The Preparation and Reactions of 1,4-Dialkoxycarbonyl-1,4-dialkyl-2-tetrazenes

WILLIAM S. WADSWORTH, JR.

Department of Chemistry, South Dakota State University, Brookings, South Dakota 57006

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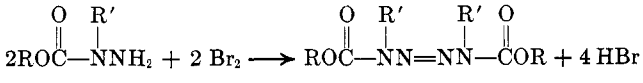
A number of 1,4-dialkoxycarbonyl-1,4-dialkyl-2-tetrazenes have been prepared by the bromine oxidation of 1-alkoxycarbonyl-1-alkylhydrazines. The tetrazenes which have a *trans* configuration react with nucleophiles to give products arising from carbon–nitrogen bond scission. One of the products, 1,4-dimethyltetrazolinone, although thermally stable, undergoes solvent assisted photodecompositions to give isoureas.

Acyclic 2-tetrazenes have been studied by a number of workers.[1] In most cases, those reported have been symmetrically substituted analogs containing nonfunctional groups.[2] It was the purpose of this work to prepare and study the chemistry of the 1,4-dialkoxycarbonyl analogs which might condense with diols or diamines to give interesting polymers.

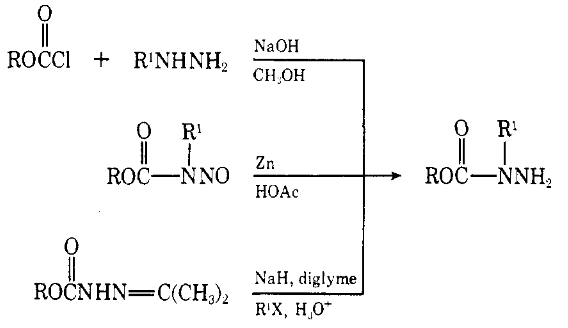
The classical synthesis of 2-tetrazenes involves oxidation of unsymmetrically substituted hydrazines under basic conditions. We have found that, in the case of 1-alkoxycarbonyl-1-alkylhydrazines, bromine oxidation is particularly successful, the 2-tetrazene precipitating from aqueous acid solution in a nearly pure state (Table I).



$$2\mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\overset{\mathrm{R}'}{\overset{|}{\mathrm{N}}}\mathrm{NH_2} + 2\,\mathrm{Br_2} \longrightarrow \mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\overset{\mathrm{R}'}{\overset{|}{\mathrm{N}}}\mathrm{N}{=}\mathrm{N}\overset{\mathrm{R}'}{\overset{|}{\mathrm{N}}}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR} + 4\,\mathrm{HBr}$$

The starting 1-alkoxycarbonyl-1-alkylhydrazines were prepared by one of three different procedures (Scheme I), each of which had its limitations. The first[3] was limited by the lack of availability of monoalkylhydrazines. Methyl N-amino-N-cyclohexylcarbamate was prepared in low yield by the zinc–acetic acid reduction of the N-nitroso precursor.[4] The product was not isolated, but was oxidized directly to the 2-tetrazene. The procedure failed when primary N-alkyl substituents were employed. The third method involved the alkylation of an alkylidene hydrazide followed by mild hydrolysis.[5] This method was particularly successful in the preparation of benzyl derivatives.

SCHEME I



The 1,4-dialkoxycarbonyl-1,4-dialkyl-2-tetrazenes were prepared by treating an acidified aqueous solution of 1-alkoxycarbonyl-1-alkylhydrazine with liquid bromine. Inverse addition or addition of bromine to an alkaline solution of the hydrazine failed to give a precipitate. Treatment of an alkaline solution of 1-alkoxycarbonyl-1-methylhydrazine with bromine caused a rapid evolution of methyl bromide. Likewise, N-amino-N-methylureas and N-amino-N-methylamides under both acidic and alkaline conditions gave rapid evolution of methyl bromide when their solutions were treated with bromine. Thus, under acidic conditions the presence of an alkoxycarbonyl group has a deciding effect on the course of the oxidation.

