Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. III. Reactions of 2-Methyl-, 4-Methyl-, and 2,4-Dimethyl-1-naphthols with Methanol. Sequential Pathways to Polymethylnaphthalenes[1a]

J. SHABTAI,[1b] L. H. KLEMM, AND D. R. TAYLOR[1c]

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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The alumina-catalyzed reactions of methanol with 1-naphthol (I), 2-methyl-1-naphthol (V), 4-methyl-1-naphthol (VI), and 2,4-dimethyl-1-naphthol (VIIa) were studied under comparable conditions at 350–420°. Quantitative identity in the composition of methylnaphthalenes from I and V indicates that methylation of I at C-2 is a primary step with no major influence on the extent of subsequent substitution. The reactions of VI and VIIa are highly selective and give 1,2,4-trimethylnaphthalene and 1,2,4,7-tetramethylnaphthalene as main products (combined yields, 61–87 mol %). A general, sequential pathway is proposed for formation of polymethylnaphthalenes from 1-naphthols. Data on the composition of the total methylnaphthalene product from I at different reaction temperatures are used to estimate the relative over-all extents of ring methylation at C-2, C-4, and C-7.

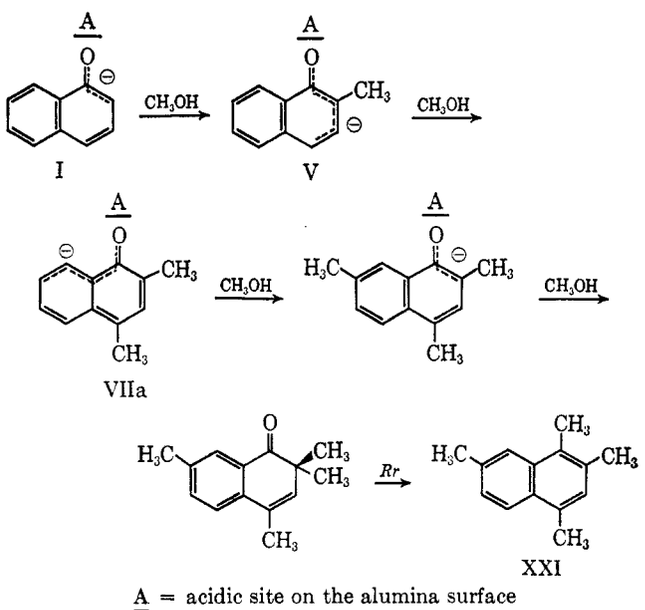
As an extension of research on alumina-catalyzed reactions of hydroxyarenes and hydroaromatic ketones,[2,3] a comparative study was made of the reactions of methanol with 1-naphthol (I), 2-methyl-1-naphthol (V), 4-methyl-1-naphthol (VI), and 2,4-dimethyl-1-naphthol (VIIa), respectively. The experimental and analytical procedures were essentially the same as described previously.[2,3] Reactions were carried out at two selected temperatures, 350 and 420°, over catalyst A (pure alumina, obtained by hydrolysis of aluminum isopropoxide) and catalyst C (Houdry hard alumina, which contains *ca.* 0.4% of sodium).[2-4] In the temperature range studied A is distinctly more acidic than C.[2,3]

As seen from Table I the composition of methylnaphthalene products formed by the reaction of V with methanol varies with reaction temperature and catalyst used. However, in all cases (expt 1–4) the di-, penta-, and hexamethylnaphthalene fractions consist only of one isomer each, *viz.* 1,2- (XIV), 1,2,3,4,6- (XXII), and (where present) 1,2,3,4,6,7- (XXIII), respectively. The yield of XIV is higher with catalyst C than with A, while yields of XXII and XXIII are higher with the more strongly acidic A. Three trimethylnaphthalenes, 1,2,3- (XVI), 1,2,4- (XVII), and 1,2,7- (XVIII), and two tetramethylnaphthalenes, 1,2,3,4- (XIX) and 1,2,4,7- (XXI), are also formed. Among the former XVIII is the major component with A (expt 3 and 4), whereas XVII predominates with C (expt 1 and 2). XXI is the major tetramethyl isomer with either catalyst. With A the composition of methylnaphthalene products from V is closely similar to that from I (*cf.* expt 3 and 11; 4 and 12). This result is consistent with previous observations that methylation of I produces V as the predominant isolable methylated naphthol under mild reaction conditions (275–350°)[2] and indicates that up to 420° methylation of I occurs more readily at C-2 than at any alternative ring position (*vide infra*).

