process dark, gummy material precipitated until about two thirds of the original volume of liquid remained, at which time a yellow solid began to precipitate. At this point the clear solution was decanted again from the solid and evaporated to dryness under reduced pressure. Recrystallization of the yellow residue (20 g.) from 500 ml. of benzene-ethyl acetate (12:1) gave 16 g. of yellow amorphous solid, m.p. 120–123°. An analytical sample was prepared by two more crystallizations from benzene, carried out quickly in order to minimize decomposition. Samples stored at room temperature underwent considerable darkening after several days. The infrared spectrum (potassium bromide) showed bands at 2.95 μ (NH), 3.35 μ (CH), 4.45 μ and 4.55 μ (conjugated $C{\equiv}N$), 5.74 μ (ethoxycarbonyl), and 6.25 μ (conjugated $C{=}C$ or $C{=}N$). The ultraviolet spectrum (ethanol) showed absorption peaks at 423 mμ ($\epsilon\lambda_{max}$ 2200), 273 mμ ($\epsilon\lambda_{max}$ 1840), 245 mμ ($\epsilon\lambda_{max}$ 4600) and 215 mμ ($\epsilon\lambda_{max}$ 5330).

Anal. Calcd. for $C_{10}H_6N_6O_2$: C, 49.59; H, 2.50; N, 34.70; mol. wt., 242. Found: C, 50.05; H, 2.66; N (Dumas) 33.56, 33.81; N (Kjeldahl) 24.02, 23.89; mol. wt. (ebullioscopic in acetone) 233, 259.

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Improved Preparation of Triphenylmethyl Perchlorate and Fluoroborate for Use in Hydride Ion Exchange Reactions[1]

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Received March 7, 1960

The synthesis of tropenium (cycloheptatrienylium) salts by hydride ion abstraction from cycloheptatriene by trityl (triphenylmethyl) carbonium ion[4] has been extended recently to the preparation of a series of substituted tropenium ions,[5] several π-tropenium ion-metal carbonyl complexes,[6,7a] perinaphthenium ion,[7a] triphenylcyclopropenium ion,[7b] and various substituted triphenylmethylcarbonium ions.[7b]

$$R{-}H + (C_6H_5)_3C^+,Y^- \longrightarrow R^+,Y^- + (C_6H_5)_3CH$$

In the course of these studies it was found that when trityl halides were used as the hydride ion abstracting reagents, reaction was slow (except in sulfur dioxide solvent) and halide salts formed frequently had undesirable properties, *e.g.*, tropenium chloride and bromide were quite hygroscopic,[5,8] some substituted tropenium ions reacted with halide ions at their substituent groups,[5] and perinaphthenium halides were found to be only transiently stable.[7a] For these reasons, use of other trityl salts, particularly those with anions of low nucleophilicity, was investigated. Trityl perchlorate and trityl fluoroborate were found to give rapid hydride ion exchange in a number of different solvents and aromatic carbonium ion salt products of unusual stability.[4–7] The consequent need for convenient routes to these trityl salts led to an examination of the known preparative methods, and has resulted in a simplified procedure for the preparation of trityl perchlorate and a convenient new synthesis of trityl fluoroborate.

Trityl perchlorate has been prepared by essentially three different methods: (i) from trityl chloride and silver perchlorate in nitrobenzene on precipitation by benzene addition[9]; (ii) from trityl chloride or triphenylcarbinol in nitrobenzene or ether and 71% perchloric acid, followed by removal of all water by evaporation in a desiccator[9,10]; and (iii) from triphenylcarbinol in acetic anhydride and 71% perchloric acid, the product separating partially from concentrated solution, or by evaporation of dilute solutions in a vacuum desiccator.[10] Method i suffers from the disadvantages of the need for prior preparation of trityl chloride and the use of explosive silver perchlorate, and method ii requires complete removal of water by slow, and potentially dangerous, evaporation. Method iii, on the other hand, employs a convenient starting material and removes the water by reaction with acetic anhydride, but possesses the disadvantage, even when run in concentrated solution, of furnishing conveniently and directly only moderate yields of pure product. However, because of the lower solubility of the salt product in acetic anhydride than in acetic acid, conduct of the reaction of triphenylcarbinol and 71% perchloric acid in an adequate excess of acetic anhydride leads to the direct separation of yellow crystals of trityl perchlorate in 76–92% yield. Circumvention of the evaporation step not only greatly simplifies the preparation but also avoids formation of a dark-colored product that is not satisfactory for most hydride ion exchange reactions; decomposition of substituted tropenium

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[4] H. J. Dauben, Jr., and D. L. Pearson, Abstracts, 126th Meeting, American Chemical Society, New York, N. Y., Sept. 13, 1954, p. 18-O.

