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PARA-SELECTIVE MONONITRATION OF ALKYLBENZENES UNDER MILD CONDITIONS BY USE OF BENZOYL NITRATE IN THE PRESENCE OF A ZEOLITE CATALYST

Keith Smith* and Karl Fry

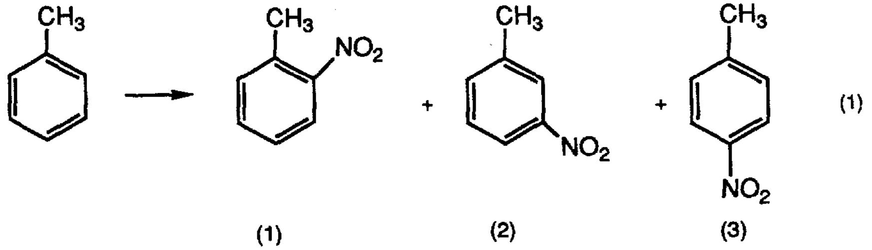
Department of Chemistry, University College of Swansea, Swansea SA2 8PP, UK

Michael Butters and Barry Nay

BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN, UK

Summary *Toluene and other alkylbenzenes are mononitrated in essentially quantitative yield at ambient temperature by benzoyl nitrate in the presence of aluminium/proton exchanged large port mordenite; the reaction is highly para-selective.*

Nitration of toluene (equation 1) is a notoriously unselective reaction. A variety of pocedures gives rise to mixtures containing *ca.* 55-70% *ortho*-nitrotoluene, **1**, *ca.* 30-45% *para*-nitrotoluene, **3**, and a small amount of the *meta*-isomer, **2**.[1,2] Few procedures are capable of producing more than 50% of *para*-nitrotoluene, and these are difficult to reproduce,[3] show other disadvantages,[4] or have not had their scope investigated.[5] Thus, there is still a great need for a convenient, general *para*-selective method for nitration of alkylbenzenes. The recent appearance of methods involving the use of reactions catalysed by K10 montmorillonite clay[6-8] prompts us to report our own method.[9]

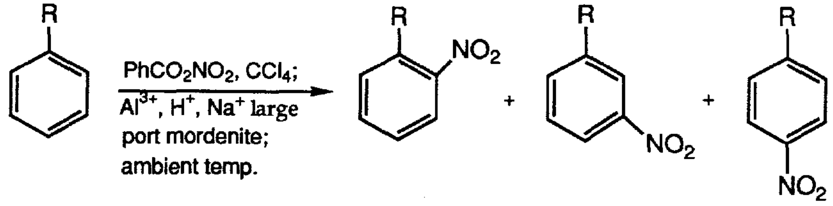


We have recently used inorganic solids such as silica to catalyse halogenation reactions of aromatic[10] and heteroaromatic[11] compounds, and in particular we have developed a highly *para*-selective chlorination of alkylbenzenes which utilizes a zeolite catalyst.[12] It was therefore of interest to investigate the possibility of developing a zeolite-catalysed *para*-selective nitration reaction for alkylbenzenes. We now report the successful development of such a reaction, utilizing benzoyl nitrate as the reagent and partially aluminium exchanged, partially proton exchanged sodium large port mordenite as the catalyst.

Benzoyl nitrate was prepared from benzoyl chloride by the literature method.[13] The solution obtained was used directly, without estimation, and quantities were based on the amount of benzoyl chloride used in the preparation. In the absence of any catalyst the reaction of benzoyl nitrate with toluene in tetrachloromethane at room temperature was slow, giving only 4% yield of nitrotoluenes after 10 days. Furthermore, the proportion of the isomeric nitrotoluenes produced was highly unusual, *viz*. **1** : **2** : **3** = 55 : 35 : 10.

Several acidic solids were tested as catalysts. All catalysed the reaction, but the o : p ratios of products varied considerably. Silica yielded predominantly *ortho*-nitrotoluene, alumina gave *ca*. 55% *para*, K10 clay gave *ca*. 60% *para*, and the most selective catalysts, under these conditions, were proton exchanged faujasite X and large port mordenite zeolites. The yield of nitrotoluenes was higher, under comparable conditions, with large port mordenite than the yield with faujasite. Thus, this catalyst was chosen for further study. Out of a range of solvents tried (hydrocarbons, ethers, acetonitrile, chlorinated hydrocarbons) tetrachloromethane appeared to be the optimum solvent, giving rise to the highest yield and best selectivity, as also observed by Laszlo *et al* in related reactions.[6] Temperature appeared to play only a minor role, only 1 - 2% improvement in the proportion of the *para*-isomer resulting from a lowering of the temperature to -20°C. Thus, further studies were carried out at ambient temperature with tetrachloromethane as solvent, under which conditions the proportions **1** : **2** : **3** were 35 : 1 : 64.

