# Isomerization of Dimethylnaphthalenes[1]

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Isomerization of di- and monomethylnaphthalenes in the system anhydrous hydrofluoric acid–boron trifluoride has been investigated. In accord with the previously reported observations with methylbenzenes the relative concentrations of di- and monomethylnaphthalenes in the isomerisates depend on the amount of boron trifluoride. The unique feature in the dimethylnaphthalene series is the existence of a number of discrete equilibrium sets of isomer groups with no interconversion between the members of the different sets. The experimental rate data are in agreement with the postulated intramolecular 1,2-methyl shift. The barriers to the intramolecular methyl shift between the adjacent $\beta$–$\beta$ as well as between the *peri* positions are rationalized in terms of the unfavorable high-energy complexes required for these migrations.

It has long been recognized that aromatic hydrocarbons dissolve in strong protonic acids. Solubility of a number of aromatic hydrocarbons in liquid hydrogen fluoride was reported by Klatt[2]; this was interpreted by Hammett[3] as involving a formation of arene conjugate acids by the protonation of the aromatic nucleus. The above postulate has been supported by the conductivity measurements of solutions of benzene and methylbenzenes in liquid HF[4] and also by the study of electronic spectra of the dissolved aromatic cations.[5]

Aromatic hydrocarbons have only a moderate solubility in liquid HF; however most of the arenes show a greatly enhanced solubility as well as the much faster H–D isotope exchange rate in the presence of added promoters such as $BF_3$.[6]

The formation of the soluble arene conjugate acids may be pictured as follows.

$$Ar + HF \rightleftharpoons ArH^+F^- \quad (1)$$

$$F^- + BF_3 \rightleftharpoons BF_4^- \quad (2)$$

$$Ar + HF + BF_3 \rightleftharpoons ArH^+BF_4^-$$

The equilibrium for the reaction (1) is far to the left; however, addition of $BF_3$ with the resulting formation of the stable fluoborate ion drives the complex formation to completion. A number of ternary arene–HF–$BF_3$ complexes have been prepared and characterized at low temperature.[7]

The alkyl groups in alkylarene cations may migrate according to intermolecular or intramolecular mechanism. Ethyl-, isopropyl-, *n*-propyl-, and *sec*-butylbenzenes disproportionate by an apparently intermolecular pathway giving a mixture of benzene, di- and trialkylbenzenes[8] while xylenes isomerize intramolecularly, presumably by a series of 1,2-shifts.[9] Recently it was demonstrated that $AlBr_3$–HBr catalyzed isomerization of toluene-1-$C^{14}$ proceeds by the intramolecular 1,2-methyl shift.[10]

Isomerization of methylbenzenes with the HF–$BF_3$ catalyst system has been investigated by McCaulay and Lien.[9] They demonstrated that the amount of $BF_3$ used had a pronounced effect on the composition of the isomerized equilibrium mixture. This result as well as the differences in the isomerization rates between xylene isomers were interpreted by the above workers on the basis of differences in the stabilities of the protonated methylbenzene complexes. Thus, the stabilities of the methylbenzene conjugate acids and hence the basicities of the corresponding hydrocarbons depend apparently on both the number and the positions of the methyl substituents. The relative basicities of methylbenzenes in HF–$BF_3$ systems have been reported in three sets of independent experimental data.[4,11,12] A quantitative estimation of basicities of methylbenzenes by a self-consistent LCAO–MO method based on the combined methyl-hyperconjugation and methyl-induction model has been shown to correlate well with the experimental data.[13]

In contrast to an extensive literature on the isomerization of alkylbenzenes little has been reported with respect to the corresponding naphthalene derivatives. Only two brief notes concerning the isomerization of a dimethylnaphthalene isomer were found in the literature.[14,15]

## Experimental

**Reagents.**—The anhydrous hydrogen fluoride and boron trifluoride were commercial reagents (Matheson Co.) and were used directly without further purification.

The 1,5-, 1,8-, 2,3-, 2,6-, and 2,7-dimethylnaphthalenes (DMNs) were purified by recrystallization from methanol from commercially available samples (Aldrich Co., Henley Co., and K and K Laboratories). These isomers were ~99% pure.

The liquid 1,2- and 1,6-isomers were less pure. The 1,2-isomer assayed as 96% pure, containing a non-DMN impurity. The 1,6-isomer analyzed as follows: 1,6-DMN, 91%; 2,6- and 2,7-DMNs, 3%; 1,7-DMN, 4%; 2,3-, 1,4-, and 1,5-DMNs, 2%. An attempt to purify the 1,6-isomer *via* the picrate salt was unsuccessful.

The 1,3- and 1,4-dimethylnaphthalenes were synthesized from *m*- and *p*-xylene, respectively, by the succinic anhydride–$\alpha$-tetralone route[16] and were ~99% pure.

The 1,7-isomer was prepared from the 1,8-isomer by isomerization with anhydrous HF by the following procedure. To a solu-

(1) Presented in part before the Division of Organic Chemistry, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, Abstracts, p. 83Q.

(2) W. Klatt, *Z. anorg. allgem. Chem.*, **234**, 189 (1937).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 293, 294.

(4) M. Kilpatrick and F. Luborski, *J. Am. Chem. Soc.*, **75**, 577 (1953).

(5) (a) C. Reid, *ibid.*, **76**, 3264 (1954); (b) G. Dallinga, E. L. Mackor, and A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).

(6) (a) D. A. McCaulay, B. H. Shoemaker, and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950); (b) Ya. M. Varshavskii, M. G. Loshkina, and A. I. Shatenshtein, *J. Phys. Chem.* (USSR), **31**, 1377 (1957).

(7) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6535 (1958).

(8) (a) A. P. Lien and D. A. McCaulay, *ibid.*, **75**, 2407 (1953); (b) D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953).

(9) D. A. McCaulay and A. P. Lien, *ibid.*, **74**, 6246 (1952).

(10) H. Steinberg and F. L. J. Sixma, *Rec. trav. chim.*, **81**, 185 (1962).

(11) D. A. McCaulay, and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951).

(12) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 186 (1958).

(13) S. Ehrenson, *J. Am. Chem. Soc.*, **84**, 2681 (1962).

(14) F. Mayer and R. Schiffner, *Ber.*, **67B**, 67 (1934).

(15) R. Tutihasi and T. Hanzawa, *J. Soc. Chem. Ind. Japan*, **45**, 273 (1942).

