methanol-water, m.p. 273-275° (dec.).[9] The filtrate was evaporated to dryness. The residue was partitioned between dilute aqueous ammonia and ether. Evaporation of the dried ether solution and distillation of the residue at 0.2 mm. gave 0.55 g. (72%) of a colorless oil (IX) whose hydrobromide salt crystallized from acetone in needles, m.p. 184-187°.

Anal. Calcd. for $C_{17}H_{28}BrNO$: C, 59.64; H, 8.24; N, 4.09. Found: C, 59.67; H, 8.06; N, 4.19.

The picrate of IX, prisms from methanol-acetone, melted at 152-153°.

Anal. Calcd. for $C_{23}H_{30}N_4O_8$: C, 56.32; H, 6.17; N, 11.42. Found: C, 56.32; H, 6.24; N, 11.54.

β-7-Methoxy-1,2-dimethyl-1-(2-dimethylaminoethyl)-1,2,3,4-tetrahydronaphthalene picrate. As described before[3] authentic V methiodide was degraded to this compound whose picrate melted at 149-150° and was markedly depressed in m.p. by IX picrate.

Anal. Calcd. for $C_{23}H_{30}N_4O_8$: C, 56.32; H, 6.17. Found: C, 56.25; H, 6.45.

The hydrobromide salt (m.p. 194-196°) of this authentic tetrahydronaphthalene derivative was also depressed in melting point by the hydrobromide of IX. Furthermore, the picrate and hydrobromide of IX proved to be different from these salts prepared by Hofmann degradation of authentic III and reduction of the resultant methine.[8]

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[9] Although the found carbon-hydrogen values (C, 53.01; H, 6.56) for the methiodide VIII were in agreement with those calculated for VII, the infrared spectrum and melting point were clearly different from the starting VII. In addition, VIII was different from the methiodide of either III or V (*cf.* ref. 3).

Formation of Isocyanides during the Thermal Decomposition of Sodium Trichloroacetate in the Presence of Arylamines

A. PAUL KRAPCHO

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Two general synthetic methods to isocyanides have been utilized most extensively since their discovery by Hofmann[1] and Gautier.[2] These methods consist of the action of silver cyanide on alkyl iodides and the reaction of chloroform-base on primary amines.[3] More recently Ugi[4] has published some excellent isocyanide syntheses by dehydration of monosubstituted formamides with phosphorus oxychloride. The chloroform-base reaction on primary amines is well known and is used qualitatively to distinguish between primary and secondary amines by making use of the disagreeable odor of isocyanides which are formed on reaction of primary amines.[5] The intermediacy of dichlorocarbene in the formation of isocyanides from primary amines is substantiated by the investigations of Hine.[6] The reaction of dichlorocarbene (from potassium *t*-butoxide and chloroform) with secondary and tertiary amines has been reported by Saunders[7] and Frankel.[8] The decarboxylation studies of Hine[9] on chlorodifluoroacetic acid in aqueous solution led to a proposed concerted decomposition to difluoromethylene. Most other trihaloacetate ions lose carbon dioxide to yield the trihalomethyl anion which is subsequently protonated by the medium. It has been demonstrated by Wagner[10] that the thermal decomposition of sodium trichloroacetate in nonprotonic solvents leads to dichlorocarbene as an intermediate (trapped in the presence of olefins). This method of formation of dichlorocarbene was investigated in the presence of aryl amines as trapping agents. In a preliminary test a distinct odor of phenyl isocyanide could readily be detected by refluxing aniline and sodium trichloroacetate in 1,2-dimethoxyethane for a few minutes. The odor of the isocyanide could also be detected on heating aniline and sodium trichloroacetate without solvent for a few minutes. A more detailed study of this decomposition showed that fair yields of isocyanides could be obtained. The results of this investigation are listed in Table I.

TABLE I

	Molarity[a]			
Amine	Amine	Sodium trichloroacetate	Hours Refluxed	% RNC
Aniline	1.1	1.1	16	15[b]
p-Toluidine	1.6	3.2	6	25[b]
p-Toluidine	1.0	3.0	3/4	43[c]
p-Anisidine	1.0	3.0	1/2	38[c]

[a] All runs are in dry 1,2-dimethoxyethane as solvent. [b] The infrared spectrum showed the presence of unchanged amine and the % isocyanide is estimated from the strong isocyanide band at 4.70 μ. [c] The infrared spectrum shows the material to be pure isocyanide.

