overnight in an ice bath, the solution was worked up by neutralization with aqueous hydrochloric acid and extraction with ether. Concentration of the dried extracts gave 535 mg (41%) of white crystals, mp 125–130°. Recrystallizations from ether produced material of mp 133.5–136° and having a characteristic tosylate absorption in its infrared spectrum at 1173 cm^{-1}, but no absorption in the hydroxyl or carbonyl regions; $\lambda_{\max}^{\mathrm{EtOH}}$ 226 mμ (ϵ 19,500), 282 (2800).

Anal. Calcd for $C_{24}H_{28}O_6S$: C, 64.84; H, 6.35. Found: C, 64.81; H, 6.53.

Oxidation of Compound I to the Neopentyl Aldehyde III.—Compound I (16.2 g, 56 mmoles) was dissolved in 250 ml of pyridine containing 1% water and to this was added 750 ml of a saturated solution of chromium trioxide in pyridine containing 1% water. The flask, flushed with nitrogen and stoppered, was allowed to stand at room temperature with gentle stirring. After 24 hr another 500 ml of the above solution of chromium trioxide in pyridine was added. The mixture was worked up after a total of 48 hr by addition of ether, filtration, concentration, and chromatography on a column of Florisil. Concentration of fractions eluted with 25–50% ether in hexane and recrystallization of the resulting solid from hexane yielded 9.94 g (62%) of aldehyde: mp 66–71°, further recrystallization raised the melting point to 69.5–72°; $\nu_{\max}^{\mathrm{CCl_4}}$ 2710, 1720 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 283 mμ (ϵ 2700); nmr (CH_2Cl_2), 1 H singlet at τ 0.1, 3 H complex at 2.8–3.4, 4 H singlet at 6.2, 3 H singlet at 6.3, 1 H triplet at 6.5 (J = 4 cps), pair of 1 H doublets at 7.1 and 7.3 (J = 15 cps), 6 H complex at 7.8–8.7.

Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.76; H, 7.01.

Reaction of Aldehyde III with Lithium Acetylide.—In a flask fitted with a Dry Ice condenser a solution was prepared of 1.260 g (180 mg-atoms) of lithium in 250 ml of dry ammonia; dry acetylene was then passed into the solution until discharge of the blue color. To the stirred suspension of lithium acetylide was then added 5.00 g (17.5 mmoles) of aldehyde III in 60 ml of dry tetrahydrofuran. The mixture was stirred for 1 hr and the ammonia was allowed to evaporate overnight. Work-up by addition of water, extraction with ether, and concentration of the dried extracts gave IV as a pale yellow viscous oil lacking infrared absorption attributable to carbonyl, but having absorption at *ca.* 3630, 3420, and 3320 cm^{-1}. The nmr spectrum (CCl_4), although somewhat messy, was consistent with structure IV: 3 H complex at τ 2.8–3.5, 1 H doublet at 5.4 (J = 14 cps), 18 H complex at 5.9–9.0, including a broad singlet at 6.15 and a sharp singlet at 6.3.

Preparation of the Methanesulfonate Ester of IV.—The crude propargyl alcohol IV from the previous step was dissolved in 133 ml of dry pyridine and the solution cooled with an ice bath. Freshly distilled methanesulfonyl chloride (2.22 ml; 3.28 g, 28.9 mmoles) was added and the flask, flushed with nitrogen and stoppered, was kept in an ice bath for 24 hr. Work-up by addition of cold aqueous hydrochloric acid to slight acidity and extraction with ether, followed by concentration of the dried extracts, produced a yellowish oil lacking infrared absorption attributable to hydroxyl, but having bands at *ca.* 3330 and 2120 cm^{-1}.

