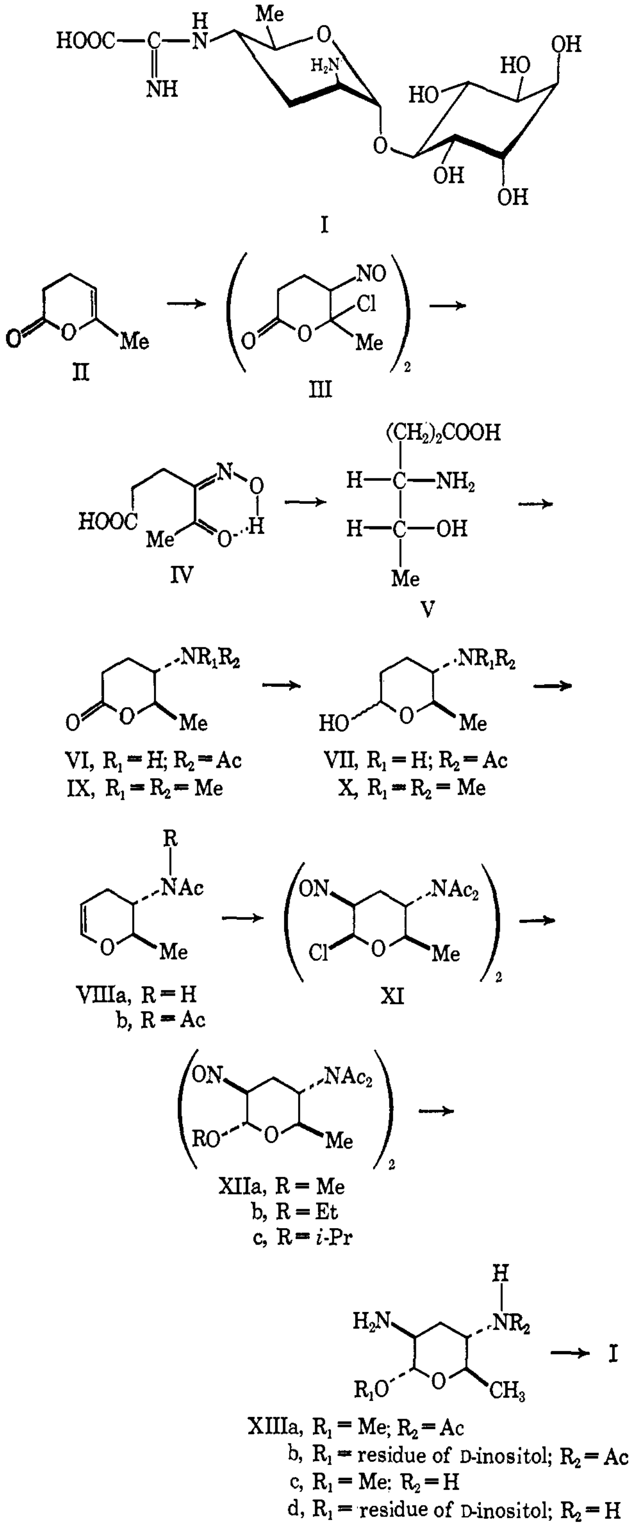
Chart I



by recrystallization from a mixed solvent of methanol and acetone, affording N^4-acetyldiamino sugar XIIIb, mp 139–142°, in low yield.[17] The synthetic material XIIIb was confirmed to be identical with the N-acetyl derivative[18] of natural kasuganobiosamine in all respects, including nmr, ir, optical rotation, and mixture melting point. The treatment of XIIIb with $Ba(OH)_2$ afforded kasuganobiosamine (XIIId). It is noteworthy that not only the displacement but also the resolution of XI has been carried out by the reaction with 1:2,3:4-di-O-isopropylidene-D-inositol, yielding the product stereochemically conforming with natural kasuganobiosamine, which is successfully crystallized in a pure state without any other procedure for the separation of the diastereoisomers. The synthesis of XIIId completes the total synthesis of kasugamycin, since kasuganobiosamine (XIIId) was previously converted to kasugamycin (I) by treatment with the diethyl ester of oxalimidic acid and subsequent mild hydrolysis with HCl in our structural studies.[2,19] (See Chart I for structures.)

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[17] Although the yield of the crude material was 10.5% based on XI, the most purified material with $[\alpha]^{20}D$ +116° (*c* 1.3, H_2O) was obtained in *ca.* 1% yield.

[18] Y. Suhara, K. Maeda, and H. Umezawa, *J. Antibiotics*, **18A**, 187 (1965).

