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# Regioselective dialkylation of naphthalene

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**Abstract**

The alkylation of naphthalene using *tert*-butanol in cyclohexane over a dealuminated H-Mordenite (HM) zeolite has been optimised to give a 60% yield of 2,6-di-*tert*-butylnaphthalene with a 2,6/2,7 ratio of over 50. This has been achieved by varying the reaction time, temperature, pressure, solvent, amount of *tert*-butanol, solvent and catalyst, Si/Al ratio of the catalyst, and the mode of addition. 

*Keywords:* Alkylation; Naphthalene; H-Mordenite; Regioselectivity

## 1. Introduction

Increasingly stringent environmental regulations and political pressure demand more selective synthetic processes [1]. Heterogeneous catalysts such as zeolites have in a number of cases proved to be central to this strategy, and careful control of reactions can maximise the selectivity and yield of a single desired product, while minimising the formation of by-products.

In previous studies, we have shown that zeolites can be used successfully for clean organic synthesis in reactions such as nitration [2], bromination [3], chlorination [4], acylation [5] and methanesulfonylation [6] of aromatic compounds. Our recent studies in this area have focussed on the regioselective dialkylation of naphthalene. This topic is of considerable interest as 2,6-dialkylnaphthalenes can be oxidised to naphthalene-2,6-dicarboxylic acid, used in the synthesis of the commercially valuable polymer, poly(ethylene naphthalenedicarboxylate) (PEN) [7] (Scheme 1). PEN has properties that are generally superior to those of poly(ethylene terephthalate) (PET) and has become the polymer of choice for a variety of applications such as in films, industrial fibres, packaging, liquid crystalline polymers, coatings, inks and adhesives [7].

World-wide PEN consumption is expected to show substantial market growth [7]. However, the high cost of naphthalenedicarboxylic acid has been the major hindrance to widespread application and substantial effort has been made to develop an economical route for its manufacture. Amoco chemicals have commercialised an interesting procedure that uses *o*-xylene as the starting material. However, this synthesis of naphthalene-2,6-dicarboxylic acid involves five steps, including an isomerisation step of 1,5-dimethylnaphthalene to 2,6-dimethylnaphthalene. The direct alkylation of naphthalene (Scheme 2) therefore appears to be more attractive, and has been investigated by, amongst others, NKK, Chiyoda and Catalytica [7]. However, the synthesis of the desired 2,6-isomer is complicated by the possible formation of nine other dialkyl isomers (10 in total), which can be difficult to separate from the 2,6-isomer [8].

