was continued until the supernatant solution was colorless (16–24 hr). The solid materials were filtered off and washed, and the acetone was evaporated. The resulting solid was recrystallized from pentane, 0.839 g (65% yield). Sublimation of this material gave white crystals, mp 55°. Using the method of Stenstrom and Goldsmith[9] and published $H_0$ values for hydrochloric acid solutions,[10] the decrease of absorbance of the peak due to the free base with increasing acid concentration was followed; a $pK_b$ value of 14.57 at room temperature was obtained for the 2-tetrazene. The molecular weight was determined with the Bendix mass spectrometer; the most intense peak corresponded to the parent peak at mass 130 (calcd mol wt 130). In addition, a prominent peak corresponding to mass 102 (1-formyl-1,2,2-trimethylhydrazine, formed by loss of $N_2$ from the parent 2-tetrazene) was observed.

The 2-tetrazene also was prepared by treating 1,1,4-trimethyl-4-(β,β-dinitrovinyl)-2-tetrazene[8] with bromine in carbon tetrachloride. After removal of the solvent, the resulting oil was treated with aqueous potassium hydroxide and the 2-tetrazene was extracted with pentane. Yields from tetramethyl-2-tetrazene by this method did not exceed 2%.

**1,4-Diformyl-1,4-dimethyl-2-tetrazene.**—Tetramethyl-2-tetrazene (1.16 g) was dissolved in 200 ml of acetone and the solution was cooled to −78°. Potassium permanganate (4.24 g) was added, the mixture was warmed to room temperature, and the solution was stirred overnight. Manganese(IV) oxide was filtered off and the solvent was evaporated to give the diformyl-2-tetrazene, 0.728 g (50%). The material recrystallized from acetone was a white solid, mp 166°. The compound was also prepared in 70% yield by oxidation of 1-formyl-1,4,4-trimethyl-2-tetrazene with potassium permanganate in acetone. Similarly, the material was prepared from 1-formyl-1-methylhydrazine[11] by oxidation with potassium permanganate.[12]

**1-Acetyl-1,4,4-triethyl-2-tetrazene.**—This material was prepared from tetraethyl-2-tetrazene (1.72 g) and potassium permanganate (2.12 g) in a calcium sulfate buffered acetone solution according to the procedure for 1-formyl-1,4,4-trimethyl-2-tetrazene. The crude product was a yellow oil; no purification of the product was attempted.

**1,4-Diacetyl-1,4-diethyl-2-tetrazene.**—After 2 days at room temperature, the crude 1-acetyl-1,4,4-triethyl-2-tetrazene was treated with potassium permanganate (2.12 g) in 200 ml of acetone. Concentrated hydrochloric acid (16 drops) was added and the mixture was stirred for 30 min. After filtration and evaporation of the solvent, 0.35 g of solid (18% from tetraethyl-2-tetrazene) was obtained; the product was recrystallized from ether, mp 78°.

**1-Propionyl-1,4,4-tripropyl-2-tetrazene.**—This material was prepared from tetra-*n*-propyl-2-tetrazene (1.14 g) and potassium permanganate (1.06 g) according to the procedure for 1-formyl-1,4,4-trimethyl-2-tetrazene. The crude product was a yellow oil.

**1,4-Dipropionyl-1,4-dipropyl-2-tetrazene.**—After a day at room temperature, the crude 1-propionyl-1,4,4-tripropyl-2-tetrazene was treated with potassium permanganate (1.06 g) in 200 ml of acetone. The procedure was similar to that for 1,4-diacetyl-1,4-diethyl-2-tetrazene. The product (about 0.3 g, 25% yield from tetra-*n*-propyl-2-tetrazene) was recrystallized twice from ether, mp 62°.