On the other hand, the composition of methylnaphthalene products formed from 4-methyl-1-naphthol (VI) or 2,4-dimethyl-1-naphthol (VIIa) differs markedly from that produced from I or V. (a) No 1,2-dimethylnaphthalene is found, but the isomeric 1,3-dimethylnaphthalene is formed in small yield instead. (b) Only a single trimethylnaphthalene, *i.e.*, the 1,2,4 isomer (XVII), is produced. In fact, at 420° with the weakly acidic catalyst C (expt 5 and 9) the reaction can be conveniently employed as a preparative method for XVII (60–66 mol %). (c) Yields of 1,2,4,7-tetramethylnaphthalene (XXI) are notably higher from VI or VIIa (40 mol % at 420° with A, *cf.* expt 6 and 10), while yields of the pentamethyl (XXII) and hexamethyl (XXIII) compounds are slightly higher than those from I or V. Thus, the initial introduction into I of a methyl group at C-4 fosters the formation of 1,2,4-trimethyl- and 1,2,4,7-tetramethylnaphthalenes, while at the same time it completely inhibits the pathways to 1,2-dimethyl- and 1,2,7-trimethylnaphthalenes.

In Schemes I and II are depicted typical proposed pathways for the formation of methylnaphthalenes from reaction of methanol with 1-naphthol, as based

SCHEME I



A = acidic site on the alumina surface

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(2) Part I: L. H. Klemm, J. Shabtai, and D. R. Taylor, *J. Org. Chem.*, **33**, 1480 (1968).

(3) Part II: J. Shabtai, L. H. Klemm, and D. R. Taylor, *ibid.*, **33**, 1489 (1968).

(4) For simplicity, compounds and catalysts are designated by the same Roman numerals and capital letters, respectively, as used in part I.[2]

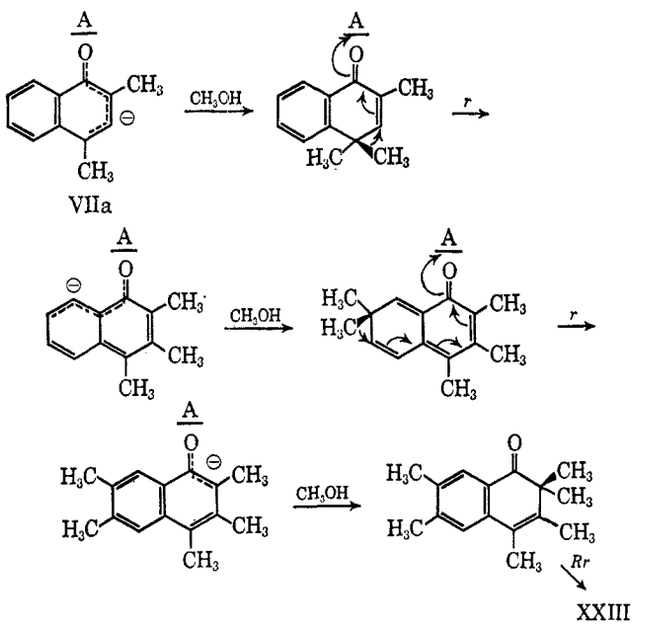
TABLE I

ALUMINA-CATALYZED REACTIONS OF 2-METHYL-1-NAPHTHOL (V), 4-METHYL-1-NAPHTHOL (VI), AND 2,4-DIMETHYL-1-NAPHTHOL (VIIa) WITH METHANOL[a]