(16) (a) E. B. Barnett and F. G. Sanders, *J. Chem. Soc.*, 434 (1933); (b) R. E. Evans, J. C. Smith, and F. B. Strauss, *J. Inst. Petrol.*, **40**, 7 (1954).

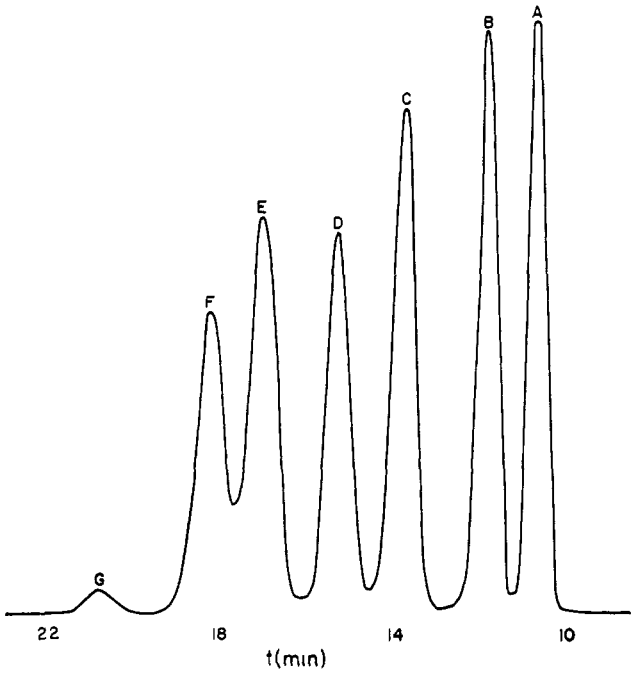



Fig. 1.—Vapor phase chromatogram on a 12-ft. column, at 215°, with a He flow of 70 ml./min. of the ten dimethylnaphthalene and two monomethylnaphthalene isomers: A, 2-methylnaphthalene; B, 1-methylnaphthalene; C, 2,6- and 2,7-; D, 1,6-, 1,7-, and 1,3-; E, 2,3-, 1,4-, and 1,5-; F, 1,2-; and G, 1,8-dimethylnaphthalene.

tion of the 1,8-isomer in benzene (3–5 wt. %) contained in a stainless steel Hoke bomb was added a large molar excess of anhydrous HF. The mixture was shaken mechanically at room temperature over a 15-min. period, then quenched in ice–water. The 1,7-dimethylnaphthalene was recovered from the benzene phase and analyzed as ~99% pure.

The 1- and 2-methylnaphthalenes (from Humphrey-Wilkinson Co. and Distillation Products, respectively) assayed at 98.4 and 99%.

The physical constants of dimethylnaphthalenes corresponded closely to those reported in the literature[17]; purity of the individual isomers was further ascertained by gas chromatography (Fig. 1) and infrared absorption techniques.

**Apparatus and Procedure.**—Isomerization of di- and monomethylnaphthalenes was carried out in 80-ml. stainless steel Hoke bombs equipped with two-needle valves; one of the valves was adapted to an internal dip tube.

A measured quantity of anhydrous HF was transferred by nitrogen pressure from a metering cylinder through a stainless steel manifold into an evacuated Hoke bomb containing the benzene or *n*-hexane solution of the DMN or MeN isomer. The bomb was immersed in a constant-temperature bath and allowed to equilibrate thermally over a short period of time (15–20 min.). In the rate study it was ascertained that no isomerization occurred under these conditions, *i.e.*, prior to the addition of $BF_3$. A calculated quantity of $BF_3$ was then added from the $BF_3$ metering cylinder, and the time count was initiated. The reactor bomb was shaken by means of a Burrell wrist-action shaker at 250 times/min.

In most of the study 10% (wt.) solutions of di- or monomethyl naphthalenes in benzene were employed, in a few instances *n*-hexane was used as a solvent. A large molar excess of anhydrous hydrogen fluoride (50–60 moles/mole of DMN and MeN) was used throughout the investigation.

The quantities of materials in a single experiment were the following: 3.0 g. of DMN or 2.7 g. of MeN, 27 g. of benzene or *n*-hexane, 20–22 g. of anhydrous HF. On some occasions, for reasons of economy, somewhat smaller quantities of DMN isomers were used (1–2 g. with 1,4-, 1,7-, and 1,8-isomers).

The equilibration experiments carried out with 10 mole % of $BF_3$ at 70° were followed by withdrawing *ca.* 1-ml. aliquots of the organic layer into a polyethylene container filled with crushed ice. The supernatant hydrocarbon layer was separated, dried over anhydrous potassium carbonate, and analyzed for the DMN and MeN isomers by gas chromatography and infrared absorption techniques.

In the isomerization rate study *ca.* 0.5-ml. aliquots of the acid layer were withdrawn at measured time intervals and quenched in crushed ice. After addition of a small quantity of pentane, the aqueous acid was neutralized with potassium carbonate and the organic layer was separated and dried with anhydrous potassium carbonate. The product was again analyzed by gas chromatography and infrared absorption techniques. Following the withdrawal of the last sample from the acid layer a 5–10-ml. aliquot of the supernatant organic solvent layer was withdrawn through the dip tube and assayed for the DMN or MeN content.

**Analytical Methods.**—Analysis of the DMN and MeN product mixtures was accomplished by gas chromatography and infrared absorption techniques by the method of King, Fabrizio, and Donnell.[18] Separation of the two methylnaphthalenes and resolution of the ten dimethylnaphthalenes into five groups (Fig. 1) was achieved with a Model 300 F and M gas chromatograph under the following conditions: 12 ft. × 0.25 in. column packed with Craig polyester succinate on Chromosorb P, 30–60 mesh. The dimethylnaphthalenes under the unresolved peaks C, D, and E (Fig. 1) were collected as the peak fractions emerged from the gas chromatograph and analyzed at 11–15 $\mu$ using Perkin-Elmer Model 21 spectrophotometer. The analytical wave lengths are listed below.

| Isomer | Wave length, $\mu$ (±0.02) |
|---|---|
| 2,6- | 12.37 |
| 2,7- | 12.03 |
| 1,6- | 12.33 |
| 1,7- | 12.18 |
| 1,3- | 12.97 |
| 2,3- | 13.49 |
| 1,4- | 13.32 |
| 1,5- | 12.76 |

Both the accuracy and the precision of the analytical method were 1% based on the whole sample.

