as spectra for solutions containing other mole ratios of the quinone to thorium were exactly similar to that given for the 1:1 combination, they are not included. Since all such solutions showed maximum absorption at 490 mμ, but a single absorbing species is present in them. The optical density difference–composition curve[4] given in Fig. 2 for data obtained at 490 mμ indicates the presence of two 2,5-dihydroxyquinone groups to one thorium in the colored substance. Decision as to whether this species is a neutral molecule, in which both of the acidic hydrogens in each of the quinone molecules have been replaced by thorium, or an ionic material, in which only a single hydrogen in each of the quinone groups has been involved, cannot be made from data presented here. In any event, a chelate structure seems likely.

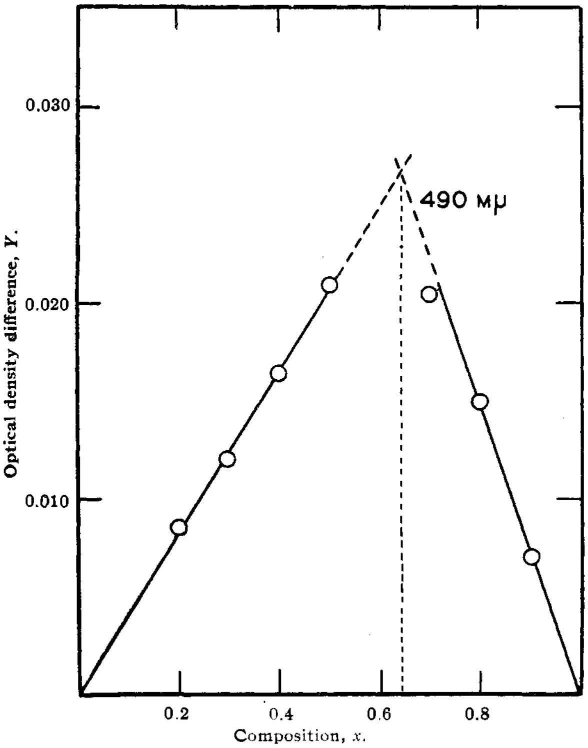

Fig. 2.—Variation of optical density difference (Y) with mole fraction (x) of 2,5-dihydroxyquinone.

Experimental

Materials Used.—Methanol solutions of thorium nitrate were prepared from the pure tetrahydrate and standardized by evaporating, igniting to the oxide and weighing. The 2,5-dihydroxyquinone was prepared by Mr. J. M. Coker[2] and purified by sublimation at 185°. Standard solutions in methanol were prepared by direct weighing.

Spectrophotometric Measurements.—All absorption spectra were obtained with a General Electric Recording Spectrophotometer, using 1-cm. cells and a 10 mμ slit width. In applying the method of continuous variations, the absorption spectra of a series of solutions, prepared by combining varying volumes of 0.001 *M* thorium nitrate and 2,5-dihydroxyquinone solutions, were measured, all solutions having the same total volume. For each the difference between the measured optical density (at the selected wave length) and that calculated for the reagents present assuming no interaction was related to solution composition as in Fig. 2. The maximum at mole fraction 0.64 for the quinone agrees well with the value of 0.67 required by a 2:1 composition for the colored complex. Data at other wave lengths yield the same result.

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Studies in the Guanidine Series. I. The Reaction of Hydrazine with Carbon Tetrachloride and Carbon Tetrabromide

BY SEYMOUR H. PATINKIN AND EUGENE LIEBER

Triaminoguanidine hydrochloride, $(H_2NNH)_2C(=NNH)\cdot HCl$, was first reported to have been prepared by Stollé[1] by the action of hydrazine hydrate on carbon tetrachloride at its boiling point in the presence of ammonia gas. No details as to actual quantities of materials used or yield obtained were stated. Stollé[1] indicated that further investigations were being carried out; however, nothing has appeared in the literature on this reaction since that time.

A repetition of this work by the writers has failed to confirm this, hydrazine monohydrochloride being identified as the only solid product of the reaction. The results of a number of runs of the reaction of hydrazine with carbon tetrachloride, at its boiling point at atmospheric pressure, either in the presence or absence of a stream of ammonia gas, are summarized in Table I. Slightly increasing the ammonia pressure above atmospheric increases the yield of solids salts in which only ammonium chloride and hydrazine monohydrochloride can be identified. An inert gas, identified as nitrogen, is continuously evolved from the reaction and an examination of the liquid volatile products by infrared analysis showed the presence of chloroform and possibly methylene dichloride. These data are sum-