[19] Satisfactory elemental analyses were obtained for all the compounds for which melting point or boiling point values were given. All the compounds cited showed reasonable spectral data. In the chart, compounds V to XIII are all racemic except XIIIb and XIIId, but only one member of the pairs is shown. The homogeneity of V and XIIa was confirmed by a combination of tlc, paper chromatography, and nmr methods.

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The Photochemical Synthesis of Thiocyanatobis(triphenylphosphine)copper(I)

Sir:

Organic azides are known to undergo several types of reactions. For example, organic azides react with olefins by 1,3 cycloaddition to form heterocyclic compounds which may decompose thermally or photolytically to yield a variety of products.[1,2] In analogy to organic azides, azido complexes of transition metals might be expected in some cases to undergo the same types of reaction. We therefore have undertaken a detailed study of the photochemistry of coordinated azides. Here we wish to report the photochemical synthesis of the thiocyanatobis(triphenylphosphine)copper(I) complex by the addition of CS_2 to azidobis(triphenylphosphine)copper(I) and its subsequent photolysis.

$((C_6H_5)_3P)_2CuN_3$[3] was prepared by the addition of a methanolic solution of NaN_3 to a chloroform solution containing cuprous chloride and excess $(C_6H_5)_3P$. The compound, mp 185° dec, has been compositionally identified by elemental analysis and a molecular weight determination in $CHCl_3$.[4] *Anal.* Calcd for $((C_6H_5)_3P)_2CuN_3$: C, 68.5; H, 4.75; N, 6.65; P, 9.75. Found: C, 68.3; H, 5.1; N, 6.75; P, 9.32. The N–N stretching[5] frequency of the azide is at 2045 cm^{-1}; mol wt: calcd, 629.5; found, 644. Judging from its composition and monomeric nature in solution we

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[1] R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, 565 (1963).

[2] R. F. Bleiholder and H. Shecter, *J. Amer. Chem. Soc.*, 90, 2131 (1968).

[3] W. Beck, M. Bauder, W. P. Fehlhammer, P. Pollmann, and H. Schachl, *Inorg. Nucl. Chem. Letters*, **4**, 143 (1968).

[4] Molecular weights were determined with a Mechrolab osmometer, Model 301A.

[5] Infrared measurements were made on a Beckman IR-5A using KBr disks.

believe that the azide complex has a trigonal-planar geometry.[6]

Addition of CS_2 to a chloroform solution of $((C_6H_5)_3P)_2CuN_3$ in a 1:1 mole ratio results in a clear yellow solution which, upon photolysis,[7] very rapidly evolves nitrogen, deposits colloidal sulfur, and leaves a colorless solution from which crystalline material was isolated. This crystalline material was shown to be $((C_6H_5)_3P)_2CuNCS$ on the basis of elemental analysis and its physical properties, which are identical with those of an authentic sample of $((C_6H_5)_3P)_2CuNCS$.[8] *Anal.* Calcd for $((C_6H_5)_3P)_2CuNCS$: C, 68.8; H, 4.65; N, 2.16; P, 9.60; S, 4.95. Found: C, 68.3; H, 4.53; N, 2.0; P, 8.88; S, 5.22. The C–N stretching frequency of the thiocyanate is at 2090 cm^{-1},[9] mp 210–213°. We can therefore write the following over-all reaction

$$((C_6H_5)_3P)_2CuN_3 + CS_2 \xrightarrow{h\nu} ((C_5H_5)_3P)_2CuNCS + S + N_2 \quad (1)$$

Since this is the first example of a photolytical conversion of a bonded azide to a bonded thiocyanate, we have decided to investigate this reaction in detail.

Prior to the photolysis we were able to isolate yellow crystalline material of the CS_2 adduct. On the basis of elemental and mass spectral analysis and a molecular weight determination in benzene, the compound is formulated as $((C_6H_5)_3PCuN_3 \cdot CS_2)_2$ (I). *Anal.* Calcd for $(C_6H_5)_3PCuN_3 \cdot CS_2$: C, 51.4; H, 3.38; N, 9.47; P, 7.0. Found: C, 50.94; H, 3.47; N, 9.20; P, 6.35. The molecular weight calculated for $((C_6H_5)_3PCuN_3 \cdot CS_2)_2$ was 887; found, 896. The loss of $(C_6H_5)_3P$ upon the formation of the yellow adduct was further verified by the isolation of triphenylphosphine from the filtrate of the CS_2 adduct. We also note that the complex $((C_6H_5)_3P)_2CuNCS$ can be obtained from I only if $(C_6H_5)_3P$ is added prior to the photolysis. In the absence of $(C_6H_5)_3P$ the products which are obtained from the photolysis of I are different, and these will be reported at a later date.

