

## CORRESPONDENCE

### Handle Azide Compounds with Caution

To the Editor:

The article "The Reaction of Azidoorganic Compounds with Acetylenes" by John A. Durden, Jr., Harry A. Stansbury, and William Catlette, [J. CHEM. ENG. DATA 9, 228 (1964)] describes the preparation of certain organic azides and triazoles. Amounts of compounds collected and worked with in one batch are reported as follows:

698 grams of bis(2-azidoethyl)ether  
264 grams of 1-azidobutane  
31 grams of 1,5-diazidopentane  
464 grams of 1-butyl-4 (and 5)-methyl-1,2,3-triazole

Unstated amount of diazides were obtained from:

439.4 grams of sodium azide and 550 grams of bis-(2-chloro-1-methylethyl)ether  
144 grams of sodium azide and 187 grams of 1,2-bis-(2 chloroethoxy)ethane  
78 grams of sodium azide and 157 grams of chloroethyl chloroacetate

We feel that these quantities are far too large to be prepared under ordinary conditions of laboratory work. It would appear that triazoles are not so treacherous but must be handled with caution. Their preparation should not be reported without proper reference to possible danger. Recently reported explosions from azides and triazoles include:

C.L. Currie and B. de B. Darwent, *Can J. Chem.* 41, 1048 (1963). Methyl azide in the presence of mercury was shown to be potentially explosive.

R.H. Wiley and J. Moffat, *J. Org. Chem.* 22, 995 (1957) report that "a sample [of vinyl azide] in a distilling flask with a ground glass joint detonated when the joint was rotated. . . . Statements in the literature that this material is 'surprisingly stable' should be regarded as misleading and erroneous." Vinyl azide was obtained in a yield of about 20 grams; however, the authors say, "This amount is probably larger than should be handled by ordinary laboratory procedures, since this amount can cause very severe damage on detonation."

An anonymous report in *Chem. Eng. News* 34, 2450 (1965) describes a powerfully destructive explosion during an attempt to distill benzotriazole at 160° (2mm. of Hg).

J.H. Boyer and F.C. Canter, *Chem. Rev.* 54, 32,33 (1954) report that methyl and ethyl azides are stable at room temperature but are apt to detonate upon rapid heating, and "Certain  $\alpha$ -azidocarbonyl compounds

have long been known to be unstable substances.  $\alpha$ -Azidoacetaldehyde could not be purified, while  $\alpha$ -azidoacetone has been reported to decompose upon storage in the refrigerator. . . . Introduction of more than one azide group into the molecule increases its instability. In the determination of the weight of a sample of 1,3-diazidopropene a violent explosion occurred which prompted cancellation of further investigation of the compound."

It is our experience that trace amounts of strong acid, certain metal salts, or conceivably other materials, may catalyze explosive reactions with organic azides. Low molecular weight alkyl azides and diazido alkanes are considered to be particularly dangerous in the absence of suitable precautions. At all times it must be remembered that they are sensitive to shock and heat. Azides generally will decompose on exposure to ultraviolet light.

In our opinion organic azides should be prepared and worked with only by experienced laboratory investigators. It is advisable to handle all azides with caution and protection against the eventuality of explosion, until experience has shown the characteristics of the particular sample at hand. Each of us has witnessed the powerfully destructive action of these compounds. When distillation is necessary, it should be restricted to minimum quantities and carried out with the best available protection for safety.

Sincerely yours,

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To the Editor:

I wish to endorse *in toto* Dr. Boyer's letter concerning the dangers involved in preparations such as those reported in our recent paper. We also wish to emphasize that, although no accidents occurred involving our personnel, chemicals such as these are inherently dangerous, particularly in the amounts employed. Our manuscript was prepared, however, on the basis of our own somewhat limited experience in this area and the contents reflect only those events recorded by us. We are therefore indebted to Dr. Boyer and his colleagues for supplementing our report with their timely and considered letter.

Very truly yours,

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