**Calculation of Rate Constants and Activation Parameters.**—The first-order rate constants were obtained from the slope of the straight-line plot of $\ln (A_0 - A_e)/(A_t - A_e)$ *vs.* time. The concentration terms $A_0$, $A_t$, and $A_e$, expressed as the weight per cent of the starting DMN or MeN isomer at times $t = 0$, $t$, and $t_\infty$, respectively, were obtained from the measurement of the peak areas on the gas chromatography scans. The rate constants were found to be reproducible in the duplicate kinetic runs.

The Arrhenius activation energy $E$ for the 2,6- → 1,6-DMN interconversion was obtained from the plot of $\ln k$ *vs.* $1/T$ at four different temperatures and for the other DMN and MeN isomers from the rate constants at two different temperatures.

The activation entropy $\Delta S^*$ was calculated from the Eyring equation

$$k = kT/h \exp(-\Delta H^*/RT) \exp(\Delta S^*/R)$$

where $\Delta H^* = E - RT$.

## Results

The isomerization procedure applied to di- and monomethylnaphthalenes was similar to that employed by McCaulay and Lien with xylenes and tri- and tetramethylbenzenes.[9] The isomerization experiments were carried out in the presence of a large molar excess of anhydrous hydrogen fluoride and with two different added boron trifluoride concentrations, 10 and 110 mole %, based on the arene used. The actual $BF_3$–arene molar ratios were probably somewhat smaller (estimated 5 and 105 mole %) owing to basic impurities in the commercial hydrogen fluoride. Since a number of dimethylnaphthalene isomers are solid, the method

(17) A. B. Bailey, K. C. Bryant, R. A. Hancock, S. H. Morrell, and J. C. Smith, *J. Inst. Petrol.*, **33**, 503 (1947).

(18) R. W. King, F. A. Fabrizio, and A. R. Donnell in "Gas Chromatography," Academic Press, New York, N. Y., 1962, p. 149.

used entailed contacting the benzene solution of the reactant arene with HF and $BF_3$ in the given order. Addition of $BF_3$ resulted in the formation of the acid-soluble complex as indicated by the pressure decrease in the system. In the presence of excess $BF_3$ only a small fraction of the (1–2%) added arene remained in the supernatant benzene layer.

It was established that the presence of $BF_3$ as a promoter was not a prerequisite for the occurrence of the isomerization reaction; thus both the 1,8- and 1,4-DMN isomers could be readily isomerized with HF alone at ambient temperature while a similar reaction with the 2,6-isomer required an elevated temperature (70°). However, the isomerization rates with HF alone were in most instances too slow for a study at a convenient temperature.

The analysis of the product mixtures was accomplished by gas chromatography and infrared absorption techniques.[18]

In accord with the findings of McCaulay and Lien,[9] with methylbenzenes the isomer distribution in the equilibrium isomerisates was found to depend on the amount of added boron trifluoride.

The unique feature of the isomerization of dimethylnaphthalenes was the discovery of a number of discrete equilibrium sets of isomer groups. Thus, isomerization of dimethylnaphthalenes within the group is facile; however no interconversion of isomers belonging to the different groups has been observed. The 1,2-isomer did neither isomerize to any of the nine other dimethylnaphthalenes nor did the other isomers give rise to 1,2-dimethylnaphthalene. The isomer groups, together with the equilibrium concentrations of the individual isomers with different amounts of added $BF_3$ are given in Table I.

TABLE I

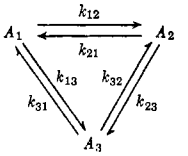
EQUILIBRIUM CONCENTRATIONS OF DI- AND MONOMETHYLNAPHTHALENES[a]

| Conditions[b] | Equilibrium | | |
|---|---|---|---|
| | 2,6-DMN ⇌ | 1,6-DMN ⇌ | 1,5-DMN |
| A | 57 | 40 | 3 |
| B | 35 | 63 | 2 |
| C | 56 | 40 | 4 |
| | 2,7-DMN ⇌ | 1,7-DMN ⇌ | 1,8-DMN |
| A | 61 | 39 | 0 |
| B | 90 | 10 | 0 |
| | 2,3-DMN ⇌ | 1,3-DMN ⇌ | 1,4-DMN |
| A | 35 | 64 | 1 |
| B | <1 | >99 | <1 |
| | 1,2-DMN ⇌ | other DMD isomers | |
| | 1-MeN ⇌ | 2-MeN | |
| A | 23 | 77 | |
| B | 12 | 88 | |

[a] Values are given as weight per cent. [b] A, benzene phase, with catalytic amount of $BF_3$, 70°; B, acid phase, with equimolar amounts of $BF_3$, 28°; C, benzene phase, with HF alone, 70°.

The rates of isomerization of individual isomers were determined in the homogeneous acid medium, with equimolar or excess $BF_3$. The constancy of the equilibrium concentration values was verified from several sides, *i.e.*, starting with all the equilibrium partners. The approach to equilibrium with the isomers of the 2,6-, 1,6-, 1,5-, and 2,7-, 1,7-, 1,8-DMN and 1-MeN and 2-MeN sets as well as the irreversible conversion of 1,4- and 2,3-DMNs to the 1,3-isomer were found to be first order in the starting arene.

The most general form, a coupled set of first-order reactions involving three components, is the following.




Any simpler set may be obtained from the general scheme by setting certain rate constants equal to zero.

From the time *vs.* the product composition analysis the sequence of the appearance of the isomers in the 2,6-, 1,6-, and 1,5-DMN set was found to be as follows: from 2,6-, first 1,6- then 1,5-; from 1,5-, first 1,6-, then 2,6-; from 1,6-, both 2,6- and 1,5-, concurrently. These observations are consistent with the postulated intramolecular 1,2-methyl shift. Thus, a reaction scheme for the two consecutive reversible first-order reactions would be applicable.

$$\text{2,6-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{1,6-} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{1,5-DMN}$$

Further simplification was based on the fact that the equilibrium concentration of the 1,5-DMN isomer was much smaller than those of the two other equilibrium partners. Consequently, $k_3$ could be, as a first approximation, neglected in comparison with the other three rate constants.

The kinetic scheme for the interconversion of the 2,6- and 1,6-isomers reduced then to a simple, reversible reaction.

$$\text{2,6-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{1,6-DMN}$$

For the 1,5-isomer it reduced to a simple, first-order reaction.

$$\text{1,5-} \xrightarrow{k_4} \text{1,6-DMN}$$

Introduction of the equilibrium concentrations into the integrated rate expression and plotting the concentration term log $A$ *vs.* time gave the effective rate constants. In the case of two reversible first-order reactions, the effective rate constant may be obtained as the sum of the rate constants for the forward and reverse reactions[19]; the individual rate constants can then be arrived at from the equilibrium constant.