TABLE I

THE REACTION OF HYDRAZINE WITH CARBON TETRACHLORIDE[a] AT ITS BOILING POINT

				Product			
Run	Hydrazine, g.	Reflux, hr.	Stream of NH_3 gas	Yield,[b] g.	M. p.,[c] °C.	Assay,[d] % N_2H_4	Benzaldehyde derivative, m. p., °C.
1	3.8[e]	48	None	3.2	89	46.73	92.5[f]
2	23.6[g]	18	Yes	4.9	89	46.67	92.5
3	20.4[h]	16	Yes	1.6	87	46.70	90.5
4	20.7[g]	20	None	0.3	88.7	46.50	92
5	18.2[g]	35	Yes	3.1	89	...	92

[a] Excess of CCl_4 used in all runs. [b] Of recrystallized product. [c] All melting points are taken on the Dennis Bar (L. M. Dennis and R. S. Shelton, THIS JOURNAL, **52**, 3129 (1930)); the m. p. of $N_2H_4\cdot HCl$ is reported to be 89° by Curtius and Jay, *J. prakt. Chem.*, [2] **39**, 27 (1889), [d] The theoretical hydrazine content of $N_2H_4\cdot HCl$ is 46.72%. [e] Anhydrous N_2H_4. [f] Benzalazine $(C_6H_5CH:N)_2$ is reported to melt at 93° (Beilstein, Vol. VII, p. 225). [g] 85% hydrazine hydrate. [h] 95% hydrazine hydrate.

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[1] R. Stollé, *Ber.*, **37**, 3548 (1904).

marized in Fig. 1. The bands at 3.40, 8.21 and 14.99 μ have little or no counterpart in the carbon tetrachloride spectrum. The evidence, accordingly, demonstrates that the hydrazine is functioning *solely as a reducing agent*, the reactions being

$$2CCl_4 + N_2H_4 \longrightarrow 2CHCl_3 + N_2 + 2HCl$$
$$2N_2H_4 + 2HCl \longrightarrow 2N_2H_5Cl$$

There is only one brief report in the literature on the reaction of hydrazine with carbon tetrabromide. Without identification of the liquid or solid products of the reaction, Macbeth and Traill[2] stated that nitrogen was evolved in an amount equivalent to the removal of one bromine atom from the carbon tetrabromide. A repetition of this reaction in dry ethyl alcohol as solvent led to the isolation of hydrazine hydrobromide as the only solid product of the reaction.

Experimental

Reaction of Hydrazine with Carbon Tetrachloride. Stollé Procedure.[1]—In view of the indefiniteness of the original directions[1] a number of runs were made at atmospheric pressure, using different types of hydrazines, with or without ammonia gas, with the sole object of determining the nature of the solid products formed. The data obtained are summarized in Table I. The products were isolated by evaporating the reaction mixture under vacuum until salts appeared and were recrystallized from ethyl alcohol. The mother liquors were similarly examined but resulted only in further small yields of hydrazine monohydrochloride.

Reaction of Hydrazine with Carbon Tetrachloride at Increased Ammonia Pressure.—Hydrazine hydrate (95%) (48.6 g.) and 200 ml. of freshly distilled carbon tetrachloride were placed in a reaction flask equipped with water condenser and inlet tube leading to the bottom of the reaction mixture, hydrostatically controlled so as to introduce ammonia gas at a pressure of approximately 800 mm. The reaction flask was electrically heated so as to maintain a vigorous reflux, the ammonia gas furnishing sufficient turbulence in the reaction mixture. The reflux was maintained, intermittently, for a 50-hour reaction period. The reaction mixture was poured into a separatory funnel and the aqueous phase separated from the carbon tetrachloride. The carbon tetrachloride was washed with water, separated and the aqueous solutions combined. The major portion of the water was removed by vacuum distillation, at which time salts had crystallized out. It was found impossible to remove the last traces of water under vacuum as considerable frothing was experienced. Accordingly, the last traces of water were removed by evaporation in a wide porcelain dish over a steam-bath. The crude salts after drying in a vacuum desiccator weighed 19.6 g. Fractionation of the crude salts yielded 11.95 g. of ammonium chloride, identified as the chloroplatinate (calcd.: Pt, 43.9. Found: Pt, 43.4) and 1.91 g. of hydrazine monohydrochloride, identified by hydrazine analysis (found: N_2H_4, 46.35) and conversion to the benzalazine (m. p. 90°, calcd.: N, 13.41. Found: N, 13.83).