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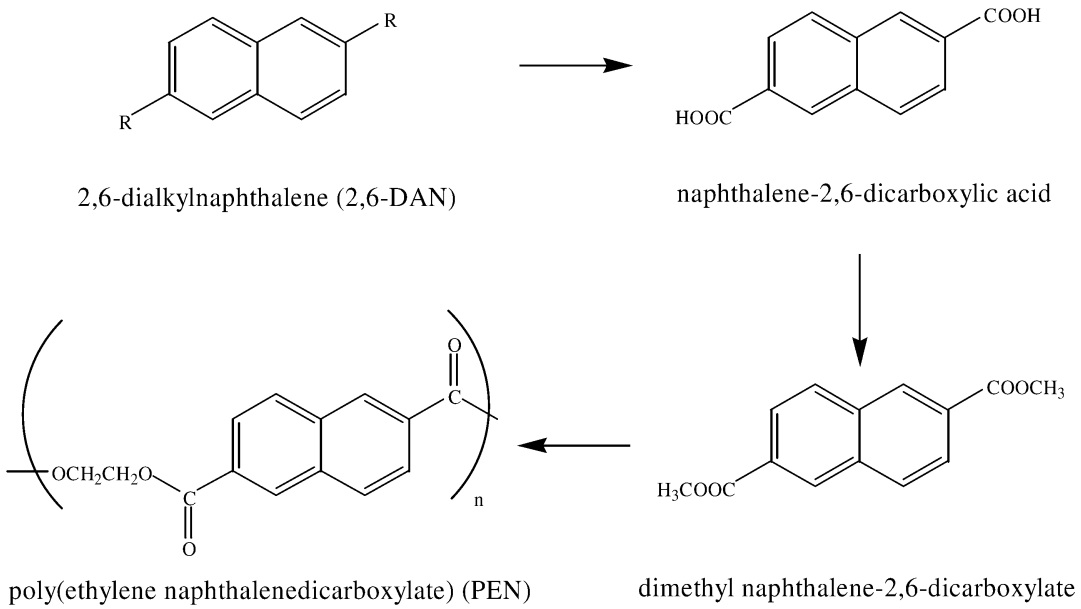
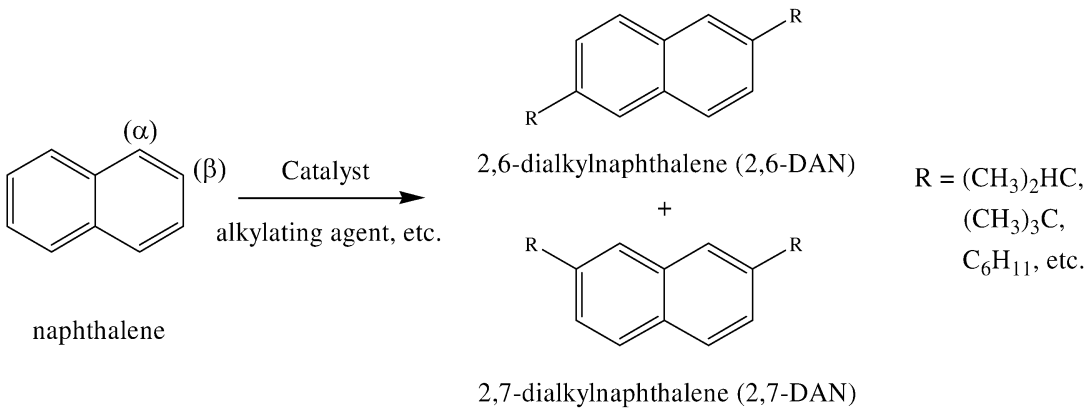



Scheme 1. Synthesis of PEN.

The selective preparation of 2,6-dialkylnaphthalenes has proved very difficult with the conventional Friedel–Crafts catalysts [9] or amorphous silica–alumina catalysts [8] as low β,β-selectivities and equal proportions of 2,6- and 2,7-isomers are obtained. Therefore, attention has focussed on the use of shape selective zeolite catalysts. Initial studies focussed on methylation of naphthalene, and it was found that β-selectivity could be obtained over zeolite HZSM-5, whereas non-selective alkylation was seen over the larger pore H-Mordenite (HM) and HY zeolites [10]. However, a poor yield of the 2,6-isomer was obtained and the ratio of 2,6/2,7 over HZSM-5 was approximately 1.

Subsequently, the *iso*-propylation of naphthalene has been studied with propene [11], *iso*-propanol




Scheme 2. Dialkylation of naphthalene.

Table 1
Recently published results for 2,6-dialkylnaphthalene selectivity[a]

| Reaction | *iso*-Propylation | Cyclohexylation | *tert*-Butylation |
|---|---|---|---|
| Catalyst | HM | HY | HY |
| Conversion of naphthalene (%) | 96.6 | 94 | 52.4 |
| Dialkylnaphthalene (%) | 69.2 | 43 | 27.8 |
| 2,6-Dialkylnaphthalene (%) | 54.2 | 19 | 23.3 |
| 2,6/2,7 Ratio | 4.0 | 1.2 | 5.9 |

[a] Results shown are taken directly from the corresponding papers or patents but converted into a common format.

