## 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.Cl.	benzaldehvde <sup>a</sup>	70	60
Propan-2-ol	C.H.	acetoneb	70	70
Cyclohexanol	CH,Čl,	cyclohexanone <sup>a</sup>	70	85
1-Phenylethanol	CCl <sub>4</sub>	acetophenone <sup>a</sup>	65	50
Diphenylmethanol	CCI	benzophenone <sup>a</sup>	65	50
Hydrazobenzene	CH,Cl,	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 <sub>2</sub> Cl <sub>2</sub>	benzyne <sup>e</sup>	80	
2-Aminobenzotriazole	$CH_{2}Cl_{2}$	cis,cis-1,4-dicyanobuta- 1,3-diene	75	85

<sup>a</sup> Isolated as the 2,4-dinitrophenylhydrazone; <sup>b</sup> estimated by g.l.c.; <sup>c</sup> isolated as tetraphenylnaphthalene after reaction with tetraphenylcyclopentadienone; two mol. of oxidant were required in this case.

product in solution. Residual traces of benzotriazole hydrochloride could be removed by washing with dilute aqueous sodium hydroxide. 1-Chlorobenzotriazole oxidised 1-aminobenzotriazole to benzyne and 2-aminobenzotriazole to



cis,cis-1,4-dicyanobuta-1,3-diene, as fast and effectively as lead tetra-acetate.

Some typical results are shown in the Table. No attempt was made to find the best conditions, nor have we investigated further the scope of oxidation by 1-chlorobenzotriazole. However, its ease of preparation, stability, reactivity under very mild conditions, and the ease of isolation of products indicate that it is potentially a useful new oxidant.

(Received, August 5th, 1968; Com. 1080.)