a kinetic "inversion" has occurred and that the major sulfoxide enantiomer is actually derived from the minor sulfinate diastereomer. We emphasize that in such instances of insufficient yields, rigorous absolute configuration assignment is impossible. Although this concept has been formulated in slightly different terms by Mislow (see footnote 17 of ref 17), it has subsequently been overlooked by the same author (ref 13), although the conclusions reached in that case are undoubtedly correct. In the case at hand, however, the alternate, independent configurational assignment makes it clear that no such inversion has occurred.
(13) M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4835 (1968).
(14) T. M. Balthazor and J. C. Martin, *J. Am. Chem. Soc.*, submitted for publication. Dr. Balthazor has kindly provided us with the experimental procedure.
(15) W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **90**, 6250 (1968).
(16) A recent study (R. L. Muntz, Ph.D. Thesis, University of Illinois, Urbana, 1972) shows that the presence of an additional basic site in each of several partially resolved sulfoxides did not interfere with the assignment of its absolute configuration via ^{1}H NMR in (*R*)-(−)-**1a**. In each case the observed sense of nonequivalence was consistent with the known absolute configuration of the sulfoxide.
(17) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965).
(18) K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Am. Chem. Soc.*, **86**, 5637 (1964).
(19) C. Djerassi and G. W. Krakower, *J. Am. Chem. Soc.*, **81**, 237 (1959).
(20) W. H. Pirkle, S. D. Beare, and T. G. Burlingame, *J. Org. Chem.*, **34**, 470 (1969).
(21) W. H. Pirkle and M. S. Hoekstra, *J. Org. Chem.*, **39**, 3904 (1974).
(22) W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **89**, 5485 (1967).
(23) Prepared from the corresponding disulfides, according to I. B. Douglass and R. V. Norton, *J. Org. Chem.*, **33**, 2104 (1968).
(24) The cyclizations leading to **11** and **12** were carried out according to the general procedure already published: N. K. Sharma, F. Jung, and T. Durst, *Tetrahedron Lett.*, 2863 (1973). The procedures for preparation of the precursors have been supplied to us by Professor T. Durst in advance of a detailed report of the synthesis and characterization of **11** and **12**.
(25) H. C. Brown and C. Groot, *J. Am. Chem. Soc.*, **64**, 2563 (1942).
(26) F. C. Whitmore and J. H. Olewine, *J. Am. Chem. Soc.*, **60**, 2570 (1938).
(27) D. M. Feigl, Ph.D. Thesis, Stanford University, 1965.
(28) H. S. Mosher and E. D. Parker, *J. Am. Chem. Soc.*, **78**, 4081 (1956).
(29) J. S. Birtswistle, K. Lee, J. D. Morrison, W. A. Sanderson, and H. S. Mosher, *J. Org. Chem.*, **29**, 37 (1964).
(30) H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *J. Am. Chem. Soc.*, **78**, 2576 (1956).

Aromatic Substitution. XXXVII.[1] Stannic and Aluminum Chloride Catalyzed Friedel–Crafts Alkylation of Naphthalene with Alkyl Halides. Differentiation of Kinetically and Thermodynamically Controlled Product Compositions, and the Isomerization of Alkylnaphthalenes

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Abstract: The $AlCl_3$- and $SnCl_4$-catalyzed Friedel–Crafts alkylation (methylation, ethylation, isopropylation, and *tert*-butylation) of naphthalene with alkyl halides was studied in nitromethane, carbon disulfide, and benzene solution. Alkylations in nitromethane show the least isomerization giving 75–100% α and 25–0% β substitution. Ready isomerization of α-alkylnaphthalenes under usual Friedel–Crafts conditions leads to substantially increased β-alkylnaphthalene formation. To ascertain the effect of acid-catalyzed isomerization, the $AlCl_3$-catalyzed isomerization of α- and β-alkyl-(methyl-, ethyl-, isopropyl-, *tert*-butyl-)naphthalenes was studied, including determination of equilibrium composition of the α/β isomeric pairs.

Compared to the extensively studied Friedel–Crafts alkylation of benzene and its derivatives,[2] the alkylation of naphthalene received relatively little attention. Whitmore and James reported the formation of β-*tert*-butylnaphthalene (and higher alkylation products) in the aluminum chloride catalyzed alkylation of naphthalene with isobutylene.[3] Other reports of the alkylation of naphthalene with olefins, alcohols, or alkyl halides also showed preferential formation of the β isomer.[4,5]

The preferential formation of the β isomer has been argued on steric grounds in the case of bulky reagent–catalyst complexes and on the basis of rearrangement of the kinetically favored α isomer.