Expt no.	1	2	3	4	5	6	7	8	9	10	11[b]	12[b]
Starting naphthol	V	V	V	V	VI	VI	VIIa	VIIa	VIIa	VIIa	I	I
Catalyst	C	C	A	A	C	A	C	A	C	A	A	A
Reaction temp, °C	350	420	350	420	420	420	350	350	420	420	350	420
Conversion,[c] mol %	65	98	76	100	100	100	86	95	100	100	87	100
Product component,[d] mol %												
1,2-Dimethyl-N[e] (XIV)	23.5	30.5	18.2	15.7	...	...	...	...	...	...	18.0	15.5
1,3-Dimethyl-N	...	...	...	...	1.3	1.1	4.5	3.4	1.5	1.5	...	...
1,2,3-Trimethyl-N (XVI)	1.7	1.9	4.6	4.0	...	...	...	...	...	...	4.5	4.0
1,2,4-Trimethyl-N (XVII)	8.4	12.5	5.2	5.8	60.3	22.4	51.0	36.1	66.2	20.3	5.3	5.7
1,2,7-Trimethyl-N (XVIII)	6.0	10.4	8.5	18.2	...	...	...	...	...	...	8.2	18.0
1,2,3,4-Tetramethyl-N (XIX)	1.4	3.0	3.2	3.0	2.2	1.9	2.5	2.9	1.6	2.4	3.6	3.1
1,2,4,7-Tetramethyl-N (XXI)	7.2	12.6	8.0	15.8	20.1	39.4	12.3	29.2	20.4	40.3	7.9	15.5
1,2,3,4,6-Pentamethyl-N (XXII)	3.2	8.1	10.5	18.4	8.6	20.1	3.6	10.8	9.2	21.0	10.2	18.7
1,2,3,4,6,7-Hexamethyl-N (XXIII)	...	Trace	1.4	5.5	0.1	6.6	...	1.6	0.2	7.5	1.3	5.6
Others	10.3	9.5	9.8	9.2[f]	1.0	7.7[g]	...	1.5	...	6.0[h]	22.0[i]	9.5[j]
Unidentified[k]	(3.5)	(9.0)	(4.8)	(3.0)	(4.4)	(0.5)	(11.7)	(8.5)	(0.5)	(0.6)	(4.5)	(3.5)

[a] A mixture of 0.0125 mol of the naphthol and 20 g (0.63 mol) of methanol was used as starting material in each experiment. This solution was introduced into the reactor at a uniform rate during a period of 2 hr. [b] Small changes from previous data[2] in the composition of products formed are ascribed to differences in the naphthol–catalyst and the naphthol–methanol ratios used. [c] Conversion of the naphthol. [d] Calculated on the basis of 100 mol of starting naphthol (including unreacted material). Differences between conversion and total products formed represent losses due to unrecoverable deposits on the catalyst. [e] N is naphthalene. [f] Includes 3.8 mol % of heptamethylnaphthalene (XXIV) and 1.7 mol % of octamethylnaphthalene (XXV), as based on gas chromatographic data only. [g] 1-Methylnaphthalene, 2.0; XXIV, 3.9; and XXV, 1.8 mol %. [h] XXIV, 3.9; XXV, 2.1 mol %. [i] Includes 10.6 mol % of V. [j] Includes XXIV, 3.8; XXV, 1.9 mol %. [k] Percentage by weight of total product. It includes unidentified chromatographic peaks and nondistillable residues.

SCHEME II



A = acidic site on the alumina surface

on the data reported in preceding papers[2,3] and the results of the present study. It is assumed that all oxygen-containing species are adsorbed on the surface of the alumina catalyst where methylation by an electrophilic species and processes of molecular rearrangement (*r*) and reduction–rearrangement (*Rr*) occur. For simplicity all naphtholic compounds are represented as anions (adsorbed to acidic sites) and the pertinent electromeric shift involved in each step of ring methylation is shown. For each naphthoxide ion there is a corresponding proton adsorbed to a basic site (not shown). Methylation is accompanied by the over-all loss of water. The oxygen function is considered to be the anchoring group for adsorption, but adsorbability should be enhanced by simultaneous flatwise orientation of the aromatic system with attendant interaction of the π-electronic system with the polarizing surface. If the methylating species is confined to the surface layer, such flatwise adsorption would be essential for methylation at positions other than C-2. Methylnaphthalenes formed would be largely displaced from the catalyst surface by the more strongly adsorbed oxygen-containing entities (including methanol).