Since 2-tetrazene formation takes place under acidic instead of the usual basic conditions used for the formation of 1,1,4,4-tetraalkyl-2-tetrazenes, it would appear that azamines ($R_2\overset{+}{N}{=}\overset{-}{N}$) postulated as intermediates in 2-tetrazene formation[1e] are not intermediates in this case. Although mechanisms can be given, there is little evidence for their support.

Permanganate was also successful in oxidizing aqueous acid solutions of 1-alkoxycarbonyl-1-alkylhydrazines to 2-tetrazenes, whereas again the aminoamides and ureas underwent decomposition. Rapid gas evolution and small yields of the corresponding N-alkylcarbamate were produced when a dioxane solution of a 1-alkoxycarbonyl-1-alkylhydrazine was warmed with yellow mercuric oxide.

The reaction of 1,4-dialkoxycarbonyl-1,4-dialkyl-2-tetrazenes with a number of nucleophiles (Nu) was studied, and the course of the reaction was found to depend upon the size of the 1,4-dialkyl groups (Scheme II). Whereas I (R = CH_3) gave a high yield of a 1,4-dialkyltetrazolinone,[6] III, when warmed with piperidine, I (R = benzyl) gave less than 1% and I (R = cyclohexyl) gave none. In the latter two, decomposition was primarily *via* route B. The effect of the increased size of the alkyl group may reflect the geometry of the transition state, which, based on least ring strain, would have the N-alkyl groups *cis* and in close proximity. Aqueous sodium hydroxide gave similar results, except that the yield of III was somewhat lower. In neither case was carbon–oxygen bond scission observed. The transition-state energy for carbon–nitrogen bond breakage is lowered by resonance stabilization of the devloping anion, II.

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[1] (a) E. Fischer, *Ann.*, **190**, 167 (1878); (b) H. Wieland, *Ber.*, **41**, 3498 (1908); (c) B. L. Erusalimsky, B. A. Dolgoplosk, and A. P. Kravunenko, *J. Gen. Chem. USSR* (Engl. Transl.), **27**, 267 (1957); (d) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1965, p 345; (e) *ibid.*, p 136.

[2] W. E. Thun and W. R. McBride, Abstracts of the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, M 130.

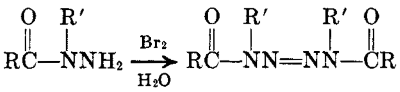
[3] C. Th. Pederson, *Acta Chem. Scand.*, **18**, 2199 (1964).

[4] C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, p 241.

[5] (a) G. Cignarella, *Chim. Ind.* (London), **42**, 145 (1966); (b) H. Yamamoto, *J. Org. Chem.*, **32**, 3693 (1967).

[6] 1,4-Dimethyltetrazolinone has been reported to be one of the products formed in low over-all yield by treating 5-hydroxytetrazole with an excess of diazomethane: K. Hattori, E. Lieber, and J. P. Horwitz, *J. Amer. Chem. Soc.*, **78**, 411 (1956).

TABLE I

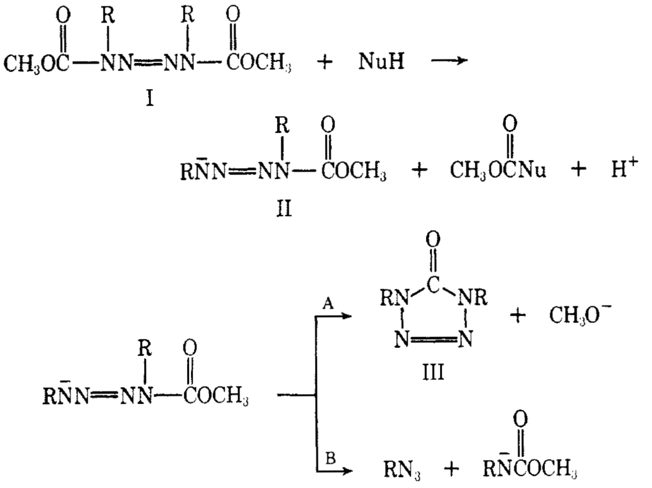


$$R\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{N}}NH_2 \xrightarrow[H_2O]{Br_2} R\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{N}}N{=}N\overset{R'}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}R$$

