chloride) was preferable in the reaction between I (X = H, Y = Me) and II (R = R′ = Ph) to give IV (X = H, Y = Me), mp 118–119°. Alternatively, the nitrilium salt [RC≡N⁺R]Z⁻ may be generated prior to the addition of the N-oxide. Otherwise, the process is the same. In another approach to aryl amination the decomposition of an aromatic diazonium salt in an acetonitrile solution of the pyridine N-oxide gave the nitrilium salt[3] *in situ* which reacted with the N-oxide.[4] The yields were much poorer, however, and many unwanted by-products were formed.

The method has been extended to five-membered-ring heterocycles. For example, 1-benzylbenzimidazole 3-oxide and N-phenylbenzimidoyl chloride in boiling chloroform gave N-(1-benzyl-2-benzimidazolyl)benzanilide (90%), mp 151.5–153.5°, which, on hydrolysis, gave 2-anilino-1-benzylbenzimidazole, mp 188–190°. We are studying the extensions of this process to other heterocyclic ring systems and to open-chain nitrones and the effect of a 3 substituent on the pyridine ring upon the orientation of the attacking group.

While this reaction bears a resemblance to the 1,3-dipolar addition of phenyl isocyanate to N-oxides[5,6] it appears to be more flexible[7] and, in addition, permits the isolation of the intermediate amides, not possible in the isocyanate procedure. The latter are important as potential analgetics or may be reduced, thus providing a convenient synthesis of tertiary amines, of value in the antihistamine field, for example. The heterocyclic amines now readily obtainable by these reactions had previously been accessible only by more tedious procedures and from starting materials (*e.g.*, substituted 2-bromopyridines) not as readily available as the required N-oxides.

In all of the reactions of pyridine N-oxides with N-phenylbenzimidoyl chloride, benzanilide was formed as a by-product and could be isolated before any water was added, though stringent precautions against the intrusion of moisture (preparation of imide chloride and addition to N-oxide carried out in a drybox under nitrogen) were taken. With pyridine N-oxide itself 3-chloropyridine was also isolated as a by-product by gas chromatography of the reaction mixture. Pathway b could account for these products and could also provide an alternate route to III and IV. This is similar to the mechanism proposed[8] for the formation of 3-methyl-5-*o*-tolylpyridine from 3-picoline and *o*-tolyllithium.

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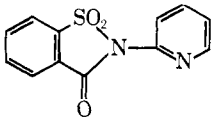
(3) H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Chem. Ber.*, **89**, 209 (1956).
(4) Preliminary work was carried out on this reaction by Mr. F. F. Gadallah.
(5) R. Huisgen, *Angew. Chem.*, 75, 604 (1963).
(6) S. Takahashi and H. Kanô, *Tetrahedron Lett.*, 1687 (1963); *Chem. Pharm. Bull.* (Tokyo), 12, 1290 (1964).
(7) For example, 3-chlorobenzoisothiazole 1,1-dioxide (ψ-saccharin chloride) reacts with pyridine N-oxide to give N-2-pyridylsaccharin (VIII), mp 210–211°.



VIII

(8) R. A. Abramovitch and G. A. Poulton, *Chem. Commun.*, 274 (1967).

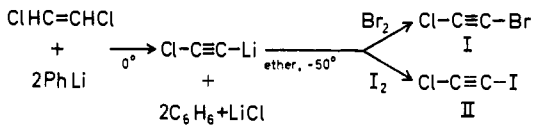
Preparation and Spectra of Pure Hetero and Homo Dihaloacetylenes

Sir:

Dihaloacetylenes, X—C≡C—Y (symmetry $C_{\infty v}$ (X ≠ Y) and $D_{\infty h}$ (X = Y) are obviously key compounds for experimental and theoretical studies of the properties of the carbon–carbon triple bond. However, their extreme chemical reactivity[1] has so far prevented their preparation in spectroscopically pure form and hence limited the investigation of their physical properties.[2,3] In this note we wish to report an alternative synthesis of the known homo dihaloacetylenes C_2Cl_2, C_2Br_2, and C_2I_2, and of the hetero dihaloacetylenes C_2BrCl and C_2ClI, hitherto unknown.[4] This method of preparation yields samples on a gram scale of a purity well in excess of those described so far in the literature, and has furthermore the advantage of allowing the handling of the highly explosive compounds in relative safety. As a consequence homo and hetero dihaloacetylenes are now available for thorough physical investigation.

The synthetic pathway for the new compounds bromochloroacetylene (I) (mp −54°; vapor pressure, 52 Torr (−1°); over-all yield 18.2%) and chloroiodoacetylene (II) (mp −37°; vapor pressure, 6 Torr (−1°); yield 26%) is summarized in Scheme I. Lithium

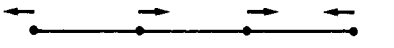
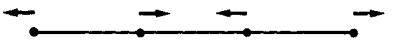
Scheme I



chloroacetylide, prepared[5] in ether solution under nitrogen from *cis*-1,2-dichloroethylene by the action of 2 equiv of phenyllithium at 0°, was allowed to react with molecular bromine or iodine at −50° to produce I and II, respectively. Dichloroacetylene (III) (mp −68 to −65°;[6] yield *ca.* 13%) and dibromoacetylene (IV) (mp −17°;[6] vapor pressure 13 Torr (−1°); yield 41%); were prepared as shown in Scheme II. Dilithium

(1) Only diiodoacetylene is a relatively stable compound.[2]
(2) For a comprehensive survey on haloacetylenes, *cf.* K. M. Smirnov, A. P. Tomilov, and A. I. Shchekotikhin, *Usp. Khim.*, **36**, 777 (1967); *Russ. Chem. Rev.*, **36**, 326 (1967), and references cited therein.
(3) Electron diffraction investigations; *cf.* H. de Laszlo, *Trans. Faraday Soc.*, 30, 825 (1934); O. Hassel and T. Taarland, *Tidsskr. Kjemi, Bergvesen Met.*, 1, 172 (1941).
(4) The English edition of ref 2 is erroneously translated regarding this statement.
(5) H. G. Viehe, *Chem. Ber.*, 92, 1950 (1959).
(6) F. Straus, L. Kollek, and W. Heyn, *ibid.*, 63, 1868 (1930), give mp −68 to −64° for dichloroacetylene and mp −25 to −23° for dibromoacetylene.