As indicated in Schemes I and II ring methylation proceeds stepwise, without loss of the oxygen function, at C-2, C-4, and C-7 positions which are favored for electrophilic substitution and are not sterically hindered.[2] Insertion of a second methyl group at C-4 or at C-7 is followed by rearrangement to 3,4-dimethyl[5] and 6,7-dimethyl derivatives, respectively (Scheme II). On the other hand, insertion of a second methyl group at C-2 terminates the methylation process with the formation of a 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene derivative. Compounds of this type serve as immediate precursors of the final methylnaphthalene products by undergoing elimination of the keto oxygen and migration of one of the geminal methyl groups from C-2 to C-1. Possible, detailed mechanisms for the methylation, reduction, and rearrangement processes were considered previously.[2,3] The average number of methyl substituents introduced into the naphthalene system depends on the reaction temperature, the catalyst acidity, and the methanol–naphthol ratio used.[2] For an individual naphthol molecule the exact number of substituents may depend on the strength of the particular acidic site to which the substrate is adsorbed, on the orientation of the ring system relative to the catalyst surface, and finally on the proximity and orientation of the methylating species.

Only one sequential pathway (that of dimethylation at C-2 followed by reduction–rearrangement, *Rr*) is visualized for formation of XIV. This sequence is represented by the notation 2,2,*Rr*, where the numbers refer to the positions of methylation on the ring. Two pathways, either successive methylations at C-2, C-4, C-2 or at C-4, C-2, C-2 and then reduction–

(5) Reference 3, Scheme IV.

rearrangement are possible for formation of XVII. These alternatives are symbolized by (2,4),2,*Rr*, where the numbers in parentheses refer to allowed permutations in the methylation sequence. Analogously, two routes (2,7),2,*Rr* would lead to XVIII. As the depth of methylation increases the number of possible pathways increases markedly. Thus, there are three routes 4,4,*r*,2,2,*Rr* and (2,4),4,*r*,2,*Rr* to XIX; six routes (2,4,7),2,*Rr* to XXI; 12 routes 4,4,*r*(2,7),2,*Rr*, (2,4),-4,*r*,7,2,*Rr*, (4,7),4,*r*,2,2,*Rr*, and (2,4,7),4,*r*,2,*Rr* to XXII; and 30 routes to XXIII. Each route involves the common steps of . . . 2, . . . ,2,*Rr*, *i.e.*, methylation at C-2 at some preceding stage, a second methylation at C-2 at a penultimate stage, and finally reduction–rearrangement to 1,2-dimethylnaphthalene or its ring-methylated derivative. Thus, the process 2,2,*Rr*, which leads to XIV, may be considered the simplest typical route. The observation that 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene (IX) is almost exclusively converted into XIV under reaction conditions[3] is consistent with this pathway. Moreover, the selective conversion of 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene (X) into XIX and XXII[3] lends credence to the pathways 4,4,*r*,2,2,*Rr* and 4,4,*r*,(2,7),2,*Rr*. On the other hand, the main route to XIX from I is probably 2,4,4,*r*,2,*Rr* and that to XXII is probably 2,(4,7),4,*r*,2,*Rr* or 2,4,4,*r*,7,2,*Rr* (or a combination of these). There are nine methylnaphthalenes which might be expected on the basis of the foregoing general pathways. These correspond to all possible combinations for the introduction of zero–two methyl groups at each of the positions C-4 and C-7. Products XIV, XVII–XIX, and XXI–XXIII correspond to seven of these possibilities. The remaining two should be 1,2,6,7-tetramethylnaphthalene (from dimethylation at C-7 but no methylation at C-4) and 1,2,4,6,7-pentamethylnaphthalene (from dimethylation at C-7 and monomethylation at C-4). Vpc analysis of mixed methylnaphthalene products failed to reveal the presence of a second pentamethylnaphthalene, in addition to the 1,2,3,4,6 isomer (XXII) found. However, a third, unidentified tetramethylnaphthalene, in addition to the 1,2,3,4 (XIX) and 1,2,4,7 (XXI) isomers, was readily detected by this method. Tentatively, this isomer (XX) has been assigned the 1,2,6,7-substitution pattern[6] on the basis of the preceding mechanistic considerations.