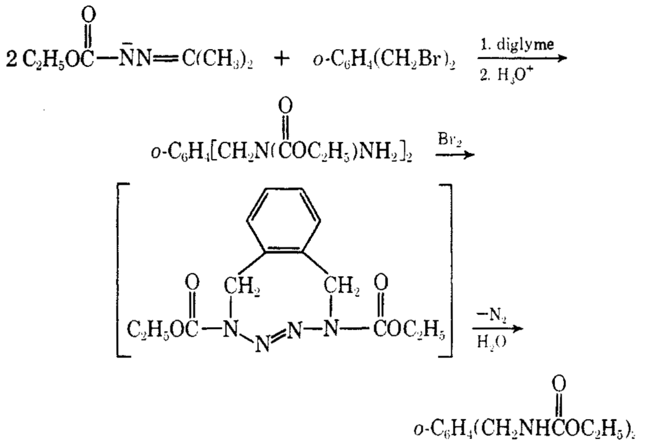
	$R\overset{O}{\overset{\|}{C}}-\overset{R}{\overset{|}{N}}NH_2$			$R\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{N}}N{=}N\overset{R'}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}R$							
						Calcd, %			Found, %		
Registry no.	R	R′	Bp (mm) or mp, °C	Registry no.	Mp, °C	C	H	N	C	H	N
20628-41-5	CH_3O	CH_3	69 (20)	760-81-6	186–187	35.29	5.88	27.45	35.15	5.87	27.42
20628-43-7	C_2H_5O	CH_3	80 (20)	20628-44-8	125–126	41.38	6.89	24.13	41.34	6.92	23.96
. . .	CH_3O	C_6H_5[a]	69–70	20628-45-9	160 dec	58.53	4.87	17.00	58.47	4.97	16.87
. . .	CH_3O	C_6H_{11}	. . .	20628-46-0	101–102	58.69	8.69	15.21	58.71	8.51	15.15
. . .	C_2H_5O	$C_6H_5CH_2$	. . .	20628-47-1	114–115	62.50	6.25	14.58	62.44	6.20	14.69

[a] R. Willstatter, *Ann.*, **477,** 161 (1929).

SCHEME II



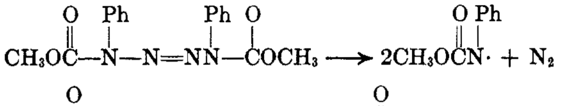
SCHEME III



The cyclization is of further interest, for the starting 2-tetrazene is most probably *trans.*[7] Thus a change in configuration must take place before cyclization. The newly formed negative charge in II is delocalized over three nitrogen atoms, giving some single-bond character to the original double bond and thereby allowing rotation to a *cis* configuration.

An attempt to prepare a cyclic 2-tetrazene (Scheme III) met with failure. The product, a biscarbamate isolated in high yield, would indicate that the intermediate cyclic tetrazene, if formed, is unstable. Such would most likely be the case if the bromine oxidation of N-aminocarbamates gave 2-tetrazenes with *trans* configurations.

The case of I (R = phenyl) was found to be unique in that, upon treatment with piperidine, the only products isolated were methyl N-phenylcarbamate and a polymeric material. Although no detailed study was made, it was apparent that the 2-tetrazene in this case



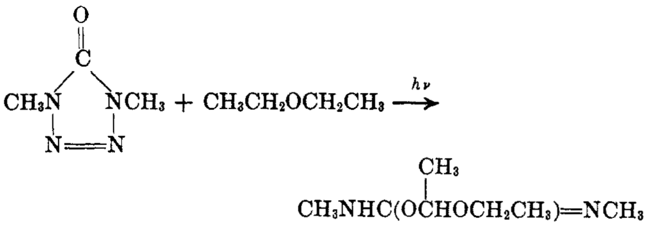
$$CH_3O\overset{O}{\overset{\|}{C}}-\overset{Ph}{\overset{|}{N}}-N{=}N\overset{Ph}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}OCH_3 \longrightarrow 2CH_3O\overset{O}{\overset{\|}{C}}\overset{Ph}{\overset{|}{N}}\cdot + N_2$$

$$CH_3O\overset{O}{\overset{\|}{C}}-\dot{N}Ph + R_2NH \longrightarrow CH_3O\overset{O}{\overset{\|}{C}}NHPh + R_2N\cdot$$

decomposed in solution to give a radical which in turn abstracted hydrogen from the amine. Similar decompositions of 2-tetrazenes are well known.[8]

