Ethyl *N*-(3-Cyclohexenyl)carbamate (22). The carbamate **22** was prepared according to the procedure described by Lwowski and Mattingly:[7] bp 81 °C (0.45 mm); IR (CCl_4) 3460, 3352, 1726, 1653 cm^{-1}, reported IR 3454, 3348, 1720, 1653 cm^{-1}.

***trans*-Ethyl *N*-(2-Chlorocyclohexyl)carbamate (23).** The carbamate **23** was prepared according to the procedure described by Swern and Foglia:[11] mp 94–95 °C (lit. mp 96–97 °C).

3,3′-Bicyclohexenyl (24). This was prepared according to the procedure described by Lwowski and Mattingly:[7] bp 90 °C (4.3 mm) (lit. bp 85–89 °C (3.7–4.0 mm)).

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Supplementary Material Available: ^{13}C NMR spectrum of compound 4 (1 page). Ordering information is given on any current masthead page.

Registry No.—**4**, 69705-71-1; **5**, 1611-51-4; **6**, 64227-21-0; **7**, 53256-17-0; **12**, 594-85-4; **13**, 51-79-6; **15**, 56488-02-9; **16**, 56488-01-8; **17**, 2955-74-0; **18**, 817-87-8; **19**, 56488-05-2; **20**, 56488-04-1; **21**, 69653-42-5; **22**, 1541-28-2; **23**, 18296-24-7; **24**, 1541-20-4; **25**, 822-86-6; 2,3-dimethyl-2-butene, 563-79-1; cyclohexene, 110-83-8.

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Regiospecific Formation of Azoxyaralkanes (Diazene *N*-Oxides) from *N,N*-Dibromo Compounds and Nitrosobenzene[1]

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An improved directed synthesis of azoxyaralkanes from *N,N*-dibromo compounds and nitrosobenzene is described. Unlike the prior related method, yields of azoxy compounds are not sensitive to the nature of the *N,N*-dihalo compound; i.e., high yields were obtained from all types (primary, secondary, and tertiary) of alkyl groups in $RNBr_2$. Several aspects of the mechanistic features are discussed.

Previously, we reported that a wide variety of azoxy compounds can be regiospecifically synthesized through the reaction of *N,N*-dichloroamines with nitroso compounds.[3,4] Although the method enjoys wide scope, yields of azoxy compounds are usually not outstanding for reactions involving primary or secondary alkyl-*N,N*-dichloroamines.

The aim of this study was to make the method more attractive by substantially increasing the yields for various types of *N,N*-dihalo substrates and to furnish additional mechanistic insight.

Results and Discussion

Synthesis. In this synthesis of azoxy compounds, the promoting effect of certain transition metal salts does not appear to involve the metal atom.[5] For example, in the case of cobaltous bromide or cupric bromide, we have shown that bromide ions are rapidly oxidized by the *N,N*-dichloroamines through a halogen exchange reaction in which the more reactive *N,N*-dibromoamines are generated (eq 1). The overall transformation resembles the conversion of hypochlorite to hypobromite by means of bromide ion.[6]

$$RNCl_2 + MBr_2 \xrightarrow{\text{fast}} RNBr_2 + MCl_2 \qquad (1)$$

In the present study, pure *N,N*-dibromo compounds, such as *N,N*-dibromo-α-aminoisobutyronitrile or *N,N*-dibromo-*tert*-butylamine, were found to react with nitrosobenzene in acetonitrile or methylene chloride to afford the corresponding *N*-alkyl-*N*′-phenyldiazene *N*′-oxides in excellent yields. At room temperature the reaction is complete within a few minutes (eq 2). Under similar conditions, the corresponding

$$RNBr_2 + C_6H_5NO \rightarrow RN{=}N(O)C_6H_5 + Br_2 \qquad (2)$$

N,N-dichloroamines do not react.[3] The progress of the transformation can be followed by observing the dramatic color change which occurs as the initial dark green mixture turns red upon liberation of free bromine. Fortunately, similar high yields of azoxy compounds can be more conveniently obtained by treatment of the readily available *N,N*-dichloroamines with 1 molar equiv each of bromide salt and nitrosobenzene in acetonitrile solution under mild conditions. High yields (70–92%) of azoxy compounds were obtained.