**1,1′-Azoperhydroazepine.**—Yellow mercury(II) oxide (10 g) was added to an ether solution of 5 g of 1-aminoperhydroazepine (N-aminohexamethyleneimine or N-aminohomopiperidine, Aldrich Chemical Co., Inc.) at −78° with continuous stirring. The mixture was allowed to warm to room temperature and was left stirring overnight. After filtration and evaporation of the ether, 4.4 g (90% yield) of nearly white crystals were obtained; recrystallization from ethanol gave white needles, mp 64°.

**1,1′-Azoperhydroazepin-2-one.**—This crystalline material was prepared according to the procedure for 1-formyl-1,4,4-trimethyl-2-tetrazene. The crude product was purified by separation on a column packed with silica gel, mp 70°.

**1,1′-Azoperhydroazepine-2,2′-dione.**—The direct oxidation of 1,1′-azoperhydroazepine with a small excess of potassium permanganate in acetone (several drops of acetic acid were added after the oxidation had proceeded for several hours) gave the

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[3] J. S. Watson, *J. Chem. Soc.*, 3677 (1956).

[4] A. Good and J. C. J. Thynne, *ibid.*, *B*, 684 (1967).

[5] W. R. McBride and W. E. Thun, *Inorg. Chem.*, **5**, 1846 (1966).

[6] E. Fischer, *Ann.*, **190**, 67 (1878).

[7] A. Wieland and C. Reisenegger, *ibid.*, **401**, 244 (1913).

[8] W. E. Thun, D. W. Moore, and W. R. McBride, *J. Org. Chem.*, **31**, 923 (1966).

[9] W. Stenstrom and N. Goldsmith, *J. Phys. Chem.*, **30**, 1683 (1926).

[10] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

[11] C. Pedersen, *Acta Chem. Scand.*, **18**, 2199 (1964).

[12] K. Ronco and H. Erlenmeyer, *Helv. Chim. Acta*, **39**, 1045 (1956).

TABLE I

ANALYTICAL, ULTRAVIOLET, AND INFRARED DATA

| 2-Tetrazene | Registry no. | Analyses, % C Calcd | C Found | H Calcd | H Found | N Calcd | N Found | Ultraviolet spectra $\lambda_{max}$, mμ | $\epsilon \times 10^{-4}$ | Infrared spectra, ν, cm$^{-1}$ C=O | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Formyl-1,4,4-trimethyl- | 20642-57-3 | 36.91 | 36.94 | 7.74 | 7.76 | 43.05 | 43.19 | 275 | 1.88 | 1650 | 1020, 1350, 738 |
| 1,4-Diformyl-1,4-dimethyl- | 20642-58-4 | 33.33 | 33.61 | 5.59 | 5.89 | 38.87 | 38.49 | 270 | 2.45 | 1670 | 1030, 1340, 668 |
| 1,4-Diacetyl-1,4-diethyl- | 20642-59-5 | 47.99 | 48.01 | 8.05 | 8.13 | 27.98 | 27.92 | 285 | 2.40 | 1680 | 1380, 1350, 1290 |
| 1,4-Dipropionyl-1,4-dipropyl- | 20642-60-8 | 56.22 | 56.97 | 9.44 | 9.70 | 21.86 | 22.57 | 287 | 2.42 | 1680 | 1380, 1065 |
| 1,1′-Azoperhydroazepine | 16504-24-8 | 64.24 | 64.33 | 10.78 | 10.78 | 24.97 | 24.87 | 289 | 1.04 | ... | 2890, 1070, 962 |
| 1,1′-Azoperhydroazepin-2-one | 20642-61-9 | 60.47 | 61.39 | 9.31 | 9.43 | 23.51 | 23.62 | 287 | ... | ... | ... |
| 1,1′-Azoperhydroazepine-2,2′-dione | 20642-62-0 | 57.12 | 56.85 | 7.99 | 7.96 | 22.21 | 22.12 | 283 | 1.7 | 1670[a] | 1125, 1380, 958 |
| 1-Formyl-4-methyl-1,4-diphenyl- | 20642-63-1 | 66.13 | 65.83 | 5.55 | 5.33 | 22.04 | 22.06 | 314 | 1.0 | 1690 | 1365, 1325, 720 |
| 1-Benzoyl-1,4,4-tribenzyl- | 20642-65-3 | 77.39 | 77.47 | 6.03 | 5.91 | 12.89 | 13.01 | 294 | 1.5 | 1625 | 697, 1380 |
| 1-Nitroso-1,4,4-trimethyl-[b] | 20642-64-2 | ... | ... | ... | ... | ... | ... | 310 | 1.3 | 1470[c] | 1325, 980, 1090 |

