100% methylcyclohexane-isopentane and OD_{4800} = 1.16 in 95% methylcyclohexane–isopentane, 5% diethyl ether.

(d) In a matrix of tetrahydro-2-methylfuran containing biphenyl or naphthalene, addition of carbon tetrachloride suppresses formation of the corresponding aromatic hydrocarbon anions. Thus in systems containing 1 mole % naphthalene, G-($C_{10}H_8^-$) was 3.96, 1.50, 0.0 with 0, 0.16 and 1.57 mole % carbon tetrachloride, respectively.

(e) Irradiation of pure ethanol produces a broad absorption band at λ_{max} 5400 Å.[5] Illumination of the ethanol band with a 4760 Å. narrow band pass filter bleaches the entire band.

9 mole % carbon tetrachloride completely removes this band and 0.1 mole % biphenyl reduces the OD_{5400} from 0.71 for pure ethanol to a value OD_{5400} = 0.40, with the appearance of biphenyl anion bands.

(f) Yields of $C_{10}H_8^-$ per 100 ev. for 0.28 mole % naphthalene in 3-methylpentane for various additives were: none, 0.15; 1% isobutylene, 0.31; 5% isobutylene, 0.44; 5% methylcyclohexane, 0.42; 1% triethylamine, 0.36.

We interpret the preceding facts in this way: (a) in classical terms, "free" electrons are produced in condensed media with about the same G-(e^-) = 3 as in gases. The average electron encounters some 10^3 molecules, given by (mole fraction $C_{10}H_8)^{-1}$ at 50% attachment in tetrahydro-2-methylfuran.

(b) Electrons are trapped and solvated in tetrahydro-2-methylfuran, and presumably other polar media, since solvent color centers photolyze to produce $C_{10}H_8^-$ in presence of naphthalene.

(c) The color center is probably CCl_4^- since this should bleach readily by photoionization whereas a neutral entity could not be photolyzed readily in a rigid medium because of an exaggerated "cage effect" in the contracted solvent. In polar media one expects CCl_4^- to solvolyze because of the enhanced solvation energy for Cl^-, which is eventually converted to HCl. The result in tetrahydro-2-methylfuran indicates that CCl_3 does not absorb in the interval examined. If the color were due to a free radical, it should not be affected by adding ether to the matrix.

(d) The ability of carbon tetrachloride to suppress aromatic anion formation supports the view that it is an efficient reagent for "free" electrons.

(e) The phenomena of electron solvation, bleaching and solute effects are not specific to tetrahydro-2-methylfuran but extend to ethanol and, presumably, to various other polar media.

(f) Enhancement of $G(C_{10}H_8^-)$ in non-polar media by chemically unreactive solutes of relatively low ionization potential indicates positive hole migration and trapping. The large $G(C_{10}H_8^-)$ in tetrahydro-2-methylfuran can be attributed in part to ion–molecule reaction forming $C_5H_{10}OH^+$, thus trapping the positive hole.

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[5] R. S. Alger, T. H. Anderson, and L. A. Webb, *J. Chem. Phys.*, **30**, 695 (1959).

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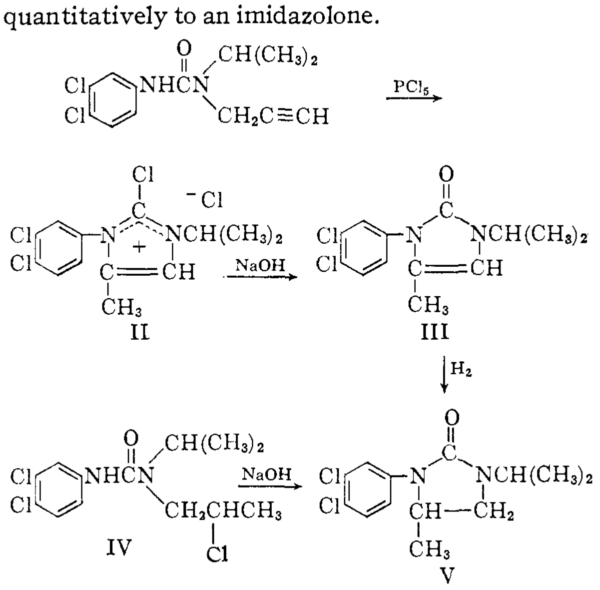
THE PREPARATION OF 2-IMIDAZOLONES: A NOVEL RING CLOSURE OF PROPYNYL UREAS WITH PHOSPHORUS PENTACHLORIDE

