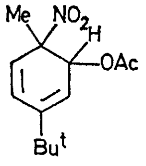
Ipso-Nitration of *p*-t-Butyltoluene. A 1,2 Adduct

By Alfred Fischer* and Rolf Röderer

(*Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada* V8W 2Y2)

Summary Nitration of *p*-t-butyltoluene in acetic anhydride gives 5-t-butyl-2-methyl-2-nitro-1,2-dihydrophenyl acetate as the major addition product.

Ipso[1] nitration at the methyl-substituted position of toluene and substituted toluenes is well established.[2] In acetic anhydride the *ipso*-methylnitrocyclohexadienyl cation, formed by addition of a nitronium ion at the 1-position of the toluene, adds acetate to give a pair of diastereoisomeric 1,4-adducts. 1,2-Adducts have not been obtained from any of the systems previously studied but we now report the isolation of a 1,2-acetoxynitro adduct as well as the expected 1,4-adducts from nitration of *p*-t-butyltoluene.



(1)

(B) and (C) are the *cis*- and *trans*-isomers of 1-t-butyl-4-methyl-4-nitro-1,4-dihydrophenyl acetate.

In the case of diene (A) the absorptions in the vinylic–allylic region of the n.m.r. spectrum appear as two AB quartets, the downfield with 10·3 and the upfield with 5·6 Hz coupling, each doublet integrating for one proton. Each peak in the upfield doublet of each quartet is further split into a doublet by a four-bond coupling while the peaks of the downfield doublets are split into quartets by two long range couplings. This spectrum is consistent with the structure of 5-t-butyl-2-methyl-2-nitro-1,2-dihydrophenyl acetate (**1**) or one of its locational isomers in which the positions of the t-butyl and methyl and/or nitro and acetate groups are interchanged. Chemical arguments against the latter structures can be adduced. Moreover, the effect‡ of the shift reagent $\mathrm{Eu}([^{2}\mathrm{H}_{9}]\mathrm{fod})_{3}$ shows that the