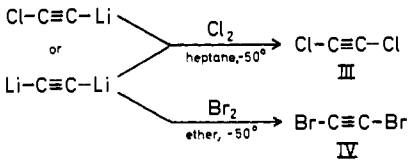
Table I. Observed Fundamental Frequencies (in cm^{-1}) and Vibrational Assignments of Dihaloacetylenes

ClC≡CBr I	ClC≡CCl II	ClC≡CCl III	BrC≡CBr IV	IC≡CI[c] V	Approximate motion XC≡CY	
2223	2191	2234[a,b]	2185[a,b]	2118[a,b]		-C≡C- str
923	886	988	832	720[a]		XC≡CY asym str
389	276[a,b]	477[a,b]	267[a,b]	190[a,b]		XC≡CY sym str
326[a,b]	325[a,b]	333[a,b]	311[a,b]	296[a,b]		XC≡CY bend
152	135	172	137	136[a]		XC≡CY bend

[a] Observed in solution. All other frequencies are vapor values. [b] In the Raman effect. [c] The spectral findings of diiodoacetylene are in good accordance with those of A. G. Meister and F. F. Cleveland, *J. Chem. Phys.*, **17**, 212 (1949); *J. Chim. Phys.*, **46**, 108 (1949), who measured all but the lowest band.

acetylide, prepared from acetylene with phenyllithium in ether, reacted (in heptane) with molecular chlorine to yield III; lithium chloroacetylide reacted similarly. In both cases phenyllithium was prepared from chlorobenzene. If the lithium base was made in the usual way from bromobenzene, the action of chlorine as well as bromine on dilithium acetylide gave dibromoacetylene (IV) exclusively.

Scheme II



When 1,2-dibromoethylene was treated with phenyllithium and iodine under similar conditions, the reaction failed to produce bromoiodoacetylene. Instead, diiodoacetylene (V) (m p 76.0°;[7] yield 18.2%) was isolated as the only reaction product.

All compounds can be gas chromatographed (except V) (Apiezon L, 50–90°). Samples were collected under helium at −80°, at which temperature the products crystallize as long needles.

The compounds have been identified by their mass spectra and by their vibration spectra. The five fundamental vibrations of the linear molecules, three stretching and two doubly denerate bending modes, have all been identified in the spectra. Table I gives the wave numbers and the assignments of the ir and Raman bands.[8]

Detailed descriptions of the preparative techniques and the vibrational spectra,[9] mass spectra, and photoelectron spectra will be published elsewhere.

(7) Several melting points varying from 74 to 82° are given in the literature.[2]

(8) The infrared spectra were recorded on Perkin-Elmer Model 225 and Beckman IR-9 spectrometers. A Michelson interferometer was employed in the far-infrared region. The Raman spectra were determined on a Cary 81 spectrometer with Spectra Physics Model 125 helium–neon laser.

(9) P. Klaboe, E. Kloster-Jensen, D. H. Christensen, and I. Johnsen, submitted for publication.

Acknowledgments. The author is indebted to Dr. P. Klaboe, University of Oslo, and Dr. D. H. Christensen, University of Copenhagen, for recording and interpretation of the infrared and Raman spectra. Financial support from the Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

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Chemistry of Cephalosporin Antibiotics. XVII. Functionalization of Deacetoxycephalosporin. The Conversion of Penicillin into Cephalosporin

Sir:

We wish to report conversions which, taken together with previous work from this laboratory,[1] constitute a transformation of the penicillin system into the cephalosporin system.

Morin and coworkers reported[1] the conversion of penicillin V *via* its methyl ester sulfoxide **1** into deacetoxycephalosporin V methyl ester (**2**). We now describe the conversion of the latter compound into cephalosporin V (**7b**).

Mild, controlled hydrolysis of methyl ester **2** in 1:1 pyridine–water with 1 equiv of sodium hydroxide afforded 7-phenoxyacetamido-3-methyl-2-cephem-4-carboxylate[1b] (**3a**, Δ^2-deacetoxycephalosporin V), mp 183–184°, in yields ranging from 45 to 60%. Acid **3a** was transformed in 90% yield into its *p*-methoxybenzyl ester **3b**,[2] mp 112–114°, by treatment with dimethylformamide dineopentyl acetal[3] and *p*-methoxy-

(1) R. B. Morin, B. G. Jackson, R. A. Mueller, E. R. Lavagnino, W. B. Scanlon, and S. L. Andrews, *J. Amer. Chem. Soc.*, **85**, 1896 (1963); (b) *ibid.*, **91**, 1401 (1969).

(2) All new crystalline compounds afforded excellent spectral and microanalytical data.

(3) H. Brechbühler, H. Büchi, E. Hatz, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **48**, 1746 (1965).