Sir:

We wish to report a novel ring closure effected by treating a propynyl urea with phosphorus pentachloride.[1] A stable imidazolium chloride is obtained which on treatment with base is converted quantitatively to an imidazolone.



The propynyl urea I with PCl_5 in refluxing benzene gives the cyclized imidazolium chloride II as a white hygroscopic crystalline solid, m.p. 275° dec. *Anal.* Calcd. for $C_{13}H_{14}Cl_4N_2$: C, 46.60; H, 4.13; Cl, 41.80; N, 8.25. Found: C, 46.40; H, 4.20; Cl, 41.95; N, 8.30. The infrared spectrum of II now shows a C=C absorption at 6.15 μ and no longer shows the C≡C band in the 4.5 μ region.

An aqueous solution of II, made slightly alkaline with NaOH, deposits the imidazolone III quantitatively: small white granules, m.p. 111.6–112.2°. *Anal.* Calcd. for $C_{13}H_{14}Cl_2N_2O$: C, 54.60; H, 3.70; Cl, 25.02; N, 9.62. Found: C, 54.75; H, 3.88; Cl, 24.95; N, 9.72.

The structural assignment for III and hence II is unambiguous as determined by proton nuclear magnetic resonance. The τ values for all protons are consistent for III[5]: a doublet at 8.72 τ (methyl

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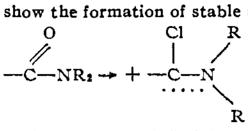
[1] The conversion of amides and ureas to imide chlorides by treatment with phosphorus pentachloride is well known. Recent reports[2,3,4] show the formation of stable amide chlorides of the type

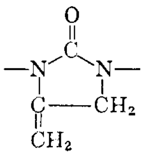


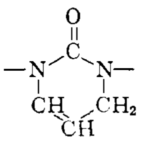
[2] I. Ugi and C. Steinbruckner, *Angew. Chem.*, **72**, 267 (1960).

[3] H. Eilingsfeld, M. Seefelder and H. Weidinger, *ibid.*, **72**, 836 (1960).

[4] F. Klages and W. Grill, *Ann.*, **594**, 21 (1955).

[5] The n.m.r. data rule out two alternate ring closures which can be postulated *a priori.*

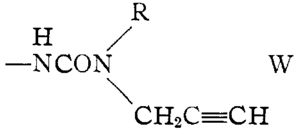




groups of isopropyl), a second doublet at 8.06 τ (CH_3 attached to a double bond) a quartet at 4.00 τ (single proton attached to olefin); the single proton of the middle carbon of isopropyl at 5.69 τ and the aromatic protons at 2.61 τ.

The fully saturated 2-imidazolidone V is obtained on hydrogenating III with platinum oxide in acetic acid as small colorless granules, m.p. 67.8–68.2°. *Anal.* Calcd. for $C_{13}H_{16}Cl_2N_2O$: C, 54.50; H, 5.58; Cl, 24.75; N, 9.77. Found: C, 54.10; H, 5.62; Cl, 24.80; N, 9.40. The infrared spectrum no longer shows the C=C band at 6.15 μ.

V is identified unequivocally by synthesis with the urea IV. IV is prepared following conventional procedures: 2-propanolamine → isopropyl-2-hydroxypropylamine → isopropyl-2-chloropropylamine → IV. IV is cyclized by treatment with sodium hydroxide in acetone to V, m.p. 67.7–68.2°. Mixed m.p. with hydrogenated III, (IV) is not depressed and infrared spectra are identical. All elemental analyses are correct as required by theory.