[a] Third most intense peak. [b] Infrared spectrum of $CCl_4$ solution. [c] Absorption due to N=O, second most intense peak.

TABLE II

NUCLEAR MAGNETIC RESONANCE DATA

| 2-Tetrazene | Shift, ppm; *J*, Hz N—CH₂— | Aryl- or —CH₂CH₃— | —COCH₂— or —COH |
|---|---|---|---|
| 1-Formyl-1,4,4-trimethyl- | 3.03 (s, 6 H)<br>3.16 (s, 3 H) | | 8.73 (s, 1 H) |
| 1,4-Diformyl-1,4-dimethyl- | 3.35 (s, 6 H) | | 8.96 (s, 2 H) |
| 1,4-Diacetyl-1,4-diethyl- | 4.06 (q, 4 H); *J* = 7.1 | 1.16 (t, 6 H); *J* = 7.1 | 2.37 (s, 6 H) |
| 1,4-Dipropionyl-1,4-dipropyl- | 3.97 (t, 4 H); *J* = 7.2 | 0.89 (t, 6 H); *J* = 7.2<br>1.20 (t, 6 H); *J* = 7.4<br>1.55 (m, 4 H) | 2.71 (q, 4 H); *J* = 7.4 |
| 1,1′-Azoperhydroazepine | 3.24 (m, 8 H) | 1.38 (m, 16 H) | |
| 1,1′-Azoperhydroazepin-2-one | 3.71 (m, 4 H)<br>3.98 (m, 2 H) | 1.72 (m, 14 H) | 2.62 (m, 2 H) |
| 1,1′-Azoperhydroazepine-2,2′-dione | 4.30 (m, 4 H) | 1.81 (m, 12 H) | 2.80 (m, 4 H) |
| 1-Formyl-4-methyl-1,4-diphenyl- | 3.52 (s, 3 H) | 7.19 (m, 10 H) | 9.01 (s, 1 H) |
| 1-Benzoyl-1,4,4-tribenzyl- | 4.38 (s, 4 H)<br>5.41 (s, 2 H) | 6.83 (m, 5 H)<br>7.31 (m, 15 H) | |
| 1-Nitroso-1,4,4-trimethyl- | 3.32 (s, 6 H)<br>3.44 (s, 3 H) | | |

desired product which was recrystallized from ethanol-water, mp 216°.

**1-Formyl-4-methyl-1,4-diphenyl-2-tetrazene.**—Dimethyldiphenyl-2-tetrazene (1.82 g) was dissolved in 300 ml of acetone at room temperature, potassium permanganate (1.62 g) was added, and the mixture was stirred until homogeneous; then glacial acetic acid (3 ml) was added. Although the color of the permanganate was depleted in about 30 min, stirring was continued overnight. The solvent was partially evaporated after filtration. The first fraction (0.43 g) was primarily starting material (23% yield), but the second fraction (0.82 g) contained the desired product (*ca.* 40% yield). Recrystallization from acetone gave a solid, mp 94°.

**1-Benzoyl-1,4,4-tribenzyl-2-tetrazene.**—Tetrabenzyl-2-tetrazene (2.14 g) and potassium permanganate (1.08 g) were dissolved in 400 ml of acetone containing glacial acetic acid (1 ml) and the solution was stirred overnight. After the manganese-(IV) oxide was filtered off, the solvent was evaporated, leaving a crude product, 1.61 g (73%). Separation on a silica gel column with methylene chloride–*n*-hexane (50:50) gave a central fraction, 0.49 g, mp 87°.