Of particular interest is the structure of the yellow CS_2 adduct.[10] The formation of I can be followed by the disappearance of the N–N stretching band of the azide and the appearance of a sharp band at 1235 cm^{-1} which can be associated with a thiocarbonyl group. It is therefore reasonable to suggest that the addition occurs at the azide moiety, possibly by a 1,3-dipolar cycloaddition. Although several possible structures could be formulated for I, we feel that we do not have compelling evidence for any particular one. We have, therefore, undertaken the study of the crystal and molecular structure of I by X-ray diffraction techniques.

Preliminary results indicate that the metal atom and the other donor atoms in azide complexes have marked effects on the photochemical behavior of the coordinated azides. In order to study these effects in detail we have prepared a series of azido complexes of Cu(I), Ag(I), Au(I), Ni(II), Pd(II), and Pt(II) with a variety of mono- and bidentate ligands containing phosphorus donor atoms, and we are currently studying the photochemical reactions of these species. The results of this study will be presented at a later date.

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[6] Crystal structure analysis of this complex is currently in progress.

[7] Photolysis was performed with a Hanovia Type L 450-W medium-pressure mercury lamp.

[8] $((C_6H_5)_3P)_2CuNCS$ was prepared by the addition of a methanolic solution of NaNCS to a chloroform solution containing cuprous chloride and an excess of $(C_6H_5)_3P$. The complex was recrystallized from a chloroform–ether solution.

[9] Although it is generally agreed that the N–C stretching frequency for an N-bonded NCS occurs below 2100 cm^{-1} (see, for example, A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 1665 (1965)), we do not rule out the possibility of an S-bonded thiocyanate in this complex.

[10] The adduct can be stored in the dark and under a nitrogen atmosphere for a long period of time with no apparent decomposition.

Gas-Phase Acidities of Alcohols. Effects of Alkyl Groups

Sir:

As part of our continuing studies of gas-phase acidities,[1] we wish to report the relative acidities of a series of simple aliphatic alcohols. This is the first direct measurement of these acidities,[2] and it provides a unique demonstration of the effect of alkyl groups in stabilizing charge. Making use of ion cyclotron resonance (ICR) spectroscopy and pulsed double-resonance studies, we have been able to detect reactions of type 1 and determine the sign of $\Delta H°$.[3] Assuming $\Delta S° = 0$, this provides a measure of relative acidities for reactions of type 1.

$$ROH + R'O^- \rightleftharpoons RO^- + R'OH \quad (1)$$

The following order of relative acidities has been found: neopentyl alcohol > *t*-butyl > isopropyl > ethyl > methyl > water; and *t*-butyl ≈ *n*-pentyl ≈ *n*-butyl > *n*-propyl > ethyl.

Formally, the energetics of acid ionization can be considered as the sum of three thermodynamic processes: bond dissociation energy (to a radical and a hydrogen atom), ionization potential of the hydrogen atom (to a proton), and electron affinity of the radical (to an anion).[4] Since in all of the simple aliphatic

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[1] J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 5636 (1968).

[2] V. L. von Trepka, *Z. Naturforsch.*, **18a**, 1122 (1963); D. Vogt and H. Neuert, *Z. Physik*, **199**, 82 (1967). These authors have observed the reactions of hydroxide ion with alcohols in the gas phase.

[3] All alcohols (except 1-butanol) were of reagent grade and were used without further purification. Degassed alcohol mixtures (1:1 gas phase, room temperature) were prepared on a vacuum line. The alcohol mixture was allowed to mix with a comparable amount of water vapor in the unheated manifold of the ICR spectrometer. For these mixtures, the ionization efficiency curves of all the alkoxide ions (as well as that of benzyl anion in the case of toluene) had a maximum ion intensity at 6.2 eV (uncor), identical with that for OH^-. Neither alkoxide nor benzyl anion could be observed unless water was present. However, this has created no difficulties in ordering these acidities, since water is the least acidic compound studied. The principal negative ion formed on electron impact with H_2O has been shown to be H^- (dissociative attachment, peak maximum 6.5 eV), and the principal negative ion–molecule reaction is the proton transfer from H_2O to H^-. See R. N. Compton and L. G. Christophorou, *Phys. Rev.*, **154**, 110 (1967), and references cited therein. Within the pressure range chosen for our studies, H^- could not be observed, possibly because of a fast reaction with water and/or alcohol.

Reactions were studied in the pressure range 1.0–2.5 × 10^{-6} torr using the pulsed double-resonance technique. See ref 1 for pertinent literature citations and a generalized description of the experiment and techniques used in studying gas-phase acidities. Transfer of only the hydroxylic proton was demonstrated with appropriate deuterium-labeled compounds.