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Electrophilic Substitution in 1,8-Di-*tert*-butylnaphthalenes

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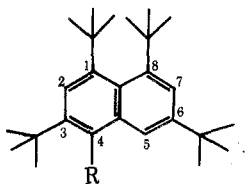
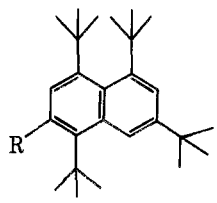
In previous reports from our laboratories on 1,8-di-*tert*-butylnaphthalenes, the focus has been primarily on synthetic and spectroscopic studies.[2] This note describes our results with probing the strained system via electrophilic aromatic substitution.

Nitration of 1,3,6,8-tetra-*tert*-butylnaphthalene (**1**) was accomplished using acetyl nitrate at −40°, followed by warming to 25°, conditions used previously for substitution on azulene, (18)annulene, and 1,3,6,8-tetramethylnaphthalene.[3] NMR and TLC of the crude reaction mixture revealed the presence of a single product which after purification yielded 4-nitro-1,3,6,8-tetra-*tert*-butylnaphthalene (**2**) in 54% yield. The structural assignment was based on its NMR spectrum (Table I), particularly the shielded peri proton at δ 7.04. This value is shifted upfield by 0.17 ppm compared to the parent compound **1**, expected since the nitro group is rotated so that its shielding cone interacts strongly with the peri H. Similar results have been obtained with methylnitronaphthalenes by Wells.[4] Our reaction conditions and results may be compared to those for *o*-di-*tert*-butylbenzene which is nitrated using concentrated nitric acid in acetic acid to afford products with no nitro insertion ortho to *tert*-butyl.[5]

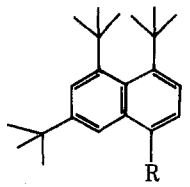
Bromination of **1** was effected in good yield with dioxane dibromide, a reagent normally used for bromination of phenols.[6] The NMR of the product (Table I) is consistent with both a rearranged structure **4** and the direct product **3**. In particular, the *tert*-butyl chemical shift of δ 1.64 is interpretable as an uncrowded peri-*tert*-butyl which is complementary to a neighboring peri H at δ 8.07. A reductive dehalogenation with butyllithium was performed on **3** to yield **1**, confirming lack of rearrangement in the bromination. Thus, the chemical shifts are due to the deshielding effects



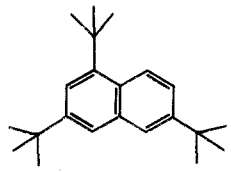
1, R = H
2, R = NO_2
3, R = Br



4, R = Br
9, R = H



5, R = H
6, R = Br
7, R = I



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of the bromine. These bromination conditions were also applied to 1,3,8-tri-*tert*-butylnaphthalene (**5**) to afford 5-bromo-1,3,8-tri-*tert*-butylnaphthalene (**6**). The lesser deshielding of the peri proton by bromine compared to that in **3** can be explained by the lack of buttressing of the bromine by the *tert*-butyl.[7] The photochemical behavior of **6** has been reported.[2] These brominations also may be compared to those of *o*-di-*tert*-butylbenzene, which requires $FeBr_3$ catalysis for rapid reaction and which results in some dealkylation as well as substitution.[5] Lastly, 5-iodo-1,3,8-tri-*tert*-butylnaphthalene (**7**) was prepared by treating **5** with iodine and yellow mercuric oxide, a combination of reagents previously used for iodination of thiophene.[8]

These results, i.e., regiospecific attack at the 4 position, are consistent with our previous study of the acid sensitivity of peri *tert*-butylnaphthalenes which demonstrated greatest reactivity at the 4 position. From the NMR data accumulated in this series, we are now able to assign α and β protons in the entire series with more certainty. Using the data obtained in unstrained naphthalene **8** as a standard, we can conclude that there is, in fact, a decrease in ring current in the naphthalenes which are strained and thus distorted from planarity. This decrease in ring current appears to result in a shielding of approximately 0.3 ppm and is consistent with the distortion effects observed with other spectroscopic techniques applied to the naphthalenes and the similar NMR observation made with 1,2,3,5-tetra-*tert*-butylbenzene.[9]