[12] and *iso*-propyl bromide [13] as reagents, over a variety of different zeolites. For example, in 1991, Katayama et al. [11] reported β,β-selectivities of over 75% with a 2,6/2,7 ratio of approximately 2 over HM. Moreau and co-workers have recently studied both the cyclohexylation [14] and *tert*-butylation [15] of naphthalene over HY zeolite, with the added advantage of an easy separation of the corresponding 2,6-dialkylnaphthalene by crystallisation.

Examples of the best *iso*-propylation [16], cyclohexylation [14] and *tert*-butylation [15] results that we could find in the literature to date are given in Table 1. Our criteria for selection were based on the 2,6-dialkylnaphthalene yields and 2,6/2,7 ratios that could be calculated from the information given in the original papers or patents, and results are reported in this form.

The most promising of the three alkylations appeared to be *tert*-butylation, as the highest β,β-selectivity and 2,6/2,7 ratio were obtained as well as an easy separation of the desired product. It has also been reported that *iso*-octane effects *tert*-butylation [17], and that naphthalene can be *tert*-butylated using pillared clay catalysts [18].

Despite the intensive effort, the selective production of a 2,6-dialkylnaphthalene still remains an elusive goal. Therefore, we have undertaken a detailed study of the *tert*-butylation reaction to see if improvements could be made in the yield and selectivity for the 2,6-isomer. We now report the successful production of 2,6-di-*tert*-butylnaphthalene in over 60% yield, with a 2,6/2,7 ratio of over 50. The product can be easily separated from the mixture in over 50% isolated yield by crystallisation from ethanol, with the remainder obtainable by Kugelrohr distillation.

## 2. Experimental

### 2.1. Materials

HPLC grade *tert*-butanol (99.5+%) and scintillation grade naphthalene (99+%) were obtained from Aldrich and cyclohexane (99+%) was obtained from Fischer Scientific. All were used directly without further purification.

### 2.2. Catalysts

Zeolyst International (formerly PQ zeolites) kindly provided zeolites. H-MMS was synthesised by a literature method [19]. All solids were freshly calcined prior to the reaction by heating in air at 550°C for a minimum of 6 h. The properties of the commercial zeolites used in this study are recorded in Table 2. Those having ammonium cations would be converted into the corresponding proton forms during the calcination process.

### 2.3. Typical reaction procedure

Quantities are recorded in the footnotes to the appropriate tables. All reactions were carried out in a 450 ml glass-lined Parr autoclave, fitted with a thermocouple, gauge block assembly and liquid charging pipette. Stirring was achieved externally by means of a magnetic stirrer.

To the glass liner of the autoclave were added a magnetic stirrer bar, naphthalene, *tert*-butanol and cyclohexane. The mixture was allowed to stir until all the naphthalene had dissolved (ca. 5 min) and then the catalyst was added. The glass liner was transferred into the autoclave, which was sealed and

Table 2
Typical properties of the commercial zeolites

| Zeolite | HZSM-5 | HM | HM | HY | Hβ |
|---|---|---|---|---|---|
| Product code | CBV 5020E | CBV 20A | CBV 30A | CBV 720 | CP 814B-25 |
| Si/Al ratio | 25 | 10 | 17.5 | 15 | 12.5 |
| Nominal cation form | H | $NH_4$ | $NH_4$ | H | $NH_4$ |
| $Na_2O$ (wt.%) | 0.05 | 0.02 | 0.02 | 0.03 | 0.05 |
| Surface area ($m^2/g$) | 425 | 500 | 600 | 780 | 720 |

heated for the appropriate reaction time and temperature, with stirring, under self-generated pressure. In a few experiments the system was artificially pressurised to 3.45 MPa with nitrogen gas prior to heating.

After the given reaction time, the heating device was removed and the autoclave was allowed to cool to room temperature (ca. 2 h). The apparatus was then washed thoroughly with acetone and the catalyst was removed by filtration. The solid was thoroughly extracted with acetone and the mother liquor was concentrated.