In more recent studies using H_3PO_4–BF_3 catalyst propylene, 1-butene, *cis*-2-butene, and *trans*-2-butene were found to give 70–74% α- and 26–30% β-alkylnaphthalenes. Isobutylene, and diisobutylene, however, gave exclusively β-*tert*-butylnaphthalene.[6] Alkylations were considered to be carried out under kinetically controlled conditions. The formation of no detectable amount of α-*tert*-butylnaphthalene in the reaction of isobutylene was explained on the basis that in this case, for steric reasons, the β isomer becomes the exclusive kinetic product.

In the H_2SO_4-catalyzed alkylation of naphthalene with 2-butene the α/β isomer ratio was found to be dependent on the temperature and varied from 1.5 to 4.[7]

The Friedel–Crafts alkylation of naphthalene thus seems to be still controversial, and no clear understanding of directive effects and selectivities was yet obtained.

Besides possible steric effects the varying isomer ratios giving generally preference of β isomer observed in the Friedel–Crafts alkylations of naphthalene could have been effected by secondary isomerization processes of the alkylnaphthalenes initially formed in the reactions. Whereas the Friedel–Crafts isomerization of alkylbenzenes was extensively investigated,[8] apparently no such study of the isomerization of alkylnaphthalenes was yet reported.

In continued study of Friedel–Crafts alkylation and isomerization reactions it was, therefore, felt of substantial interest to carry out a study of the alkylation of naphtha-

Table I. $AlCl_3$-Catalyzed Methylation of Benzene and Naphthalene with Methyl Iodide in Benzene and Nitromethane Solution

Time	k_N/k_B	% methylnaphthalenes α-	% methylnaphthalenes β-
In Benzene Solution at 25 °C			
2 min	44	65	35
10 min	41.6	58.5	41.5
1 h	32	40	60
6 h	25	32	68
In Nitromethane Solution at 25 °C			
1 h	44	65	35
6 h	44	65	35

Table II. $AlCl_3$-Catalyzed Ethylation of Naphthalene with Ethyl Bromide at 25 °C in Carbon Disulfide and Nitromethane Solution

Time	k_N/k_B	% α-ethylnaphthalene	% β-ethylnaphthalene
In CS_2 Solution			
0.5 min		51.0	49.0
1 min		39.4	60.6
3 min		30.8	69.2
5 min		18.4	81.6
10 min		11.7	88.3
15 min		10.6	89.4
60 min		9.9	90.1
In Nitromethane Solution			
1 h	10	72	28
2 h	9.3	70	30
6 h	5.5	69	31

lene, as well as of the isomerization of alkylnaphthalenes, in order to clarify the kinetically vs. thermodynamically controlled nature of product compositions.

Results and Discussion

A. Alkylation of Naphthalene. In order to study the alkylation and to establish both positional and substrate selectivity of the reaction of naphthalene with alkyl halides (methyl and ethyl iodide, as well as isopropyl and *tert*-butyl bromide were preferentially used in our experiments), we first studied the aluminum chloride catalyzed competitive reaction of naphthalene and benzene with alkyl halides in benzene, nitromethane, and carbon disulfide solution. It became obvious that in both benzene and carbon disulfide solution the substrate selectivity, as expressed by the relative reaction rates of naphthalene and benzene (k_N/k_B), and the positional selectivities (as reflected by the isomeric α- and β-alkylnaphthalene ratios) widely varied with reaction conditions, primarily with reaction time and temperature, particularly in the case of isopropylation and *tert*-butylation reactions. In contrast, when using nitromethane as solvent, k_N/k_B values and α-/β-alkylnaphthalene isomer ratios at 25 °C stayed quite constant in case of methylation and ethylation, showed relatively slow variation in case of isopropylation, and only in case of *tert*-butylation was the change fast, even at 0 °C. Tables I–IV summarize the data.

Considering the alkylation data summarized in Tables I–IV, it is obvious that alkylations in nitromethane show substantially less isomerization (both intramolecular, primarily affecting α/β isomer ratios, and intermolecular, affecting k_N/k_B rate ratios). From the time dependence of the data showing decrease of both α/β isomer ratios and k_N/k_B values, one can summarize, as done in Table V, the initial alkylation data characteristic of conditions of minimal product isomerization.

