A Convenient Oxidation of Hydroxylamines to Nitroso-compounds

By EDWARD C. TAYLOR and FUMIO YONEDA
(*Department of Chemistry, Princeton University, Princeton, New Jersey*)

DIETHYL AZODICARBOXYLATE (I) has recently been shown to be an effective hydrogen-abstracting reagent for the oxidation of alcohols to carbonyl compounds,[1,2] and of several other electron donors (mercaptans, anilines, hydrazobenzenes) to the corresponding oxidation (hydrogen-abstraction) products, with concomitant formation of diethyl hydrazodicarboxylate (II).[1] Here, we report that (I) is also a convenient reagent for the oxidation of hydroxylamines to nitroso-compounds.

A solution of the hydroxylamine in ether is treated with a solution of (I) in ether.* The mixture is maintained at 0° for a few hours, the precipitated diethyl hydrazodicarboxylate (II) removed by filtration, and the ether filtrate concentrated to give the nitroso-compound, usually in crystalline form and in a high state of purity.

The reaction proceeds in good yield with aromatic hydroxylamines (see Table), but is less satisfactory with aliphatic hydroxylamines. For example, *N*-benzylhydroxylamine gave α-nitrosotoluene dimer in only 10% yield, with the simultaneous formation of 1-benzylidene-2,3-diethoxycarbonyltriazane [$PhCH:N{\cdot}N(CO_2Et){\cdot}NH{\cdot}CO_2Et$] [presumably by Michael addition of the hydroxylamine to (I), followed by dehydration] in 63% yield. Similarly, cyclohexylhydroxylamine and (I) gave a mixture of nitrosocyclohexane dimer (25%) and 1-cyclohexylidene-2,3-diethoxycarbonyltriazane (32%).

TABLE

Hydroxylamine	Nitroso-compound (% yield)
Phenylhydroxylamine	89
p-Tolylhydroxylamine	79
p-Chlorophenylhydroxylamine	70
p-Nitrophenylhydroxylamine	67
o-Hydroxylaminobiphenyl	76

Diethyl azodicarboxylate (I) appears to be a

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* When working on a small scale (0·01–0·1 molar) these solutions can be mixed without precaution. However, larger-scale oxidations are better carried out by a slow simultaneous mixing of ether solutions of the two reagents.

superior oxidizing agent for the conversion of *NN*-disubstituted hydroxylamines into nitrones; *NN*-dibenzylhydroxylamine was converted in quantitative yield by this reagent (chloroform solution, R.T.) into *N*-benzylbenzaldoxime.

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[2] R. C. Cookson, I. D. R. Stevens, and C. T. Watts, *Chem. Comm.*, 1966, 744.