A New Reagent for Oxidation of Alcohols to Ketones in Neutral Solution at Room Temperature

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INCIDENTALLY to an account of the photochemical addition of alkyl ethers to diethyl azodicarboxylate[1] we mentioned that the ester oxidizes cyclohexanol to cyclohexanone in the dark, though only in low yield. In fact we had carried out many experiments on a variety of alcohols under various conditions in an attempt to develop a useful preparative method of oxidation, but could not achieve yields above 20 to 30% (except for n-butanol 70%).

However, Yoneda, Suzuki, and Nitta[2] have just reported the oxidation of several alcohols to aldehydes and ketones in yields varying from 55 to 87% under conditions that we had already tried with little success (*e.g.*, in boiling benzene). We have now repeated the work, and under the conditions described[2] we still find yields of only half or less of Yoneda's. No significant improvement resulted from the use of samples of azo-ester prepared by different procedures or those to which possible impurities or potential catalysts had been added.

The more reactive azo-compound, 4-phenyl-1,2,4-triazoline-3,5-dione,[3,4] oxidises alcohols to aldehydes or ketones at room temperature over a few hours in high yield. Dry benzene is a convenient solvent, from which the phenylurazole separates during the reaction. Some examples of the method with equimolar quantities of azo-compound and alcohol are given in the Table.

TABLE

Alcohol	Yield (%)* Ketone	Unreacted alcohol
Benzyl alcohol	78†	17
Benzhydrol	90	—
Cyclopentanol	62	34
Cyclohexanol	84	12
4-t-Butylcyclohexanol ..	75	22

* Measured by gas chromatography, except benzophenone, which was estimated as 2,4-dinitrophenylhydrazone.
† Benzaldehyde.

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[1] R. C. Cookson, I. D. R. Stevens, and C. T. Watts, *Chem. Comm.*, 1965, 259.
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[3] J. Thiele and O. Stange, *Annalen*, 1894, **283**, 1; J. Stollé, *Ber.*, 1912, **45**, 273.
[4] R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Letters*, 1962, 615.