**1-Nitroso-1,4,4-trimethyl-2-tetrazene.**—An excess of dinitrogen tetroxide or dinitrogen trioxide was bubbled into a solution of tetramethyl-2-tetrazene in chloroform or carbon tetrachloride, cooled to about −20°. Most of the solvent was evaporated and a nearly white solid was collected on a sintered glass disk, mp 38–40°. However, in some cases a dark oil was the product of the reaction. The oil was washed several times with a total of 300 ml of pentane, and the pentane solution was evaporated to a volume of 50 ml and cooled to −78° to precipitate the product prior to filtration. Further purification by sublimation gave a slightly yellow solid, mp 40°. A parent peak corresponding to *m/e* 131 and prominent peaks corresponding to *m/e* 43, 59, 28, and 15 were observed in the mass spectrum. A precise mass determination of the parent peak was 131.0813; calcd for $C_3H_9N_5O$, 131.0807. A broad unsymmetrical absorption at 1480–1440 cm$^{-1}$ and absorption at 1045 cm$^{-1}$ were observed in the infrared region, corresponding to the N=O and N-N stretching frequencies, respectively.[13] The analysis for the nitroso functional group was determined by adding acid to a solution of the material in an inert atmosphere to form nitrous acid. The nitrous acid thus produced liberated iodine from iodide and the iodine was titrated with thiosulfate.[14] *Anal.* Calcd wt of samples from thiosulfate titration: 0.0623 and 0.1323 g. Found: 0.0626 and 0.1279 g, respectively. *Caution!* This material is sensitive to friction and impact. Preliminary results indicate a kilogram weight dropped onto the solid from 7 cm will initiate detonation.

## Results

**Tetramethyl-2-tetrazene.**—Oxidation of 1,1,4,4-tetramethyl-2-tetrazene with potassium permanganate in acetone solution and at room temperature provides a good synthesis for 1-formyl-1,4,4-trimethyl-2-tetrazene. The latter compound, p$K_b$ = 14.57, is a much weaker base than tetramethyl-2-tetrazene, p$K_b$ = 7.80.[15] This new synthesis gives material identical with that obtained from the reaction of trimethyl(β,β-dinitro-

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[13] (a) E. Müller and H. Haiss, *Chem. Ber.*, **95**, 1255 (1962); (b) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 4172 (1955).

[14] (a) F. Sutton, "A Systematic Handbook of Volumetric Analysis," Butterworth and Co. Ltd., London, 1955, pp 398–400. (b) For a more recent procedure which may be useful, see J. Gal, E. R. Stedronsky, and S. I. Miller, *Anal. Chem.*, **40**, 168 (1968).

[15] W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, **79**, 572 (1957).

vinyl)-2-tetrazene with bromine and aqueous potassium hydroxide. The time required for the oxidation, as judged by the disappearance of the permanganate, varies according to the amount of moisture in the acetone; greater amounts of moisture necessitate shorter reaction times. Although acidic aqueous solutions accelerate the completion of the oxidation to a few minutes, yields are lower and evolution of nitrogen indicates an alternative reaction resulting in the cleavage of the nitrogen chain. 1-Formyl-1,4,4-trimethyl-2-tetrazene is a product of the permanganate oxidation of tetramethyl-2-tetrazene over the pH range from 1 to 13; in fact, the product can be detected even from oxidation in acetic acid. In one experiment, an electron paramagnetic resonance spectrum of a slightly acidic solution at room temperature indicated both absorption due to $Mn^{2+}$ and a more complex spectrum, attributed to the tetramethyl-2-tetrazene cation radical. The epr spectrum of this latter species, however, is better resolved under different conditions.[16]