The rate constants for the 2,7-, 1,7-DMN, and 1- and 2-MeN isomerization were obtained in an analogous manner. Conversion of 1,4- and 2,3-DMNs to the 1,3-isomer was practically complete and the rate constants were obtained from the simple, first-order rate expression.

The rate of the irreversible isomerization of the 1,8-isomer in the presence of $BF_3$ was too rapid for measurement; thus at −22° 97% of the above isomer was converted to the 1,7-isomer in less than 4 min. Even in the absence of $BF_3$, *i.e.*, with HF alone, 98% of the 1,8-isomer had reacted in 10 min. at room temperature. Isomerization of the 1,4-isomer to 1,3-DMN was also

(19) A. A. Frost and R. P. Pearson, "Kinetics and Mechanism" 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 186.

TABLE II

EFFECT OF TEMPERATURE ON THE EQUILIBRIUM PRODUCT COMPOSITION OF THE 2,6-, 1,6-, AND 1,5-DMN SET

| Temp., °C. | Time, min. | Composition of product, % DMN 2,6- | 1,6- | 1,5- | Other |
|---|---|---|---|---|---|
| 20 | 15 | 94 | 6 | 0 | ... |
| 20 | 2880 | 35 | 63 | 2 | 1 |
| 28 | 15 | 82 | 18 | 0 | ... |
| 28 | 1000 | 35 | 63 | 2 | 1 |
| 28 | 7500 | 34 | 64 | 2 | 4.5 |
| 40 | 15 | 57 | 42 | 1 | ... |
| 40 | 180 | 35 | 62 | 3 | |
| 50 | 15 | 38 | 59 | 3 | ... |
| 50 | 180 | 35 | 62 | 3 | |

too fast to be measured at 28°; however measurable rates could be obtained at −22 and −12°. The 1,2-DMN isomer was not converted to any of the other DMN isomers under the above described conditions.

The equilibrium concentrations of isomers varied little over the temperature range employed, thus essentially identical distributions were found in the experiments at 20, 28, 40, and 50° (Table II).

Disproportionation of both di- and monomethylnaphthalenes under the reaction conditions was found to be negligible, *e.g.*, *ca.* 1% at 28° over a 10-half-life period.

The rate data for the homogeneous phase isomerization of di- and monomethylnaphthalenes are sum-

TABLE III

RATES OF ISOMERIZATION OF 2,6-, 1,6- AND 1,5-DIMETHYLNAPHTHALENES[a]

2,6-DMN[b]

| Time, min. | Composition of product, % DMN 2,6- | 1,6- | 1,5- |
|---|---|---|---|
| 0 | 100 | 0 | 0 |
| 10 | 88 | 12 | 0 |
| 15 | 82 | 18 | 0 |
| 20 | 80 | 20 | 0 |
| 32 | 71 | 29 | 1 |
| 44 | 62 | 37 | 1 |
| 56 | 57 | 42 | 1 |
| 68 | 52 | 47 | 1 |
| 80 | 48 | 50 | 2 |
| 92 | 46 | 53 | 2 |
| 170 | 37 | 61 | 2 |
| 1000 | 35 | 63 | 2 |

2,6-DMN[c]

| Time, min. | Composition of product, % DMN 2,6- | 1,6- | 1,5- |
|---|---|---|---|
| 0 | 100 | 0 | 0 |
| 5 | 93 | 7 | 0 |
| 10 | 86 | 14 | 0 |
| 20 | 75 | 25 | 0 |
| 30 | 64 | 36 | 1 |
| 40 | 58 | 42 | 1 |
| 1000 | 35 | 63 | 2 |

2,6-DMN[d]

| Time, min. | Composition of product, % DMN 2,6- | 1,6- | 1,5- |
|---|---|---|---|
| 0 | 100 | 0 | 0 |
| 25 | 78 | 22 | 0 |
| 35 | 68 | 32 | 0 |
| 50 | 60 | 39 | 1 |
| 70 | 51 | 48 | 1 |
| 90 | 47 | 52 | 1 |

1,6-DMN[b]

| Time, min. | Composition of product, % DMN 2,6- | 1,6- | 1,5- |
|---|---|---|---|
| 5 | 4 | 95 | 1 |
| 10 | 7 | 92 | 1 |
| 15 | 11 | 88 | 1 |
| 20 | 13 | 86 | 1 |
| 30 | 20 | 79 | 1 |
| 45 | 22 | 77 | 1 |
| 60 | 27 | 72 | 1 |

1,6-DMN[e]

| Time, min. | Composition of product, % DMN 2,6- | 1,6- | 1,5- |
|---|---|---|---|
| 10 | 11 | 88 | 1 |
| 20 | 17 | 82 | 1 |
| 30 | 21 | 78 | 2 |
| 45 | 25 | 73 | 2 |
| 75 | 32 | 67 | 2 |
| 120 | 35 | 63 | 2 |
| 1160 | 36 | 62 | 2 |

1,5-DMN[b]

| Time, min. | Composition of product, % DMN 2,6- | 1,6- | 1,5- |
|---|---|---|---|
| 0 | 0 | 0 | 100 |
| 10 | 0 | 10 | 90 |
| 21 | 1 | 20 | 79 |
| 30 | 2 | 28 | 70 |
| 41 | 4 | 34 | 62 |
| 60 | 7 | 43 | 50 |
| 80 | 11 | 52 | 37 |
| 100 | 15 | 56 | 29 |
| 121 | 19 | 59 | 21 |
| 140 | 22 | 60 | 18 |
| 1000 | 35 | 62 | 3 |

1,5-DMN[c]

| Time, min. | Composition of product, % DMN 2,6- | 1,6- | 1,5- |
|---|---|---|---|
| 0 | 0 | 0 | 100 |
| 10 | 1 | 15 | 84 |
| 20 | 2 | 28 | 70 |
| 30 | 4 | 37 | 59 |
| 60 | 12 | 53 | 35 |

[a] 1.1 moles of $BF_3$ and 55 moles of HF/mole of DMN at 28°. [b] Dissolved in benzene, 10% solution. [c] Dissolved in *n*-hexane, 10% solution. [d] Dissolved in benzene, 2% solution (275 moles of HF/mole of DMN). [e] No solvent.