Whereas most of the lower precursors required by the proposed mechanism, *i.e.*, compounds V–X, were isolated from the products at 275–300°,[2] only very small amounts (*ca.* 1% by weight) of the precursors of higher methylnaphthalenes are indicated at this mild temperature. The formation of such intermediates apparently requires somewhat higher temperature, where conversion into methylnaphthalenes is fast. Chromatograms of the products obtained at 300–350° showed a number of small peaks in the range of tri- and tetramethylnaphthalenes. Since a preparative sample enriched in these minor components gave carbonyl absorption in the infrared region (*ca.* 1690 cm^{-1}), it is possible that these peaks are due to the higher precursors.

On the basis of the proposed general mechanism it is possible to approximate the relative over-all extents of methylation of 1-naphthol at C-2, C-4, and C-7 by calculating the total number of substituents at C-1 plus C-2, C-3 plus C-4, and C-6 plus C-7, respectively, in all product components.[6] For example, over catalyst A, at 300° the ratio of over-all methylation at the 2, 4, and 7 positions found by this method is 1.0:0.2:0.02; at 350° the corresponding ratio is 1.0:0.36:0.20; at 420° it is 1.0:0.46:0.31; and at 470° it is 1.0:0.31:0.35. The change in the ratios reflects the gradual increase in the extent of methylation at C-4 and C-7 relative to that at C-2 up to 420°, a temperature at which maximal depth of methylation is attained. A possible cause for the decrease in relative extent of methylation at C-4 above 420° is that enhanced thermal out-of-plane and in-plane deflections of the hydrogen at C-5 may sterically hinder approach of the methylating agent to the *peri* (*i.e.*, to the C-4) position.[7]

The importance of *peri* interactions in the methylation of naphthols is illustrated by the practical absence of substitution at C-5 and C-8 in the reactions of I, V, VI, and VIIa. Lack of methylation at the 5 position is especially significant in view of the higher calculated superdelocalizability for electrophilic attack at C-5 than at C-7 in I.[2] At 275–350° neither 5- nor 7-methyl-1-naphthol is formed from I. On the other hand, the lack of reaction at C-5 at higher temperature (350–550°) where polymethylation, including attack at C-7, takes place can be essentially attributed to the steric interference of a methyl substituent[7] introduced at C-4 in an earlier step.

The results of the reactions of 4-methyl-1-naphthol (VI) and 2,4-dimethyl-1-naphthol (VIIa) are fully consistent with the proposed mechanism. Since methylation occurs to a lesser over-all extent at C-4 than at C-2 (for the initial precursor I), the preliminary introduction of a methyl substituent at the former position facilitates the formation of 1,2,4-trimethylnaphthalene (XVII) and 1,2,4,7-tetramethylnaphthalene (XXI). At the same time the presence of the 4-methyl group in VI and VIIa excludes the possibility of reaction sequences leading to 1,2-dimethyl- and 1,2,7-trimethylnaphthalenes. The formation of XVII as main product in expt 5 and 9 indicates that over the weakly acidic catalyst C at 420° a *second* methylation of VI or VIIa at C-2 occurs to a larger extent than a second methylation step at C-4 or than a first one at C-7. On the other hand, the high yield of XXI in expt 6 and 10 shows that in the presence of the strongly acidic catalyst A at 420° methylation occurs to a large extent at C-7 prior to a second (terminal) methylation at C-2. With 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene (X) as substrate[3] over A, the gradual change with temperature of relative over-all extent of methylation at C-2 and C-7 (as based on comparison of yields of XIX, XXII, and XXIII) can also be noted. The ratios of methylation at the 2 and 7 positions, in this case, are 4.9:1 at 320°, 3.6:1 at 350°, 2.3:1 at 375°, and 2.0:1 at 420°.

It was shown previously[6] that for reaction of I below 420° values for average depth of ring methylation and for mole percentage conversion are higher with the pure alumina catalyst A than with the sodium-containing catalysts B or C. These gross differences probably arise from a higher concentration of strongly acidic sites on the surface of A than on either of the other

(6) Reference 2, Table I.

(7) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

catalysts.[8,9] At 420–470°, however, these values tend to converge for catalysts A and C. A marked increase in the catalytic activity of alumina for hydrocarbon reactions has been observed to occur above 400° and has been ascribed to the conversion of passive acidic sites into active ones.[10] In the present case the production of active sites for the methylation process may be especially large on catalyst C for temperatures above 400°. However, it should be noted that A, B, and C do not show equivalent catalytic properties even in this temperature range, since differences in the distribution of methylated naphthalenes and in isomeric compositions still persist.[6] This may be due to nonequivalence in the nature and geometric arrangements of active sites on A and C, with attendant differences in orienting influences on the adsorbed substrates.

