

## Polybromination of naphthalene using bromine over a montmorillonite clay and regioselective synthesis of 2,6-dibromonaphthalene

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Received mm-dd-yyyy

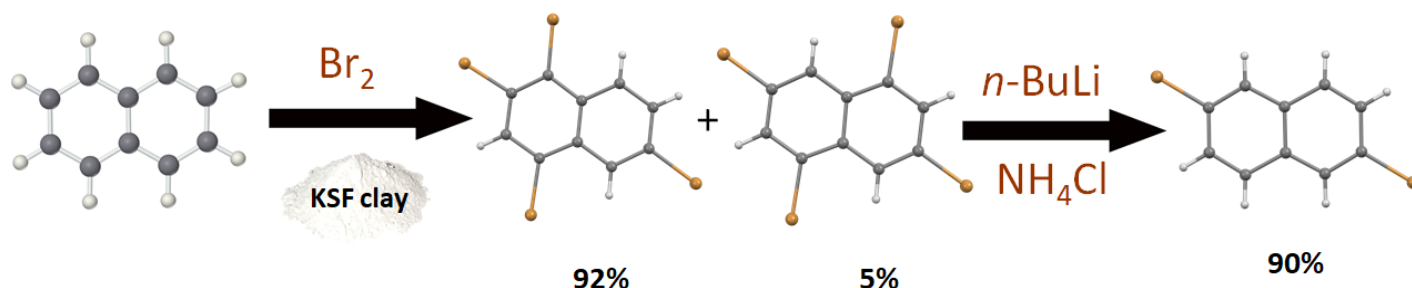
Accepted Manuscript mm-dd-yyyy

Published on line mm-dd-yyyy

Dates to be inserted by editorial office

### Abstract

Reaction of naphthalene and bromine (three mole equivalents) at room temperature gave 1,4,6-tribromonaphthalene (66%) along with 1,4-dibromonaphthalene (8%) and 1,5-dibromonaphthalene (10%). Crystallization of the crude product gave pure 1,4,6-tribromonaphthalene in 50% yield. Bromination of naphthalene using four mole equivalents of bromine over KSF clay gave 1,2,4,6-tetrabromonaphthalene (92%) along with 1,3,5,7-tetrabromonaphthalene (5%). Crystallization of the crude products gave 1,2,4,6-tetrabromonaphthalene, a previously unreported compound, and 1,3,5,7-tetrabromonaphthalene in 70% and 4% isolated yields, respectively. Proto-debromination of the crude tetrabromination product, using two mole equivalents of *n*-butyllithium at a low temperature for a short reaction time, gave 2,6-dibromonaphthalene regioselectively in 82% yield after crystallization.



**Keywords:** naphthalene; polybromination; regioselective catalysis; structured solids; 2,6-dibromonaphthalene; 1,2,4,6-tetrabromonaphthalene

## Introduction

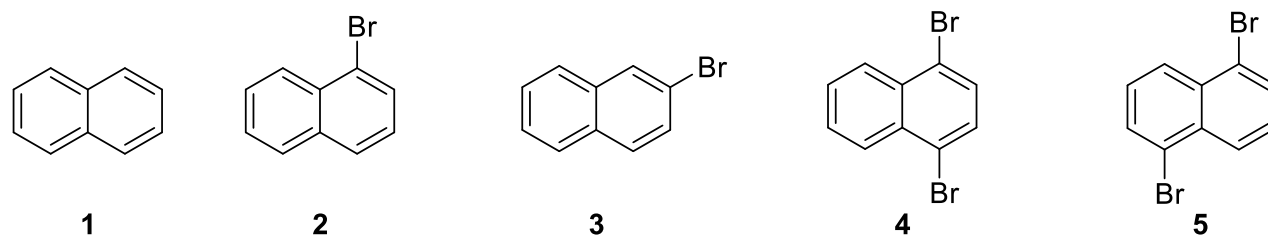
Reactions of aromatic compounds with electrophiles are among the most common routes for the production of substituted derivatives.<sup>1-3</sup> Traditional processes involve use of an acid or other activator, which generates toxic and hazardous materials during work-up. In addition, such reactions often require harsh reaction conditions and lead to low yields because of the production of mixtures of isomers that require separation.<sup>4</sup> Therefore, attention has shifted to the use of greener chemical processes to overcome many of the limitations associated with traditional ones.<sup>5-7</sup> In particular, certain solid catalysts can provide high selectivity towards the more linear disubstituted aromatics (for example as a result of shape-selectivity within the pores of zeolites)<sup>8,9</sup> in good yields, have the possibility to be reused several times, and may allow simple procedures that do not require long reaction times or harsh conditions.<sup>10-12</sup>

Bromonaphthalenes are used as precursors for the production of valuable materials with interesting applications.<sup>13,14</sup> Polybromonaphthalenes can be produced by direct bromination of naphthalene or by further bromination of bromo- or dibromonaphthalenes. Common reagents used in such brominations include bromine (Br<sub>2</sub>) in chlorinated solvents at -30 °C to 77 °C,<sup>15,16</sup> dioxane dibromide at 40 °C,<sup>17</sup> copper bromide in chlorobenzene at 120 °C,<sup>18</sup> *N*-bromosuccinimide in ionic liquid at 28 °C,<sup>19</sup> and 3-methylimidazolium tribromide at 70 °C.<sup>20</sup> However, many of the procedures require the use of excess brominating reagents, several purification stages, or have been applied only on a small scale.<sup>21</sup>