Conversion of V to the Allene VI.—The crude methanesulfonate ester V from the previous step, as a viscous liquid, was dissolved in 250 ml of dry ether and treated with excess lithium aluminum hydride by refluxing for 2.5 hr. Work-up by dropwise addition with stirring of saturated aqueous sodium sulfate and decantation of the organic liquors (and washing of the inorganic precipitate with ether) gave, on concentration, a yellow oil which was dissolved in hexane and chromatographed on Merck basic alumina. Reconcentration of appropriate fractions gave 4.06 g (78.5% from III) of crystalline allene which, when recrystallized from hexane, melted at 66–68°: $\nu_{\max}^{\mathrm{CCl_4}}$ 1960 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 228 mμ (ϵ 7200), 282 (2700); nmr (CCl_4), 3 H complex at τ 2.8–3.5, 1 H triplet at 4.3 (J = 7 cps), 2 H doublet at 5.25 (J = 7 cps), complex absorption at 6.0–9.0, including a 4 H singlet at 6.2 and a 3 H singlet at 6.3.

Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.48; H, 7.18.

Conversion of VI to Keto Acetylene VIII.—The ketal allene VI (3.0 g, 10 mmoles) was dissolved in 15 ml of dry tetrahydrofuran and added with stirring to a solution of potassium amide prepared from 725 mg of potassium (18.5 mg-atom), 150 ml of dry ammonia, and a trace of ferric chloride. The mixture was stirred at reflux temperature for 1 hr and worked up by addition of solid ammonium chloride, evaporation of ammonia, addition of water, and extraction with ether and pentane. Concentration of the dried extracts gave about 2.8 g of a colorless oil exhibiting infrared absorption at *ca.* 3340 and 2130 cm^{-1}, attributable to terminal acetylene. Since the product could not be induced to crystallize and since the ketal was no longer required for our purposes,[12] the entire product was deketalized by stirring at room temperature for 1.5 hr in a mixture of 100 ml of methanol, 20 ml of water, and 3 ml of hydrochloric acid. Work-up by neutralization with aqueous sodium bicarbonate and extraction with ether yielded, on concentration, 2.1 g (82%) of crude crystalline VIII. Recrystallization from hexane–ether gave material melting at 71–72°: $\nu_{\max}^{\mathrm{CCl_4}}$ 3310, 1710 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 282 mμ (ϵ 2700); nmr (CCl_4), 3 H complex at τ 2.8–3.5, 3 H singlet at 6.3, 1 H triplet at 6.8 (J = 4 cps), pair of 1 H doublets at 7.1 and 7.4 (J = 16 cps), 8 H complex at 7.5–8.0, 1 H triplet at 8.1 (J = 2.5 cps).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.30; H, 7.25.

Registry No.—II, 13758-72-0; III, 13673-64-8; IV, 13673-65-9; VI, 13673-66-0; VIII, 1149-97-9.

Acknowledgment.—The author is indebted to Professor Gilbert Stork of Columbia University, where this work was done, for originating the problem described and for essential suggestions and discussions during its resolution. The author is also grateful to the U. S. Public Health Service, whose National Institutes of Health Postdoctoral Fellowship, No. 2-F2-GM-17,148-02, in part supported this work. Additional support through funds supplied by The National Science Foundation to Professor Stork is also acknowledged.

Pyrolysis of Tetrakis(dimethylamino)methane

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The recently reported tetrakis(dimethylamino)methane[1] was observed to decompose slowly at temperatures slightly above its melting point (122.5–124.5°) and it was of interest to examine this decomposition in some detail.