Further oxidation of tetramethyl-2-tetrazene (or 1-formyl-1,4,4-trimethyl-2-tetrazene) with potassium permanganate in acetone at room temperature forms 1,4-diformyl-1,4-dimethyl-2-tetrazene in good yield. The latter compound was prepared independently by oxidation of 1-formyl-1-methylhydrazine directly to the 2-tetrazene. 1,4-Diformyl-1,4-dimethyl-2-tetrazene is a weaker base than 1-formyl-1,4,4-trimethyl-2-tetrazene; a $pK_b$ value at 25° for the diformyl derivative is estimated at 18. The formyl-2-tetrazenes differ from tetramethyl-2-tetrazene not only because they exist as free bases rather than as conjugate acids in dilute acid, but also because they decompose in moderately basic solution. Preliminary studies of formyl-2-tetrazenes in dilute aqueous solution at 20° established that the decomposition is initially pseudo first order and that the decomposition rate for a given tetrazene is 4 to 6 times faster at pH $\sim$ 13 than at pH $\sim$ 1, indicating decomposition due to hydrolysis of the formyl group.[17]

The usual reduction product of permanganate in these reactions is manganese(IV) oxide. Since Henbest and Thomas[18] were able to oxidize dimethylaniline to formylmethylaniline in 80% yield with a fiftyfold excess of "activated" manganese dioxide, conditions similar to those they described were used to oxidize tetramethyl-2-tetrazene. Yields of several per cent of formylmethyl-2-tetrazenes were recovered from such reactions, but, because of the poor yields and the excessive amount of manganese dioxide employed, we conclude that permanganate is the principal oxidant in our reaction.

At room temperature, tetramethyl-2-tetrazene can be oxidized to 1-formyl-1,4,4-trimethyl-2-tetrazene within 10 min in solutions buffered at pH 5; under these conditions, there is negligible oxygen exchange between the permanganate ion and water.[19] The mass spectral data for the formyl-2-tetrazene reveal that $^{18}O$ is incorporated in the 2-tetrazene when $Mn^{16}O_4^-$ is the oxidant and $H_2{}^{18}O$ is the solvent, but not *vice versa*. Thus, it is highly unlikely that any kind of manganate ester is involved in the oxidation mechanism.

Tetramethyl-2-tetrazene was also oxidized by nitrogen oxides during the present investigation. Again, an epr spectrum of the cation radical of tetramethyl-2-tetrazene[16] is observed on the addition of gaseous dinitrogen tetroxide to an aqueous solution of the 2-tetrazene. If the reaction is performed in chloroform or carbon tetrachloride with dinitrogen tri- or tetroxide, an easily sublimable, explosive material, 1-nitroso-1,4,4-trimethyl-2-tetrazene, is obtained.

**Classes of Tetrasubstituted 2-Tetrazenes.**—The permanganate oxidation is a general reaction of tetraalkyl-2-tetrazenes. With tetraethyl- and tetra-*n*-propyl-2-tetrazene, the monoacyl derivatives were obtained only as light yellow oils and were not purified for chemical analysis. However, further oxidation of these oils gave solid diacyl derivatives. In all cases, a methyl or methylene group alpha to a terminal nitrogen (the 1,4 positions) of the 2-tetrazene chain is oxidized to a carbonyl group; under the conditions employed, the oxidation is terminated on the formation of the symmetrical diacyl-substituted 2-tetrazene. The generality of the synthesis was extended to cycloalkyl derivatives of 2-tetrazenes containing a methylene group $\alpha$ to the 1,4 nitrogens. 1,1′-Azoperhydroazepine (1,1,4,4-dihexamethylene-2-tetrazene) was used as the model compound for the permanganate oxidation.

Tetrabenzyl- and 1,4-dimethyl-1,4-diphenyl-2-tetrazenes were chosen as being representative of 2-tetrazenes containing pseudoalkyl and alkyl–aryl substitution. In these examples, oxidation with permanganate proved to be more difficult than with the alkyl- or cycloalkyl-substituted 2-tetrazenes; only the monoacyl-substituted 2-tetrazenes were successfully isolated as products. Elemental analyses and various spectral data indicated further oxidation to diacyl-substituted derivatives, but these products, in low yield, were not obtained in satisfactory purity for good elemental analysis.