The results are summarized in Table I. Although the reaction does not require exclusive use of arylnitroso substrates, this study mostly involved nitrosobenzene since it gave higher yields, can be easily purified, and is more stable in solution than most alkylnitroso compounds.[7] Product yield with $(CH_3)_3CNO$ was somewhat lower. With the bromide-promoted synthesis, there appear to be no great differences in yields of azoxy compounds with tertiary, secondary, or primary alkyl-*N,N*-dichloroamines. In addition, high yields were obtained from *N,N*-dichloroneopentylamine and *N,N*-dichloro-*tert*-octylamine, even though the corresponding *N,N*-dibromoamines are too unstable for isolation via the halogen exchange reaction.[5] Although our main attention was focused on *N,N*-dihaloamines, good results were also realized with analogous derivatives of urethane and arylsulfonamide. The products from $RNCl_2$ exhibited various degrees of instability on standing, as evidenced by a darkening in color. As a result, some difficulties were experienced in obtaining high purity samples for microanalyses, e.g., the product from **4**. All azoxy materials gave satisfactory IR and NMR spectra. Those containing primary or secondary alkyl groups showed no molecular ion in the mass spectrum.

The low yield from primary and secondary alkyl groups

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Table I. Preparation of *N*-Alkyl-*N'*-phenyldiazene *N'*-Oxides

$RNCl_2$	no.	azoxy yield, %, using promoter $CuBr_2$[a]	$CuCl$[b]	KOH[c]
$(CH_3)_2C(CN)NCl_2$	1	92		72
t-$BuNCl_2$	2	80	44	
$(n$-$Bu)_2C(CH_3)NCl_2$	3	70		
$(CH_3)_3CCH_2C(CH_3)_2NCl_2$	4	70		
$(CH_3)_2CHNCl_2$	5	90		4
c-$C_6H_{11}NCl_2$	6	75	58	7
n-$BuNCl_2$	7	79	83	36
$(CH_3)_3CCH_2NCl_2$	8	87		
$(CH_3)_2CHCH_2NCl_2$	9	90		
EtO_2CNCl_2	10	80	65	
p-$CH_3C_6H_4SO_2NCl_2$	11	87[d]		

[a] Similar yields were obtained with $CoBr_2$; several hours were required for completion of the reaction with NaBr due to low solubility. Only results with $CuBr_2$ are presented; desirable solubility drastically reduced reaction time.[5] [b] Reference 3. [c] Reference 4. [d] Melting point and spectral (IR, NMR) properties were essentially identical with data reported for authentic material: W. V. Farrar and J. Masson Gulland, *J. Chem. Soc.*, 368 (1944).

($RNCl_2$) in the prior investigations was attributed to the tendency of these materials to undergo competing dehydrohalogenation in the presence of alkali or certain inorganic salts.[4,8] Also, the previous method in many cases possessed the undesirable features of heterogeneity and workup procedures which were not as simple as the present one.

Stoichiometry. At 0 °C, the reaction proceeds quite slowly. Liberation of free bromine is quantitative. A 50% decrease (essentially 100% of theory for eq 2) in positive bromine content is observed upon completion of reaction with a 1:1 molar ratio of *N,N*-dibromo compound and nitroso substrate. Superior yields of azoxy compounds are obtained only with at least a 1:1 molar ratio of $CuBr_2/RNCl_2$. When *N,N*-dichloro-α-aminoisobutyronitrile is exposed to only 0.5 mol of cupric bromide in the presence of 1 mol of nitrosobenzene, the yield is halved (eq 3). Scheme I sets forth various routes which