A few studies have reported the production of tribromonaphthalenes by bromination of either naphthalene or bromonaphthalenes. For example, bromination of 1-bromonaphthalene using 1.5 mole equivalents of Br<sub>2</sub> in carbon tetrachloride (CCl<sub>4</sub>) under photolytic conditions (250 W lamp) for 2.5 hour at 77 °C gave a mixture of 1,5-dibromonaphthalene (92%) and 1,3,5-tribromonaphthalene (8%),<sup>16</sup> while photo-bromination of 1-bromonaphthalene using Br<sub>2</sub> (2.5 mole equivalents) in CCl<sub>4</sub> at -30 °C for 45 minutes led to a mixture of 1,5-dibromonaphthalene (8%), *trans,cis,trans*-1,2,3,4,5-pentabromo-1,2,3,4-tetrahydronaphthalene (10%), and *trans,trans,trans*-1,2,3,4,5-pentabromo-1,2,3,4-tetrahydronaphthalene (63%) after purification.<sup>16</sup> Treatment of *trans,trans,trans*-1,2,3,4,5-pentabromo-1,2,3,4-tetrahydronaphthalene with potassium *tert*-butoxide (2.4 mole equivalents) in tetrahydrofuran (THF) at 20 °C overnight gave 1,3,5-tribromonaphthalene in 91% yield.<sup>16</sup> Treatment of monobromonaphthalenes with aluminum chloride gave mixtures of naphthalene and polybromonaphthalenes.<sup>22</sup> Bromination of 1-bromonaphthalene using excess Br<sub>2</sub> in the presence of iron gave 1,4,6-tribromonaphthalene in 20% yield.<sup>23</sup> 1,4,6-Tribromonaphthalene was obtained in a better yield (43%) from bromination of 1,4-dibromonaphthalene using excess Br<sub>2</sub> at 80 °C.<sup>24</sup>

Reaction of either 1,5-dibromonaphthalene or 1,8-dibromonaphthalene with Br<sub>2</sub> (two mole equivalents) in the presence of traces of iodine in a sealed tube heated at 200 °C for 5 hours gave, what was believed at the time to be, 1,4,5,8-tetrabromonaphthalene in 82% crude yield.<sup>25</sup> In fact, the tetrabromonaphthalene obtained was 1,3,5,7-tetrabromonaphthalene, as proved later by X-ray diffraction.<sup>26</sup> 2,3,6,7-Tetrabromonaphthalene was obtained in 53% yield from reaction of a solution of Br<sub>2</sub> in CCl<sub>4</sub> with 2,3,6,7-tetrakis(trimethylsilyl)naphthalene in pyridine for 10 hours.<sup>27</sup> Higher brominated naphthalenes such as 1,2,3,4,6,7-hexabromonaphthalene have been obtained from bromination of naphthalene using Br<sub>2</sub> in the presence of iron powder in boiling dichloromethane (DCM) for 4 hours.<sup>27</sup> As can be seen from these examples, few of the methods for preparation of specific polybromonaphthalenes are convenient. Therefore, there are still needs for convenient and simple synthetic procedures to produce such polybrominated naphthalenes.

Recently, we have shown that dibromination of naphthalene (**1**) over Synclyst 13 gave 1,4-dibromonaphthalene (**4**; Figure 1) selectively in 91% yield after purification, while the use of calcined montmorillonite KSF clay led to the production of a mixture of **4** and 1,5-dibromonaphthalene (**5**; Figure 1).

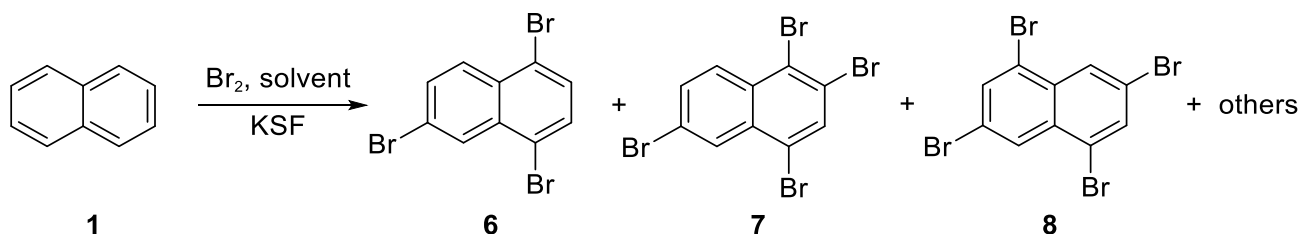


**Figure 1.** Structures of compounds **1**–**5**.

Following crystallization of the latter mixture, **5** was obtained in 40% yield.<sup>28</sup> The current work deals with polybromination of **1** using Br<sub>2</sub> (three or four mole equivalents) over the same clay to produce tri- or tetrabromonaphthalenes, respectively. In addition, proto-debromination of tetrabromonaphthalenes using butyllithium (BuLi) was investigated in an attempt to produce the linear derivative, 2,6-dibromonaphthalene. Success has been achieved on both fronts, which is now reported.

## Results and Discussion

As reported previously, dibromination of **1** using two equivalents of Br<sub>2</sub> in DCM over KSF clay that had been calcined by heating in air for 6 hours had given a small amount (up to 5%) of 1,4,6-tribromonaphthalene (**6**) as an impurity.<sup>28</sup> Reaction of **1** (7.64 mmol) with three mole equivalents of Br<sub>2</sub> over freshly calcined KSF clay (4.0 g, based on our previous experience<sup>26</sup>) in different solvents was attempted (Scheme 1) and the reaction time was varied from 30 minutes to 65 hours (Table 1).



**Scheme 1.** Polybromination of **1** using Br<sub>2</sub> over calcined KSF.

The use of a non-polar solvent (hexane) resulted in a 20% yield of **6** after a reaction time of 3 hours, but the reaction continued slowly thereafter, so that by 65 hours the yield of **6** had risen to only 51%, while the yields of **4** and **5** fell to about half of what they were after 3 hours. The reaction proceeded more quickly in the more polar solvent DCM, giving **6** in 66% yield after 24 hours, by which time only a small amount of both **4** (8%) and **5** (10%) remained. The crude product obtained from this reaction was purified by crystallization to give pure **6** in 50% yield. The structure of **6** was established using different spectroscopic tools (see experimental section) and X-ray diffraction (Figure 2).