The results of our investigation indicate that cyclization will occur with propynyl ureas of the type 

$$-\overset{H}{N}CON\begin{matrix}\diagup R\\ \diagdown CH_2C\equiv CH\end{matrix}$$

When R = H, the parent urea is regenerated on treatment with water or base presumably through formation of a carbodiimide. The reaction offers a simple and facile route to 1,3-disubstituted imidazolones. A discussion of the mechanism and scope of the reaction will be published shortly.

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RECEIVED DECEMBER 7, 1961

BOOK REVIEWS

Azo and Diazo Chemistry. Aliphatic and Aromatic Compounds. By HEINRICH ZOLLINGER, Professor in the Eigenössische Technische Hochschule, Zurich, Switzerland. Translated by HARRY E. NURSTEN, Lecturer in the University of Leeds, Great Britain. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1961. 444 pp. 17.5 × 24.5 cm. Price, $16.50.

This book bears a close relationship to the German-language book by the same author, "Chemie der Azofarbstoffe," Birkhäuser Verlag, Basel, Switzerland, 1958; but the relationship is not the simple one of translation from German to English, or even of second edition to first with translation as an extra flourish.

"Chemie der Azofarbstoffe" dealt exclusively with the chemistry of aromatic diazonium and azo compounds. Throughout, its point-of-view was that of reaction mechanisms and physical chemistry as it treated the major phenomena of interest to the organic chemist or the dye-works chemist dealing with these compounds. Important aspects of the dyeing process received their share of attention.

About three-quarters of the content of the original book has been transferred, with modifications to keep it up-to-date and with translation, to form the main substance of "Azo and Diazo Chemistry." Those chapters devoted to technical aspects of azo dyes and dyeing were not carried over. In the new book their place, so to speak, is taken by several chapters or sections on *aliphatic* azo compounds which, altogether, comprise about a quarter of the work.

The new book is about 30% longer than its predecessor.

Professor Zollinger writes of aromatic diazonium and azo chemistry with the confidence and command that one would expect from the world's leading investigator in that area. Though respectful of the worthwhile contributions of earlier decades, he discards much of the older systematization and nomenclature in favor of a presentation organized largely according to the precepts of modern physical organic chemistry. His lucid presentation clears away the clutter of outmoded views which had made the area of pure chemistry to which azo dye technology is related as unfashionable as Whist. The many fascinating phenomena and challenging problems which Zollinger has revealed offer a stirring opportunity to the investigator willing to suffer the slights of the style-conscious for the rewards of discovery in an exciting but neglected field.

In presenting aliphatic azo chemistry, Zollinger is more the competent critic than the practicing master. Nevertheless, what he writes is authoritative and valuable.

It is inevitable that any general treatment of a fast-moving field should be partially out of date on the day of publication. The absence of Schmitz' work on cyclodiazomethane and of Huisgen's interpretation of the cycloaddition of diazomethane to olefinic bonds (as a concerted 1,3-dipolar addition) are cases in point.

The translation from German into English seems faithful. Indeed, it is occasionally too much so. Traces of German word order or idiom now and then show through.

The book is beautifully printed and produced, and errors are not obvious. However, the reviewer got a bit of peevish satisfaction out of seeing (p. 409) Burnett misspelled "Bunnet" for a change.

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Industrial Organic Nitrogen Compounds, ACS Monograph No. 150. By MELVIN J. ASTLE, Professor of Organic Chemistry, Case Institute of Technology, Cleveland, Ohio. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1961. vii + 392 pp. 16 × 23.5 cm. Price, $14.00.

"This book has been written in an attempt to summarize the chemistry of most of the types of organic nitrogen compounds. No single book has appeared in recent years which has accomplished this goal. Many very excellent treatises are available describing the chemistry of amino acids and proteins, alkaloids and heterocyclic nitrogen compounds. Accordingly these compounds are not discussed extensively in this monograph. In order to present a comprehensive survey of nitrogen chemistry it has been necessary to discuss the simple heterocyclic nitrogen ring systems in some detail.

"Considerable attention has been given to the patent literature in order to present developments from the indus-