$$RNCl_2 + Br^- + C_6H_5NO \rightarrow 0.5RN{=}N(O)C_6H_5 + 0.5RNCl_2 + 0.5C_6H_5NO + 0.5Br_2 + Cl^- \quad (3)$$

may account for this result. The suggestion that an intermediate *N*-chloro-*N*-bromoamine may be involved is justified since we recently reported isolation of mixtures of *N,N*-dibromo- and *N*-chloro-*N*-bromoamines under conditions in which a large excess of *N,N*-dichloroamine is used in the halogen exchange reaction.[5] Also, since under the conditions used very little halogen exchange occurs between bromine and *N,N*-dichloroamine (eq 4), reaction cannot be effected by only

$$RNCl_2 + Br_2 \overset{\text{slow}}{\rightleftharpoons} RNBr_2 + Cl_2 \quad (4)$$

a small amount of bromide with perpetuation by the bromine byproduct (Scheme I). Thus, when an equimolar mixture of bromine and *N,N*-dichloro-α-aminoisobutyronitrile was allowed to stand for 3 h at 0 °C, only starting materials were detected.

Scheme I

$$RNCl_2 + Br^- \xrightarrow{k_1} 0.5RNClBr + 0.5Cl^- + 0.5Br^- + 0.5RNCl_2$$

$$0.5RNClBr + 0.5Br^- \xrightarrow{k_2} 0.5RNBr_2 + 0.5Cl^-$$

$$(\text{or } 2RNClBr \rightarrow RNCl_2 + RNBr_2)$$

$$0.5RNBr_2 + 0.5C_6H_5NO \xrightarrow{k_3} 0.5RN{=}N(O)C_6H_5 + 0.5Br_2$$

$$k_2 >> k_1$$

Scheme II

$$RNBr_2 \overset{\text{slow}}{\rightleftharpoons} R\dot{N}Br + Br\cdot$$

$$R\dot{N}Br + C_6H_5NO \overset{\text{fast}}{\rightleftharpoons} RN(Br)N(\dot{O})C_6H_5 \xrightarrow{-Br\cdot} RN{=}N(O)C_6H_5$$

$$2Br\cdot \rightarrow Br_2$$

Scheme III

$$2RNBr_2 \overset{\text{slow}}{\rightleftharpoons} 2R\dot{N}Br + 2Br\cdot$$

$$2R\dot{N}Br \xrightarrow{\text{fast}} RN(Br)N(Br)R \xrightarrow[-Br_2]{} RN{=}NR$$

$$2Br\cdot \rightarrow Br_2$$

Halogen Exchange. *N,N*-Dihalo compounds can react via ionic, free-radical, or nitrene intermediates.[8] Difficulties associated with these versatile, unstable entities have, for the most part, discouraged quantitative studies. Hence, even a minor contribution in this area is significant.

Since azoxy product can be synthesized under conditions in which halogen exchange occurs, it would be of interest to determine whether this process might be associated with azoxy formation. An S_N2 displacement of chloride by bromide appears unlikely. If such a pathway were operative, one would predict sluggish behavior for **2, 3,** and **4** since they are nitrogen analogues of neopentyl halides which are relatively unreactive toward nucleophilic substitution. Furthermore, in related studies[9] of halogen exchange in the $HOCl$–Br^- system, the possibility of chloride loss in a single step from $(HOClBr)^-$ was excluded. Involvement of a redox process (oxidation of bromide and reduction of positive chlorine) suggests that electron transfer may occur (eq 5). Alternatively, it is reasonable[9] to expect attack of bromide on positive chlorine (eq 6). The necessity of a 1:1 molar ratio of $CuBr_2/RNCl_2$ indicates that conversion to $RNBr_2$ quite likely occurs initially, rather than capture by C_6H_5NO of an intermediate[10] (e.g., $R\dot{N}Cl$) in the exchange. Also, any radicals of type $R\dot{N}Cl$ are not undergoing dimerization with eventual formation of azo compound. Further speculation is not warranted due to complexity of the mechanistic picture and the limited amount of experimental data available.