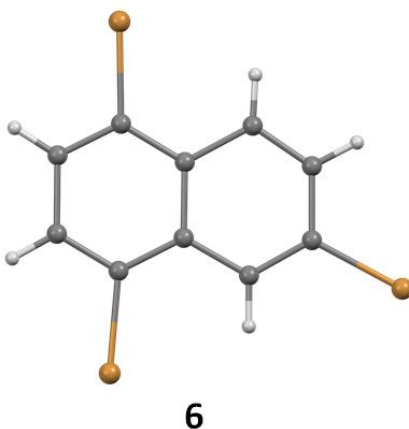
**Table 1.** Polybromination of **1** using Br<sub>2</sub> (three mole equivalents) over calcined KSF clay according to Scheme 1<sup>a</sup>

Reaction time (h)	Solvent	GC Yield (%) of products	Mass balance (%) <sup>b</sup>
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		<b>2</b>	<b>4</b>	<b>5</b>	<b>6</b>	
0.5	DCM	67	18	14	—	99
1	DCM	1	47	38	11	97
3	DCM	1	25	24	45	95
3	Hexane	—	63	14	20	97
24	DCM	—	8	10	66	84
24	Hexane	—	43	8	37	88
65	DCM	1	15	16	53	85
65	Hexane	—	34	8	51	93

a: A solution of Br<sub>2</sub> (3.66 g; 22.92 mmol) in a solvent (10 mL) was added slowly to a stirred mixture of **1** (0.979 g, 7.64 mmol) and calcined KSF clay (4.0 g) in a solvent (50 mL). The mixture was stirred in the dark for the specified reaction time at 25 °C, then quenched with an aqueous solution of sodium metabisulfite; b: Sum of the yields of the listed compounds. A low mass balance indicates that other naphthalene derivatives were also formed in the reaction. For example, small quantities of unidentified isomeric tribromonaphthalenes were present in some reaction mixtures.

Leaving the reaction for a longer time (65 hours) led to a decrease in the yield of **6** from 66% to 53% and an increase in the proportions of **4** and **5**. Such an observation suggests that the bromination process may be reversible and that over time some bromine might be lost from the system. Reactions conducted under similar conditions (DCM, 25 °C), in the absence of the clay, with 3–8 equivalents of bromine for up to 5 days in most cases gave only mono- and dibromonaphthalenes and even after 5 days with 8 equivalents of bromine the amount of tribromonaphthalene formed was only 5%, clearly indicating that the KSF clay was significant in bringing about these results.

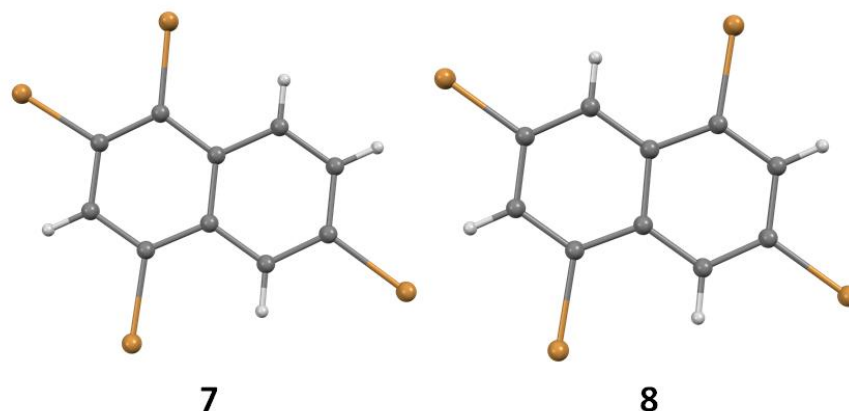


**Figure 2.** Molecular structure of **6** by X-ray diffraction.

Next, our attention was turned to polybromination of **1** using four mole equivalents of Br<sub>2</sub> over calcined KSF (Scheme 1) in DCM as solvent at 25 °C, over reaction periods from one to four days.

A reaction carried out for 72 hours led (according to GC) to the major formation of an unidentified compound, along with a small proportion of 1,3,5,7-tetrabromonaphthalene (**8**). The crude product was purified by fractional crystallization to give the unidentified product in pure form and pure **8** (4% isolated yield). Mass spectrometry showed that the unidentified product was also a tetrabromonaphthalene and its NMR spectra suggested that it was the previously unknown 1,2,4,6-tetrabromonaphthalene (**7**). Full details of the

spectroscopic identification are given in the experimental section. The structures of **7** and **8** were confirmed by X-ray diffraction (Figure 3). With the identity of the novel compound confirmed and the availability of pure samples of **7** and **8** with which to determine their GC response factors, the yields of **7** and **8** in the different reactions could be calculated and the figures are recorded in Table 2. The mass balance for the identified products in the reaction carried out over 96 h was low (84%) due to formation of pentabromonaphthalenes (*ca.* 10%) along with other unidentified products (*ca.* 5%) that could not be included in the mass balance figure because their response factors were not known.



**Figure 3.** Molecular structures of **7** and **8** determined by X-ray diffraction.

**Table 2.** Polybromination of **1** according to Scheme 1 using Br<sub>2</sub> (four mole equivalents) over calcined KSF clay in DCM<sup>a</sup>

Time (h)	GC Yield (%) of products			Mass balance (%)
	<b>6</b>	<b>7</b>	<b>8</b>	
24	33	59	8	100
72	—	92	5	97 <sup>b</sup>
96	2	61	21	84 <sup>c</sup>

a: A solution of Br<sub>2</sub> (4.88 g; 30.6 mmol) in DCM (10 mL) was added slowly to a stirred mixture of **1** (0.979 g, 7.64 mmol) and calcined KSF clay (4.0 g) in DCM (50 mL). The mixture was stirred in the dark for the specified reaction time at 25 °C, then quenched; b: Unidentified isomeric tetrabromonaphthalenes were also present; c: Unidentified products including pentabromonaphthalenes were also present.