**Methylated Hydrazines.**—The permanganate oxidation was extended to another class of substituted hydro nitrogens, methylated hydrazines. Formylmethyl-2-tetrazenes were recovered in very low yield by the direct oxidation of 1,1-dimethylhydrazine. It is not presently known whether the reaction proceeds *via* formation and oxidation of tetramethyl-2-tetrazene or *via* oxidation of 1,1-dimethylhydrazine to 1-formyl-1-methylhydrazine and subsequent formation of formylmethyl-2-tetrazenes. Tetramethylhydrazine was oxidized to both formyltrimethylhydrazine and 1,2-diformyl-1,2-dimethylhydrazine. Qualitative identification of formyltrimethylhydrazine was made from mass spectral data, and diformyldimethylhydrazine was identified from comparison of glpc elution time and mass, nmr, and ir spectra with data from an authentic sample of diformyldimethylhydrazine.[20]

## Discussion

The most unusual feature of the oxidation of tetrasubstituted 2-tetrazenes—whether with potassium permanganate, nitrogen oxides, or tetranitromethane — is the retention of the four-membered nitrogen chain. Electron impact data indicate that the bond dissociation energy of the nitrogen–nitrogen single bond in

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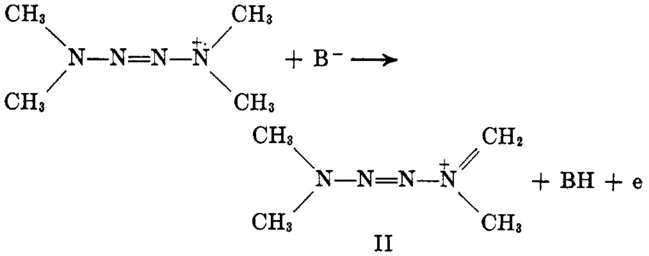
tetramethyl-2-tetrazene is 16.5 kcal/mol.[21] Only the nitrogen oxides, dinitrogen tri- and tetroxide, have weaker nitrogen–nitrogen single bonds.[22] It is therefore somewhat surprising that an alkyl group of the 2-tetrazene is altered without rupture of the relatively weak nitrogen–nitrogen bonds.

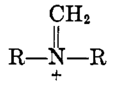
Experimentally, it has been observed that each of the oxidants mentioned above can react with tetramethyl-2-tetrazene to form the cation radical, a species with one electron removed. It now seems obvious that most, if not all, of the oxidation reactions leading to the retention of the 2-tetrazene nitrogen chain occur *via* a cation radical. From the published epr spectrum of the tetramethyl-2-tetrazene cation radical, relatively small nitrogen coupling constants[16] were determined for the 1,4 positions compared with those predicted for tetrahedral nitrogen atoms. This evidence supports $sp^2$ hybridization on the terminal nitrogen positions.

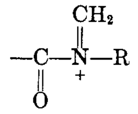
The $sp^2$ hybridization in the tetramethyl-2-tetrazene cation radical should both strengthen the nitrogen–nitrogen single bond and reduce the likelihood of an elimination reaction of the stable diatomic nitrogen molecule. Although pertinent bond dissociation energy data are not available, this point may be crudely illustrated from bond energies. Bond energies for the nitrogen–nitrogen single and double bonds are 37 and 61 kcal/mol, respectively, and that for the carbon–nitrogen single bond is 66 kcal/mol.[23] During the formation of 1-nitroso-1,4,4-trimethyl-2-tetrazene, a carbon–nitrogen single bond in the 2-tetrazene is replaced by a nitrogen–nitrogen single bond. This would suggest that the stabilization energy of the nitrogen chain in the cation radical is greater than 29 kcal/mol, the difference between the carbon–nitrogen and nitrogen–nitrogen single-bond energies. Recent results from infrared spectra of hydrazine derivatives indicate that, as the configuration on the nitrogen atom changes from $sp^3$ to $sp^2$, a corresponding decrease in repulsion between lone pairs occurs, accompanied with a shortening and strengthening of the nitrogen–nitrogen single bond.[24]