$$RNCl_2 + Br^- \rightarrow R\dot{N}Cl + Br\cdot + Cl^- \quad (5)$$

$$RNCl_2 + Br^- \rightarrow R^-NCl + BrCl \quad (6)$$

Azoxy Formation. At least three reaction mechanisms can be visualized for formation of azoxy products from *N,N*-dibromo and nitroso substrates, one of which entails a nitrene intermediate. Under certain conditions nitrenes have been reported as intermediates from *N,N*-dichloroamines.[11] *N,N*-Dihalosulfonamides[12] and *N,N*-diiodoamides[13] have also been shown to be efficient sources. However, when *N,N*-dibromo-α-aminoisobutyronitrile was allowed to decompose in dioxane, no evidence for the characteristic C–H insertion product was found.[12,14]

A second possibility involves a radical pathway (Scheme II). Since *N,N*-dibromo compounds are thermally unstable and photosensitive (often decomposing with violence after a brief induction period), a free-radical mechanism seems plausible. The reversibility of the initiation step is suggested by the very slow decomposition of *N,N*-dibromo-α-aminoisobutyronitrile in chloroform or carbon tetrachloride at room temperature. Without the presence of a nitroso scavenger, the positive halogen content of the solution does not change significantly until several hours after mixing. AIBN (10–20%) was isolated from the reaction mixture after 24–48 h (Scheme III).[5] A similar result was obtained upon pyrolysis of the solid *N,N*-dibromoamine.

A third approach (eq 7) consists of a bimolecular reaction between the *N,N*-dibromoamine and nitroso compound.

$$RNBr_2 + C_6H_5NO \underset{}{\overset{\text{slow}}{\rightleftharpoons}} \begin{matrix} Br & \bar{O} \\ | & | \\ RN^{+}-NC_6H_5 \\ | \\ Br \end{matrix} \xrightarrow[-Br_2]{\text{fast}} RN{=}N(O)C_6H_5 \quad (7)$$

Reaction Order. Highly purified *N,N*-dibromo-α-aminoisobutyronitrile reacts very slowly with nitrosobenzene in acetonitrile or methylene chloride at 0 °C. Under certain conditions, the time for completion (4–5 half-lives) can be determined by measuring the time needed for positive halogen content to decrease to the theoretical value of 50%. Unfortunately, points between the start and finish of the reaction cannot be ascertained iodometrically since the unreacted nitrosobenzene interferes with the analysis, perhaps as set forth in eq 8.[15] The total time required for reaction of $RNBr_2$ and

$$C_6H_5NO \overset{e}{\rightleftharpoons} C_6H_5NO^{-}\cdot \quad (8)$$

C_6H_5NO (1:1 molar ratio) was determined at two different initial concentrations. A mixture initially 0.137 M in both substrates reacted at 0 °C within the same interval as another mixture initially 0.068 M in both materials. For both solutions, the average total reaction period was determined to be 5.56 ± 0.23 h. Although this analytical method becomes impractical beyond the fourth half-life (>94% completion), accuracy is within the requirements for distinguishing between a first- and second-order reaction. Since the half-life, and hence the total time for a first-order process, is independent of the initial reagent concentration, azoxy formation appears to be first order in one component and zero order in the other. This rules out a bimolecular mechanism. On the reasonable assumption that the reaction is zero order in nitrosobenzene, these results are consistent with a free-radical or nitrene route. The negative results from the dioxane scavenging experiment gives added credence to a free-radical pathway which is also supported by prior studies demonstrating efficacy of silver metal, redox metal salts, and MgI_2/Mg as promoters.[3,4] However, a definite conclusion concerning mechanism is not yet possible.

Experimental Section

Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. NMR spectra were taken on a Varian T-60A with tetramethylsilane as an internal standard. Positive halogen content was determined by iodometric titration.[16] Melting and boiling points are uncorrected. Elemental analyses were performed in part by Galbraith Laboratories, Knoxville, Tenn.