In order to try to understand the results of the polybromination reactions, we considered the likely reactivity of the different positions around the naphthalene ring. It is well known that  $\alpha$ -positions are more reactive towards electrophilic substitution than  $\beta$ -positions and it is therefore not surprising that dibromination led to mixtures of **4** and **5**.<sup>28</sup> Further bromination of **4** would be sterically hindered at the remaining  $\alpha$ -positions due to the presence of bulky bromine substituents at the nearby *peri* positions, 1 and 4. Therefore, it would not be surprising that further bromination of **4** might take place at one of the identical positions 6 or 7, leading to the production of **6**. However, since **5** was also formed in a substantial amount in the reaction of two equivalents of bromine with naphthalene over calcined KSF clay,<sup>28</sup> it would be reasonable on the same basis to expect a significant amount of 1,3,5-tribromonaphthalene to be formed in the reaction with three equivalents of bromine, possibly with a smaller quantity of 1,2,5-tribromonaphthalene, which would require attack of bromine at a position adjacent to an existing bromine substituent. However, only small quantities of any tribromonaphthalenes other than **6** were seen in the reactions with three equivalents

of bromine, even when the yield of **6** was as high as 66% (Table 1). It might be expected that further bromination of **6** would take place preferentially at the 2-, 3- and 7-positions on steric grounds, with attack at the 3-position being least favored on electronic grounds because of the contribution of the bromine at the 6-position, but it is not obvious why isomer **7** should predominate over the 1,4,6,7-tetrabromonaphthalene isomer (formed by attack at the 7-position on **6**). Formation of **8** might be expected to result from attack at the least hindered position of 1,3,5-tribromonaphthalene, which in turn would have resulted from attack at the least hindered position of **5**.

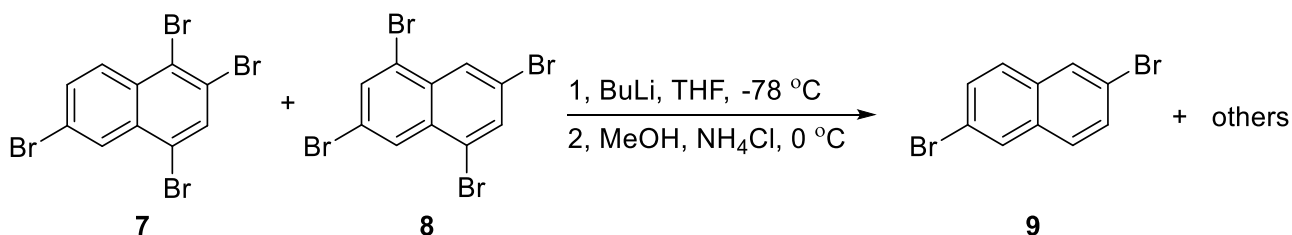
On the basis of the above analysis, involving successive further bromination steps on pre-formed bromo derivatives, it should be possible to enhance the selectivity towards particular polybromo isomers by starting with an appropriate pure dibromonaphthalene precursor rather than relying on the mixture of isomeric dibromonaphthalenes formed during dibromination of naphthalene itself over calcined KSF. Therefore, further brominations were attempted on a reaction mixture from dibromination over Synclyst 13 (an amorphous silica-alumina), which was virtually pure 1,4-dibromonaphthalene (**4**),<sup>28</sup> with two mole equivalents of additional Br<sub>2</sub> in DCM, with and without added calcined KSF clay. Surprisingly, no further bromination occurred under these conditions in either case and **4** remained as the almost exclusive component of the reaction mixtures. However, when a small amount of naphthalene (10%) was added to such a reaction mixture, **7** was obtained in 48% yield, along with **6** (33.5%) and **8** (9%). This result is not very different to that obtained from reaction of **1** and Br<sub>2</sub> (4 mole equivalents) over KSF after 24 hours (Table 1). Clearly, something more complicated than a series of successive electrophilic brominations on preformed bromo compounds, leading sequentially to mono-, di-, tri- and tetrabromonaphthalenes, is occurring in these reactions. It is possible that the KSF is inducing radical reactions or catalyzing addition of bromine, either of which processes might occur with naphthalene but not with a less reactive dibromonaphthalene. If the intermediates produced could then transfer bromine between different naphthalene and bromonaphthalene derivatives, the eventual mixture produced would depend on the specific reaction conditions and components rather than particularly on the starting materials. Further research would be needed in order to gain a better understanding of the mechanism.

Various attempts were made to test the effect of temperature, solvent and amount of KSF clay on the rate of formation of both **7** and **8**. However, none of the conditions attempted improved the yields of the specific components. Also, a reaction was attempted over KSF clay dried at 120 °C rather than calcined at 550 °C to see what the effect of calcination could have on the yield of products. However, the products obtained using four mole equivalents of Br<sub>2</sub> over the dried clay were **4** (75%), **5** (15%), and **6** (8%). Calcination had evidently been important in encouraging the processes reported above that had given greater proportions of more highly brominated products.

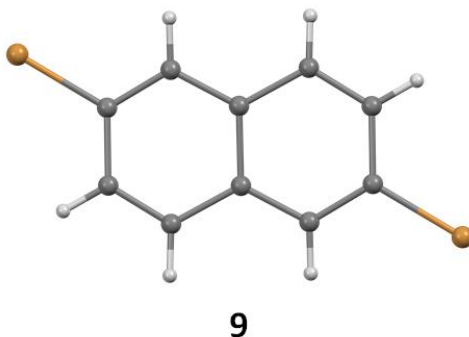
An intriguing possibility emerged as a result of the virtually exclusive formation of a mixture of **7** and **8** in the reaction of **1** with 4 equivalents of bromine over calcined KSF. One of the initial drivers behind our studying the bromination of naphthalene over solid catalysts had been the desire to produce 2,6-dibromonaphthalene (**9**), which could be a very valuable intermediate for the synthesis of a range of linear disubstituted naphthalenes. We had previously developed several regioselective synthetic processes that allowed the selective production of (linear) 1,4-disubstituted benzenes<sup>8,12,29–31</sup> or 2,6-dialkyl naphthalenes<sup>32,33</sup> using solid catalysts such as zeolites. However, the production of **9** by direct dibromination of **1** over solid catalysts was not successful, the reaction giving **4** and/or **5** instead.<sup>28</sup> Based on our experience in the use of organolithium intermediates in organic synthesis,<sup>34–36</sup> we thought it might be possible to debrominate a mixture of tetrabromonaphthalenes **7** and **8** selectively to give 2,6-dibromonaphthalene (**9**). Both **7** and **8** contain two bromine atoms in the same relative orientation at  $\beta$ -positions (2- and 6-positions or 3- and 7-positions) in

