

Nitration of *p*-Quaterphenyl

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Summary Nitration of *p*-quaterphenyl with acetyl nitrate generated *in situ* affords 4-nitro- and 4,4'-dinitro-quaterphenyl, no products of *ortho*- or *meta*-nitration of inner or outer rings being detected.

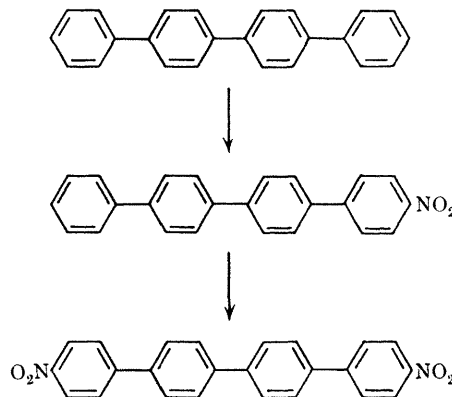
NITRATION studies of biphenyl have shown poor selectivity toward the *para*-positions; depending upon experimental conditions, the *ortho*:*para* ratio for monosubstituted product varies from 0.6 to 1.5.¹ *p*-Terphenyl undergoes nitration with 40–63% selectivity toward the 4-position, 25–41% selectivity toward the 2-position, and 15–20% nitration of middle ring.² The possibility of realizing higher selectivity to nitration of the end positions with *p*-quaterphenyl was considered.

In any attempt at aromatic monosubstitution of an oligophenylene, the formation of disubstituted by-product must be expected. If one end of a *p*-quaterphenyl molecule is substituted, the other end of the molecule is hardly less activated than that of an unsubstituted hydrocarbon. There will necessarily be a competition between monosubstituted product and unreacted starting material for reaction with the nitrating agent. Even if limited quantities of nitrating agent are employed, both mono- and di-nitro-products, as well as recovered hydrocarbons, are obtained.

The reaction products of *p*-quaterphenyl with *in situ* generated acetyl nitrate were separated by column chromatography on silica gel, employing gradually increasing ratios of benzene-hexane as eluent. Mononitroquaterphenyl‡ is separated first (36% selectivity). It can be distinguished from dinitro-compound by its u.v. absorption maximum at 275 nm (ϵ 3.5×10^4); the dinitro-compound has λ_{\max} 340 nm (ϵ 3.5×10^4).

The course of substitution was determined by oxidative degradation of the aromatic nitro-compounds with chromium trioxide in acetic acid at 100° to *p*-nitrobenzoic acid. The oxidation products were contaminated with benzoic acid but

no products derived from inner or outer ring *ortho*-nitration or *meta*-nitration were detected by g.l.c. examination of the methyl ester. Reduction of 4-nitro-*p*-quaterphenyl with stannous chloride affords 4-amino-*p*-quaterphenyl.‡



Recrystallization of the crude dinitroquaterphenyl (53% selectivity) affords a yellow crystalline solid whose n.m.r. spectrum exhibits a symmetrical pattern as expected for 4,4'-dinitro-*p*-quaterphenyl‡ and can be degraded to *p*-nitrobenzoic acid. The principal course of *p*-quaterphenyl nitration proceeds through 4-nitro-*p*-quaterphenyl, which is partially converted into 4,4'-dinitro-*p*-quaterphenyl. It appears that the selectivity of nitration toward the 4-position increases in the series: biphenyl < *p*-terphenyl < *p*-quaterphenyl.

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¹ R. Taylor, *J. Chem. Soc. (B)*, 1966, 727.

² G. W. Gray and D. Lewis, *J. Chem. Soc.*, 1961, 5156.