***N,N*-Dichloroamines and -amides.** All *N,N*-dichloro compounds were prepared by a literature procedure.[17] After removal of solvent, the crude products were used without further purification.

General Procedure for Diazene *N*-Oxides. A solution of cupric bromide (2.23 g, 0.01 mol) in 50 mL of acetonitrile was cooled with stirring to 0 °C. Nitrosobenzene (1.07 g, 0.01 mol, Aldrich) was added in one portion, followed by dropwise addition of the *N,N*-dichloro substrate (0.01 mol) over 15 min. After the stirring was continued for 30 min at 0 °C, the mixture was allowed to warm to room temperature (red color intensified). Copper salts were removed by diluting the dark acetonitrile solution with 350 mL of ice water. The dark oil which separated was extracted into chloroform and washed with water. Drying over anhydrous sodium sulfate followed by rotoevaporation of solvent afforded the azoxy compound as a dark oil. Column chromatography on silica gel with hexane/methylene chloride (10:1) yielded orange oils which were distilled under vacuum (short-path). **Warning! These compounds may be toxic (mutagenic).**

Diazene *N*-Oxides from *N,N*-Dibromoamines. A solution of the *N,N*-dibromoamine (0.005 mol) in 50 mL of methylene chloride or acetonitrile was cooled to 0 °C. A solution of nitrosobenzene (0.51 g, 0.005 mol) in 10 mL of solvent was added in one portion with vigorous stirring. The initial dark green reaction mixture developed a bright red color a few minutes after removal of the ice bath. Evaporation of solvent (and Br_2) afforded near quantitative yields of the azoxy compound as a red-orange oil.

***N*-(Isobutyronitrilo)-*N'*-*tert*-butyldiazene *N'*-Oxide.** A solution of the *N,N*-dibromoamine (0.51 g, 0.002 mol) in 25 mL of acetonitrile was chilled to 0 °C. 2-Methyl-2-nitrosopropane (0.18 g, 0.002 mol) was added in one portion with rapid stirring. The deep blue solution was allowed to warm to room temperature. After a few minutes, a red-brown color developed. TLC analysis (Al_2O_3/hexane) revealed a complex mixture. Rotoevaporation afforded a dark oil which was eluted with hexane through a 1 × 15 cm, silica gel column. The azoxy compound (0.2 g, 54%) was isolated as a light brown oil whose IR and NMR spectra were identical with those of an authentic sample.

Characterization of Diazene *N*-Oxides. Compounds from **1, 2, 5, 6, 7, 10,** and **11** (Table I) were identified by comparison with previously prepared samples.

***N*-(1-Methyl-1-butylpentyl)-*N'*-phenyldiazene *N'*-Oxide:** bp 112–113 °C (4 mm); NMR ($CDCl_3$) δ 8.10 (m, Ph, 2 H), 7.38 (m, Ph, 3 H), 2.30–0.80 (m, $C_{10}H_{21}$, 21 H); IR (neat) 1475 (N=N), 1280 (N–O), 765 and 650 (aromatic) cm^{-1}; mass spectrum, *m/e* 262 ($M^{+}\cdot$).

Anal. Calcd for $C_{16}H_{26}N_2O$: C, 73.28; H, 9.92; N, 10.69. Found: C, 73.03; H, 10.31; N, 10.55.

***N*-Neopentyl-*N'*-phenyldiazene *N'*-Oxide:** bp 81–83 °C (5 mm); NMR ($CDCl_3$) δ 8.20 (m, Ph, 2 H), 7.40 (m, Ph, 3 H), 3.42 (s, CH_2, 2 H), 1.05 (s, *t*-Bu, 9 H); IR (neat) 1475 (N=N), 1300 (N–O), 765 and 660 (aromatic) cm^{-1}.

Anal. Calcd for $C_{11}H_{16}N_2O$: C, 68.75; H, 8.33; N, 14.58. Found: C, 68.29; H, 7.92; N, 14.02.