addition to two bromine atoms in  $\alpha$ -positions (1,4- or 1,5-positions, respectively). The selective proto-debromination of the bromine at the  $\alpha$ -position in 1,6-dibromo-2-naphthol had been reported using tin in the presence of hydrogen bromide.<sup>37</sup> Therefore, it was hoped that selective proto-debromination from the  $\alpha$ -positions in both **7** and **8** through bromine-lithium exchange followed by hydrolysis with aqueous ammonium chloride solution could lead to the production of **9**. Compound **9** had previously been obtained in only 35% crude yield from reaction of 6-bromo-2-naphthol with Br<sub>2</sub> in the presence of triphenylphosphine in boiling MeCN for 2 hours.<sup>38</sup>

Treatment of the crude product containing **7** (92%) and **8** (5%) with *tert*-BuLi in anhydrous tetrahydrofuran (THF) at a low temperature (Scheme 2) under an inert atmosphere for 1 hour at  $-78\text{ }^{\circ}\text{C}$  was attempted (Table 3). The use of one mole equivalent of *tert*-BuLi led to the production of 2% of 2,6-dibromonaphthalene (**9**) and a single predominant peak in the tribromonaphthalene (TriBN) region of the gas chromatogram, which was not due to **6**, but would correspond to around a 70% yield if its response factor were comparable to that of **6**. However, NMR spectra of the product mixture suggested that the single GC peak subsumed at least two different TriBN components, most likely 1,3,7-TriBN and 1,2,6-TriBN by removal of one or the other of the  $\alpha$ -bromo substituents. A significant increase in the yield of **9** (to 45%) and a substantial decrease in the proportion of the TriBN compounds took place when two mole equivalents of *tert*-BuLi were used. Following work-up, the crude product was crystallized to provide a pure sample of **9** and its structure was established (see experimental section and Figure 4).<sup>39</sup> Table 3 shows that the first Br–Li exchange (one mole equivalent of *tert*-BuLi) was fast and probably selective at the  $\alpha$ -position to give a high proportion of the TriBN compounds. The second Br–Li exchange (two mole equivalents of *tert*-BuLi) was selective to produce **9** (45%) but **1**, and monobromonaphthalenes **2** and **3**, were also obtained.



**Scheme 2.** Synthesis of **9**.



**Figure 4.** Molecular structure of **9** revealed by X-ray diffraction.

**Table 3.** GC yields of products obtained from treatment of a mixture of **7** and **8** with *tert*-BuLi<sup>a</sup>

<i>tert</i> -BuLi (mole equivalents)	GC Yield (%) of products
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	<b>1</b>	<b>2</b>	<b>3</b>	<b>TriBN<sup>b</sup></b>	<b>7</b>	<b>8</b>	<b>9</b>
0	—	—	—	—	92	5	—
1 <sup>c</sup>	6	1	—	70	6	3	2
2 <sup>c</sup>	3	2	1	38	—	—	45

a: A solution of *tert*-BuLi (1.7 M) in pentane was added dropwise over 10 minutes to a cold (−78 °C) stirred solution of a mixture of **7** and **8** (1.776 g, 4.0 mmol) in dry THF (30 mL) under N<sub>2</sub>. The mixture was stirred for one hour at −78 °C then warmed up to room temperature and quenched; b: Based on the area of a single GC peak and an assumption of a response factor equal to that of **6**; c: Unidentified bromonaphthalenes (10–11%) were also obtained.

Next, *tert*-BuLi was added in stages in order to control the second Br–Li exchange. The first mole equivalent of *tert*-BuLi was added to the mixture of **7** and **8** at −78 °C and the mixture was stirred for 10 min. An aliquot was drawn from the mixture, quenched, and analyzed by GC. Another half equivalent of *tert*-BuLi was added and the mixture was stirred for 10 min. The process was repeated one more time to bring the total to two mole equivalents of *tert*-BuLi. In addition, other alkyllithium reagents (*sec*-BuLi and *n*-BuLi) were used to test the effect of the lithium reagent on the rate of the proto-debromination process. The GC yields of products obtained are shown in Table 4.

**Table 4.** GC yields of product obtained from treatment of a mixture of **7** and **8** with BuLi in stages<sup>a</sup>

BuLi isomer	Mole equivalents	GC Yield (%) of products						
		<b>1</b>	<b>2</b>	<b>3</b>	<b>TriBN<sup>b</sup></b>	<b>7</b>	<b>8</b>	<b>9</b>
—	—	—	—	—	—	92	5	—
<i>tert</i> -BuLi	1	—	—	—	84	5	4	5
<i>tert</i> -BuLi	1.5 <sup>c</sup>	—	3	1	32	2	3	56
<i>tert</i> -BuLi	2 <sup>c</sup>	4	19	16	3	—	—	48
<i>sec</i> -BuLi	1	—	—	—	82	3	4	9
<i>sec</i> -BuLi	1.5 <sup>c</sup>	—	20	6	9	—	5	59
<i>sec</i> -BuLi	2 <sup>c</sup>	31	13	10	7	—	—	21
<i>n</i> -BuLi	1	—	—	—	61	—	2	33
<i>n</i> -BuLi	1.5 <sup>c</sup>	—	12	5	34	—	—	48
<i>n</i> -BuLi	2 <sup>c</sup>	3	12	7	19	—	—	43

a: A solution of BuLi (1.0 mole equivalent) was added dropwise to a cold (−78 °C) stirred solution of a mixture of **7** and **8** (0.888 g, 2.0 mmol) in dry THF (30 mL) under N<sub>2</sub>. The mixture was stirred for 10 minutes before another half of a mole equivalent of BuLi was added and the mixture was stirred for 10 min. The last portion of BuLi (half mole equivalent) was added and the mixture was stirred for 10 minutes, warmed up to room temperature and quenched; b: Based on the area of a single GC peak and an assumption of a response factor equal to that of **6**; c: Unidentified bromonaphthalenes (1–18%) were also present in these reactions.