[5] (a) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957); (b) H. J. Dauben, Jr. and K. M. Harmon, Abstracts, 134th Meeting, American Chemical Society, Chicago, Ill., Sept. 9, 1958, p. 35-P; (c) K. M. Harmon, Ph.D. thesis, University of Washington, 1958.

[6] H. J. Dauben, Jr. and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958); Abstracts, 15th Southwest Regional Meeting, American Chemical Society, Baton Rouge, La., Dec. 3, 1959, p. 89.

[7] (a) L. R. Honnen, Ph.D. thesis, University of Washington, 1960; (b) L. L. McDonough, Ph.D. thesis, University of Washington, 1960.

[8] *Cf.* W. v. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

[9] M. Gomberg and L. H. Cone, *Ann.*, **370**, 142 (1909).

[10] K. A. Hofmann and H. Kirmreuther, *Ber.*, **42**, 4856 (1909).

and perinaphthenium perchlorate salt products appears to be strongly influenced by impurities in the trityl salt use in the exchange reaction.

Trityl fluoroborate has been prepared by Seel[11] from trityl chloride or tritanol and preformed acetyl fluoroborate in chloroform or sulfur dioxide, followed by ether precipitation, or from the chloride with equivalent amounts of acetyl fluoride and boron trifluoride on similar work-up. These related methods give good yields but are inconvenient to use routinely, primarily because of difficulties involved in the preparation of the acetyl fluoride and acetyl fluoroborate reactants. Witschonke and Kraus[12] have employed addition of boron trifluoride to trityl fluoride in benzene for the preparation of the fluoroborate salt but the properties reported for their trityl fluoride and fluoroborate products are probably indicative of the presence of impurities. Similar difficulty in the preparation of pure trityl fluoride has been encountered by others.[5c,13] As neither method provides a convenient route to this salt from readily available reactants, attempts were made to adapt the excess acetic anhydride method to the preparation of trityl fluoroborate. Triphenylcarbinol and 48% fluoroboric acid in acetic anhydride produce trityl fluoroborate but due to its greater solubility, compared with trityl perchlorate, direct separation of the product may not be effected by the use of excess acetic anhydride, and only moderate yields may be realized by addition of large volumes of dry ether. However, conduct of the reaction of tritanol with 48% fluoroboric acid in excess propionic anhydride furnishes directly on cooling yellow crystalline trityl fluoroborate in 95% yield. Trityl fluoroborate prepared by this extremely convenient procedure is very satisfactory for use in hydride ion exchange reactions, and has been used to prepare fluoroborate salts of a number of different types of aromatic carbonium ions.

When first prepared both of these trityl salts are brilliant yellow to orange compounds, depending on crystal size, and both contain traces of acid anhydride solvent, which does not interfere with the hydride ion exchange reaction but may be removed almost completely by trituration with dry ether. Recrystallization of both salts may be effected from minimum quantities of acetonitrile, but recoveries are low unless the mother liquor is recycled. In most organic solvents trityl fluoroborate is appreciably more soluble than trityl perchlorate. Trityl perchlorate keeps well in the dark at deep-freeze temperatures but darkens on exposure to light; the causative factors and the course of this decomposition are not fully known but low yields of 9-phenylfluorene have been isolated from darkened samples.[14] Trityl fluoroborate is much more stable and, once dried, may be stored in a desiccator without protection from light. This increased stability, coupled with the explosive nature of the perchlorate salts of trityl and tropenium ions (particularly when complexed with metal carbonyls[6,7a]), makes trityl fluoroborate the preferred compound for the preparation of aromatic carbonium ion salts by the hydride ion exchange reaction.