The optimum yield of the isocyanide can be obtained utilizing a 3:1 molar ratio of sodium trichloroacetate to amine and is not contaminated by unreacted amine. Unchanged amine was found to be present in runs having less than a 3:1 molar ratio of sodium trichloroacetate to amine. Undoubtedly this arises from the reaction of CCl_3^-

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[1] A. Hofmann, *Ann.*, **144** (1867); **146**, 107 (1868).

[2] A. Gautier, *Ann. chim. et phys.*, [4] **17**, 108 (1869).

[3] P. A. S. Smith and N. W. Kalenda, *J. Org. Chem.*, **23**, 1599 (1958), and references cited therein.

[4] I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).

[5] J. Houben, *Die Methoden der organischen Chemie*, Vol. 4 (3rd ed.), p. 587, Georg Thieme Verlag, Leipzig (1941).

[6] J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).

[7] (a) M. Saunders and R. W. Murray, *Tetrahedron*, **11**, 1 (1960). (b) M. Saunders and R. W. Murray, *Tetrahedron*, **6**, 88 (1959).

[8] M. B. Frankel, H. Feuer, and J. Bank, *Tetrahedron Letters*, **7**, 5 (1959).

[9] J. Hine and D. C. Duffey, *J. Am. Chem. Soc.*, **81**, 1131 (1959), and references cited therein.

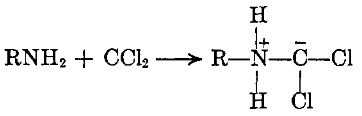
[10] W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

(formed in reaction 2 below) with the amine salt (formed in reaction 4 below) to produce chloroform and the free amine (reaction 5 below).[11] In one run utilizing approximately a 2:1 molar ratio of sodium trichloroacetate to *p*-chloroaniline, a 60% yield of chloroform (based on acetate) was obtained. In all runs black, tarlike material remained after distillation.

These observations are consistent with the mechanistic sequence of reactions depicted in the following steps:

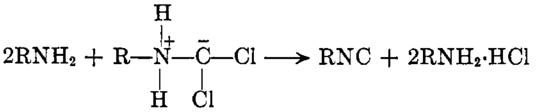
$$CCl_3CO_2^- \longrightarrow CCl_3^- + CO_2 \qquad (1)$$

$$CCl_3^- \longrightarrow CCl_2 + Cl^- \qquad (2)$$



$$RNH_2 + CCl_2 \longrightarrow R-\overset{H}{\underset{H}{\overset{+}{N}}}-\underset{Cl}{\overset{-}{C}}-Cl$$

(3)



$$2RNH_2 + R-\overset{H}{\underset{H}{\overset{+}{N}}}-\underset{Cl}{\overset{-}{C}}-Cl \longrightarrow RNC + 2RNH_2{\cdot}HCl$$

(4)

$$RNH_2{\cdot}HCl + CCl_3^- \longrightarrow CHCl_3 + RNH_2 + Cl^- \qquad (5)$$

The over-all stoichiometry can be represented by the following equation:

$$RNH_2 + 3CCl_3CO_2Na \longrightarrow RNC + 2CHCl_3 + 3CO_2 + 3NaCl$$

Further extensions of this reaction with other amines are currently under investigation and will be reported shortly.