The use of *tert*-BuLi (1.5 mole equivalents) over two stages led to the formation of **9** in 56% yield along with around 32% of tribromonaphthalenes (TriBN). The addition of an extra half mole equivalent of *tert*-BuLi led to a decrease in the yield of both tribromonaphthalenes and **9** in addition to formation of 1- and 2-



bromonaphthalenes (**2** and **3**) in significant proportion (35%). Clearly, the proto-debromination at this stage was not highly selective since **2**, which still retains an  $\alpha$ -bromo substituent, was formed in 19% yield.

Table 4 also shows that the yield of **9** was 59% after the addition of the first half of the second mole equivalent of *sec*-BuLi, which is very similar to that obtained using *tert*-BuLi (56%). However, the yield of **9** decreased significantly to 21% after the addition of the second half of the second mole equivalent of *sec*-BuLi. Clearly, there was no significant gain from the use of *sec*-BuLi instead of *tert*-BuLi.

The proto-debromination reaction after the addition of the first mole equivalent of *n*-BuLi was fast and selective towards the removal of  $\alpha$ -protons. Under such conditions, the yield of **9** was 33% along with TriBN (*ca.* 61%), indicating that at least 1.27 equivalents of bromine had been removed by just 1 equivalent of *n*-BuLi. The yield of **9** was increased to 48% when 1.5 mole equivalents of *n*-BuLi was used, along with significant quantities of TriBN (*ca.* 34%), **2** (12%) and **3** (5%), indicating that 1.81 equivalents of bromine had been removed by 1.5 equivalents of *n*-BuLi. Finally, when two mole equivalents of BuLi (*tert*-BuLi, *sec*-BuLi, or *n*-BuLi) were used, the result suggests that 2.4–2.8 mole equivalents of bromo substituents were removed. The reasons for these observations are not clear, but one possible explanation might be that the interaction between THF and the lithionaphthalene intermediates leads to lithium-proton exchange with the solvent, giving a lithiated THF species, which might play a role in further Br–Li exchange reactions.

Since *n*-BuLi was very selective towards **9** after the addition of the first mole, it was chosen for further investigation. Next, the effect of dilution of both **1** and *n*-BuLi was investigated to see what effect the dilution could have on the yield of **9**. In addition, a pre-cooled ( $-78$  °C) solution of *n*-BuLi in hexane was used to avoid formation of local hot spots. Moreover, a short reaction time (20 or 5 minutes) was employed to minimize any side reactions that might take place. The results obtained are shown in Table 5.

**Table 5.** GC yields of products obtained from treatment of a mixture of **7** and **8** with *n*-BuLi in two stages<sup>a</sup>

Mole equivalents	Time (min)	GC Yield (%) of products						
		<b>1</b>	<b>2</b>	<b>3</b>	TriBN <sup>b</sup>	<b>7</b>	<b>8</b>	<b>9</b>
—	—	—	—	—	—	92	5	—
1	20	—	—	1	63	—	3	31
2	20	—	—	7	15	—	—	77
1	5	—	—	—	81	4	2	12
2 <sup>c</sup>	5	—	—	1	6	—	—	90

a: A pre-cooled ( $-78$  °C) solution of *n*-BuLi (4.0 mmol, 2.5 M in hexane) diluted with dry hexane (5 mL) was slowly added to a cold ( $-78$  °C) stirred solution of a mixture of **7** and **8** (1.776 g, 4.0 mmol) in dry THF (40 mL) under N<sub>2</sub>. The mixture was stirred for 20 or 5 minutes and the second mole equivalent of *n*-BuLi (4.0 mmol) was then added. The mixture was stirred for another 20 or 5 minutes and then quenched; b: Based on the area of a single GC peak and an assumption of a response factor equal to that of **6**; c: Unidentified bromonaphthalenes (*ca.* 3%) were also obtained.

The addition of a pre-cooled diluted solution of *n*-BuLi (4 mmol) in hexane to a mixture of **7** and **8** (4 mmol) at  $-78$  °C for 20 minutes led to the production of **9** in 31% yield along with TriBN (*ca.* 63%). The addition of the second equivalent of *n*-BuLi led to an increase in the yield of **9** to 77%. For the shorter reaction time (5 min), the yield of **9** was only 12% after the addition of the first mole equivalent of *n*-BuLi. Under such conditions the yield of TriBN was very high (*ca.* 81%). The yield of **9** increased to 90%, the highest ever obtained, when the second mole equivalent of *n*-BuLi was added. In addition, the yield of TriBN was only 6%

under such conditions. Crystallization using a mixture of hexane and Et<sub>2</sub>O gave **9** in 82% isolated yield. Clearly, the use of *n*-BuLi (two mole equivalents) can be used as a selective process to produce **9** by proto-debromination of a mixture of **7** and **8**.

## Conclusions

Simple and efficient synthetic procedures have been developed for the regioselective production of 1,4,6-tribromonaphthalene and 1,2,4,6-tetrabromonaphthalene by direct bromination of naphthalene using bromine (three or four mole equivalents, respectively) over calcined montmorillonite KSF clay at room temperature. Proto-debromination of a mixture of 1,2,4,6-tetrabromonaphthalene and 1,3,5,7-tetrabromonaphthalene using two equivalents of *n*-butyllithium at a low temperature afforded 2,6-dibromonaphthalene regioselectively in high yield.

