ity of thiamine when determined by microbiological assay with either *L. fermenti*[6] or *L. viridescens*.[7]

(6) H. Sarett and P. Cheldelin, *J. Biol. Chem.*, **155**, 153 (1944).

(7) R. H. Deibel, J. B. Evans and C. F. Niven, Jr., *J. Bacteriol.*, **74**, 818 (1957).

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A STABLE DIPOSITIVE CARBONIUM ION[1]

Sir:

We wish to report the formation of a stable carbonium ion produced formally by loss of two anions from a single carbon atom. Trichloromethylpentamethylbenzene (I)[2] dissolves readily in 100% sulfuric acid (> 5 g./25 ml.) to give an intensely red solution (though neither benzotrichloride nor pentamethylbenzene are readily soluble in this solvent at 15°). The van't Hoff *i*-factor is 5 (4.97, 4.79, 4.96, 5.16) and is unaltered after 24 hours.[3] The spectrum in 100% sulfuric acid showed the following $\lambda_{\max}$ in mμ (ϵ): 545 (1031), 393 (16,160), 265 (3860) and 235 (5120), with an inflection at 382 mμ of slightly lower intensity than the 393 mμ band. Such solutions, when poured on ice or cold methanol, gave pentamethylbenzoic acid, m.p. 208–210°,[4] or its methyl ester, m.p. 67–67.5°, respectively, in essentially quantitative yield. When a stream of dry nitrogen was passed through a cold solution of I in 100% sulfuric acid, *two* moles of hydrogen chloride were collected in an alkaline trap within fifteen minutes; twelve more hours gave essentially no additional hydrogen chloride. The remaining solution had a spectrum identical with the original, an *i*-factor of 3 (2.91, 2.74) and when poured on ice gave pentamethylbenzoic acid essentially quantitatively; the third chlorine was accounted for in the water solution after hydrolysis.

Data to this point indicated that of the five particles produced when I dissolves in 100% sulfuric acid, two were hydrogen chloride, and that no drastic structural changes occurred. It seemed reasonable that the two hydrogens (for the hydrogen chloride) must come from the solvent, requiring that two bisulfate ions be produced, and that the fifth particle have two positive charges and be capable of producing a chloride ion and pentamethylbenzoic acid on hydrolysis.

It seemed necessary to demonstrate experimentally that indeed two bisulfate ions were formed. The elegant work of Gillespie and Wasif[5] clearly demonstrated that the principal conducting particle produced when bisulfates are dissolved in 100% sulfuric acid is the bisulfate ion, and that one can determine from molar conductivity the number of bisulfates produced per mole of solute. The molar conductivity[3] of solutions of I in 100% sulfuric acid (see Table) are consistent only with the production of two bisulfate ions.

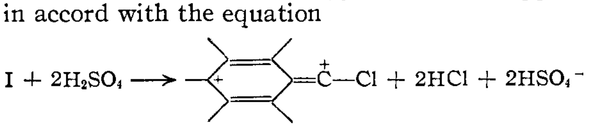
TABLE I

MOLAR CONDUCTIVITIES IN 100% H_2SO_4 AT 25°

M	$KHSO_4$	o-C_6H_4-$(NH_2)_2$	I
0.05	...	304 (306)[a]	304
0.10	157 (156)[a]	212 (236)	213
0.20	122 (116)	164 (187)	155

[a] Values in parentheses are taken from Gillespie and Wasif, ref. 5.

The ionization of I in 100% sulfuric acid appears in accord with the equation



II

ion II having numerous contributing structures and being responsible for the color. Relief of steric strain and the need to produce a linear substituent may be factors in its formation. The same species (II) appears to be produced when I is dissolved in nitromethane containing a large molar excess of aluminum chloride ($\lambda_{\max}$ (ϵ) = 542 (1032), 395 (14,610), inflection at 385 mμ).

Extensions to related systems, and to other possible sources of dipositive carbonium ions are being investigated.

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(1) First presented at the 7th Organic Reaction Mechanisms Conference, University of Chicago, Chicago, Illinois, September 3, 1958.

(2) We are indebted to Dr. R. J. Rolih, Standard Oil Company (Indiana), Whiting, Indiana, for samples of this compound, and for its method of synthesis.

(3) We are indebted to Professor James L. Dye for preliminary van't Hoff *i*-factor determinations, and for invaluable assistance with the cryoscopic and conductance measurements.

(4) O. Jacobsen, *Ber.*, **22**, 1215 (1889), reported 210 and 67° for the acid and methyl ester, respectively.

(5) R. J. Gillespie and S. Wasif, *J. Chem. Soc.*, 204, 209, 221 (1953).

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TRIPHOSPHONITRILIC HEXA-ISOTHIOCYANATE[1]

Sir:

Many attempts have been made to replace the chlorine atoms of the phosphonitrilic chlorides by other structural units in order to prepare derivatives which might then be subjected to polymerization to yield elastomeric inorganic–organic polymeric products of greater hydrolytic and thermal stability. The chlorine atoms have been replaced partially and/or completely by the solvolytic action of water, alcohols, ammonia, amines, and most recently, of hydrazine.[2] Except for evidence that the chlorine atoms can be replaced by azide groups, no previous attempts have[3] been reported entailing introduction of other halogenoid groups

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(1) This research was supported by Contract AF 33(616)-5486 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. Reproduction of this Communication in whole or in part is permitted for any purpose of the United States Government.

(2) R. J. A. Otto and L. F. Audrieth, THIS JOURNAL, **80**, 3575 (1958).

(3) C. Grundmann and R. Rätz, *Z. Naturforschung*, **10B**, 116 (1955).