For routine preparations it is not necessary to isolate the trityl salt before conducting the hydride ion exchange reaction. For example, tropenium fluoroborate may be prepared in quantity and in good yield (89%) from triphenylcarbinol, 48% fluoroboric acid and cycloheptatriene in essentially a single step by adding cycloheptatriene to the yellow solution of triphenylcarbinol and fluoroboric acid in acetic anhydride until the color is discharged and then flooding with ether to effect separation of the product. Use of acetic, rather than propionic, anhydride in this sequence avoids separation of the trityl fluoroborate and thereby enables rapid and complete hydride ion abstraction on addition of the cycloheptatriene. Caution should be used in extending this simplified procedure to the preparation of tropenium perchlorate as darkened samples result, and impurities are known to increase the shock sensitivity of this explosive product.

Impurities in the triphenylcarbinol reactant markedly affect the color and the stability of the trityl perchlorate or fluoroborate produced by the above methods. Commercially available samples of triphenylcarbinol vary in color from white to yellow and it has been found that only white samples that give colorless solutions in the acid anhydride furnish products with good color and stability. The yellow impurities in commercial triphenylcarbinol usually can be removed by chromatography over alumina using 25% benzene-75% pentane as eluant and subsequent evaporative recrystallization from acetone or benzene. Satisfactory triphenylcarbinol may also be synthesized by a modification of the standard method of preparation of trityl chloride[15] as described in the Experimental.

EXPERIMENTAL

Triphenylcarbinol. The procedure of Hauser and Hudson[15] for the synthesis of trityl chloride was modified and the work-up of the reaction mixture altered so as to effect hydrolysis to the carbinol. Pure white, commercially sublimed aluminum chloride (Baker and Adamson; 425 g., 3.19 moles) was placed in a 5-l. three-necked flask equipped with a mechanical stirrer, a large Allihn condenser, and a 500-ml.

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[11] F. Seel, *Z. anorg. allgem. Chem.*, **250**, 331 (1943).

[12] C. R. Witschonke and C. A. Kraus, *J. Am. Chem. Soc.*, *69*, 2472 (1947).

[13] C. G. Swain and R. B. Mosely, *J. Am. Chem. Soc.*, **77**, 3727 (1955).

[14] On the other hand, it has been reported that surface darkening of trityl perchlorate crystals does not alter their X-ray pattern nor affect conductivity of their solutions (private communication from N. N. Lichtin, Boston University).

[15] C. R. Hauser and R. E. Hudson, Jr., *Org. Syntheses*, **Coll. Vol. III**, 842 (1955).

pressure-equalizing dropping funnel, and thiophene-free benzene (Baker and Adamson Reagent Grade; 1.30 l., 14.6 moles) added with stirring and external cooling in an ice bath. A solution of carbon tetrachloride (Baker Analyzed; 335 ml., 3.48 moles) in benzene (0.50 l., 6.63 moles) was added with continued stirring and ice bath cooling over the period of about 90 min.; adequate cooling must be used to moderate the quite exothermic reaction. Stirring of the dark red reaction mixture was continued for 30 min. in the ice bath and for about 8 hr. at room temperature. The reaction mixture was poured into an enamel bucket half-filled with chopped ice and the bucket heated on a steam cone until all of the red color of the aluminum chloride complex had disappeared. The separated benzene layer was washed thoroughly several times with water and twice with dilute sodium hydroxide, concentrated until almost all solvent had been removed, and allowed to cool to room temperature before placing in a refrigerator to crystallize. Separation of the successive crops by concentration of mother liquors and recrystallization from the recovered benzene by the usual cascade procedure gave four crops of triphenylcarbinol: (i) 249 g., white, m.p. 162.5°; (ii) 243 g., very slightly yellow, m.p. 161.5–162.5°; (iii) 118 g., tan, m.p. 159.5–161.5°; (iv) 34 g., brown, m.p. 152–158°; total yield, 644 g., 77%. Material from the first three crops is satisfactory for the preparation of trityl perchlorate or fluoroborate.