For the reactions that involved multistages, after the above procedure the product mixture was concentrated and fresh catalyst, *tert*-butanol and solvent were added. The reaction was then allowed to proceed again under the same conditions.

### 2.4. Quantification of products

Product mixtures were subjected to gas chromatography on a Hewlett Packard HP 5890 (series II) gas chromatograph, fitted with an RTX-1 (100% dimethyl polysiloxane; 30 M, 0.32 mm ID) column. The GC conditions used for analysis were: 100°C for 5 min, ramped to 200°C at 10°C/min and held for 10 min, then ramped to 250°C at 5°C/min and held for 30 min. Tetradecane was used as an internal standard. A known weight was added to a measured aliquot of the final product solution prior to running the GC.

The EPSRC Mass Spectrometry Centre, University of Wales, Swansea, performed GC–MS. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker WM-400 spectrometer, operating at 400 MHz for $^1H$ and 100 MHz for $^{13}C$. $CDCl_3$ was used as the solvent and chemical shifts are reported as $\delta$ (ppm) from TMS. $J$ values are recorded in Hz.

### 2.5. Isolation and quantification of 2,6-di-tert-butylnaphthalene

Approximately 85% of the 2,6-DTBN present in the product could be obtained by concentrating the reaction mixture following the optimum reaction and then allowing the product to crystallise out. Purification was obtained by recrystallisation from hot ethanol (m.p.=148°C, lit. m.p.=147–148°C [20]). Separation of the remaining 2,6-DTBN (ca. 15% of the total) was obtained by Kugelrohr distillation under reduced pressure.

$^1H$ NMR, $\delta$: 7.75 (2H, d, $J$=8.6); 7.72 (2H, d, $J$=1.8); 7.55 (2H, dd, $J$=8.6 and 1.8); 1.40 (18H, s). $^{13}C$ NMR, $\delta$: 147.9, 131.5, 127.5, 124.7, 122.3, 34.7, 31.3. MS, $m/z$ (% abundance): 240 (26) [$M^+$], 226 (17), 225 (100), 77 (20), 57 (43).

## 3. Results and discussion

### 3.1. Preliminary screening of zeolites

Initially, a range of different solids was screened for efficacy in the *tert*-butylation reaction, under conditions used by Moreau and co-workers [15]. The results are given in Table 3.

The trends in the results were consistent with the findings of Moreau and co-workers [15], where direct comparison was possible. The minor variations can be understood in terms of the use of different zeolite samples and a different autoclave with different dimensions and different temperature control. Thus, HY was the most active solid and Hβ was essentially non-selective for the 2,6- over the 2,7-isomer (2,6/2,7 ratio of 1.1). In addition, we found that HZSM-5 gave no reaction, presumably because the pores were too small to allow the reaction to occur. With mesoporous

Table 3
Varying the catalyst in the *tert*-butylation of naphthalene[a]

| Catalyst | HY | HM | Hβ | HZSM-5 | H-MMS[d] |
|---|---|---|---|---|---|
| Si/Al ratio of catalyst | 15 | 10 | 12.5 | 25 | 10 |
| Conversion of naphthalene (%)[b] | 89 | 24 | 49 | 0 | 47 |
| 2-*tert*-Butylnaphthalene (%)[b] | 39 | 22 | 46 | – | 37 |
| Total di-*tert*-butylnaphthalene (%)[b] | 45 | 2 | 4 | – | 9 |
| 2,6-Di-*tert*-butylnaphthalene (%)[b] | 33 | 2 | 2 | – | 6 |
| 2,7-Di-*tert*-butylnaphthalene (%)[b] | 12 | – | 2 | – | 3 |
| 2,6/2,7 Ratio[c] | 2.7 | – | 1.1 | – | 1.9 |

[a] 2 h stirred autoclave reactions at 160°C; catalyst (0.5 g), cyclohexane (100 ml), naphthalene (10 mmol, 1.28 g), *tert*-butanol (20 mmol, 1.48 g).
[b] Proportions determined by GC. Numbers expressed as percentages have been rounded to the nearest whole number.
[c] The 2,6/2,7 ratio is a direct comparison of GC peak areas.
[d] MMS (a mesoporous molecular sieve) was synthesised by a literature procedure (see Section 2). The solid is similar to HMS.