## Experimental Section

**General.** Montmorillonite KSF clay, solvents, and reagents were obtained from Aldrich Chemical Company (Gillingham, UK). Some properties of KSF clay have been reported.<sup>40</sup> The KSF clay was calcined at 550 °C for 6 h before its use. The concentrations of organolithium reagents were determined prior to use.<sup>41</sup> Melting points were recorded on a Gallenkamp apparatus (Calgary, Canada). The FTIR spectra were recorded on a FTIR-660 plus Fourier transform infrared spectrometer (Jasco, Tokyo, Japan). UV-visible spectra (KBr disc) were measured using a U-750 UV-visible spectrophotometer (Jasco, Tokyo, Japan). <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra were recorded on a Bruker AV400 spectrometer (Zürich, Switzerland) in CDCl<sub>3</sub>. High- and low-resolution mass spectra were recorded on Waters Q-TOF and GCT Premier mass spectrometers (Milford, MA, USA), respectively. The X-ray crystal diffraction data was collected using a Nonius Kappa CCD diffractometer (Bruker, Madison, WI, USA) equipped with a graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation source. The X-ray crystallographic data for compounds **6–9** were deposited at the Cambridge Crystallographic Data Center with CCDC reference numbers 2088776–2088779.

**GC Measurements.** The products from polybromination reactions of **1** were analyzed by GC using a Hewlett Packard 5890 Series II Gas Chromatograph fitted with a ZEBRON ZB-5 column (100% poly(dimethylsiloxane) with a 0.32 mm ID and a 30 m length). The GC temperature was 170 °C for 0.5 min, ramped to 300 °C at 4 °C/min. The temperature was 295 °C for both injector and flame ionization detector. Hexadecane was used as an external standard to quantify the products.

**Synthesis of 1,4,6-tribromonaphthalene (6).** A solution of **1** (0.979 g, 7.65 mmol) in DCM (10 mL) was added to a stirred mixture of calcined montmorillonite KSF clay (4.05 g) and DCM (30 mL). The mixture was stirred for 45 minutes in the dark and a solution of Br<sub>2</sub> (3.67 g, 22.95 mmol) in DCM (10 mL) was added slowly. The mixture was stirred for 24 h at 25 °C. The solid was removed through filtration and washed with DCM (3 × 10 mL), then the filtrates were combined. The combined filtrate was washed with sat. aq. Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> solution (20 mL) and the organic layer was separated and dried (MgSO<sub>4</sub>), then the solvent was removed under reduced pressure. The GC analysis of the crude product showed the presence of **4** (8%), **5** (10%), and **6** (66%). The crude product was recrystallized using a mixture of DCM and Et<sub>2</sub>O (4:1 by volume) in a freezer (−15 °C) for three days, to give **6** (1.40 g, 50%) as a white powder, Mp 85–87 °C (lit. 86–87 °C<sup>15</sup>). Further recrystallization

gave crystals suitable for X-ray crystallographic analysis. FTIR  $\nu_{\max}$  3060, 1645, 1558, 1071, 963, 814, 619. UV-Visible  $\lambda_{\max}$  315 nm, Abs. 1.68,  $\epsilon$   $16.8 \times 10^2$  L mol<sup>-1</sup> cm<sup>-1</sup>,  $c$   $1 \times 10^{-3}$  M (25 °C). <sup>1</sup>H NMR  $\delta$  8.42 (d,  $J$  = 2.0 Hz, 1H), 8.09 (d,  $J$  = 9.0 Hz, 1H), 7.70 (dd,  $J$  = 2.0 & 9.0 Hz, 1H), 7.64 (d,  $J$  = 8.0 Hz, 1H), 7.62 (d,  $J$  = 8.0 Hz, 1H). <sup>13</sup>C NMR  $\delta$  134.3, 132.0, 131.9, 131.5, 130, 130.4, 130.0, 123.5, 122.9, 121.7. EI-MS  $m/z$  (%) 368 ([M<sup>81</sup>Br<sub>3</sub>]<sup>+</sup>, 18), 366 ([M<sup>79</sup>Br<sup>81</sup>Br<sub>2</sub>]<sup>+</sup>, 52), 364 ([M<sup>79</sup>Br<sub>2</sub><sup>81</sup>Br]<sup>+</sup>, 55), 362 ([M<sup>79</sup>Br<sub>3</sub>]<sup>+</sup>, 19), 288 (48), 286 (100), 284 (50), 126 (32), 82 (43). HRMS (EI)  $m/z$  calculated for C<sub>10</sub>H<sub>5</sub><sup>79</sup>Br<sub>2</sub><sup>81</sup>Br (M<sup>+</sup>) 363.7933, found 363.7930.

**Synthesis of 1,2,4,6-tetrabromonaphthalene (7) and 1,3,5,7-tetrabromonaphthalene (8).** The procedure was identical with that described for the synthesis of **6** except that Br<sub>2</sub> (4.89 g, 30.6 mmol) was used and the mixture was stirred for 72 h at 25 °C. The crude product was purified by double crystallization using a mixture of DCM and Et<sub>2</sub>O (4:1 by volume) to give **7** (2.38 g, 70%) as colorless crystals, Mp 151–153 °C. The KSF was further extracted with DCM (3 × 20 mL) and the solvent was removed under reduced pressure. The residue obtained was purified by double crystallization using a mixture of DCM and Et<sub>2</sub>O (4:1 by volume) to give **8** (0.14 g, 4%) as a white powder, Mp 239–241 °C (lit. 308 °C<sup>25</sup>). Further recrystallization gave crystals suitable for X-ray crystallographic analysis.