The structure of 1,4-dimethyltetrazolinone was determined by spectral and analytical means and through its decomposition products. Unlike other tetrazoles, which decompose on heating,[9] 1,4-dimethyltetrazolinone was found to be thermally stable. Heating a sample to over 300° did not induce decomposition. The possibility that the water-soluble tetrazolinone has an ionic structure and is aromatic cannot be excluded.

In contrast to the lack of nitrogen evolution on heating, 1,4-dimethyltetrazolinone [λ 225 mμ (ϵ 6200)] does eliminate nitrogen photochemically, giving products arising from solvent incorporation. Photolysis in diethyl ether gave a single product, an isourea, IV,



IV

which partially decomposed upon distillation. The structure of the product was determined by spectral and chemical analysis. A strong imine band at 1620 cm^{-1} and no carbonyl absorption characterized the ir spectrum. The nmr spectrum showed a single absorption for the methyl hydrogens at δ 2.58. The nmr of N,N′-dimethyl-O-benzylisourea, prepared by adding benzyl chloride to the anion of *sym*-dimethylurea, also

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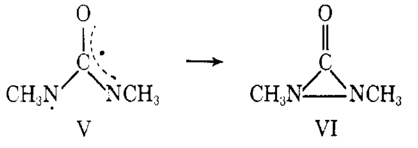
[7] P. S. Forgione, G. S. Sprague, and H. J. Trottkin, *J. Amer. Chem. Soc.* **88**, 1079 (1966).

[8] (a) B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961); (b) F. O. Rice and C. J. Crelecki, *J. Amer. Chem. Soc.*, **79**, 2679 (1957).

[9] (a) J. E. Baldwin and S. Y. Hong, *Tetrahedron*, **24**, 3787 (1968); (b) F. R. Benson, in "Heterocyclic Compounds," Vol. 8, R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, pp 86–95.

gave a single peak with an identical chemical shift for its methyl hydrogens. The ir and nmr spectra of the crude photolysis product before distillation were nearly identical to the spectra of the purified material. There was no trace of a trialkylurea, $CH_3NH(C{=}O)N(CH_3)CH(CH_3)OCH_2CH_3$, which would easily be detected from its spectra. The hydrogens of the N-methyl groups of the latter would not have identical chemical shifts and one would be split into a doublet. Such is the case for N,N′-dimethyl-N-ethylurea and N,N′-dimethyl-N-benzylurea.

Although a diradical,[10] V, may be an intermediate, there was no evidence of its existence. By direct



V VI

coupling, spin inversion, or bond rotation, the diradical might, as in the decomposition of alkylidenepyrazolines[11] and pyrazolinones,[12] be expected to undergo ring closure to yield in this case a diazacyclopropanone, VI, a single example of which has been reported.[13] No such product was isolated, nor did the ultraviolet spectrum of the mixture give rise to new absorption bonds during the photolysis while the disappearance of the single band at 225 mμ was monitored.

The photodecompositions increased in rate when more efficient hydrogen donor solvents than diethyl ether were used. Thus, in tetrahydrofuran, absorption in the ultraviolet region had disappeared after 40 hr. The ir and nmr spectra of the crude product, which decomposed on heating, verified that it was primarily an isourea. Besides the imine stretching absorption at 1610 cm^{-1} and lack of carbonyl absorption observed in the ir, the nmr spectrum gave a single peak for the methyl hydrogens at δ 2.75. Photodecomposition was complete after only 2 hr when carried out in ethanol or water. In both cases, a mixture of heat-sensitive products were obtained which were not characterized further. When carried out in 2-propanol, nearly quantitative yields of *sym*-dimethylurea and pinacol were obtained.

