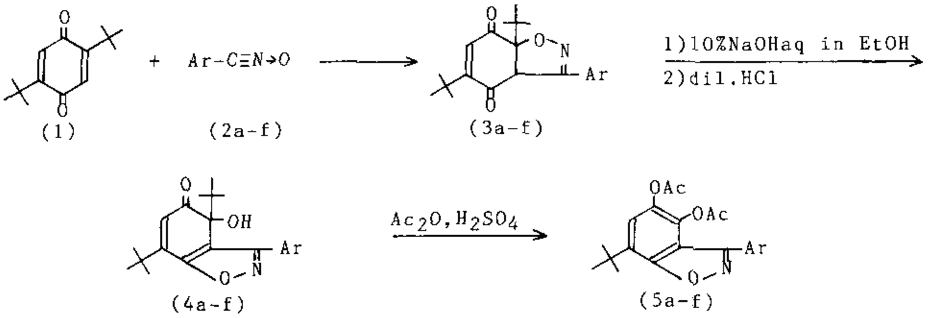
BASE-CATALYZED REARRANGEMENT REACTIONS OF THE 1:1-C=C-ADDUCTS FROM THE REACTIONS OF DIALKYL-SUBSTITUTED-p-BENZOQUINONES WITH NITRILE N-OXIDES

Shinsaku Shiraishi, B.S.Holla and Kiyoshi Imamura
Institute of Industrial Science, The University of Tokyo
Roppongi, Minato-ku, Tokyo 106, Japan

The 1:1-C=C-adducts(3a-f) of 2,5-di-tert-butyl-p-benzoquinone(1) with aromatic nitrile N-oxides(2a-f) behaved very interestingly in the presence of base. Thus, as soon as dropwising sodium hydroxide aqueous solution to the ethanol solutions of adducts(3a-f), the solutions turned bluish, purple and then colourless. Neutralizing the solutions with dil. chloric acid, rearranged products(4a-f) were obtained almost quantitatively. And the 1:1-C=C-adducts of 2,6-diisopropyl-p-benzoquinone and 2-tert-butyl-5-methyl-p-benzoquinone with nitrile N-oxides(2a-f) also gave the rearranged products, but the adducts of the other dialkyl-substituted-p-benzoquinones with (2a-f) did not undergo rearrangement.

Furthermore, the products(4a-f) were almost never acetylated by usual method with acetic anhydride and pyridine, but in the presence of sulfuric acid, they were acetylated almost quantitatively and led to catechol derivatives(5a-f).



Ar: a=phenyl, b=p-chlorophenyl, c=p-bromophenyl, d=2,4,6-trimethylphenyl
e=2,3,5,6-tetramethylphenyl, f=2,6-dichlorophenyl