

Action of Chlorine on a 2-Substituted Benzotriazole

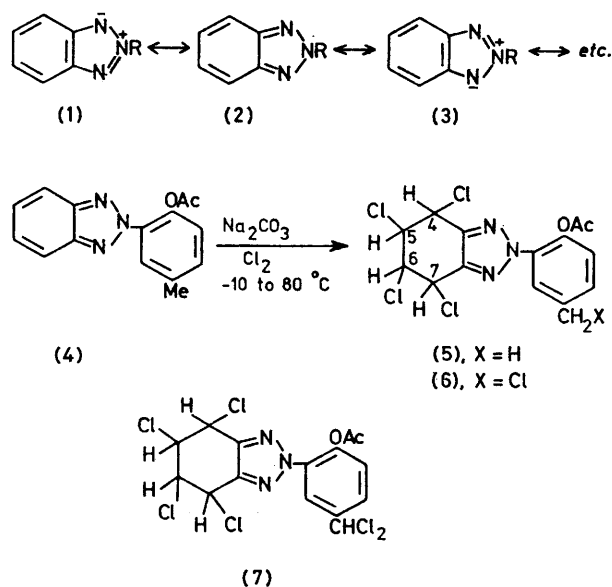
By TIMOTHY NORRIS,* ALAN PAYNE, and DAVID T. SOUTHEY

(Research Division, Kodak Limited, Headstone Drive, Harrow, Middlesex HA1 4TY)

Summary Chlorine gas reacts with 2-(2-acetoxy-5-methylphenyl)benzotriazole in the presence of anhydrous sodium carbonate to form novel addition derivatives of the benzotriazol-2-yl nucleus, namely configurational isomers of 2-(2-acetoxy-5-methylphenyl)-4,5,6,7-tetrachloro-4,5,6,7-tetrahydrobenzotriazole and 2-(2-acetoxy-5-chloromethylphenyl)-4,5,6,7-tetrachloro-4,5,6,7-tetrahydrobenzotriazole.

2-SUBSTITUTED benzotriazoles have a structure that can be represented in valence bond terms by canonical forms (1), (2), and (3) *etc.* The nature of the bonding in the fused benzo ring is interesting, in that from the former molecular description it could have either a benzenoid or quinonoid character.^{1†} It has been claimed² (without substantiation) that the quinonoid form probably contributes least to the overall structure of these molecules. Also the stability of 2-methylbenzotriazole to oxidative attack by conc. HCl-conc. HNO₃ at reflux temperatures (the product is 2-methyl-4,5,6,7-tetrachlorobenzotriazole) has been cited as evidence against any simple *o*-quinonoid structure for 2-substituted benzotriazole.³

We now report that the reaction of chlorine gas with a 2-substituted benzotriazole in the presence of anhydrous sodium carbonate illustrates the non-benzenoid character of the benzo ring in the benzotriazol-2-yl system. Thus, when chlorine gas was passed into a solution of 2-(2-acetoxy-5-methylphenyl)benzotriazole (4) in 1,2-dichloroethane in



the presence of a suspension of anhydrous sodium carbonate at temperatures between -10 and 80 °C, a mixture of polychlorinated products was formed. The 100 MHz ¹H n.m.r. spectrum of these products indicated that they were a

† Recent X-ray analysis of 2-(2-*H*-benzotriazolyl)-*N*-(quinoxalin-6-yl)aniline shows that the 2*H*-benzotriazolyl ring system is planar but that a bias towards either the benzenoid or quinonoid form is not definitive (P. Luger, J. Malkowski, and P. Skrabal, *Helv. Chim. Acta*, 1977, **60**, 1545).

ca. 50:50 mixture of configurational isomers of tetrachloro- (5) and pentachloro- (6) derivatives of (4). The mixture of products can be separated by medium pressure liquid chromatography and fractional crystallization into two main isomeric types. The n.m.r. spectrum of the mixture of exclusively tetrachloro-isomers (5) was consistent with this structural assignment: δ 2.32 (s, OAc), 2.44 (s, ArMe), 4.36—4.44 (m) and 5.24—5.32 (m) (4-, 5-, 6-, and 7-H), and 7.1—7.8 (ArH); the assignment of structures (5) and (6) was confirmed by the chlorine isotope patterns in the mass spectrum, elemental analysis of the separated tetrachloro-isomers (5), and the accurate mass of the molecular ions of the configurational isomers of (5) (m/e 406.9771) and (6) (m/e 440.9378). Major mass spectral peaks were observed at m/e 365 and 399 for (5) and (6), respectively ($M^+ - \text{CH}_2\text{CO}$).

The reaction mixture also contained traces of a third product with a very weak molecular ion at m/e 475 corresponding to a hexachloro-compound [$M^+ - \text{CH}_2\text{CO}$, m/e 440.8778 ($\text{C}_{13}\text{H}_9^{35}\text{Cl}_2^{37}\text{Cl}_4\text{N}_3\text{O}$)], which is probably the dichloromethyl derivative (7). This is consistent with observations that heteroarylmethyl compounds are reported⁴

to yield mainly monochloromethyl derivatives on treatment with $\text{Cl}_2\text{-Na}_2\text{CO}_3$, and the di- and tri-chloromethyl derivatives as minor products.

Although the 1-substituted benzotriazoles and benzotriazole itself can undergo substitution in conc. HCl -conc. HNO_3 to form unsaturated 4,5,6,7-tetrachloro products³ these systems do not readily undergo addition reactions analogous to the type observed for 2-substituted benzotriazoles. Thus, 1-methylbenzotriazole in 1,2-dichloroethane solution is virtually unaffected by the action of chlorine in the presence of anhydrous sodium carbonate at 10 °C.

It is felt that the hitherto unreported addition of chlorine to the 2H-benzotriazole nucleus illustrates the quinonoidal nature of this system which has been under-emphasized in structural discussions.¹⁻³

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¹ F. R. Benson and W. L. Savell, *Chem. Rev.*, 1950, **46**, 1 (see pp. 54—58); J. H. Boyer, 'Heterocyclic Compounds,' Vol. 7, Wiley, New York, 1961, p. 386.

² H. J. Heller, *European Polymer J. (Suppl.)*, 1969, 105 (see p. 125).

³ R. H. Wiley, K. H. Hussung, and J. Moffat, *J. Amer. Chem. Soc.*, 1955, **77**, 5105.

⁴ W. Mathes and H. Schulz, *Angew. Chem. Internat. Edn.*, 1963, **2**, 144.