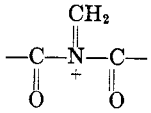
If the chemical oxidation of these substituted 2-tetrazene hydro nitrogens is similar to the electrochemical oxidation of primary aliphatic amines,[25] the initial step in the oxidation is the removal of an electron from a nitrogen atom. It is proposed that such a mechanism indeed does extend to the tetrasubstituted 2-tetrazenes currently studied. In a reaction analogous to the electrochemical oxidation of dimethylaniline[26] and the permanganate oxidation of tertiary aliphatic amines,[27] electron abstraction gives a cation radical as the first step. A basic medium assists in deprotonation of the cation radical, and this is rapidly followed by loss of a second electron. The resultant cation (II), like those derived from substituted amides[28] (IV), is hydrolyzed to a primary alcohol which can then be readily oxidized by permanganate to formyltrimethyl-2-tetrazene.


II

The stabilization by conjugation of the iminium cations II and IV possibly precludes the direct hydrolysis[29] of II to formaldehyde and other fragments. Cations containing structures III, IV, and V can hydrolyze and subsequently lose a proton to give corresponding N-hydroxymethyl compounds; the order of stability toward hydrolysis is V > IV > III. The importance of both moisture and a basic medium has been recognized in the permanganate oxidation of a benzyl to a benzoyl group in aryl-substituted amines,[30] compounds possibly capable of forming cation radicals.[31] Although the optimum medium and pH for the oxidation of tetrasubstituted 2-tetrazenes were not definitely established, it is clear that extremes in pH should be avoided. A strongly basic medium contributes to the rapid hydrolysis of the desired product, while strongly acidic conditions accelerate the decomposition of the starting 2-tetrazene; qualitatively, permanganate catalyzes this latter reaction.


III


IV


V

Oxidation of pseudoalkyl- and alkyl–aryl-substituted 2-tetrazenes can be complicated by competitive reactions. This is noted in the oxidation of dimethylaniline upon removal of an electron; redistribution of the free electron density in the phenyl group leads to other reaction products.[26] Choice of experimental conditions can become most important. Thus, benzoyldibenzylamine was obtained by the permanganate oxidation of tribenzylamine in a slightly basic medium[30] but not in a neutral medium.[32] Other reactions might involve hydrogen instead of electron abstraction in the first step[27] and hydrolysis of the cation in a different manner[29] owing to acyl substitution in the 2-tetrazene.

The formation of 1-nitroso-1,4,4-trimethyl-2-tetrazene is believed to involve a free-radical mechanism similar to one proposed for the oxidation of tertiary amines[33] and the transient formation of trimethyl-2-tetrazene; 1-nitroso-1,2,2-trimethylhydrazine is pre-

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pared from trimethylhydrazine and nitrous acid.[34] A 1,4-disubstituted 2-tetrazene has been proposed as an intermediate in the reaction of *p*-toluenesulfonyl azide with a halomagnesium salt of aniline.[35] Thermally, 1-nitroso-1,4,4-trimethyl-2-tetrazene is more stable than similar 1-nitroso-1,3-diaryltriazenes.[13]

The permanganate oxidation was extended successfully to the alkyl-substituted hydronitrogen, tetramethylhydrazine. According to electron-impact studies, this material has a relatively strong nitrogen–nitrogen single bond,[21] but it is quite easily oxidized to a cation–radical.[36] This latter fact accounts for the analogous reaction. Although the permanganate oxidation of tetra-*n*-propylhydrazine to 1,2-dipropionyl-1,2-dipropylhydrazine has been reported,[37] tetra-*n*-propylhydrazine was not isolated, but was only proposed as an intermediate in the oxidation of dipropylamine, a supposition not consistent with a more recent investigation.[32]

