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).

[8] This investigation at Western Reserve University was supported in part by a grant (Contract No. AT(30-1)-1050) from the Atomic Energy Commission, and in part by a research grant (E-253) from the United States Public Health Service.

DEPARTMENT OF MICROBIOLOGY
SCHOOL OF MEDICINE
WESTERN RESERVE UNIVERSITY
CLEVELAND 6, OHIO
LESTER O. KRAMPITZ[8]
GERHARD GREULL
MERCK SHARP AND DOHME RESEARCH LABORATORIES
DIVISION OF MERCK AND CO., INC.
WEST POINT, PENNSYLVANIA
CHARLES S. MILLER
JOHN B. BICKING
HELEN R. SKEGGS
JAMES M. SPRAGUE

RECEIVED AUGUST 21, 1958

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.

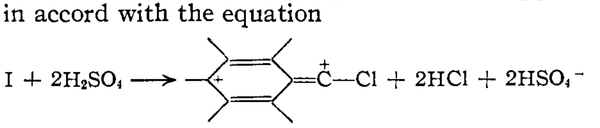
TABLE I

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.

---

[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).

KEDZIE CHEMICAL LABORATORY
MICHIGAN STATE UNIVERSITY
EAST LANSING, MICHIGAN
HAROLD HART
RICHARD W. FISH

RECEIVED SEPTEMBER 17, 1958

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

---

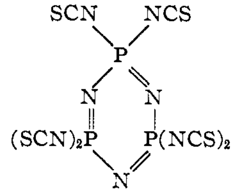
[1] This research was supported by Contract AF 33(616)-5486 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. Reproduction of this Communication in whole or in part is permitted for any purpose of the United States Government.

[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).

in the inorganic, but aromatic-like triphosphonitrilic ring system.

We have found that the interaction of potassium thiocyanate and triphosphonitrilic chloride in acetone results in the rapid quantitative precipitation of potassium chloride with formation of the triphosphonitrilic hexa-isothiocyanate which can be recovered from the solvent medium as a white crystalline product melting at 42°. Analytical data verify complete replacement of chlorine atoms by thiocyanate groups. (Calcd. for $P_3N_3(NCS)_6$: P, 19.2; S, 39.5; C, 14.8; N, 26.1. Found: P, 19.8, 19.7; S, 39.5, 40.1; C, 15.1; N, 26.0). Molecular weights were determined cryoscopically in benzene (calcd. for $[PN(NCS)_2]_3$, 483. Found, 466, 475, 479, 488). Strong absorption in the infrared at ~1200 cm.$^{-1}$ indicates retention of the trimeric P_3N_3 ring system.[4] Two other strong absorptions at 1016 cm.$^{-1}$ and 1960 cm.$^{-1}$ suggest that the product contains the isothiocyanate[5] grouping. The product therefore can be represented by the structural formula



The triphosphonitrilic hexa-isothiocyanate undergoes polymerization to an elastomeric product by heating in vacuum at 150°. It has been found to react with a wide variety of active hydrogen compounds such as ammonia, amines, alcohols, hydrazine and substituted hydrazines to give condensation products, characteristic of substances containing the isothiocyanate group.

(4) L. W. Daasch, THIS JOURNAL, **76**, 3403 (1954).

(5) J. Goubeau and J. Reyling, *Z. anorg. allgem. Chem.*, **294**, 96 (1958).

NOYES LABORATORY OF CHEMISTRY
UNIVERSITY OF ILLINOIS R. J. A. OTTO
URBANA, ILLINOIS L. F. AUDRIETH

RECEIVED SEPTEMBER 27, 1958

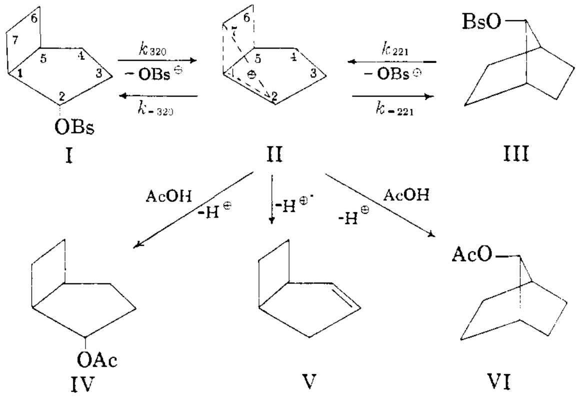
A TRICYCLOHEPTONIUM NON-CLASSICAL CATION[1]