H-MMS, reaction occurred with a naphthalene conversion similar to that with Hβ but with higher yield and a surprisingly higher 2,6/2,7 ratio of 1.9. However, our attention was attracted mostly by the result with HM. Although HM was quite inactive (only a 24% conversion of naphthalene and a 2% yield of DTBN (di-*tert*-butylnaphthalene)), it was potentially the most promising for selectivity as the only dialkyl isomer detected under these conditions was 2,6-DTBN. Therefore, we undertook a more detailed study of the reaction with HM as catalyst in the hope of enhancing the conversion into dialkylnaphthalene while retaining the high selectivity.

### *3.2. Optimisation of the conditions using HM as catalyst*

We attempted to increase the conversion into desirable product by using more forcing conditions (increasing the time and temperature) and by adding more catalyst and/or alkylating agent. Doubling the amount of catalyst to 1.0 g under the original conditions increased the conversion by 13% and the DTBN yield by 5%. Also, it was then possible to identify the 2,7-isomer in the mixture and a 2,6/2,7 ratio of 17.3 could be determined, already a significant improvement over all previously reported selectivities. The general trend when the amount of HM catalyst was increased further was increased conversion and DTBN yield, but decreased 2,6/2,7 ratio.

Further studies were conducted using different times, temperatures, pressures, *tert*-butylating species, solvents, amounts of *tert*-butanol, solvent and catalyst, Si/Al ratios of the HM catalyst, and modes of addition. Increasing the reaction time increased the conversion, yield of 2,6-DTBN and the 2,6/2,7 ratio. Increasing the reaction temperature initially improved the conversion and yield of 2,6-DTBN but these reached a maximum, with further increase in temperature having a negative effect on both. The 2,6/2,7 ratio was seen to fall with increasing temperature (cf. results of Moreau and co-workers [15]). An artificial pressure increase resulted in improvements to the conversion and yield of 2,6-DTBN but at the expense of the 2,6/2,7 ratio. Changing the Si/Al ratio of HM from 10 to 17.5 gave a marginal improvement in selectivity at a similar conversion. However, with more substantially dealuminated samples of HM the conversion fell considerably, though there were further increases in the 2,6/2,7 ratio.

No other solvents tried proved to be more beneficial than cyclohexane. Furthermore, a reduction in the volume of solvent used was advantageous both to the conversion and to the yield of desirable product, whilst having little effect on selectivity (although a poor result was achieved without solvent). Increasing the amount of *tert*-butanol brought about increase in both the conversion and the yield of 2,6-DTBN, although excessive amounts caused both to fall. However, the 2,6/2,7 ratio was seen to increase with increasing *tert*-butanol without reaching a maximum.

Following this study, we found that the optimum conditions for maximising the yield while retaining selectivity involved two successive 1 h autoclave

Table 4
*tert*-Butylation of naphthalene under optimised conditions[a]

| | Stage 1 | Stage 2 |
|---|---|---|
| Conversion of naphthalene (%)[b] | 84 | 96 |
| Total di-*tert*-butylnaphthalene (%)[b] | 50 | 61 |
| 2,6-Di-*tert*-butylnaphthalene (%)[b] | 50 | 60 |
| 2,7-Di-*tert*-butylnaphthalene (%)[b] | 1 | 1 |
| 2,6/2,7 Ratio[c] | 58.5 | 50.6 |

[a] Each stage involved a 1 h stirred autoclave reaction at 180°C; HM (Si/Al 17.5, 4.0 g), cyclohexane (10 ml), naphthalene (10 mmol, 1.28 g), *tert*-butanol (80 mmol, 5.93 g).