When tetrakis(dimethylamino)methane is kept at 150°, it gradually loses dimethylamine (identified by mass spectral and nmr analyses) and the resulting residue is a mixture of an unknown, distillable liquid and a polymeric tar. The nuclear magnetic resonance (nmr) spectrum of the distillable liquid is relatively simple, being composed of a doublet centered at τ 5.34 (J = 10.6 cps), a singlet at 7.42, a broadened singlet at 7.52, and another singlet at 7.70 in the ratio 1:6:3:6 (in benzene solvent, tetramethylsilane internal standard). On the basis of this spectrum and other data presented below, structure I was assigned to this compound. Additional nmr evidence is obtained from a sample to which dimethylamine was added as a source of exchangeable protons. The doublet at τ 5.34 becomes a singlet and the broad peak at τ 7.52 also becomes a sharp singlet, while the peaks at τ 7.42 and 7.70 remain unchanged. This corroborates the $=CHNHCH_3$ arrangement of structure I. The infra-

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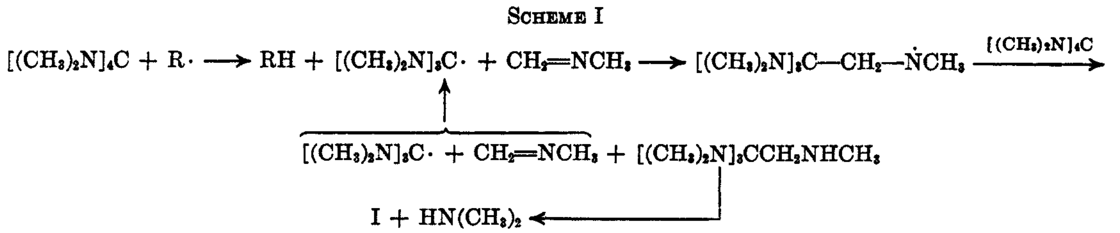
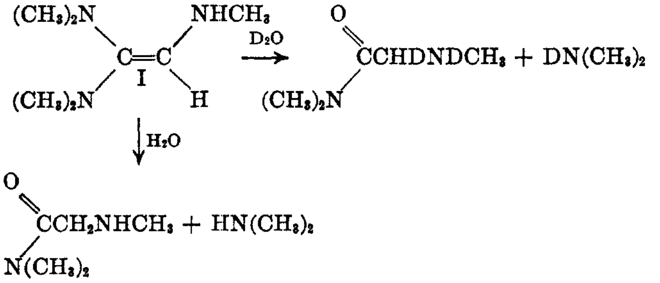
[1] H. Weingarten and W. A. White, *J. Am. Chem. Soc.*, **88**, 2885 (1966).

SCHEME I



red spectrum of I is generally consistent with the structure proposed and specifically it exhibits an adsorption at 3500 cm^{-1} for the NH bond.

A powerful chemical confirmation of structure I is obtained on hydrolysis which yields sarcosine dimethylamide[2] and an equivalent of dimethylamine. When the hydrolysis is carried out in D_2O the sarcosine product has a deuterium atom in the α position as expected.



Freshly purified samples of the tetraamine require 15–20 hr at 150° to complete the conversion while samples stored for several months react much more rapidly. This suggests free radical pathways and indeed the addition of a free radical initiator, azobisisobutyronitrile, greatly accelerates the pyrolysis of freshly purified tetraamine. A possible mechanistic scheme is Scheme I.

Experimental Section

Proton nmr spectra were obtained from a Varian Model A-60 spectrometer. Authentic sarcosine dimethylamide was prepared by the method of Waley and Watson.[3]

Pyrolysis of Tetrakis(dimethylamino)methane.—To 5 g of tetrakis(dimethylamino)methane in a 25-ml round-bottom flask was added 0.05 g of azobisisobutyronitrile and the reaction vessel was immersed in an oil bath maintained at 150°. The mixture was kept under a small positive pressure of dry nitrogen throughout the reaction. After 5 hr the reaction mixture was distilled through a small Vigreux column yielding 1.85 g (50%)[4] of tetramethyl(2-methylamino)vinylidenediamine [bp 165–170° (1 atm), $n^{25}\mathrm{D}$ 1.4716], which fumes in air.

Anal. Calcd for $C_7H_{17}N_3$: N, 29.4; mol wt, 143. Found: N, 29.3; mol wt, 140 ± 5 (cryoscopy in benzene).