Experimental Section[10]

4-Nitro-1,3,6,8-tetra-*tert*-butylnaphthalene (2). A solution of 30 mg (0.08 mmol) of naphthalene **1**[2] in 2 ml of acetic anhydride was placed in a Dry Ice–ethanol bath and allowed to stir until it reached −40°. To this solution was added acetyl nitrate (2 ml over a 10-min period) prepared as follows: 160 mg of $Cu(NO_3)_2$ was

Table I
NMR Data for *tert*-Butylnaphthalenes. Chemical Shift and *J* (Hertz), CCl_4

Compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
9[a]	1.22	7.43 (2)	1.42	7.90 (2)	1.57	7.28 (8)	7.10 (8)	1.24
8[a]	1.65	7.78 (2)	1.43	7.57 (2)	7.57 (2)	1.43	7.48 (2, 9.2)	8.34 (9.2)
1[a]	1.30	7.48 (2)	1.40	7.22 (2)	7.22 (2)	1.40	7.48 (2)	1.30
2	1.33	7.62	1.48	NO_2	7.04 (2)	1.42	7.65 (2)	1.33
3	1.30	7.59	1.64	Br	8.07 (2)	1.45	7.59 (2)	1.28
6	1.30	7.63 (2.5)	1.47	7.79 (2.5)	Br	7.48 (8)	7.32 (8)	1.32
7	1.28	7.61 (2)	1.45	7.66 (2)	I	7.80 (8)	7.19 (8)	1.28

[a] Data taken from ref 2a.

added to 10 ml of acetic anhydride and 5 ml of acetic acid and then gently heated in a water bath. Ten minutes after the acetyl nitrate was added, the reaction was allowed to warm to room temperature. Water was then added and the reaction was worked up in a conventional manner. Preparative TLC of the product on silica gel eluting with hexane afforded 22 mg of nitronaphthalene (2) whose NMR was essentially identical with that of the analytical sample obtained by recrystallization from methanol (18.5 mg, 54% yield), mp 124.5–125.5°.

Anal. Calcd for $C_{26}H_{39}NO_2$: C, 78.98; H, 9.80; N, 3.40. Found: C, 78.89; H, 9.90; N, 3.43.

4-Bromo-1,3,6,8-tetra-*tert*-butylnaphthalene (3). A solution of 50 mg (0.14 mmol) of naphthalene 1[2] in 4 ml of anhydrous ether was cooled in an ice–salt bath (−3°) and treated with a solution of 110 mg (0.41 mmol) of dioxane dibromide in 4 ml of ether. The reaction was complete in 45 min. The solution was allowed to warm to room temperature, diluted with ether, washed with sodium thiosulfate solution, and worked up in the usual manner. Preparative TLC of the product on silica gel eluting with hexane afforded 41 mg of crude bromo product whose NMR was essentially identical with that of the analytical sample prepared by recrystallization from 80:20 ethanol–ethyl acetate (27 mg, 39%), mp 142.5–144.0°.

Anal. Calcd for $C_{26}H_{39}Br$: C, 72.72; H, 9.01; Br, 18.65. Found: C, 72.46; H, 9.14; Br, 18.68.

Debromination of Bromonaphthalene 3. A solution of 18 mg (0.04 mmol) of bromonaphthalene 3 in 2 ml of anhydrous ether was prepared in an oven-dried flask equipped with a serum cap. Excess butyllithium in hexane was then injected into the solution. After the resulting solution was stirred for 1.5 hr, 10 ml of water was added. The solution was then worked up in the normal way to afford 13 mg of naphthalene 1 identical with an authentic sample by TLC and NMR comparison.