TABLE IV

RATES OF ISOMERIZATION OF 1,7- AND 2,7-DIMETHYLNAPHTHALENES[a]

1,7-DMN[b]

| Time, min. | Composition of product, % DMN 1,7- | 2,7- |
|---|---|---|
| 0 | 99 | 1 |
| 10 | 91 | 9 |
| 15 | 86 | 14 |
| 27 | 78 | 22 |
| 50 | 63 | 37 |
| 100 | 39 | 61 |
| 145 | 26 | 74 |
| 1140 | 10 | 90 |

2,7-DMN[b]

| Time, min. | Composition of % product, DMN 2,7- | 1,7- |
|---|---|---|
| 0 | 100 | 0 |
| 15 | 98 | 2 |
| 30 | 97 | 3 |
| 45 | 96 | 4 |
| 60 | 95 | 5 |
| 75 | 94 | 6 |
| 90 | 93 | 7 |
| 400 | 90 | 10 |
| 1000 | 90 | 10 |

[a] 1.1 moles of $BF_3$ and 55 moles of HF/mole of DMN at 28°. [b] Dissolved in benzene, 10% solution.

TABLE V

RATE OF ISOMERIZATION OF 2,3-DIMETHYLNAPHTHALENE[a]

| Time, min. | Composition of product, % DMN 2,3- | 1,3- |
|---|---|---|
| 0 | 100 | 0 |
| 5 | 85 | 15 |
| 10 | 71 | 29 |
| 13 | 68 | 32 |
| 17 | 59 | 41 |
| 20 | 54 | 46 |
| 30 | 38 | 62 |
| 40 | 28 | 72 |
| 60 | 15 | 85 |
| 360 | 1 | 99 |

[a] 1.1 moles of $BF_3$ and 55 moles of HF/mole of DMN (dissolved in benzene, 10% solution).

TABLE VI

RATE OF ISOMERIZATION OF 1,4-DIMETHYLNAPHTHALENE[a]

| Time, min. | Composition of product, % DMN— 1,4- | 1,3- |
|---|---|---|
| | At −22° | |
| 0 | 100 | 0 |
| 3.7 | 88 | 12 |
| 8 | 72 | 28 |
| 13 | 57 | 43 |
| 18 | 45 | 55 |
| 33 | 25 | 75 |
| 75 | 3 | 97 |
| 120 | 1 | 99 |
| | At −12° | |
| 0 | 85 | 15[b] |
| 3.0 | 56 | 44 |
| 7.2 | 29 | 71 |
| 11.0 | 13 | 87 |
| 15.1 | 8.5 | 91.5 |
| 19.0 | 5.5 | 94.5 |

[a] 1.1 moles of $BF_3$ and 55 moles of HF/mole of DMN (dissolved in *n*-hexane). [b] The extent of isomerization of the 1,4-isomer prior to the addition of $BF_3$.

TABLE VII

RATES OF ISOMERIZATION OF 1- AND 2-METHYLNAPHTHALENES[a]

| | 1-MeN[b] | | | 2-MeN[b] | |
|---|---|---|---|---|---|
| | Composition of product, —% MeN— | | | Composition of product, —% MeN— | |
| Time, min. | 1-MeN | 2-MeN | Time, min. | 1-MeN | 2-MeN |
| 0 | 100 | 0 | 0 | 0 | 100 |
| 3 | 86 | 14 | 5 | 4 | 96 |
| 5 | 80 | 20 | 10 | 5 | 95 |
| 7 | 69 | 31 | 15 | 8 | 92 |
| 10 | 62 | 38 | 20 | 9 | 91 |
| 12 | 55 | 45 | 35 | 10 | 90 |
| 15 | 49 | 51 | 120 | 12 | 88 |
| 20 | 40 | 60 | 300 | 12 | 88 |
| 35 | 25 | 75 | | | |
| 130 | 14 | 86 | | | |
| 230 | 12 | 88 | | | |
| 390 | 12 | 88 | | | |

[a] 1.1 moles of $BF_3$ and 55 moles of HF/mole of DMN at 28°. [b] Dissolved in benzene, 10% solution.

marized in Tables III–X and illustrated in Fig. 2 by the kinetic plot for the conversion of the 2,6-, 1,6-, and 1,5-DMN set. It must be emphasized that the product compositions given in Tables III–VII refer to the isomer distribution in the acid phase.

The temperature dependence of the rate of isomerization of 2,6-dimethylnapthalene is shown in Fig. 3.

## Discussion

There are no apparent restrictions to an intramolecular migration of methyl groups around the periphery of the benzene nucleus; thus the three xylene isomers give rise to the same equilibrium mixture on isomerization with a catalytic amount of $BF_3$.[9] Therefore, the existence of the discrete equilibrium groups of dimethylnaphthalene isomers under similar circumstances may, at first sight, appear surprising.

It is evident from the isomer composition of the equilibrium sets that there exist, in effect, migrational barriers between the adjacent $\beta$–$\beta'$-positions as well as between the two rings of the naphthalene nucleus (Fig. 4).

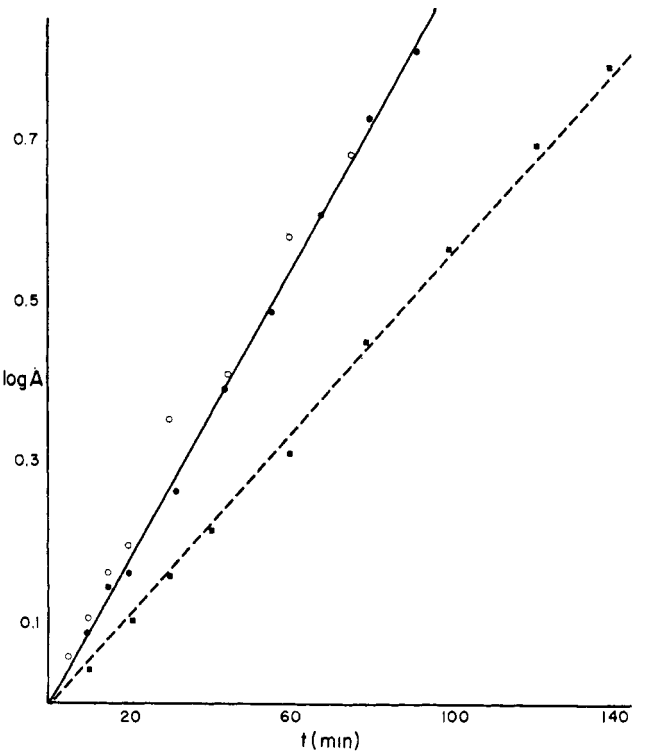



Fig. 2.—Rates of isomerization of 1,6- (○), 2,6- (●), and 1,5-dimethylnaphthalene (■) at 28°, 10 wt. % solution in benzene (Table III); $\log A = \log (A_0 - A_e/A_t - A_e)$.