Table III. $AlCl_3$-Catalyzed Isopropylation of Naphthalene and Benzene with Isopropyl Bromide at 25 °C in Carbon Disulfide and Nitromethane Solution

Time, min	k_N/k_B	% isopropylnaphthalenes α-	% isopropylnaphthalenes β-
In CS_2 Solution			
1		9.6	90.4
5		4.0	96.0
15		2.5	97.5
45		2	98
In CH_3NO_2 Solution			
5	4.7	82.5	17.5
10	6.5	74	26
60	7.5	70	30

Table IV. $SnCl_4$-Catalyzed *tert*-Butylation of Naphthalene and Benzene with *tert*-Butyl Bromide in Nitromethane Solution

Time, min	% *tert*-Butylnaphthalenes α-	% *tert*-Butylnaphthalenes β-
25 °C		
0.25	13.5	85.5
0.5	10	90
1	8.1	91.9
2	2.3	97.7

0 °C

Time, min	k_N/k_B	α, %	β, %
0.5	21.6	95	5
1	13.7	67	33
2	7.4	57.5	42.5
10	16	39.5	60.5
60	14	7	93

Table V. Competitive $AlCl_3$- and $SnCl_4$-Catalyzed Alkylation of Naphthalene and Benzene with Alkyl Halides in CH_3NO_2 Solution under Conditions of Minimal Product Isomerization

Alkyl halide	Catalyst	Time, min	k_N/k_B	% alkylnaphthalenes α-	% alkylnaphthalenes β-
CH_3I	$AlCl_3$	60	44	65	35
C_2H_5Br	$AlCl_3$	60	10	72	28
i-C_3H_7Br	$AlCl_3$	5	4.7	82.5	17.5
t-C_4H_9Br	$SnCl_4$	0.5	21.5	95	5

It should be, however, emphasized that nonisomerizing conditions, as observed in nitromethane solution, only relate to isomerization of formed alkylnaphthalene products. As in the case of the alkylation of toluene, it is also possible that in the alkylation of naphthalene alkyl shifts can take place in the arenium ion type intermediates (i.e., the alkylnaphthalenium ions) prior to their deprotonation to products. As methyl and ethyl group migration takes place predominantly via intramolecular processes, these can be less suppressed than those of isopropyl or *tert*-butyl groups, which tend to migrate intermolecularly. Indeed, in our preceding studies the preparation of alkylnaphthalenium ions was achieved, and these stable carbocations show a tendency to rearrange from α- to the more stable β-substituted ions. The higher positional selectivity (reflected by the higher α/β isomer ratios) observed in the sequence *tert*-butylation > isopropylation > ethylation > methylation is thus considered to be affected, at least in part, by the increasing preference for intramolecular (as contrasted to intermolecular)

Table VI. Aluminum Chloride Catalyzed Isomerization of Alkylnaphthalenes in CS_2 Solutions

	Reflux temperature		Reflux temperature	
Time	β-Methyl-naphthalene	α-Methyl-naphthalene	α-Methyl-naphthalene	β-Methyl-naphthalene
0 min	100%		100	
1	99.5	0.5	98.4	0.6
5	96	4	86	14
10	93.8	6.2	67	33
20	89.2	10.8	60	40
30	87.4	12.6	41	59
45			37	63
1 h	84.9	15.1		
2	80.8	19.2	32.5	67.5
3			30.5	69.5
5	80.4	19.6		
6			22.5	77.5
8	77.4	22.6		
10			25	75
24	75.5	24.5		

	Reflux temperature		Reflux temperature	
Time	β-Ethyl-naphthalene	α-Ethyl-naphthalene	α-Ethyl-naphthalene	β-Ethyl-naphthalene
0	2	98		
1 min	6	94	2	98
2	39	61	3.5	96.5
3	58.5	41.5	5	95
5	75.4	24.6	6	94
8	84.5	15.5	7.5	92.5
12	90.5	9.5	8.5	91.5
30	90.5	9.5	9.5	90.5

	0 °C		25 °C	
Time	β-Isopropyl-naphthalene	α-Isopropyl-naphthalene	α-Isopropyl-naphthalene	β-Isopropyl-naphthalene
0 min	1.5	98.5		100
0.5	17	83		
2	29.5	70.5	0.8	99.2
5	32.5	67.5	1.3	98.7
10	42.5	57.5	1.6	98.4
15	51.7	48.3	1.5	98.5
20	60	40		
30	75	25		
45	89	11		
1 h	97	3		
2	98.5	1.5		
3	98.5	1.5		