**Compound 7.** FTIR  $\nu_{\max}$  1558, 1474, 1079, 969, 850, 618. UV-Visible  $\lambda_{\max}$  320 nm, Abs. 1.68,  $\epsilon$   $16.8 \times 10^2$  L mol<sup>-1</sup> cm<sup>-1</sup>,  $c$   $1 \times 10^{-3}$  M (25 °C). <sup>1</sup>H NMR  $\delta$  8.38 (d,  $J$  = 2.0 Hz, 1H), 8.20 (d,  $J$  = 9.1 Hz, 1H), 8.01 (s, 1H), 7.70 (dd,  $J$  = 2.0 & 9.1 Hz, 1H). <sup>13</sup>C NMR  $\delta$  134.3, 132.6, 132.5, 132.4, 130.6, 130.0, 124.7, 123.7, 123.0, 121.4. EI-MS  $m/z$  (%) 448 ([M<sup>81</sup>Br<sub>4</sub>]<sup>+</sup>, 15), 446 ([M<sup>79</sup>Br<sup>81</sup>Br<sub>3</sub>]<sup>+</sup>, 91), 444 ([M<sup>79</sup>Br<sub>2</sub><sup>81</sup>Br<sub>2</sub>]<sup>+</sup>, 100), 442 ([M<sup>79</sup>Br<sub>3</sub><sup>81</sup>Br]<sup>+</sup>, 96), 440 ([M<sup>79</sup>Br<sub>4</sub>]<sup>+</sup>, 27), 365 (20), 363 (22), 286 (28), 284 (60), 282 (28), 124 (40), 92 (93), 84 (100), 72 (18). HRMS (EI)  $m/z$  calculated for C<sub>10</sub>H<sub>4</sub><sup>79</sup>Br<sub>4</sub> (M<sup>+</sup>) 439.7046, found 439.7057.

**Compound 8.** FTIR  $\nu_{\max}$  3090, 1568, 1460, 1174, 866, 619. UV-Visible  $\lambda_{\max}$  315 nm, Abs. 1.68,  $\epsilon$   $16.8 \times 10^2$  L mol<sup>-1</sup> cm<sup>-1</sup>,  $c$   $1 \times 10^{-3}$  M (25 °C). <sup>1</sup>H NMR  $\delta$  8.36 (d,  $J$  = 2.0 Hz, 2H), 7.96 (d,  $J$  = 2.0 Hz, 2H). <sup>13</sup>C NMR  $\delta$  134.6, 132.1, 129.6, 122.5, 121.05. EI-MS  $m/z$  (%) 448 ([M<sup>81</sup>Br<sub>4</sub>]<sup>+</sup>, 8), 446 ([M<sup>79</sup>Br<sup>81</sup>Br<sub>3</sub>]<sup>+</sup>, 37), 444 ([M<sup>79</sup>Br<sub>2</sub><sup>81</sup>Br<sub>2</sub>]<sup>+</sup>, 58), 442 ([M<sup>79</sup>Br<sub>3</sub><sup>81</sup>Br]<sup>+</sup>, 42), 440 ([M<sup>79</sup>Br<sub>4</sub>]<sup>+</sup>, 12), 284 (24), 92 (63), 84 (100), 72 (12). HRMS (EI)  $m/z$  calculated for C<sub>10</sub>H<sub>4</sub><sup>79</sup>Br<sub>4</sub> (M<sup>+</sup>) 439.7046, found 439.7050.

**Synthesis of 2,6-dibromonaphthalene (9).** A pre-cooled (−78 °C) solution of *n*-BuLi in hexane (2.5 M; 1.6 mL, 4.0 mmol) diluted with hexane (5 mL) was added slowly to a stirred, cold (−78 °C) solution of a crude product containing **7** and **8** (1.776 g, 4.0 mmol) in THF (40 mL) under N<sub>2</sub>. The mixture was stirred for 5 minutes and a second portion of a pre-cooled (−78 °C) solution of *n*-BuLi in hexane (2.5 M; 1.6 mL, 4.0 mmol) diluted with hexane (5 mL) was added. The mixture was stirred for 5 minutes then quenched with MeOH (20 mL) and warmed up to 0 °C. A sat. NH<sub>4</sub>Cl solution (10 mL) was added followed by Et<sub>2</sub>O (10 mL). The organic layer was separated and washed with aq. NaCl (20 mL) and NaHCO<sub>3</sub> solutions (20 mL). The organic layer was separated, dried (MgSO<sub>4</sub>), filtered, and evaporated under reduced pressure. The crude product, containing 90% of **9** according to GC, was purified by crystallization using a mixture of hexane and Et<sub>2</sub>O to give **9** (0.94 g, 82%) as a creamy powder, Mp 156–158 °C (lit. mp 160.3–161.3 °C<sup>42</sup>). Further recrystallization gave crystals suitable for X-ray crystallographic analysis. FTIR  $\nu_{\max}$  3055, 1601, 1462, 1063, 885, 817, 688. UV-Visible  $\lambda_{\max}$  340, Abs. 1.83,  $\epsilon$   $18.3 \times 10^2$  L mol<sup>-1</sup> cm<sup>-1</sup>,  $c$   $1 \times 10^{-3}$  M (25 °C). <sup>1</sup>H NMR  $\delta$  7.98 (d,  $J$  = 2.0 Hz, 2H), 7.63 (d,  $J$  = 9.0 Hz, 2H), 7.57 (dd,  $J$  = 9.0 & 2.0 Hz, 2H). <sup>13</sup>C NMR  $\delta$  134.3, 130.2, 129.8, 128.5, 120.1. EI-MS  $m/z$  (%) 288 ([M<sup>81</sup>Br<sub>2</sub>]<sup>+</sup>, 57), 286 ([M<sup>79</sup>Br<sup>81</sup>Br]<sup>+</sup>, 100), 284 ([M<sup>79</sup>Br<sub>2</sub>]<sup>+</sup>, 64), 207 (29), 205 (30), 126 (64). HRMS (EI)  $m/z$  calculated for C<sub>10</sub>H<sub>6</sub><sup>79</sup>Br<sub>2</sub> (M<sup>+</sup>) 283.8842, found 283.8836.

## Acknowledgements

We thank Cardiff University for technical support. A. K. H. Al-Khalaf thanks the Iraqi Government and Al-Qasim Green University for financial support. G. A. El-Hiti thanks the Researchers Supporting Project number (RSP-2021/404), King Saud University, Riyadh, Saudi Arabia.

## Supplementary Material

The Supporting Information is available free of charge and contains the NMR spectra of compound **7** (new compound).

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