Triphenylmethyl perchlorate. Triphenylcarbinol (20.0 g., 0.077 mole) was dissolved in acetic anhydride (Mallinckrodt Reagent Grade; 225 ml., 2.38 moles) in a 500-ml. round bottomed flask fitted with a drying tube by warming on a steam cone. After cooling to room temperature or slightly below, 71% perchloric acid (Baker and Adamson Reagent Grade; 15 ml., 0.18 mole) was added in portions (0.5 ml.) with cooling at such a rate that the temperature was maintained at or slightly below room temperature to avoid formation of a darkened product; cooling during addition of the first third of the perchloric acid is done best under a stream of tap water to avoid cocrystallization of triphenylcarbinol and trityl perchlorate, after which an ice bath may be used. Separation of the perchlorate salt began during addition of the first few portions of perchloric acid and was completed, after all of the perchloric acid had been added, by cooling in an ice bath for at least 30 min. As moisture in the air rapidly hydrolyzes the product on simple suction filtration, removal of the mother liquor is effected best by use of a large dropper. The moist crystalline residue was rinsed with dry ether (5 × 25 ml.), the ether rinses removed by a dropper, and the yellow crystals of trityl perchlorate dried in the flask by evacuation before transferral to a tightly stoppered amber bottle for storage in a deep-freeze refrigerator; yield, 85% (22.5 g.). Cold, dry ethyl acetate or acetonitrile, followed by dry pentane, also may be used for rinsing without appreciable decrease in yield. The product contains a trace of acetic anhydride impurity, which does not interfere with its use in hydride ion exchange reactions, and may be removed by recrystallization from a minimum volume of hot, dry acetonitrile. Recovery of trityl perchlorate as yellow prisms, m.p. 143° (lit.,[10] m.p. 143–144°), was only 40–50% but may be increased by reuse of the mother liquor as solvent for recrystallization of successive portions. Somewhat larger proportions of the acetic anhydride and perchloric acid reactants may be used to lessen the possibility of cocrystallization of triphenylcarbinol and trityl perchlorate during the reaction; triphenylcarbinol (1.0 g., 0.0038 mole), acetic anhydride (15 ml., 0.16 mole), and 71% perchloric acid (1.25 ml., 0.015 mole) by the above procedure gave a yield of 76% (1.0 g.), and cooling of the mother liquor in a deep-freeze refrigerator furnished an additional 16% (0.21 g.).

A dry solid sample of trityl perchlorate (*ca.* 2 g.) in a stoppered flask exposed to ordinary overhead fluorescent lights for about 2 weeks gradually darkened to a deep red-purple color. The solution resulting from partial dissolution of this darkened sample in acetonitrile (*ca.* 4 ml.) and treatment with pentane (*ca.* 100 ml.) was decanted and evaporated to dryness. Chromatography of a pentane solution of the residue on alumina using pentane as a developer gave as the first fraction, on evaporation, a colorless crystalline residue (85 mg., *ca.* 6%) of 9-phenylfluorene, m.p. 146–146.5° after three recrystallizations from pentane (lit.,[16] m.p. 147–148°); $\lambda_{\max}^{\mathrm{CH_3CN}}$, 258(sh), 265, 275(sh), 292, and 303.5 mμ, virtually identical with that reported[17] for 9-phenylfluorene in ethanol. Other materials from the chromatogram were isolated in quantities too small to identify.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.17; H, 5.82. Found: C, 93.85; H, 5.89.