Experimental Section

Proton nuclear magnetic resonance spectra were determined on a Varian A-60A spectrometer; chemical shifts are reported in δ units (parts per million from tetramethylsilane internal standard). Infrared measurements were made using a Beckman IR-5 instrument. Ultraviolet spectral measurements were made on a Beckman DK-2A recording spectrophotometer. A Hanovia 679A-36 high-pressure mercury lamp with a water-cooled quartz immersion well was used in all photolyses. Photolyses were carried out under an atmosphere of nitrogen at about 15°, in magnetically stirred solutions. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting and boiling points are uncorrected.

1-Methoxycarbonyl-1-methylhydrazine.—Methyl chloroformate (189.0 g, 2.0 mol) was added dropwise with cooling and stirring to a mixture of methylhydrazine (96.0 g, 2.0 mol) and sodium hydroxide (80.0 g, 2.0 mol) dissolved in 500 ml of methanol. After stirring at room temperature for 1 hr, the mixture was filtered, the solvent was removed by distillation, and the residue was distilled to give 90.1 g (43% yield) of liquid, bp 69° (15 mm).

Anal. Calcd for $C_2H_6N_2O_2$: C, 34.61; H, 7.69; N, 26.92. Found: C, 34.57; H, 7.71; N, 26.87.

In a similar manner, using ethyl chloroformate, 1-ethoxycarbonyl-1-methylhydrazine was prepared in 62% yield, bp 82° (15 mm).

Anal. Calcd for $C_4H_{10}N_2O_2$: C, 40.67; H, 8.47; N, 23.72. Found: C, 40.75; H, 8.51; N, 23.64.

1,4-Dimethoxycarbonyl-1,4-dimethyl-2-tetrazene.—To a sample of 1-methoxycarbonyl-1-methylhydrazine (90.1 g, 0.86 mol) was added 500 g of ice, 1 equiv of dilute HCl, and liquid bromine (dropwise with stirring until color persisted). The slurry was stirred at room temperature for 1 hr and filtered. The precipitate was recrystallized twice from ethanol to give 46.9 g of white crystalline product (53.3% yield); nmr (CS_2) δ 3.38 (s) and 1.41 (s), equal intensities.

1,4-Diethoxycarbonyl-1,4-dimethyl-2-tetrazene was prepared exactly as the 1,4-dimethoxycarbonyl analog had been (62.3% yield); nmr (CS_2) 4.32 (q, 4 H), 3.38 (s, 6 H), and 1.39 (t, 6 H).

1,4-Diethoxycarbonyl-1,4-dibenzyl-2-tetrazene.—To a slurry of 50% sodium hydride[14] (9.6 g, 0.2 mol) in 200 ml of freshly distilled diglyme was added dropwise with cooling and stirring a solution of ethyl isopropylidene carbazate (28.8 g, 0.2 mol, mp 65–67° from hexane) dissolved in 50 ml of dry diglyme. After gas evolution had ceased, benzyl chloride (25.4 g, 0.2 mol) was added and the solution was heated at 120° for 3 hr. The solution was cooled, suction filtered, and stripped under reduced pressure. The residue, when distilled, gave 32.4 g (69.1% yield) of 1-ethoxycarbonyl-1-benzyl-2-isopropylidenehydrazine, bp 108–109° (0.4 mm); nmr δ 0.78 (t, 3 H), 1.42 (d, 6 H), 3.78 (q, 2 H), 4.39 (s, 2 H), and 6.95 (s, 5 H). The distillate was dissolved in dilute HCl, the solution was cooled in an ice bath, and liquid bromine was added until color persisted. The precipitate was collected and recrystallized twice from ethanol, yield 15.30 g (57.7%); nmr ($CDCl_3$) 1.40 (t, 6 H), 4.49 (q, 4 H), 5.20 (s, 4 H), and 7.35–7.67 (m, 10 H).