	0 °C		25 °C
Time	β-*tert*-Butyl-naphthalene	α-*tert*-Butyl-naphthalene	β-*tert*-Butyl-naphthalene
0 min	1.7	98.3	100.0
1	3.5	96.5	No change, only dis-
1.5	7.6	93.4	proportionation
2	9.3	90.7	
2.5	12.7	87.3	
3	15.6	84.4	
4	22.6	77.4	
5	33.0	67.0	
7	47.2	52.8	
10	78.3	21.7	
15	100.0	0	

alkyl group migrations in the alkylnaphthalenium ion intermediates (σ complexes).

In order to gain a better understanding of the concurrent and consecutive Friedel–Crafts type isomerization of alkylnaphthalenes we also carried out a study of the isomerization of isomeric α- and β-alkyl-(methyl-, ethyl-, isopropyl-, and *tert*-butyl-) naphthalenes by following (with gas–liquid chromatographic analysis) the time-dependent isomerization.

Isomerization of Alkylnaphthalenes. The aluminum chloride catalyzed isomerization of the isomeric α- and β-methyl-, ethyl-, isopropyl-, and *tert*-butylnaphthalenes was studied by determining time-composition data until equilibrium was reached.

Table VII. Equilibrium Composition of Alkylnaphthalenes

Alkyl	α, %	β, %
Methyl	24.5	75.5
Ethyl	9.5	90.5
Isopropyl	1.5	98.5
tert-Butyl	0	100

Isomerization of alkylnaphthalenes with aluminum chloride was advantageously studied in carbon disulfide solution, and followed by capillary gas–liquid chromatography (see Experimental Section). Isomerization of the neat compounds or their hydrocarbon solutions is too fast to be conveniently followed. Table VI summarizes the data of isomerization.

From the data of Table VI, the following equilibrium compositions of alkylnaphthalenes are apparent, as summarized in Table VII.

The data of the Friedel–Crafts alkylation of naphthalene with alkyl bromides (iodides) clearly show the ease with which the kinetically controlled alkylations can be affected by thermodynamically controlled isomerizations. The predominantly kinetic reactions give high α/β alkylnaphthalene isomer ratios, which seem to be characteristic for all electrophilic substitutions of naphthalene. Increasing β substitution is indicative of isomerization, as shown by the equilibrium composition of alkylnaphthalenes in which the β isomers predominate. Intermolecular isomerizations (disproportionation) affect relative reactivities as expressed by competitive $k_{\text{naphthalene}}/k_{\text{benzene}}$ rate ratios. When evaluating data of Friedel–Crafts alkylations, before any consideration to selectivity data can be given it must be ascertained that the data were obtained under conditions of minimal isomerization, thus under predominantly kinetically controlled conditions.

Experimental Section

Benzene, naphthalene, alkyl halides, and solvents used were of highest commercially available purity. α- and β-methylnaphthalene and β-ethylnaphthalene (Aldrich) and α-ethylnaphthalene (K and K Laboratories) were purified by standard methods, and analyzed by gas–liquid chromatography. Isopropylnaphthalenes were prepared according to Haworth,[10] *tert*-butylnaphthalenes according to Illingsworth and Peters,[11] as well as Romadane.[12]

General Procedure for Competitive Alkylation. Benzene (10 g, 0.125 mol), 16 g (0.125 mol) of naphthalene, and 3.33 g (0.025 mol) of anhydrous aluminum chloride (or 0.025 mol of anhydrous stannic chloride) were dissolved in 50 mol of spectroscopic grade nitromethane (or carbon disulfide). In order to assure uniform reaction conditions one drop of water was added to the reaction mixture. To the well-stirred mixture, at the temperature given in the tables, 0.025 mol of alkyl halide in 15 ml of nitromethane was then added. Samples were withdrawn at intervals indicated, quenched with ice water, extracted with ether, and analyzed by gas–liquid chromatography.

General Procedure of Isomerization. To a solution of 0.05 ml of pure isomeric α- or β-alkylnaphthalene and 3.33 g (0.025 mol) of anhydrous aluminum chloride in 25 ml of spectroscopic grade carbon disulfide was added a drop of water (to ascertain a uniform level of moisture in the system). The mixture was stirred at the temperatures shown in Table VI, and samples were withdrawn at intervals specified. After quenching and extraction with ether, isomer compositions were determined by gas–liquid chromatographis analysis.

