Crystal and Molecular Structure of Methyltin Trinitrate

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Summary *X*-Ray crystal structure analysis of methyltin trinitrate shows the co-ordination about tin to be approximately pentagonal bipyramidal.

RECENT studies[1] on the series of complexes $Me_nSn(NO_3)_{3-n}$ ($n = 0, . . 3$) have permitted a detailed comparison to be made of their chemical and physical properties. So far only the tetranitrate ($n = 0$) itself has had its crystal structure determined by *X*-ray analysis[2] and we now report the crystal and molecular structure of methyltin trinitrate ($n = 1$). Prior to this analysis it was expected that these two members of the series would resemble each other structurally more closely than those with $n = 2$ and 3. The chemical reactivity and vibrational spectra of methyltin trinitrate and tin tetranitrate are similar, suggesting that the nitrate groups are bound in a similar bidentate fashion,[1] while the complexes where $n = 2$ [3] and $n = 3$ [4,5] are thought to be polymeric and to contain bridging nitrate groups. (However, in apparent conflict with i.r. data on the solid and the solution and with mass-spectral data, a report of an unrefined *X*-ray analysis[6] gives the nitrate groups in dimethyltin dinitrate, $n = 2$, as unsymmetrical bidentate.)

X-Ray analysis of methyltin trinitrate was carried out using 2079 reflections collected with Mo-K_α radiation on a four circle diffractometer. The crystal system is monoclinic, space group $C2/c$, with a unit cell $a = 21{\cdot}205(10)$, $b = 6{\cdot}550(4)$, $c = 12{\cdot}500(8)$Å, $\beta = 90{\cdot}21°$.

The structure has been refined to a conventional $R = 0{\cdot}052$. The mean e.s.d. of the tin-oxygen bond-lengths is 0·006 Å and of the oxygen–nitrogen bonds is 0·009 Å.

The results confirm that all three nitrate groups are bidentate The methyl group appears to have brought about some asymmetry in the bidentate bonding for in each nitrate group one Sn · · · O distance is longer than the other (see Figure). The seven atoms nearest to Sn form an approximate pentagonal bipyramid the axial positions being occupied by the carbon atom and by O(1). However, as the Figure shows, the 'axis' of the bipyramid is far from straight, the CH_3–Sn–O(1) angle in question being 159°. Two nitrate groups are vitrually coplanar (7° twist) but the third, labelled O(1)–N–O(2), is approximately normal to them. In fact this nitrate ligand compromises between an axial O(1) axial and equatorial O(2).

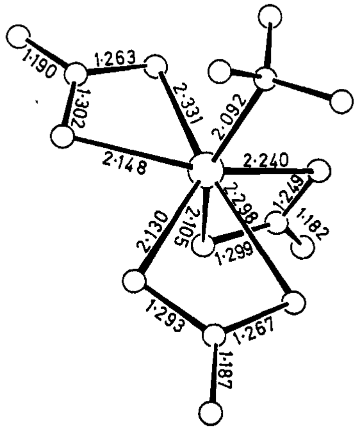

FIGURE. *The structure of methyltin trinitrate, showing the distorted pentagonal bipyramidal co-ordination. The refined values of the bond-lengths are shown. The hydrogen positions were not refined although the hydrogens were located.*

Final structure details will be published elsewhere.

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Cupric Chloride Oxidative Rearrangement of 2-Hydroxy-3,6-di-t-butyl-1,4-benzoquinone to 2-Chloro-2,4-di-t-butylcyclopentene-1,3-dione

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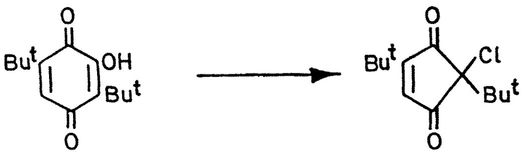
Summary 2-Hydroxy-3,6-di-t-butyl-1,4-benzoquinone reacts with $CuCl_2,6H_2O$ in hot glacial acetic acid to give 2-chloro-2,4-di-t-butylcyclopentene-1,3-dione.

HYDROXYQUINONES undergo a variety of oxidative ring contractions.[1] However, no general method exists for their conversion into cyclopentene-1,3-diones,[2] a ring system of some importance on account of its natural occurrence.[3] We report here an example of such a rearrangement; the hydroxyquinone, 2-hydroxy-3,6-di-t-butyl-1,4-benzoquinone

(1) reacts with $CuCl_2,6H_2O$ in hot glacial acetic acid to give 2-chloro-2,4-di-t-butylcyclopentene-1,3-dione (2) in 55% isolated yield.†

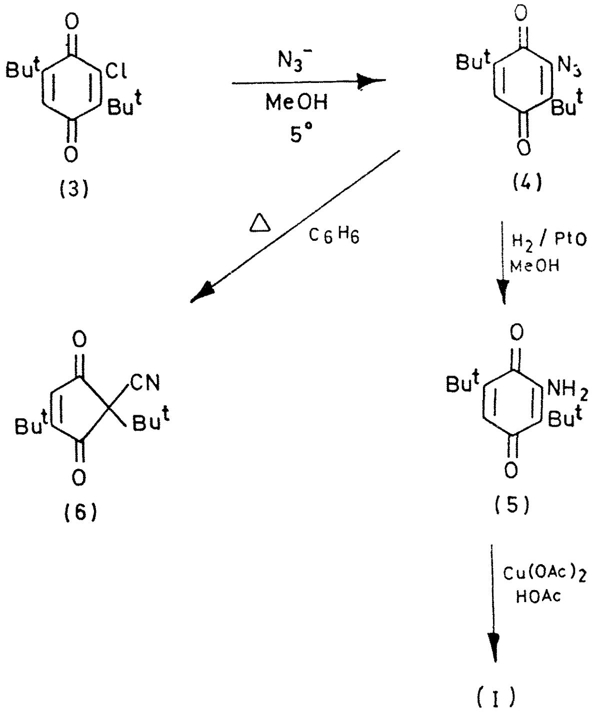


(1) (2)

The hydroxyquinone[4] (1) was prepared from 2-chloro-3,6-di-t-butyl-1,4-benzoquinone[5] as outlined below. The last step of this synthesis, *i.e.*, (5) → (1) can be accomplished by hydrolysis with $CuCl_2,6H_2O$–HOAc.[6] However, an improved method uses $Cu(OAc)_2$–HOAc, which avoids oxidative rearrangement of the product hydroxyquinone (1).

Of particular aid in assigning the cyclopentene-1,3-dione structure to (2) was the fact that its u.v. spectrum (λ_{max} EtOH 233 and 390, log ϵ 4·069 and 1·575) is nearly identical with that of 2-cyano-2,4-di-t-butylcyclopentene-1,3-dione (6) (λ_{max} EtOH 235 and 388, log ϵ 4·030 and 1·562). The latter compound was prepared in nearly quantitative yield by the known[7] pyrolytic rearrangement of the azidoquinone (4). C, H, N, and halogen analysis, i.r., u.v., and n.m.r. spectra, and also mass-spectroscopic molecular-weight determinations are in strict agreement with the formulations of all new compounds.

The scope of this oxidative ring contraction of hydroxyquinones has not yet been explored. However, 2-hydroxy-3-methyl-1,4-naphthoquinone and 2-hydroxy-5-chloro-3,6-diphenyl-1,4-benzoquinone appear to undergo analogous transformations.



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† The reaction is complete within 12 h when a solution of 0·9 g of the hydroxyquinone (1) and 1·0 g of $CuCl_2$, $6H_2O$ in 10 ml of glacial acetic acid is heated at 70—75°.

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