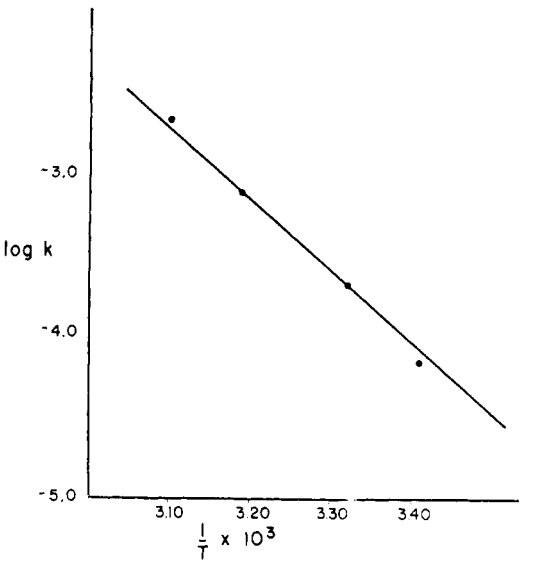



Fig. 3.—Temperature dependence of the rate of isomerization of 2,6-dimethylnaphthalene (10 wt. % solution in benzene).

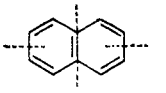


Figure 4.

A similar conclusion was reached recently by Russian workers based on their results of an isomerization study of 1-$C^{14}$-labeled 1-methylnaphthalene over a heterogeneous catalyst.[20]

(20) N. N. Vorozhtsov, and V. A. Koptyug, *J. Gen. Chem. USSR*, **30**, 999 (1960).

TABLE VIII

RATES OF ISOMERIZATION[a]

| Reactant | Temp., °C. | $k$, sec.$^{-1}$ × $10^4$ | $\left(\frac{k_1}{k_2}\right)_{eq}$[b] | $t_{1/2}$, min. |
|---|---|---|---|---|
| 2,6- $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ 1,6-DMN | 20 | 1.1[c] | | 104.0[d] |
| | 28 | 3.3[c] | 1.80 | 34.8[d] |
| | 40 | 12.0[c] | | 9.6[d] |
| | 50 | 34.0[c] | | 3.4[d] |
| | 28 | 3.2[e] | | 36.0 |
| | 28 | 4.4[f] | | 26.2 |
| 1,5- $\overset{k}{\rightleftharpoons}$ 1,6-DMN | 28 | 2.1 | | 54.7 |
| | 40 | 7.7 | | 14.9 |
| | 28 | 3.0[f] | | 38.4 |
| 2,7- $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ 1,7-DMN | 28 | 2.0[c] | 0.11 | 57.5[d] |
| 2,3- $\xrightarrow{k_2}$ 1,3-DMN | 28 | 5.3 | | 21.7 |
| | 40 | 19.0 | | 6.05 |
| 1,4- $\xrightarrow{k}$ 1,3-DMN | −22 | 7.6 | | 15.1 |
| | −12 | 26.0 | | 4.42 |
| 1- $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ 2-MeN | 28 | 9.6[c] | 7.33 | 12.0[d] |
| | 40 | 39.0[c] | | 2.95[d] |

[a] 1.1 moles of $BF_3$ and 55 moles of HF/mole of DMN. [b] Determined experimentally as $K_{eq}$. [c] The effective rate constant, the sum of the constants $k_1 + k_2$ for the forward and reverse directions. [d] Half-life of the over-all equilibration reaction. HF–DMN molar ratio, 275:1. [f] In the presence of *n*-hexane.

TABLE IX

ACTIVATION ENERGIES AND ENTROPIES OF ISOMERIZATION

| Reactant | Product | $E$,[a] kcal. | $\bar{T}$, °K. | $-\Delta S^*$,[b] (301.1° K.), cal. deg.$^{-1}$ mole$^{-1}$ |
|---|---|---|---|---|
| 2,6-DMN | 1,6-DMN | 20.1 | 307.6 | 12.6 |
| 1,6-DMN | 2,6-DMN | | | 13.7 |
| 1,5-DMN | 1,6-DMN | 20.3 | 307.1 | 12.0 |
| 2,3-DMN | 1,3-DMN | 20.3 | 307.1 | 10.2 |
| 1,4-DMN | 1,3-DMN | 16.0 | 256.1 | 12.8[c] |
| 1-MeN | 2-MeN | 22.0 | 307.1 | 3.5 |
| 2-MeN | 1-MeN | | | 7.5 |

[a] Estimated experimental uncertainty 1.0 kcal. [b] Based on $\Delta H^*$. [c] At 251.1°K.

TABLE X

ISOMERIZATION OF DI- AND MONOMETHYLNAPHTHALENES[a,b]

2,6- ⇌ 1,6- ⇌ 1,5-DMN

| Reactant | Reaction time, min. | Composition of product, % DMN 2,6- | 1,6- | 1,5- |
|---|---|---|---|---|
| 2,6-DMN | 90 | 57 | 41 | 2 |
| | 180 | 57 | 41 | 2.5 |
| | 240 | 56 | 41 | 3 |
| 1,5-DMN | 90 | 57 | 40 | 3 |
| | 180 | 57 | 40 | 3 |
| | 240 | 57 | 40 | 3 |

2,7- ⇌ 1,7- ⇌ 1,8-DMN

| | | 2,7- | 1,7- | 1,8- |
|---|---|---|---|---|
| 2,7-DMN | 90 | 64 | 36 | 0 |
| | 180 | 62 | 38 | 0 |
| | 240 | 61 | 39 | 0 |
| | 360 | 61 | 39 | 0 |
| 1,8-DMN | 60 | 56 | 44 | 0 |
| | 150 | 61 | 39 | 0 |
| | 340 | 61 | 39 | 0 |

2,3- ⇌ 1,3- ⇌ 1,4-DMN[c]

| | | 2,3- | 1,3- | 1,4- |
|---|---|---|---|---|
| 2,3-DMN | 90 | 42 | 58 | ... |
| | 180 | 38 | 62 | ... |
| | 240 | 37 | 63 | 0 |
| 1,3-DMN | 90 | (24) | 76 | (24) |
| | 180 | (36 | 64 | (36) |
| | 240 | 35.5 | 64 | 0.5 |
| 1,4-DMN | 90 | 28 | 69 | 3 |
| | 180 | (34) | 66 | (34) |
| | 240 | 34 | 64 | 2 |