Fate of the Carbon Tetrachloride and Identification of Evolved Gas.—This was studied under a fractionating column fitted at the head with a Dry Ice condenser and a gas buret. Carbon tetrachloride (200 ml.) and 33 g. of anhydrous hydrazine were continually refluxed under the column for a period of 52 hours. Gas evolution was very rapid at the start of the reaction and fell off continuously throughout the reaction as shown by the following data:

Time of reaction, hr.	2	8	16	24	35	48
Gas evolution, ml./hr.	232	146	108	85	69	58

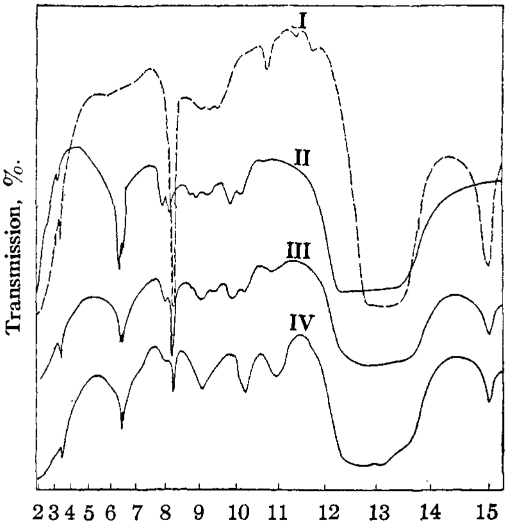

Fig. 1.—Infrared spectra of I, chloroform; II, carbon tetrachloride; and III, IV distillates obtained in the reaction of hydrazine with carbon tetrachloride.

During the reaction period of four to six hours a sample of gas was collected over saturated salt solution and analyzed by the mass spectrometer. Nitrogen was identified. During this same period over the reaction range of five to seven hours, three successive samples were collected, under very slow column equilibrium conditions, in ampoules immersed in a Dry Ice–acetone-bath. After the samples (1 to 3 ml.) were collected they were sealed off and analyzed by the infrared spectrometer. The results of the infrared analyses are summarized in Fig. 1 for two of the fractions collected. The third fraction showed a similar infrared tracing and is not reproduced. The reaction was discontinued after 52 hours and the solid salts isolated as previously described. A total of 7.3 g. of recrystallized product was obtained melting at 89° (Dennis bar). Further identification was by hydrazine analysis (Found: N_2H_4, 46.65).

Reaction of Carbon Tetrabromide with Hydrazine Hydrate. Identification of Solid Products.—Carbon tetrabromide (15.0 g., 0.045 mole) and 5.4 g. (0.108 mole) of hydrazine hydrate (95%) were dissolved in 150 ml. of dry ethyl alcohol and refluxed continuously for seventeen hours. On mixing the two reagents, a slight evolution of gas was observed and this continued slowly throughout the reaction period. The reaction mixture was cooled in an ice-salt-bath and the crystals so obtained recovered. Recrystallization from alcohol yielded 1.90 g. of a white powder melting sharply at 84°. This corresponds to the melting point for hydrazine monohydrobromide which has been reported to melt at 80°,[3] 81–82°[4] and 84.5°.[5]

Anal. Calcd. for N_2H_5Br: N, 24.80; Br, 70.74. Found: N, 24.97; Br, 71.11.

Discussion

Stollé's[1] purported formation of triaminoguanidine by the hydrazinolysis of carbon tetrachloride has been quoted by Franklin[6a] and Audrieth[6b] as a good example of the comparative behavior of

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[2] A. K. Macbeth and D. Traill. *J. Chem. Soc.*, **127**, 894 (1925).

[3] Curtius and Schulz, *J. prakt. Chem.*, [2] **42**, 521 (1890).

[4] W. V. Fuckler, Jr., Thesis, University of Illinois, 1948.

[5] Gilbert and Cobb, This Journal, **57**, 339 (1935).

[6] (a) E. C. Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corp., New York, N. Y., 1935, p. 202; (b) L. F. Audrieth, N6ORI-71-Chemistry Task. No. XX, Chapter 11, p. 8.

hydrazine and ammonia in the nitrogen system of compounds, since the reaction of ammonia and carbon tetrachloride leads to the formation of guanidine,[7] although the literature on this is very scanty. It is interesting to note that Ponzio[8] attempted to prepare triphenylguanidine by the reaction of aniline and carbon tetrabromide but obtained only aniline hydrobromide, while the corresponding reaction with phenylhydrazine gave only phenylhydrazine monohydrobromide. The results of the present investigation emphasize the need for careful study on the reaction of carbon tetrachloride and related compounds with ammonia, amines and other nitrogen compounds. As pointed out by Huntress[9] there is practically nothing in the literature in this field. Our own investigations along this line are being continued.

[7] Stähler, *Ber.*, **47**, 909 (1914).

[8] Ponzio, *Chem. Zentr.*, **77**, I, 1691 (1906).

[9] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 580.