Hydrolysis of Tetramethyl(2-methylamino)vinylidenediamine, I.—To an nmr tube containing 0.1 g of tetramethyl(2-methylamino)vinylidenediamine was added about 1 ml of water. The triamine, at first insoluble, reacts exothermically to give a clear solution of dimethylamine and sarcosine dimethylamide. The nmr spectrum of this solution exhibits singlets at τ 6.57, 7.00, 7.07, and 7.68 in the ratio of 2:3:3:3 [3-(trimethylsilyl)-1-propane sulfonic acid sodium salt internal standard]. The dimethylamine peak appears at τ 7.71 and the above ratio and its relationship to dimethylamine is obtained by nmr spectra made before and after the dimethylamine is removed in a stream of nitrogen. This nmr spectrum of the hydrolysis product was identical with that of authentic sarcosine dimethylamide.

When this procedure was carried out using D_2O in place of H_2O the only change in the nmr was the decrease of the τ 6.57 peak. The α-protons of sarcosine dimethylamide do not exchange with D_2O under these conditions.

Registry No.—I, 13958-59-3; tetrakis(dimethylamino)methane, 10524-51-3.

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[2] The sarcosine dimethylamide was not isolated; see Experimental Section.

[3] S. G. Waley and J. Watson, *Proc. Roy. Soc.* (London), **A199**, 499 (1949).

[4] Slightly better yields were obtained when the reaction was carried out in a sealed tube.

Formation of Hydrocarbons in Model Primitive Earth Atmospheres

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While studying the formation of amino acids by electrical discharges in a model primitive earth atmosphere of the Urey[1] type (methane, ammonia, water, and hydrogen), Miller[2] noted incidentally that under certain conditions a considerable quantity of hydrocarbons formed. He did not identify any of them and no one else seems to have followed up this interesting observation.[3]

Electrical discharges in pure methane are well known to produce a horrendous variety of higher hydrocarbons.[4,5] Ponnamperuma and Pering[6] have demonstrated that the hydrocarbon mixture produced by a spark discharge in methane is very similar to the mixture of hydrocarbons present in the ancient Mountsorrel sediment which they therefore suggest is possibly abiogenic in origin. Conceivably such mixtures formed in the *atmosphere* of the primitive earth, although, in the presence of oxygen- and nitrogen-containing gases, the reactive intermediates would tend to be diverted into the synthesis of such end products as amino acids. However, there is at present no necessity for assuming that equilibrium conditions were reached in the primitive earth atmosphere[7] and we thought it would be

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[1] H. C. Urey, "The Planets," Yale University Press, New Haven, Conn., 1952, p 149.

[2] S. L. Miller, *J. Am. Chem. Soc.*, **77**, 2353 (1955).

[3] C. Palm and M. Calvin [*ibid.*, **84**, 2115 (1962)] found ethane, ethylene, and "C_2–C_7 hydrocarbons" in a cursory examination of the gaseous products of electron bombardment of a similar model atmosphere.

[4] For a review, see G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939, p 149.

[5] C. Ponnamperuma and F. Woeller [*Nature*, **203**, 272 (1964)] observed that a change in the type of electrical discharge changed the C_6 to C_9 hydrocarbon products from primarily aliphatic to primarily aromatic.

[6] C. Ponnamperuma and K. Pering, *ibid.*, **209**, 979 (1966).

[7] The amounts of many hydrocarbons, including those found in this work, which would be present in a C–H–N–O system at or near equilibrium at various temperatures and pressures have been computed by R. V. Eck, E. R. Lippincott, M. O. Dayhoff, and Y. T. Pratt, *Science*, **153**, 628 (1966). Whether or not the atmosphere of the prebiological earth ever approached chemical equilibrium is still an open question; A. E. Ringwood [*Geochim. Cosmochim. Acta*, **21**, 295 (1961)] goes so far as to suggest that the surface temperature may have been below 0° 5 billion years ago.