***N*-Isobutyl-*N'*-phenyldiazene *N'*-Oxide:** bp 74–75 °C (5 mm); NMR ($CDCl_3$) δ 8.10 (m, Ph, 2 H), 7.35 (m, Ph, 3 H), 3.35 (d, CH_2, 2 H), 2.00 (m, CH, 1 H), 0.95 (d, $2CH_3$, 6 H); IR (neat) 1465 (N=N), 1280 (N–O), 770 and 665 (aromatic) cm^{-1}.

Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.42; H, 7.87; N, 15.73. Found: C, 67.44; H, 7.70; N, 15.42.

***N*-*tert*-Octyl-*N'*-phenyldiazene *N'*-Oxide:** bp 95–97 °C (4 mm); NMR ($CDCl_3$) δ 8.10 (m, Ph, 2 H), 7.35 (m, Ph, 3 H), 2.00 (s, CH_2, 2 H), 1.58 (s, $(CH_3)_2C$, 6 H), 0.95 (s, *t*-Bu, 9 H); IR (neat) 1465 (N=N), 1280 (N–O), 770 and 650 (aromatic) cm^{-1}; mass spectrum, *m/e* 234 ($M^{+}\cdot$).

Stoichiometry. A solution of cupric bromide (0.402 g, 0.0018 mol) in 25 mL of acetonitrile was cooled with stirring to 0 °C. After nitrosobenzene (0.390 g, 0.0036 mol) was added in one portion, *N,N*-dichloro-α-aminoisobutyronitrile (0.550 g, 0.0036 mol, 98% Cl^{+}) in 5 mL of acetonitrile was added over 15 min. The mixture was stirred for 0.5 h at 0 °C and then allowed to warm to room temperature. After the general workup procedure, the azoxy compound (0.465 g, 46%) was isolated as a light brown oil. Nitrosobenzene (0.091 g, 47%) was also recovered. Attempts to isolate unreacted *N,N*-dichloroamine quantitatively were not fruitful, although the compound could be detected by TLC (Al_2O_3/hexane) before workup.

Bromine and *N,N*-Dichloro-α-aminoisobutyronitrile. The *N,N*-dichloro compound (1.05 g, 0.0043 mol) was dissolved in 50 mL of acetonitrile at 0 °C. Bromine was added dropwise (0.695 g, 0.0043 mol) over 10 min. The red solution was allowed to stand for 3 h at 0 °C, after which a 10-mL aliquot was diluted with 50 mL of ice water. No crystals of *N,N*-dibromo-α-aminoisobutyronitrile precipitated; only a crude red oil separated. TLC (Al_2O_3/hexane) revealed only starting material. The remainder of the reaction mixture was rotoevaporated to remove most of the solvent and bromine. The crude yellow oil (0.73 g) was shown to consist mostly of starting material by TLC.

Attempted Nitrene Trapping with Dioxane. Freshly prepared *N,N*-dibromo-α-aminoisobutyronitrile (0.714 g, 0.003 mol) was added to 25 mL of freshly distilled, dry *p*-dioxane. A light orange solution developed. Progress of the reaction was followed by TLC (Al_2O_3/hexane). After 4 h at room temperature, little decomposition of starting material was noted. The orange solution was rotoevaporated to yield 0.4 g of a water-soluble, white solid after standing for 48 h. An NMR (D_2O) spectrum of the crude substance revealed no incorporation of the dioxane ring. The spectrum was similar to that of the hydrochloride salt of α-aminoisobutyronitrile: (D_2O, 60 MHz) δ 2.40 (s, 6 H, $(CH_3)_2C$).

Pyrolysis of *N,N*-Dibromo-α-aminoisobutyronitrile. Freshly prepared *N,N*-dibromoisobutyronitrile (0.605 g, 0.0025 mol) was placed in a 10 × 1 cm test tube. Vigorous heating with a microburner produced a dark melt from which a red-brown gas evolved. The white solid which deposited on the upper wall was crystallized from cold methanol (0.103 g, 25%). The material was identical with AIBN on the

basis of physical and spectroscopic properties. The residual tar from the reaction was not investigated.