1,4-Dimethoxycarbonyl-1,4-dicyclohexyl-2-tetrazene.—Ethyl N-cyclohexylcarbamate (8.6 g, 0.05 mol) and 3.0 g of $NaNO_2$ were added to 50 ml of H_2O. Concentrated HCl was added dropwise until reaction ceased. The upper oily layer was separated and diluted with 20 ml of acetic acid. The acetic acid solution was added dropwise with rapid stirring to a slurry of 10 g of zinc dust in 100 ml of H_2O held at 0–2°. After the addition, the mixture was allowed to come to 10° and filtered. Liquid bromine was added dropwise to the filtrate until color persisted. After standing overnight, the precipitate was collected and recrystallized from acetonitrile to give 3.8 g of white crystals (41.3% yield).

1,4-Dimethoxycarbonyl-1,4-diphenyl-2-tetrazene.—1-methoxycarbonyl-1-phenylhydrazine (10 g, 0.06 mol) was added to 50 ml of dilute HCl. The solution was cooled to 0°, and liquid bromine was added until color persisted. The percipitate was collected and recrystallized twice from ethanol; yield 4.4 g (44.7%); nmr ($CDCl_3$) 3.75 (s, 6 H) and 7.22–7.71 (m, 10 H).

When a sample (3.3 g, 0.01 mol) of the 2-tetrazene was warmed with 1 equiv of piperidine at 120° for 2 days and distilled, a liquid, bp 150° (20 mm), was obtained which solidified on standing; mp 50°, yield 2.2 g (72%). The ir and nmr of the solid were identical to those of an authentic sample of methyl N-phenylcarbamate obtained by adding methanol to phenylisocyanate. A dark tarry residue remained from the distillation.

1,4-Dimethyltetrazolinone.—1,4-Dimethoxycarbonyl-1,4-dimethyl-2-tetrazene (20.4 g, 0.1 mol) was added to 20 g of piperidine and the solution was gently refluxed overnight. The mixture was stripped of excess piperidine, chilled, and suction filtered. The precipitate was recrystallized twice from ethanol to give 6.75 g (65.8%) of white, water-soluble crystals, mp 116–117°; ir (Nujol) broad band at 1695 cm^{-1}; nmr (CCl_4) 3.50 (s).

Anal. Calcd for $C_3H_6N_4O$: C, 31.58; H, 5.26; N, 49.12. Found: C, 31.65; H, 5.18; N, 48.96.

The filtrate, when distilled, gave 10.3 g (71.5%) of methyl-N-cyclohexylidene carbamate, bp 87–88° (20 mm), identified by comparison with an authentic sample. In a similar manner

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[10] Molecular orbital calculations indicate the diradical to have three bonding orbitals. The electron density on oxygen, although less in the excited state than in the ground state, is greater than the electron densities at the two nitrogens. The excited electron is, however, located only on nitrogen and may in part be responsible for the initial abstraction of hydrogen to give IV.

[11] S. D. Andrews and A. C. Day, *J. Chem. Soc., B*, 1271 (1968).

[12] N. J. Turro and W. B. Hammond, *Tetrahedron*, **24**, 6017 (1968).

[13] F. D. Greene and J. C. Stowell, *J. Amer. Chem. Soc.*, **86**, 3569 (1964).

[14] Sodium hydride, 50% in mineral oil, was supplied by Metal Hydrides, Inc.

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$_4$O: 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, α,α'-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$_2$O$_4$: 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-mμ 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$_7$H$_{16}$N$_2$O$_2$: 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$_2$O: 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-mμ 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.

Permanganate Oxidation of Tetrasubstituted 2-Tetrazenes[1]

WAYNE E. THUN AND WILLIAM R. MCBRIDE

Chemistry Division, Research Department, Naval Weapons Center, China Lake, California 93555

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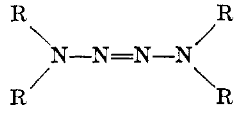
Tetraalkyl-2-tetrazenes, derivatives of the unsaturated hydronitrogen N$_4$H$_4$, are oxidized by potassium permanganate in acetone solution to 2-tetrazenes containing a carbonyl group α to a terminal nitrogen of the 2-tetrazene. Further oxidation results in the formation of symmetrically substituted 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 α 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.