5-Bromo-1,3,8-tri-*tert*-butylnaphthalene (6). To an anhydrous ether solution of 60 mg (0.2 mmol) of 1,3,8-tri-*tert*-butylnaphthalene (5)[2] was added an ether solution of 100 mg (0.4 mmol) of dioxane dibromide. The reaction was cooled in an ice–salt bath initially and then allowed to warm to room temperature over a 2-hr period. Work-up included washing the ether with 15% sodium thiosulfate. The crude product was an oil which was distilled in a Kugelrohr, oven temperature 120° (0.1 Torr), to afford 60 mg (90%) of bromonaphthalene 6 as a clear oil.

Anal. Calcd for $C_{22}H_{31}Br$: C, 70.57; H, 8.35; Br, 21.34. Found: C, 70.40; H, 8.36; Br, 21.32.

5-Iodo-1,3,8-tri-*tert*-butylnaphthalene (7). To a solution of 131 mg (1 mmol) of iodine and 50 mg (0.5 mmol) of naphthalene 5[2] in 3 ml of benzene was added 110 mg (0.5 mmol) of mercuric oxide (yellow). The mixture was stirred overnight after which time it became orange colored. Work-up afforded a mixture of product 7 (28 mg) and starting material which was separated by preparative TLC on silica gel. Crude 7 was rechromatographed on silica and then distilled at 65° and 1 Torr to yield 18 mg of a clear oil which was used as the analytical sample.

Anal. Calcd for $C_{22}H_{31}I$: C, 62.57; H, 7.35; I, 30.08. Found: C, 62.89; H, 7.60; I, 29.70.

Registry No.—**1**, 22495-86-9; **2**, 55669-70-0; **3**, 55669-71-1; **5**, 22495-89-2; **6**, 53535-11-8; **7**, 55669-72-2; acetyl nitrate, 591-09-3; dioxane dibromide, 21992-70-1.

References and Notes

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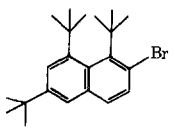

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Synthesis of Benzoquinone-1,4-aldehyde Diacetate

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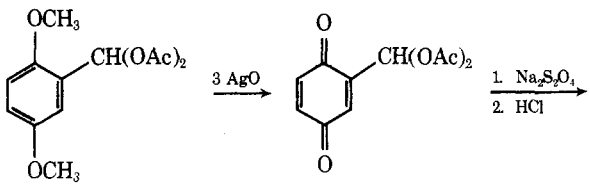
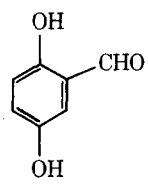
The oxidative demethylation of unsubstituted and several substituted hydroquinone and naphthohydroquinone ethers to give the corresponding quinones with argentic oxide (AgO) in excellent yields was reported by Rapoport and coworkers.[1] In our efforts related to the demethylation of 2,5-dimethoxybenzaldehyde,[2] we examined this method in order to see if benzoquinone-1,4-aldehyde could be readily obtained. Aldehydic groups are reported to remain intact under the specified mild reaction conditions.[1]

Treatment of 2,5-dimethoxybenzaldehyde with argentic oxide in the presence of nitric acid produced only small amounts of benzoquinone-1,4-aldehyde, as evidenced by the detection of traces of gentisaldehyde (by TLC) after reduction of the reaction products with sodium dithionite. In contrast, reaction of 2,5-dimethoxybenzaldehyde diacetate (1)[3] with 3 equiv of argentic oxide in the presence of 6 *N* HNO_3 produced the previously unreported benzoquinone-1,4-aldehyde diacetate (2) in 96% yield. The spectral data



1 2



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and elemental analysis agree with structure 2, and further proof was provided by the reduction of 2 with sodium dithionite, followed by hydrolysis to give gentisaldehyde (3) in 69% yield. In our attempts to further extend this method to monosubstituted alkylhydroquinone ethers, difficulties were encountered. For example, oxidation of 2,5-dimethoxytoluene (4) with argentic oxide gave a mixture of the expected methyl-1,4-benzoquinone (5) and 4,4′-dimethylbiphenyl-2,5,2′,5′-diquinone (6) in approximately equal amounts with an overall yield of 83%. The formation of 6 was due to the arylation of 5 by the starting ether 4, as evidenced by the isolation of 7, when only 1 equiv of argentic oxide was used. The formation of diquinones was also re-