1-MeN ⇌ 2-MeN

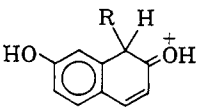
| | | % MeN 1-MeN | 2-MeN |
|---|---|---|---|
| 1-MeN | 90 | 23 | 77 |
| | 180 | 23 | 77 |
| | 240 | 23 | 77 |
| 2-MeN | 90 | 22 | 78 |
| | 180 | 22 | 78 |
| | 240 | 22 | 78 |

[a] 0.1 mole of $BF_3$ and 65 moles of HF/mole DMN at 70°. [b] Composition of the product in the organic phase. [c] Values in parentheses are composite values of 1,4- and 2,3-DMN.

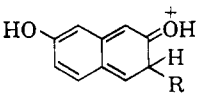
The asymmetric nature of the naphthalene bond structure is well established. The physical evidence indicates different degrees of bond order but no pure double or single bonds in the naphthalene nucleus while the chemical reactivity suggests bond fixation in the positions of the symmetrical Erlenmeyer formula (Fig. 4.).[21]

The apparent conflict between the theoretical quantum mechanical *vs.* the chemical reactivity concept of the naphthalene molecule arises from the different points of reference, *i.e.*, ground state as contrasted to polarization and localization of $\pi$-electron charge by a reagent.

The subject matter has been treated by Wheland[22] who suggested that the exclusive diazo coupling at the 1- or 8-positions of 2,7-dihydroxynaphthalene could be explained on the basis of differences in the stabilities of the corresponding activated complexes (transition states) for the coupling at 1- and 3-positions (I and II, R = diazonium radical).




I




II

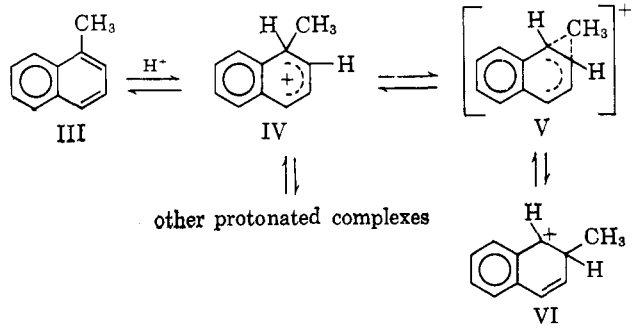
Since the complex I retains the resonance energy of the intact benzene ring it is much more stable than the complex II and consequently the difference in the rates of coupling at positions 1 and 3 would be of several orders of magnitude.

The above rationale clearly obviates the necessity of postulating bond fixation in the unreacting molecule and may be extended to a variety of reactions of the naphthalene nucleus.

The apparent existence of the migrational barriers in di- and monomethylnaphthalenes may be similarly rationalized on the above basis. Thus the postulated first step in the isomerization reaction is the rapid, reversible addition of a proton from the acid catalyst to di- or monomethylnaphthalene to form the cor-

(21) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, Chapter 27.

(22) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942); also G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 496, 497.




responding conjugate acid, formulated as a $\sigma$-complex (IV).

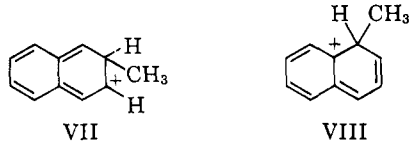
The protonation step is followed by the reversible, rate-determining, 1,2-methyl shift from an essentially tetrahedral carbon to the adjacent electron-deficient carbon with the result of formation of the new $\sigma$-complex (VI).

The above treatment is analogous to the mechanism proposed by McCaulay and Lien[9] for the isomerization of methylbenzenes.

There are ten available positions for the proton attachment to the naphthalene nucleus; however addition to the central C-9 and/or -10 would interrupt the benzenoid resonance of both rings and would be energetically unfavorable. The relative concentrations of the various complexes formed in the initial protonation step should be proportional to their relative stabilities, *i.e.*, the extent of delocalization of the positive charge and relief of steric strains present in the original hydrocarbon.

By analogy to the previously suggested explanation of the orientation of the diazo coupling in 2,7-dihydroxynaphthalene[22] it may be postulated that the bond structure of the protonated complexes would maintain an intact benzene ring. Since the intramolecular methyl shift between the adjacent $\beta$–$\beta'$-positions would require an unfavorable, high-energy quinonoid complex VII the migrational barriers are corollary to the proposed protonation–isomerization mechanism.

A similar reasoning applies to the intramolecular migration of methyl groups from one ring to the other. Here again the consecutive methyl shifts would involve quinonoid intermediates such as VIII.




As seen from Table I the equilibrium concentrations of di- and monomethylnaphthalenes within the defined groups depend on the amount of added boron trifluoride. This result is in accord with the observations of McCaulay and Lien on methylbenzenes[9] who suggested that with the equimolar or excess boron trifluoride the effective equilibrium exists between the protonated complexes in the acid (HF) phase, while with less than equimolar or catalytic amounts the concurrent equilibrium between the protonated complexes and their conjugate bases, *i.e.*, hydrocarbons in the organic phase, results ultimately in the thermodynamic distribution of isomers in the latter phase. The same process should be operable with di- and monomethylnaphthalenes—however, with the distinction that the attainment of the true thermodynamic equilibrium is here precluded by the limitation of the particular mechanism.

Assuming that with excess boron trifluoride the fraction of nonprotonated, *i.e.*, physically dissolved, di- and monomethylnaphthalenes in the acid (HF) phase is small and that the equilibrium distribution coefficients between the protonated and the nonprotonated species in the acid phase are comparable with the various isomers, then the order of the decreasing complex stabilities within the groups is 1,6-, 2,6-, 1,5-; 2,7-, 1,7-, 1,8; 1,3-, 2,3-, 1,4-DMN; 2-MeN, 1-MeN.

It should be noted that the observed equilibrium concentration values for each isomer represent a sum of the concentrations of a number of possible protonated complexes with the added proton at different ring carbons and do not necessarily reflect the relative basicities of the corresponding isomers as determined by competitive extraction experiments under nonequilibrating conditions.