In contrast with degradation reactions commonly associated with oxidation of amines,[38] Davis and Rosenblatt[39] recently oxidized an N-methyl to an N-formyl group in tertiary amines with oxygen and a platinum catalyst at room temperature. Tertiary amines containing aryl groups were more difficult to oxidize; under similar conditions, an N-benzyl group was not oxidized. Both the oxidizing species and the structure of the amine are especially important where dual mechanisms of electron and hydrogen abstraction are possible.[27] Dual oxidation mechanisms were discussed recently in a review of the electrochemical oxidation of amines.[40] While oxidation at low potentials forms a cation radical, at higher potentials another electron and a proton are lost rapidly to form an iminium salt. With amines, oxidants such as chlorine dioxide react according to the low-potential mechanism; oxidants such as permanganate yield products expected from oxidation at higher potentials. Since a cation radical which is more stable than the corresponding radical from amines is formed during the oxidation of the 2-tetrazenes, it is not surprising in retrospection that some chemical oxidants associated with the higher potential reaction for amines would react according to the low-potential mechanism during the oxidation of the tetrasubstituted 2-tetrazenes.

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# The Fischer Indole Cyclization of Several *ortho*-Substituted Phenylhydrazones[1,2]

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Fischer indole cyclization of ethyl pyruvate *o*-methoxyphenylhydrazone in ethanolic hydrogen chloride gave 2-carbethoxy-6-chloroindole as the main product. Minor products included 2-carbethoxy-3-chloroindole, the expected 2-carbethoxy-7-methoxyindole, and several indolic dimers. Similarly, ethyl pyruvate *o*-benzyloxyphenylhydrazone gave 2-carbethoxy-6-chloroindole. Cyclization of cyclohexanone *o*-methoxyphenylhydrazone in dilute sulfuric acid yielded 8-methoxy-1,2,3,4-tetrahydrocarbazole as the major product. The only isolated by-product, previously reported to be "12-methoxy-1,2,3,4-tetrahydroisocarbazole," has now been shown to have a dimeric structure. When the reaction was run in ethanolic hydrogen chloride, the dimer hydrochloride became the main product and 8-methoxy-1,2,3,4-tetrahydrocarbazole is formed in lower yield. The structure of the dimers and the reaction mechanism are discussed.

The simplest approach to 7-methoxyindole, an intermediate in a synthetic program on indole chemistry, appeared to be the Fischer indole cyclization of ethyl pyruvate *o*-methoxyphenylhydrazone (**1**). The transformation of *o*-anisidine to 2-carbethoxy-7-methoxyindole (**2**), *via* the hydrazone (**1**), has been reported[3] to proceed in 30% over-all yield; the preparation of the ethoxy analog of **2** by cyclization of the corresponding phenylhydrazone has also been described.[4] However other workers[5] found that cyclization of **1** with ethanolic hydrogen chloride gave an unidentified indole, mp 168°, different from **2**. Our results on the Fischer cyclization of **1** and related compounds are described.

While the reaction of diazotized *o*-anisidine with ethyl $\alpha$-methylacetoacetate afforded the hydrazone **1** as an oil, use of ethyl $\alpha$-ethoxalylpropionate[6] yielded crystalline **1**. The latter could be separated into two forms which are presumably the *syn* and *anti* isomers as indicated by analytical and spectral properties and the fact that the mixture and both forms yielded the same product mixtures when cyclized in acid media.

Cyclization of the isomeric hydrazone mixture **1** in ethanolic hydrogen chloride gave a mixture of polar and faster moving components. Fractional crystallization yielded a single compound, mp 177–178°, whose empirical formula corresponded to $C_{11}H_{10}ClNO_2$ (yield 36%). The melting point suggested that the product was 2-carbethoxy-6-chloroindole (**3**),[7] and this was verified by comparison of the product (**3**) and its corresponding acid (**4**) with authentic samples prepared by

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[2] This work was carried out under Contract SA-43-ph-3021 with the Psychopharmacology Research Branch, National Institute of Mental Health, Bethesda, Md.

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