Triphenylmethyl fluoroborate. In a 1-l. round bottomed flask equipped with a drying tube triphenylcarbinol (45 g., 0.17 mole) was dissolved in propionic anhydride (Distillation Products White Label Grade, redistilled; 450 ml., 3.49 moles) by warming on a steam cone. After cooling to about 20° under a water tap, 48% fluoroboric acid (Harshaw Chemical Co.; 45 ml., 0.38 mole) was added in small portions (*ca.* 0.5 ml.) with swirling and cooling under a water tap so as to maintain temperature at 15–25°; excessive heating or excessive cooling (induces cocrystallization of triphenylcarbinol) must be avoided to obtain a satisfactory yield of pure product. Separation of yellow crystals of trityl fluoroborate began well before an equivalent of the acid had been added and was completed, after the remaining acid had been added, by cooling in an ice bath for about 30 min. The bulk of the supernatant liquid was removed by decantation and discarded, as little trityl fluoroborate is recoverable from this mother liquor. Residual amounts of solvent were removed by a large dropper and the mass of crystals triturated with portions of cold, dry ether (25 ml.) until the washings, also removed by a dropper, were colorless (*ca.* 5 washings); prolonged contact with ether should be avoided, as trityl fluoroborate (or perchlorate) slowly abstracts hydride ion from ether to produce triphenylmethane. Rinsing by cold, dry ethyl acetate followed by dry pentane, may also be used, but with slight decrease in yield. Vacuum drying of the moist residue in the flask afforded yellow crystals of trityl fluoroborate (54 g., 95%) suitable for use in hydride ion exchange reactions. Removal of residual traces of propionic anhydride may be effected by recrystallization from a minimum volume of hot, dry acetonitrile with only low recovery (*ca.* 25%) unless a recycling technique is employed; use of a small volume of solvent, removal of the hot solution by a dropper, cooling to effect crystallization, and continued reuse of the saturated mother liquor for recrystallization of successive portions gave greatly increased recovery; yellow prisms, m.p. *ca.* 200° dec.[18] (lit., m.p. 215° dec.,[11] m.p. 195–196°[12]). Recrystallized trityl fluoroborate may be stored in a tightly stoppered bottle or in a desiccator over a good desiccant at room temperature and exposed to light without discoloration or decomposition for a period of at least several months.

Tropenium fluoroborate by in situ technique. Triphenylcarbinol (40 g., 0.165 mole) was dissolved in acetic anhydride (400 ml., 4.23 moles) by heating on a steam cone in a 1-l. round bottomed flask. After cooling to room temperature, 48% fluoroboric acid (25 ml., 0.21 mole) was added

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(16) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 708 (1930).

(17) R. N. Jones, *J. Am. Chem. Soc.*, **67**, 2021 (1945).

(18) Trityl fluoroborate shows no real melting point but decomposition with blackening and gas evolution usually begins around 200°; a sample recrystallized from propionic anhydride showed the highest initial decomposition range, 207–210°. The melting point of 215° dec. reported by Seel[11] is probably somewhat too high, as the melting point given for triphenyl carbinol in the same paper is at least 5° higher than any found in the literature or in the present work.

in portions with external cooling by cold water to maintain this temperature, and then cycloheptatriene (91% cycloheptatriene-7% toluene sample, generously supplied by the Shell Chemical Co.) added with swirling to the solution in an ice bath until the characteristic yellow color of trityl carbonium ion had vanished and precipitation of tropenium fluoroborate had commenced. Dry ether (600 ml.) was added to precipitate the remainder of the salt, and the white microcrystalline product filtered and washed with ether; yield of tropenium fluoroborate, 89% (23.5 g.), m.p. *ca.* 210° dec.,[19] $\lambda_{max}^{96\%\ H_2SO_4}$ 273.5 mμ (ϵ 4320) (lit.[5a]: m.p. >210° dec., $\lambda_{max}^{96\%\ H_2SO_4}$ 273.5 mμ (ϵ 4350)).

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(19) Tropenium fluoroborate also does not show a definite melting point; darkening begins at about 210° and continues to about 260–270° where the last trace of crystal faces disappears and only a crumbled darkened powder remains.

Triphenylmethyl Isothiocyanate

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Received January 15, 1960

This report deals with the structure of the product (I) m.p. 138–138.5°, which is obtained in the reaction of triphenylmethyl (trityl) halides (chloride or bromide) with alkali thiocyanates[1–3] or thiocyanic acid.[4] This compound is also referred to in the recent literature[2,5] as trityl thiocyanate. Experimental evidence obtained by us shows that the compound is trityl isothiocyanate.