Kinetic Study. A purified sample of *N,N*-dibromo-α-aminoisobutyronitrile (0.831 g, 0.0034 mol) was dissolved in 15 mL of methylene chloride. An aliquot (0.20 mL) was analyzed iodometrically for positive bromine with 0.008 N $Na_2S_2O_3$ solution. The solution was transferred to a 50-mL round-bottom flask (magnetic stirrer, ice bath, and drying tube). In a separate vial, recrystallized nitrosobenzene (0.367 g, 0.0034 mol) was dissolved in 10 mL of methylene chloride and chilled to 0 °C. After equilibration, the time was recorded and the solution of nitrosobenzene was added in one portion to the vigorously stirred solution of *N,N*-dibromoamine. Progress of the reaction at 0 °C was followed by observing the progressive color change: dark green, light brown, orange, and finally red. Upon development of a pronounced red color, 0.20-mL aliquots of reaction mixture were quickly withdrawn and titrated iodometrically. The process was repeated every 15–20 min until the assay for positive bromine was within 50 ± 3% of the initial value (adjusted for dilution with 10 mL of nitrosobenzene solution). By this method, reaction time was estimated to be 5.50 h. Further titration (12 h) of aliquots revealed no additional decrease in positive bromine.

According to the same procedure, the *N,N*-dibromoamine (0.410 g, 0.00169 mol) was reacted with nitrosobenzene (0.181 g) in 25 mL of methylene chloride. Estimated total reaction time was 5.25 h. Duplicate runs with reaction mixtures initially 0.00380 (25 mL) and 0.00182 mol (25 mL) in both starting materials required 6.00 and 5.50 h, respectively, for completion.

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References and Notes

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Chemical Evolution. 33. Photochemical Decarboxylation of Orotic Acid, Orotidine, and Orotidine 5'-Phosphate

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Orotic acid, orotidine, and orotidine 5'-phosphate are photochemically converted to uracil, uridine, and uridine 5'-phosphate in chemical yields of 13, 45, and 23%, respectively. The chemical yields for uracil and uridine formation are 1.6×10^{-5} and 1.7×10^{-2}, respectively. The chemical yield of uracil increases 2.5-fold when the orotic acid concentration is decreased 10-fold, indicating that bimolecular reactions limit the uracil yield. The reaction proceeds from the singlet excited state as shown by the absence of quenching by paramagnetic ions and the absence of sensitization by benzophenone and acetone. The Fe(III)- and Cu(II)-promoted photochemical formation of uracil from orotic acid proceeds in up to 17% yield. Small amounts of barbituric acid are also observed. A plausible pathway for the prebiological formation of uracil and its derivatives from HCN via orotic acid and its derivatives is discussed.

Hydrogen cyanide is considered to have been a likely starting material for the synthesis of biomolecules on the primitive Earth.[1] It is formed in a variety of primitive Earth simulation experiments, and it is present in interstellar space.[1,2] Dilute aqueous solutions of HCN condense to give oligomers which in turn undergo hydrolytic decomposition to purines, pyrimidines, and amino acids. In addition, two of the compounds formed by the hydrolysis of HCN oligomers, 4-aminoimidazole-5-carboxamide and orotic acid (**1a**), are intermediates in the contemporary biosynthesis of purine and pyrimidine nucleotides, respectively. Primitive life forms may have had enzymes for the utilization of these compounds for nucleic acid synthesis once the supply of preformed purines and pyrimidines was exhausted.[3] Probably the first enzymes were not very efficient and only enhanced the rates of chemical processes modestly over that of the rate in the absence of an enzyme. It is likely that the same chemical processes also occurred under primitive Earth conditions in the absence of enzymes. The chemical conversion of 4-aminoimidazole-5-carboxamide to purines under primitive Earth conditions has

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