On the *ortho*:*para* Ratio in Activation of Nucleophilic Aromatic Substitution by the Nitro-group

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Summary Contrary to recent criticism,[1] previously obtained[2] high *ortho* :*para* ratios in activation of nucleophilic aromatic substitution by the nitro-group prove to be genuine.

RECENTLY, Shein and Jevstifeyev[1] have put in doubt our results[2] concerning the high *ortho* :*para* activation ratio in the reactions of twice sublimed potassium t-butoxide with X-2- or X-4-nitrobenzenes (X = fluorine or chlorine) in t-butyl alcohol. In fact, they have reported that (i) 2- or 4-nitrophenyl t-butyl ether, because of their (presumed) high instability in the basic medium, are not the end products of such reactions, this being inferred from the isolation of nitrophenols instead of ethers, and (ii) chloride ion determination affords an *ortho* :*para* ratio of only five.[1]

As modern theories concerned with primary steric effects in aromatic nucleophilic substitution rely largely on our results,[2 3] it is important to warn that the above criticism of Shein and Jevstifeyev is completely unwarranted. In fact, both g.c. and u.v. analysis showed that 2-nitrophenyl t-butyl ether, 0·08 M, in the presence of potassium t-butoxide, 0·13 M, in t-butyl alcohol remained unaltered after 3·5 h at 70° and decomposed only 12% after 24 h at 90°. 4-Nitrophenyl t-butyl ether, 0·11 M, also remained unaltered after 40 h at 90° in the presence of potassium t-butoxide, 0·13 M, in t-butyl alcohol. When these results are compared with those in our original work,[2] one sees that both ethers are formed from the corresponding fluoro-compounds at a much higher rate than they are decomposed by potassium t-butoxide in t-butyl alcohol. Also, both ethers are sufficiently stable that their yield data of formation at 90° from the corresponding chloro-compounds, when only a small amount of the latter has already disappeared, can properly be used to obtain our previous conclusions[2] on the *ortho* :*para* ratio values.

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[1] S. M. Shein and A. V. Jevstifeyev, *Reakts. spos. org. Soedinenii*, 1969, **6**, (2, 20), 371.
[2] F. Pietra and F. Del Cima, *Chem. Comm.*, 1968, 216.
[3] F. Pietra, *Quart. Rev.*, 1969, **23**, 504.