Azoalkane Synthesis by Direct Oxidation of Semicarbazides with Copper Halide

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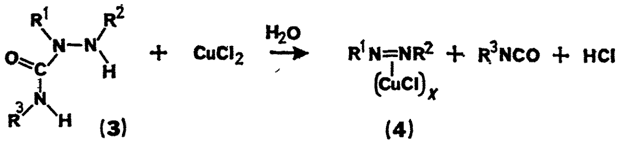
Summary Easily prepared cyclic semicarbazides are oxidised by cupric chloride, in high yield and a single step, to *cis*-azoalkane–cuprous chloride complexes and isocyanates.

DI-IMIDE derivatives† (**2**) are generally prepared by oxidation of the corresponding hydrazo-precursors (**1**) (reaction 1). Diacyl di-imides

$$\underset{(1)}{R^1NH\text{-}NHR^2} \xrightarrow{(O)} \underset{(2)}{R^1N{=}NR^2} \qquad (1)$$

(**2**; $R^1 = R^2 = COR^3$) have been generated with a variety of strong oxidants including t-butyl hypochlorite, lead tetra-acetate, and nitrogen tetroxide.[1] Cuprous halide complexes of phenyl diazene (**2**; R^1 = Ph, R^2 = H) are derived by treatment of phenylhydrazine with cupric chloride or bromide.[2] The action of mercuric oxide,[3] cupric chloride,[4] hydrogen peroxide,[3a,5] or molecular oxygen[6] on 1,2-dialkylhydrazines provides azoalkanes (**2**; $R^1 = R^2$ = alkyl) either directly or as the easily dissociated cuprous halide complexes. In the preparation of *cis*-azoalkanes, cyclic dialkylhydrazine precursors are often obtained as air-sensitive oils which are difficult to purify.[4,6] Conversion of the crude hydrazine directly into the azoalkane or its complex usually simplifies handling but storage and simple structural characterization of the intermediate hydrazine is frequently prevented by oxidation.

We now report that air-stable, crystalline semicarbazides‡ (**3**) are conveniently oxidised in high yield directly to organo-copper complexes (**4**).



The polycyclic semicarbazides (**6**) used here are prepared by 2 + 4 cycloaddition of *N*-methyl-1,2,4-triazoline-3,5-dione and a cyclic diene,[1,7] followed by hydrogenation and

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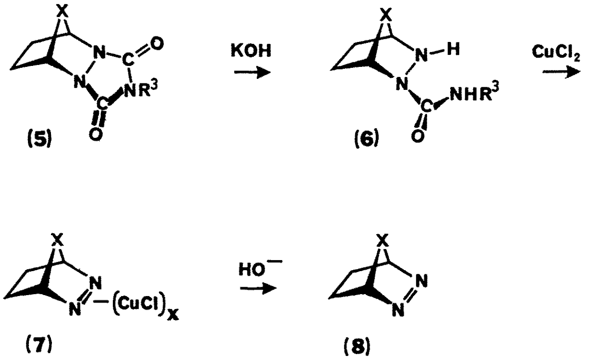
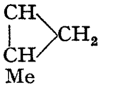
† Two related nomenclature systems often used for unsymmetrical derivatives of $R^1N{=}NR^2$ refer to the parent compound H–N=N–H as di-imide or diazene. Thus MeN=NH is deonoted methyl di-imide or methyl diazene; MeN=N·OMe may be called *N*-methoxy-N′-methyl di-imide. For symmetrical disubstituted derivatives of (2) the *azo*-nomenclature is most commonly used; Me–N=N–Me becomes azomethane. When R^1 and R^2 are α-carbonyl groups, a fourth nomenclature system is operable; *e.g.* MeCO–N=N–COMe can be designated azodiacetyl or diacetyldi-imide. For further details see: P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," vol. 2, Benjamin, New York, pp. 270—271, 1966.

‡All new compounds give satisfactory analyses and have been characterized spectroscopically.

partial hydrolysis; *e.g.* semicarbazide (**6a**) was obtained from cycloadduct (**5a**) in 90% yield.



	a	b	c	d
X	CH_2	$(CH_2)_2$	$(CH_2)_4$	
R^3	Me Ph	Me	Me	Me

An aqueous solution of diazabicycloheptane (**6a**) and cupric chloride cleanly deposits complex (**7a**)[4a] at room temperature. The pH of the initially neutral solution dropped to 1 during the oxidation consistent with the generation of HCl. Readjustment of the pH to 6·5 with aqueous ammonium hydroxide gave more of the complex. Gases evolved from the mixture were trapped at −78° and methyl isocyanate was characterized as *N*-methyl-*N*′-phenylurea. Decomposition of complex (**7a**) with aqueous ammonium hydroxide led to 2,3-diazabicycloheptene (**8a**) (77%).[4a] The phenyl substituted semicarbazide (**6a**; R^3 = Ph) is oxidised by cupric halides in water as well, but tarring reduces the yield of azoalkane (**8a**). Improved yields are obtained in methanol solvent.

Other azo–cuprous chloride complexes prepared in this manner are *cis*-azo-derivatives (**7b**, **c**, and **d**).§ The corresponding azo-ligands are obtained in good to excellent yields by treatment of the complex with base. Semicarbazide itself gives a blue cupric chloride complex under similar conditions.

We thank the National Institutes of Health for support.

(*Received, November 17th,* 1970; *Com.* 1988.)

§ Isolated as the azoxy-derivative.[5]

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