Sir:

An instructive example of carbon participation in solvolysis is available in acetolysis of *trans*-2-bicyclo[3.2.0]heptyl and 7-bicyclo[2.2.1]heptyl *p*-bromobenzenesulfonates, I and III, respectively.

The *trans*-2-bicyclo[3.2.0]heptanol, m.p. of I 61–62°, was available from hydrogenation of the predominantly *trans* 2-bicyclo[3.2.0]heptene-4-ol, the allylic alcohol from solvolysis of *syn*-7-norbornenyl toluenesulfonate.[2] Ester I acetolyzes with extensive rearrangement[3] and ion pair return. In acetic acid solvent at 50°, the product contains 83% of 7-bicyclo[2.2.1]heptyl bromobenzenesulfonate III. Of the remaining 17% of product analyzed by vapor phase chromatography, 94% is the rearranged acetate VI, 5% is the unrearranged acetate IV and 1% is the unrearranged olefin[4] V. The per cent. of III obtained varies from 86 at 25° to 79 at 100°.

Ionization of the 2-bicyclo[3.2.0]heptyl bromobenzenesulfonate I is clearly anchimerically accelerated, the rate constant for acetolysis at 50°, 5.66 × 10^{-4} sec.$^{-1}$, being some 10^2 times that of the epimeric *cis*-isomer. The corresponding *cis*-alcohol, m.p. of bromobenzenesulfonate 57–59°, was obtained by lithium aluminum hydride reduction of the corresponding ketone.



The product of acetolysis of the very unreactive[5] 7-bicyclo[2.2.1]heptyl bromobenzenesulfonate III at 205° for one hour contains 91% unrearranged acetate VI, 7% rearranged acetate IV and 2% rearranged olefin V. Formation of the 2-bicyclo[3.2.0]heptyl acetate from I and III is stereospecific, none of the *cis*-isomer of acetate IV being observed.

The observed results indicate formation of the common bridged ion II by ionization of either I or III. Ion pair return at C_1 gives rise to III. Acetates IV and VI arise from solvent attack at C_2 and C_1, respectively, while olefin V presumably arises from proton loss from C_3. The effect of temperature on the product composition shows that the energy of activation for formation of solvolysis product exceeds that for ion pair return by 1.3 kcal./mole. Also, the energies of activation for solvent reactions at C_2 and C_3 are higher than that for solvent attack at C_1 by 0.7–1.4 kcal./mole.

An estimate of the difference in ground state free energies of esters I and III may be based on the available kinetic information. As shown in equation 1, K_e, the equilibrium constant between the two materials, is the product of two ratios, (k_{221}/k_{320}) being the ratio of rates[5] of ionization, *ca.* 10^{-9} at 25°, and (k_{-320}/k_{-221}) being the partition factor for reaction of the intermediate cation II with bromobenzenesulfonate ion. Approximating the partition

$$K_e = \frac{[3.2.0]}{[2.2.1]} = \left(\frac{k_{221}}{k_{320}}\right)\left(\frac{k_{-320}}{k_{-221}}\right) \qquad (1)$$

---

(1) (a) This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund; (b) research sponsored by the Office of Ordnance Research, U. S. Army; (c) research supported in part by the National Science Foundation.

(2) S. Winstein and E. T. Stafford, THIS JOURNAL, **79**, 505 (1957).

(3) P. Schleyer, *ibid.*, **80**, 1700 (1958), recently has quoted the unpublished observation that hydration of olefin V gives rise to 7-bicyclo[2.2.1]heptanol.

(4) A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

(5) (a) C. Norton, Dissertation, Harvard University, 1955; (b) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955).