The infrared absorption spectrum of I shows a complex band with a maximum at 2046 cm.$^{-1}$ (chloroform). Position, intensity, and form of the band are characteristic of isothiocyanates, and not of thiocyanates which show a weaker (by a factor of 10) sharp absorption band around 2150 cm.$^{-1}$ (These two bands have been ascribed to the asymmetric stretching vibration of the isothiocyano- and thiocyano- groups respectively.)[6]

Elbs reports that I can be distilled at high temperature without undergoing any change.[1] Its high thermal stability has been confirmed in an experiment, in which I was heated at 150° for two hours and was recovered unaltered. If I were a thiocyanate, one would expect it to isomerize readily under these conditions. This prediction is based upon the consideration of the thermal isomerization rate of arylmethyl thiocyanates: While benzyl thiocyanate is known to isomerize with great difficulty (repeated distillation at 250°),[7] benzhydryl thiocyanate isomerizes at a measurable rate at 70° (half-time, sixty-six hours in methyl ethyl ketone) and its 4-methyl derivative isomerizes with greater ease (half-time four hours under the same conditions).[8] This and other ancillary evidence (solvent and salt effects) all showing that the isomerization reaction proceeds through an electron deficient transition state, point out that the isomerization is facilitated by increasing the ability of the organic substrate to support a positive charge. The inference therefore is that trityl thiocyanate would isomerize very rapidly. The fact that upon heating, I remains unaltered indicates that it already is an isothiocyanate.

Thioureas can be obtained by the reaction of I with amines. Thus, allylamine reacts with I yielding an adduct which has been proved to be 1-trityl-3-allylthiourea.

Assumption that I is a thiocyanate has led in the past to some misunderstanding about its reactivity toward amines. Such is the case of Swain and Dittmer concerning the 'aminolysis' of I.[5] These workers report that, while aniline rather rapidly reacts with I giving the quaternary ammonium thiocyanate, no reaction is observed with *n*-butylamine, even after months.[9] It has been presently established that *n*-butylamine reacts readily with I, both in the pure state and in cyclohexane solution, to give an adduct which, while not showing any reaction of thiocyanate ion, appears to be 1-trityl-3-*n*-butylthiourea.

The above evidence points out the isothiocyanate structure of I. It must be emphasized, however, that owing to its organic residue, I is an isothiocyanate of a particular nature. The peculiarities of its chemical behavior arise from the stability of the trityl carbonium ion and the consequent cleavage, contrary to most isothiocyanates, of the alkyl carbon-to-nitrogen bond, (1):[10]

$$(C_6H_5)_3C\text{—}NCS \rightleftarrows (C_6H_5)_3C^+NCS^- \rightleftarrows (C_6H_5)_3C^+ + NCS^- \quad (1)$$

Because of this, the reaction of I with a nucleophile may frequently lead to displacement of the thiocyanate ion. In such cases, the familiar reactions of isothiocyanates with nucleophiles (arising from

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(1) K. Elbs, *Ber.* **17**, 700 (1884).

(2) C. G. Swain, C. B. Scott, and R. H. Lohmann, *J. Am. Chem. Soc.*, **75**, 136 (1953).

(3) H. Bredereck and E. Reif, *Ber.*, **81**, 426 (1948).

(4) E. Bilmann and N. V. Due, *Bull. Soc. Chim.*, [4], **35**, 384 (1929).

(5) C. G. Swain and D. C. Dittmer, *J. Am. Chem. Soc.*, **77**, 3924 (1955).

(6) For a detailed discussion of the infrared spectra of I and similar isothiocyanates see: U. Mazzuccato, A. Foffani, A. Iliceto, and G. Svegliado; paper presented at the meeting of European Molecular Spectroscopists, Bologna (Italy) Sept. 7-12 (1959).

(7) H. Hennicke, *Ann.*, **344**, 24 (1906).

(8) A. Iliceto, A. Fava, and U. Mazzuccato, *Tetrahedron Letters*, No. 11, 27 (1960).

(9) Swain and Dittmer's statement as to the unreactivity of I towards *n*-butylamine was based solely on the lack of formation of thiocyanate ions.[5]

(10) As expected, the cleavage occurs unimolecularly: This is shown by the solvolysis of I,[2] and by the kinetics of the isotopic exchange between I and labeled thiocyanate ions which is first order in I and zero order in SCN$^-$ (A. Iliceto, A. Fava, and S. Bresadola, to be published).