Other acyl nitrates gave only minor variations in product proportions. In some experiments anisoyl nitrate appeared to give somewhat improved selectivity (*ca*. 67% **3**), but this reagent was more difficult to handle and the results could not be consistently reproduced. A variety of different cation-exchanged forms of large port mordenite also produced only relatively small variations in product proportions. The optimum form appeared to be the proton-aluminium-exchanged form,[14] which gave 67% of **3**, and this was selected as the catalyst of choice. A quantitative yield of mononitrotoluenes was obtained within 4 minutes using benzoyl nitrate obtained from 1.3 equivalents of benzoyl chloride. Estimation of the benzoyl nitrate solution showed that the amount of reagent produced from 1.3 equivalents of benzoyl chloride was only *ca*. 1.0 equiv., thus showing that the nitration reaction is essentially stoichiometric.



(2)

(4) (5) (6)

These reaction conditions were applied to a range of alkylbenzenes (eq. 2) *without* attempt to optimize the individual examples. The results are given in the Table.

Table

Products of nitration of alkylbenzenes according to equation 2[a]

R	Reaction period (Min)	Total yield[b] of 4 + 5 + 6 (%)	Product distribution[b]	Regioselectivity[d]
CH_3	10	99	32 : 1 : 67	4.2 (2.6)
CH_2CH_3	80	100	25 : 2 : 73	5.8 (5.2)
$CH_2CH_2CH_3$	130	81[c]	26 : 2 : 72	5.5 (4.9)
$(CH_2)_5CH_3$	100	76[c]	28 : 2 : 70	5.0 -
$CH(CH_3)_2$	70	86[c]	14 : 2 : 84	12.0 (11.9)
$C(CH_3)_3$	70	76[c]	5 : 3 : 92	36.8 (21.5)

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a) To the zeolite (1.5 g) was added a solution of alkylbenzene (2.5 mmol) in tetrachloromethane (10 ml); the mixture was stirred magnetically and benzoyl nitrate (*ca*. 2.5 mmol) in tetrachloromethane (6.5 ml) was added. The mixture was stirred at ambient temperature for the stated period.

b) Determined by GC using an internal standard

c) The remaining mass balance was accounted for by unreacted alkylbenzene

d) Expressed as ratio *para*: (0.5 x *ortho*) in order to allow comparison with the results of Laszlo (given in parentheses wherever available) (ref. 8).

As can be seen from the Table the yields are consistently high and all reactions are *para*-selective; the selectivity increases as the bulk of the alkyl group increases.

A preparative scale reaction was performed on toluene (8g) using proportionately much less zeolite (2g). Initial mixing was carried out with stirring at -20°C in order to avoid significant decomposition of the benzoyl nitrate, and the temperature was maintained at -20°C for 1.5 h before being allowed to rise to ambient (*ca*. 15°C). The reaction was quite slow, requiring 42 h for 95% conversion. In order to complete the reaction an extra quantity of benzoyl nitrate (*ca*. 10%) was then added. During the early stages of the reaction the *para*-selectivity was relatively low (*ca*. 55%), presumably as a result of a significant contribution from the uncatalysed reaction in free solution. However, as the reaction progressed the selectivity improved and the final mixture contained 64% *para*-nitrotoluene. At this point the zeolite was removed by filtration. Washing of the filtrate with sodium bicarbonate and water followed by distillation of the product provided a 90% isolated yield of mononitrotoluene containing 60% of the *para*-isomer. Thus, it is clear that the reaction can easily be used on a preparative scale. It is probable that the selectivities in preparative scale reactions would approximate those in the analytical scale reactions with minor adaptations of the above reaction procedure.

Acknowledgement

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14. The sodium form of large port mordenite (20g) is stirred at 100°C for 1 h with 1M ammonium chloride solution (200 ml), cooled, filtered, washed with water, dried and calcined at 550°C. The solid is then stirred at 100° with 1M aqueous aluminium chloride solution (200 ml), cooled, filtered, washed thoroughly with distilled water, dried and calcined again at 550°C. After cooling, the solid is stored in dry conditions. Simple calcination of commercial proton form mordenite produces a catalyst which is effective but a little less selective than the one prepared as described here.

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