

NITROCYCLOHEXADIENONES : CONVENIENT NEW MONO-NITRATING
AGENTS FOR AROMATIC COMPOUNDS

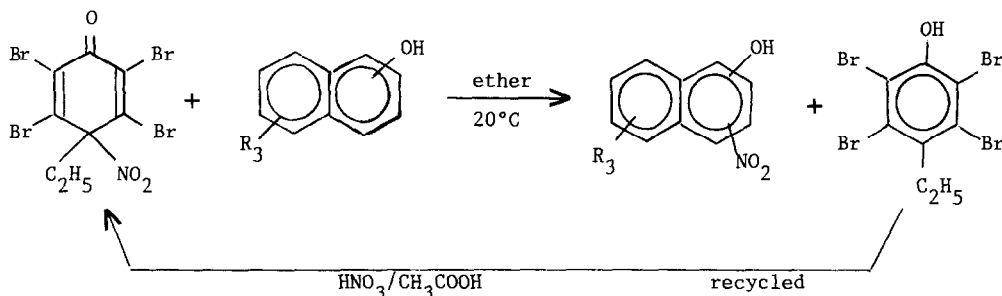
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SUMMARY : Nitrocyclohexadienones are effective nitrating agents for naphthols in dry ether at room temperature to give good yields of mononitrated products.

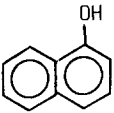
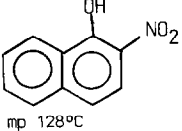
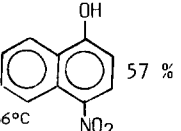
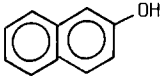
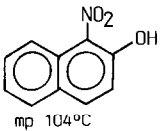
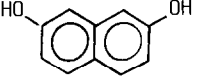
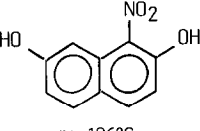
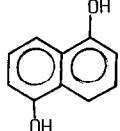
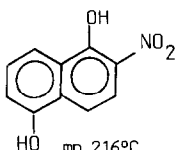
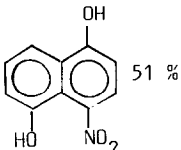
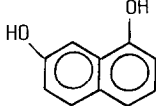
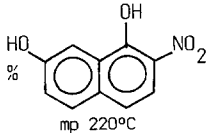
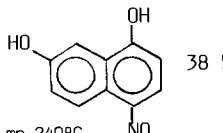
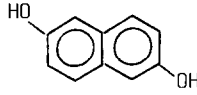
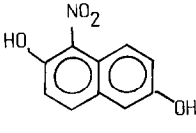
Nitration of highly sensitive substrates using nitric acid mainly gives oxidation and polynitro-compounds (1). This problem can be avoided in certain cases by the use of other nitrating agents (2), which represent a major step forward but are generally difficult to use, unstable and/or dangerous (3).

Recently we showed (4) that it is possible to use the driving force of aromatization to induce selective chlorination of aromatic compounds with hexachlorocyclohexadienones. Here we report the application of the same approach to nitration and describe a new method for the mononitration of aromatic compounds using perhalo-nitrocyclohexadienones. The latter reagents were readily prepared in excellent yields from the corresponding halophenols by nitration with nitric acid (5). Good yields of mononitrated naphthols were easily obtained at room temperature using ether as solvent. Oxidation products were obtained in contrast when nitric acid was used as nitrating agent.



TYPICAL PROCEDURE : The substrate (5 mmol) in 10 ml of dry ether was allowed to react with 5 mmol of reagent for one night at room temperature. The ether was removed and the product was separated by silicagel chromatography. Nitro-compounds gave the correct CHN, and ¹H NMR data which can be sent on demand. Perhalogenated phenols were also recovered in this way.

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Substrates	mononitration yield	nitro-products
	70 %	 
	56 %	
	50 %	
	49 %	 
	53 %	 
	62 %	

The nitrocyclohexadienone is a stable and efficient nitrating agent for sensitive aromatic compounds. Simplicity of "work-up" and the possibility of precursor recycling, are the major advantages of this type of reagent.

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