[b] Proportions determined by GC. Numbers expressed as percentages have been rounded to the nearest whole number.

[c] The 2,6/2,7 ratio is a direct comparison of GC peak areas.

Table 5
*tert*-Butylation of naphthalene over various catalysts under the optimised conditions[a]

| Catalyst | HM | HY | Hβ |
|---|---|---|---|
| Si/Al ratio of catalyst | 17.5 | 15 | 12.5 |
| Conversion of naphthalene (%)[b] | 84 | 94 | 87 |
| Total di-*tert*-butylnaphthalene (%)[b] | 50 | 55 | 38 |
| 2,6-Di-*tert*-butylnaphthalene (%)[b] | 50 | 37 | 19 |
| 2,7-Di-*tert*-butylnaphthalene (%)[b] | 1 | 18 | 19 |
| 2,6/2,7 Ratio[c] | 58.5 | 2.0 | 1.0 |

[a] 1 h stirred autoclave reactions at 180°C; catalyst (4.0 g), cyclohexane (10 ml), naphthalene (10 mmol, 1.28 g), *tert*-butanol (80 mmol, 5.93 g).

[b] Proportions determined by GC. Numbers expressed as percentages have been rounded to the nearest whole number.

[c] The 2,6/2,7 ratio is a direct comparison of GC peak areas.

reactions at 180°C, using HM (4.0 g, Si/Al ratio 17.5), *tert*-butanol (80 mmol) and cyclohexane (10 ml) for an initial 10 mmol of naphthalene (Table 4). Under these conditions, a 2,6-DTBN yield of 50% and a 2,6/2,7 ratio of 58.5 was achieved after the first reaction, and a 60% yield with a ratio of 50.6 after the second stage.

The optimum product mixture, in addition to 61% of di-*tert*-butylnaphthalenes contained 4% of residual naphthalene, 10% of 2-*tert*-butylnaphthalene and significant quantities of several other 2,6-dialkylnaphthalenes in which one or both of the alkyl groups contained more than four carbon atoms (e.g. 2,6-di-*tert*-amylnaphthalene). In addition, small quantities of tri-*tert*-butylnaphthalenes were detected.

For comparison, reactions with HY and Hβ were conducted under the conditions optimised for HM, though only for a single stage reaction. The results are given in Table 5.

The results confirmed that HY and Hβ remain more active than HM under these conditions. In the case of HY, the total DTBN yield obtained was also higher than with HM, but the results confirmed the significance of the HM catalyst for obtaining selectivity as HY achieved a 2,6/2,7 ratio of only 2 and Hβ proved to be non-selective. Therefore, the actual 2,6-DTBN yield was significantly higher with HM (50%) than with HY (37%) or Hβ (19%). Also, the absence of significant quantities of other di-*tert*-butylnaphthalene isomers would make its separation from the mixture much easier.

## 4. Conclusions

Highly regioselective dialkylation of naphthalene can be achieved over a dealuminated HM zeolite using *tert*-butanol as an alkylating agent. By optimisation of the reaction parameters, 2,6-di-*tert*-butylnaphthalene was obtained in an yield of 60% with a 2,6/2,7 ratio of over 50. To the best of our knowledge, this is the highest yield of any 2,6-dialkylnaphthalene and easily the highest 2,6/2,7 ratio yet reported. The yield of total 2,6-dialkylnaphthalenes in our reaction mixture is even higher (ca. 70%) when the higher dialkylnaphthalenes are taken into account.

Although this method is easily the most selective yet discovered for production of a 2,6-dialkylnaphthalene, it may be difficult to oxidise the *tert*-butyl groups to carboxyl groups [21]. Also, there would be a loss of six carbon atoms during this process, which is wasteful. Therefore, there is still a room for considerable improvement in the clean and selective synthesis of naphthalene-2,6-dicarboxylic acid.

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