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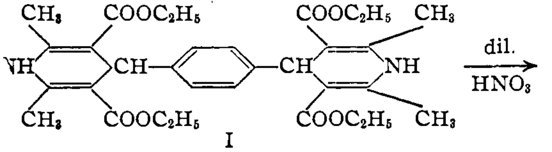
Some Condensation Products from Terephthalaldehyde

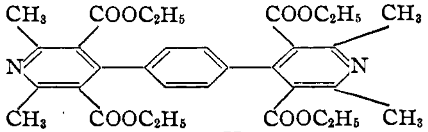
BY ARTHUR P. PHILLIPS

Other work in these laboratories concerned with attempts to prepare synthetic curare substitutes[1] suggested the preparation of symmetrical, "double-ended" molecules from terephthalaldehyde.

Condensation of terephthalaldehyde with β-aminocrotonic ester gave I, resulting from the Hantzsch dihydropyridine synthesis at both the 1- and 4-positions. Oxidation of I with dilute nitric acid gave II, having the true pyridine structure in both positions.

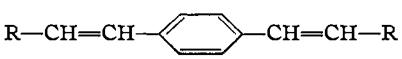


I



II

Reaction of the aldehyde with 2- and 4-methylpyridine methiodides gave III and IV, respectively.



III, R = 2-pyridine methiodide
IV, R = 4-pyridine methiodide

Experimental

Preparation of I.—Terephthalaldehyde, 13 g. (0.1 mole), and 52 g. (0.4 mole) of β-aminocrotonic ester were mixed well and heated for three hours on a steam-bath. The originally clear solution became solid in about thirty minutes. After digesting with alcohol, in which the product was insoluble, the cooled mixture was filtered and gave 16 g. (28%) of I. I was insoluble in most common solvents, though very sparingly soluble in hot glacial acetic acid. After crystallization from acetic acid it melted at 295-296°.

Anal. Calcd. for $C_{32}H_{40}O_8N_2$: C, 66.21; H, 6.90. Found: C, 65.58; H, 6.88.

Oxidation of I to II.—Eight grams of the bis-dihydropyridine I was suspended in 120 cc. of 4 *N* nitric acid and the mixture was warmed at 100° until a clear solution resulted and gas evolution had stopped (about three hours). After basifying with potassium carbonate the cooled solution gave 7 g. (90%) of II. When crystallized from alcohol, it melted at 211-212°.

Anal. Calcd. for $C_{32}H_{36}O_8N_2$: C, 66.67; H, 6.25. Found: C, 66.77; H, 6.48.

Preparation of III.—Four grams (0.03 mole) of terephthalaldehyde, 17 g. (0.07 mole) of 2-picoline methiodide, 100 cc. of methanol, and 10 drops of piperidine were mixed and refluxed five hours. Cooling gave 12 g. (70%) of yellow crystals of III, insoluble in the usual solvents. After crystallization from a large volume of hot water the crystals melted above 300°.

Anal. Calcd. for $C_{22}H_{22}N_2I_2$: C, 46.46; H, 3.91. Found: C, 46.63; H, 3.89.

Preparation of IV.—Using 4-picoline methiodide with the same quantities and conditions as in the formation of III a yield of 7 g. (41%) of an insoluble yellow product was obtained. After crystallization from much hot water these melted above 305°.

Anal. Calcd. for $C_{22}H_{22}N_2I_2$: C, 46.46; H, 3.91. Found: C, 46.68; H, 3.91.

Acknowledgment.—The author is indebted to Samuel W. Blackman and Walter S. Ide for the microanalyses included here.

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[1] Phillips, THIS JOURNAL, **71**, 3264 (1949); *ibid.*, **71**, 4003 1949); *J. Org. Chem.*, **12**, 333 (1947); **14**, 302 (1949).

The Preparation of Ultramarines[1]

BY JEROME S. PRENER[2] AND ROLAND WARD[3]

In a search for substances which might behave as base materials for infrared-sensitive phosphors, we had occasion to examine some complex silicates of the ultramarine type. The alkali ultramarines have an ideal composition $M_8Al_6Si_6O_{24}S_x$ where x may vary from one upwards to perhaps 4 and M is an alkali metal. The excess sulfur is presumably present in a polysulfide grouping and the depth of color of the ultramarines apparently depends on the amount of sulfur. Closely related to the ultramarines is sodalite $Na_8Al_6Si_6O_{24}Cl_2$ in which the two chloride ions replace a $S_x^{=}$ ion in the ultramarines.[4]

While none of the compounds studied was found to give an infrared-sensitive phosphor, methods of

[1] This work was carried out under Contract NObsr 39045 between the Bureau of Ships and the Polytechnic Institute of Brooklyn.

[2] General Electric Research Laboratory, Schenectady, N. Y.

[3] Department of Chemistry, University of Connecticut, Storrs.

[4] Linus Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 387.