EXPERIMENTAL

Preparation of isocyanides. (a) *p-Tolyl isocyanide.* To a solution of 5.4 g. (0.05 mole) of *p*-toluidine in 100 ml. of 1,2-dimethoxyethane (distilled from lithium aluminum hydride) was added 28 g. (0.15 mole) of sodium trichloroacetate. A slight exothermic reaction occurred and a fine pasty-white solid separated. On gentle warming, a clear solution resulted which was refluxed for 30 min. During this time a copious evolution of carbon dioxide occurred, and after refluxing for 15 min. a yellow solid separated. After 30 min. the solid settled to the bottom and the mixture was colored brown. The mixture was cooled, filtered, and the solid (weight 10 g.) washed with ether. The reddish-black filtrate was concentrated on a Rinco rotary evaporator. Near the end of the evaporation a solid separated. Ether was added to the pasty mass; the ethereal layer was washed twice with water and dried over sodium sulfate. The ether was removed by distillation and the residual red-black oil distilled under reduced pressure to yield 2.5 g. (43% based on amine) of a pale yellow liquid boiling at 38°/1 mm.; m.p. 19–20°. Reported:[12] b.p. 94°/25 mm.; m.p. 20°. The product exhibited a strong isocyanide infrared absorption band at 4.69 μ and contained no unchanged amine.

(b) *p-Methoxyphenyl isocyanide.* As in procedure (a) above using 6.2 g. (0.05 mole) of *p*-anisidine, 100 ml. of dry 1,2-dimethoxyethane and 29 g. (0.16 mole) of sodium trichloroacetate. The mixture was refluxed for 30 min. On work-up and distillation under reduced pressure there was obtained 2.5 g. (38% based on amine) of material boiling at 45°/1 mm. which solidified in the receiver. This material was crystallized from ether at low temperature; m.p. 28-30°. Reported:[12] m.p. 30°. The infrared absorption spectrum (20% solution in carbon tetrachloride) exhibited strong isocyanide absorption at 4.70 μ and the product contained no unreacted amine.

(c) *Phenyl isocyanide.* As in (a) above using 5.0 g. (0.05 mole) of aniline, 50 ml. of dry 1,2-dimethoxyethane, and 10.0 g. (0.05 mole) of sodium trichloroacetate. The mixture was refluxed for 15 hr. On work-up and distillation under reduced pressure there was obtained 2.8 g. of a pale yellow liquid boiling at 43–44°/1.5 mm. The product on examination in the infrared was contaminated with unchanged amine. From the intensity of the isocyanide band at 4.69 μ the product contained about 40% phenyl isocyanide. This constitutes a 20% yield of phenyl isocyanide based on amine.

(d) *p-Chlorophenyl isocyanide.* As in (a) above using 6.4 g. (0.05 mole) of *p*-chloroaniline, 50 ml. of dry 1,2-dimethoxyethane and 17 g. (0.09 mole) of sodium trichloroacetate. The mixture was refluxed for 45 min., cooled, and poured into ice water. The dark bottom layer was separated and dried over sodium sulfate (weight 11 g.). On distillation there was obtained 7 g. (64% yield based on acetate) of chloroform and 4 g. of a dark black pot residue. The infrared spectrum of this undistilled material (in KBr window) showed the presence of an isocyanide band at 4.70 μ and also unreacted amine. No further work-up was effected.

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[11] F. H. Verhoek, *J. Am. Chem. Soc.*, **56**, 571 (1934) reports that the decomposition of anilinium trichloroacetate yields chloroform.

[12] D. Ll. Hammick, R. C. A. New, N. V. Sidgwick, and L. E. Sutton, *J. Chem. Soc.*, 1876 (1930).

Preparation of Heterocyclic Dihydroxyphosphonium Salts

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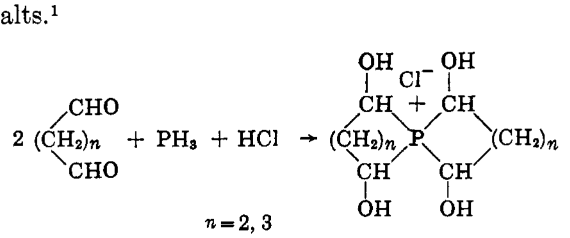
Previous reports from this laboratory described the preparation of *spiro*-tetrahydroxyphosphonium salts.[1]



We now report the preparation of a number of monocyclic dihydroxyphosphonium salts (I and II) by the reaction of secondary phosphines with succinaldehyde or glutaraldehyde in the presence of hydrochloric acid. The heterocycles III and IV,

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[1] S. A. Buckler and V. P. Wystrach, *J. Am. Chem. Soc.* **80**, 6454 (1958). *J. Am. Chem. Soc.*, **83**, 168 (1961).