The formation of several minor product components, *viz.* naphthalene (XI), 1-methylnaphthalene (XII), 2-methylnaphthalene (XIII), 2,7-dimethylnaphthalene (XV), and 1,2,3-trimethylnaphthalene (XVI), cannot be accounted for by the proposed general mechanism. Direct reduction of the naphtholic group in I, VI, and V would, however, lead to XI, XII, and XIII, respectively. In fact XII (free from XIII) was found as a minor product from VI (Table I, footnote *g*). The small yield of 1,3-dimethylnaphthalene from 2,4-dimethyl-1-naphthol (expt 7 and 8) indicates that the same type of reaction occurs. Analogously XV could be derived from an intermediate 2,7-dimethyl-1-naphthol (not experimentally detected). The low yields of XI–XIII and XV from reactions of I[2] up to 550° imply that sequential methylation steps proceed in preference to direct reduction of the naphtholic group. A different pathway is likely for the formation of XVI, which is the main by-product in the reaction of methanol with 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene (IX).[3] As noted previously IX may be methylated at C-3 before reduction–rearrangement occurs.[3]

(8) H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, **82**, 2471 (1960).
(9) J. B. Peri, *J. Phys. Chem.*, **69**, 231 (1965).
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Experimental Section

Apparatus, Materials, and Procedure.—The apparatus and experimental procedure were essentially the same as described previously.[2,3] For each run 35 g of fresh alumina catalyst (A, from aluminum isopropoxide; or C Houdry hard alumina)[2] was employed and the methanol–naphthol molar ratio was 50:1 (methanol, 0.63 mol; naphthol, 0.0125 mol). The methylnaphthols V, VI, and VIIa (about 99% pure, as based on chromatographic analysis) were synthesized by the methods given previously.[2] Product components (Table I) were isolated by gas chromatography and were identified by comparison of their pmr and infrared spectra, as well as their relative chromatographic retention volumes, with those of pure reference samples.[2] Gas chromatographic analysis of methylnaphthalene products was effected by means of a modified Bentone-34 column; and that of acidic (naphtholic) fractions, by means of Bentone-34 and Carbowax 20M columns.

Registry No.—Methanol, 67-56-1; I, 90-15-3; V, 7469-77-4; VI, 10240-08-1; VII, 4709-20-0.

Electrophilic Substitution in Acenaphthene and Related Compounds. I. Monobromination

I. K. LEWIS, R. D. TOPSOM,[1] J. VAUGHAN, AND G. J. WRIGHT

Departments of Chemistry, University of Canterbury, Christchurch, New Zealand, and La Trobe University, Bundoora, Victoria, Australia

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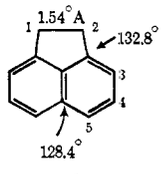
Isomer distribution in the bromination of acenaphthene has been determined for a variety of conditions and reagents. A wide variation was found in the per cent of *ortho* product. Isomer distributions for 1,8-dimethylnaphthalene, perinaphthane, and pleiadane were similar to those for acenaphthene using similar procedures.

There has been considerable recent interest[2-6] in the reactions of acenaphthene (1) and the related 1,8-dimethylnaphthalene (2). Electronic considerations suggest electrophilic attack would lead to a mixture of 3- and 5-substituted acenaphthenes or the corresponding 2- and 4-substituted 1,8-dimethylnaphthalenes.



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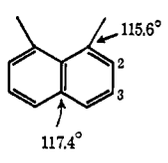

2

Molecular dimensions[7,8] suggest that substitution *ortho* to the ethylene bridge in acenaphthene might not be as sterically hindered as 2-substitution in 1,8-dimethylnaphthalene.

Whereas it has been known[9] that reasonable (approximately 20%) yields of 3-nitroacenaphthene can be separated from 5-nitroacenaphthene after the treatment of acenaphthene with nitric acid in acetic anhydride, until recently no investigation had been made into isomer proportions in monosubstitution reactions of acenaphthene. Electrophilic substitution in 1,8-dimethylnaphthalene has been assumed to enter the 4

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