

1-Chlorobenzotriazole: a New Oxidant

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WHEN aqueous sodium hypochlorite is added to benzotriazole in 50% aqueous acetic acid, 1-chlorobenzotriazole separates rapidly and almost quantitatively; crystallisation from CH_2Cl_2 -light petroleum gives colourless needles (90%), m.p. 105–106°. The structure was confirmed by analytical and spectral data; the i.r. showed no N-H and the u.v., n.m.r., and mass spectra were typical of a 1-substituted benzotriazole.

This new positive-halogen compound oxidises alcohols to aldehydes or ketones, hydrazo-compounds to azo-compounds, and 1,1-disubstituted

hydrazines, all in high yield under mild conditions. Thus, when equimolar amounts of 1-chlorobenzotriazole and an alcohol were warmed alone or in CH_2Cl_2 , CCl_4 , or benzene, a short induction period was followed by a rapid exothermic reaction to give the corresponding carbonyl compound. With 1,1- and 1,2-disubstituted hydrazines and with phenylhydroxylamine the oxidations occurred rapidly in the cold. In all cases the products of reduction of the oxidant, benzotriazole and hydrogen chloride, largely separated as benzotriazole hydrochloride, leaving the pure oxidation

TABLE

Starting material	Solvent	Product	% Yield	% Yield of benzotriazole hydrochloride
Benzyl alcohol	CH_2Cl_2	benzaldehyde ^a	70	60
Propan-2-ol	C_6H_6	acetone ^b	70	70
Cyclohexanol	CH_2Cl_2	cyclohexanone ^a	70	85
1-Phenylethanol	CCl_4	acetophenone ^a	65	50
Diphenylmethanol	CCl_4	benzophenone ^a	65	50
Hydrazobenzene	CH_2Cl_2	azobenzene	90	70
Ethyl quinoline-2-hydrazocarboxylate	CH_2Cl_2	ethyl quinoline-2-azocarboxylate	95	90
1-Amino-4,5-diphenyl-1,2,3-triazole	CH_2Cl_2	diphenylacetylene	75	80
1-Aminobenzotriazole	CH_2Cl_2	benzynes ^c	80	—
2-Aminobenzotriazole	CH_2Cl_2	<i>cis,cis</i> -1,4-dicyanobuta-1,3-diene	75	85

^a Isolated as the 2,4-dinitrophenylhydrazine; ^b estimated by g.l.c.; ^c isolated as tetraphenyl-naphthalene after reaction with tetraphenylcyclopentadienone; two mol. of oxidant were required in this case.