The isomerization studies of methylbenzenes[9,23] and presently of methylnaphthalenes support an intramolecular, 1,2-methyl shift as the mechanism of the rearrangement. However, the term intramolecular 1,2-methyl shift implies no insight into the mechanism of rearrangement, *i.e.*, the structures and the location along the reaction coordinate of the intermediates and/or transition states. If one accepts a gross mechanism based on the primary protonation of the arene followed by the reversible, rate-determining methyl migration step, two factors, discussed by McCaulay and Lien in their study on isomerization of methylbenzenes, could affect the rates of rearrangement of methylnaphthalenes. First, the rate of isomerization must depend on the concentration of the protonated complexes in a "migrational configuration," *i.e.*, with a proton attached to the ring carbon carrying the methyl group, and secondly on the relative charge stabilizations in the initial protonated complex and the unstable tricentric intermediate and/or transition state in which the methyl group is shared by two ring carbons. A question relevant to the overall isomerization picture concerns the mechanism of interconversion of various protonated complexes involving the change in the site of attachement of the added proton.

The facile interconversion of protonated complexes is a corollary to the proposed intramolecular, 1,2-methyl shift mechanism in which the rate-determining step is the migration of a methyl group. The interconversion may proceed either through (1) a reversible intramolecular, 1,2-hydrogen shift analogous to the proposed methyl shift and hence presumably subject to the same migrational restrictions or (2) *via* a fast equilibrium between the protonated complexes and their respective conjugate bases either in the homogeneous acid (HF) or in the hydrocarbon–solvent phase. No migrational barriers should apply in this intermolecular exchange with the result of a complete equilibration between all the possible protonated complexes. Obviously, both of the above processes may proceed

(23) M. Kilpatrick, J. A. S. Bett, and M. L. Kilpatrick, *J. Am. Chem. Soc.*, **85**, 1038 (1963).

through the intervening $\pi$-complexes not indicated on the previous scheme. Presently there is not sufficient experimental evidence to distinguish between the several possibilities, consequently the over-all isomerization mechanism must remain speculative.

It follows from the preceding discussion that restraint should be exercised in drawing mechanistic conclusions on the basis of the experimental rate and equilibrium data.

Furthermore, the differences in the rate constants (Table VIII) of various di- and monomethylnaphthalene isomers are, with two exceptions, small, while even smaller differences in the activation parameters (Table IX) are well within the limit of the experimental error.

Comparison of the rates of isomerization of mono- and dimethylnaphthalenes with those of *p*- and *o*-xylenes[9] shows that the first-order rate constants are, with the exception of the 1,4- (and 1,8-) DMN isomer, of the same order. However, there are significant differences in the activation parameters of the two series. The activation energies for the naphthalene series are *ca.* 7 kcal. higher than those for the benzene series, while the activation entropies are more positive by *ca.* 20 entropy units. A possible explanation for these differences may be the extra resonance stabilization of the charge by the intact benzenoid nucleus in the initially formed dimethylnaphthalenonium ions, with the result of increase in the activation energy for the isomerization. Correspondingly, the more positive activation entropy may derive from the decrease in the solvent electrostriction due to the delocalization of the charge in the above ions.

The observed rates of conversion of the 1,4- and the 1,8-DMN isomers to the 1,3- and 1,7-DMN isomers, respectively, are much faster than the isomerization rates of the other DMN isomers[24]; thus the extrapolated rate constant for the 1,4-isomer exceeds the experimental rate constants for the other DMN isomers by three orders of magnitude, while the conversion of the 1,8-isomer is too fast for measurement even at low temperatures. It is seen from Table IX that the rate enhancement for the 1,4-isomer is almost entirely due to the lowering of the activation energy.

The magnitude of the rate enhancement for the 1,4- and 1,8-DMN isomers is difficult to rationalize on the basis of the previously discussed simple protonation–methyl migration model (*vide supra*). Certainly, the fraction of the protonated complexes in the migrational configuration, *i.e.*, with a proton added to the ring carbon carrying a methyl group, must be close to unity with the 1,4- and 1,8-DMN isomers; hence this concentration effect would result in a faster over-all isomerization rate. Also, if the transition state (or an intermediate) resembles the tricentric intermediate V, the additional stabilization of the charge by the benzenoid resonance and methyl induction–hyperconjugation would lower the energy in the 1,4-DMN case but not in the case of 1,8-DMN.

An argument could be made for the rate enhancement on the basis of the relief of the steric strain present in 1,8- and 1,4-DMNs; thus a strain energy of 7.6 kcal./mole has been estimated[25] for the 1,8-isomer while 3.2 kcal./mole of strain energy may be assumed for 1,4-DMN from the estimate of 1,6 kcal./mole for the 1-MeN isomer. However, the above strain energies present in the parent hydrocarbons would be relieved to a large extent in their conjugate acids if the latter are indeed $\sigma$-complexes where the ring carbons with the attached methyl group and the added proton are essentially tetrahedral. Furthermore, the isomerization rate of the third *peri*-disubstituted isomer, 1,5-DMN, is normal.

Consequently, neither the concentration effect nor the steric strain inherent in a dimethylnaphthalene with two *peri*-methyl groups seem to be adequate to account for the magnitude of the rate increase in either the 1,4- or the 1,8-DMN isomer.

It is quite likely that the isomerization process involving the protonation of the naphthalene nucleus followed by the 1,2-methyl shift is more complex than suggested by the previous scheme, there may be an intervention of $\pi$-complexes of both the proton and the methyl group in the rate-determining step. However, since neither the $\pi$- nor the $\sigma$-complex stabilities of dimethylnaphthalenes are presently known, no correlation of the latter with the rates of isomerization is possible.

Thus, determination of the complex stabilities in the alkylnaphthalene series in general, and mono- and dimethylnaphthalenes in particular, would lead to a better understanding of the mechanism of acid-catalyzed migration of methyl groups in methylnaphthalenes.

**Acknowledgment.**—The authors wish to thank Mr. R. Urban for carrying out the experimental work, the Analytical Section of Sun Research and Development for their valuable assistance, and Sun Oil Company for the permission to publish the results.

(24) The electronic absorption spectra of 1,4- and 2,3-DMNs in HF-$BF_3$ have been reported not to correlate with the calculated spectra.[5b] It is likely that under the experimental conditions, conversion of both 1,4- and 2,3-DMNs to the 1,3- isomer occurred; indeed the observed spectra of the two isomers are quite similar.

(25) J. Packer, J. Vaughan, and E. Wong, *J. Am. Chem. Soc.*, **80**, 905 (1958).