Gas-Liquid Chromatographic Analysis. All analyses were carried out on a Perkin-Elmer Model 226 fractometer equipped with a 150-ft length, 0.01-in. i.d. open tubular (Golay) column, coated with *m*-bis(*m*-phenoxyphenoxy)benzene modified with 20% Apiezon. A hydrogen flame-ionization detector with helium carrier gas of 30 psi was used, columns being operated at 145 °C, with detector temperature of 185–190 °C and injector block temperature of 310–320 °C. Peak areas were directly determined by use of a high-speed Infotronics electronic integrator. Characteristic retention times of the isomeric alkylnaphthalenes follow: 1-methylnaphthalene, 17.2 min; 2-methylnaphthalene, 15.5 min; 1-ethylnaphthalene, 22.9 min; 2-ethylnaphthalene, 21.9 min; 1-isopropylnaphthalene, 29.8 min; 2-isopropylnaphthalene, 28.8 min; 1-*tert*-butylnaphthalene, 37.7 min; 2-*tert*-butylnaphthalene, 34.1 min.

Acknowledgment. Support of our alkylation work by the National Institutes of Health is gratefully acknowledged.

References and Notes

(1) Part XXXVI: G. A. Olah and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 2214 (1974).
(2) G. A. Olah, "Friedel-Crafts Chemistry", Wiley-Interscience, New York, N.Y., 1973.
(3) F. C. Whitmore, and W. H. James, *J. Am. Chem. Soc.*, **65**, 2088 (1943).
(4) G. A. Olah, Ed., "Friedel-Crafts and Related Reactions", Vol. II, Wiley-Interscience, New York, N.Y., 1964, Chapter XIV.
(5) H. E. Nursten and A. T. Peters, *J. Chem. Soc.*, 729 (1950).
(6) H. M. Friedman and A. L. Nelson, *J. Org. Chem.*, **34**, 3211 (1969).
(7) M. Martan, J. Manassen, and D. Vofsi, *Chem. Ind. (London)*, 434 (1970).
(8) For a review see D. A. McCauley in ref 4, Vol. III, p 1049.
(9) G. A. Olah, G. D. Mateescu, and Y. K. Mo, *J. Am. Chem. Soc.*, **95**, 1865 (1973).
(10) R. D. Haworth, B. M. Letsky, and C. R. Marvin, *J. Chem. Soc.*, 1790 (1932).
(11) E. Illingsworth and A. T. Peters, *J. Chem. Soc.*, 1602 (1951).
(12) I. Romadane, *Zh. Obshch. Khim.*, **27**, 1939 (1957); *Chem. Abstr.*, **52**, 5356*b* (1958).

Nitrogen Inversion Rates in Bicyclo[2.2.2]octyl Hydrazines and Amines by ^{13}C NMR

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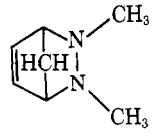
Abstract: Activation parameters for conformational change were determined by carbon NMR for 2,3-dimethyl-2,3-diazabicyclo[2.2.2]oct-5-ene, 2,3-dimethyl-2,3-diazabicyclo[2.2.2]octane, the 2,3-diethyl analogue, the 1,2,3,4-tetramethyl analogue, 2-methyl-1,2-diazabicyclo[2.2.2]octane, 2-methyl-2-azabicyclo[2.2.2]octane, 1,2-dimethyl-2-azabicyclo[2.2.2]octane, and 4,4-diethyl-2,6-diazatricyclo[5.2.2.$0^{2,6}$]undecane, and the results are discussed in terms of the shape of the potential barrier for such compounds.

Introduction

Hydrazine conformations have aroused considerable interest in recent years, largely because of the interesting interplay of steric and electronic effects upon N–N bond rotation and N inversion barriers.[1] Although acyclic hydrazines are known from several lines of evidence to have lone pair–lone pair dihedral angles near 90°,[2] cyclic hydrazines with dihedral angles of various sizes are known.[3] Dynamic NMR spectroscopy has been particularly frequently applied to cyclic hydrazines, and many studies of the barriers to conformational interconversion have appeared.[4-15] Anderson and Lehn[4c] discussed the form of the potential curve for methyl equilibration of 2,3-dimethyl-2,3-diazabicyclo[2.2.1]hept-5-ene (**1**) in detail, pointing out that the mirror image anti



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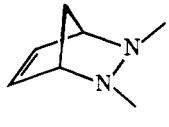
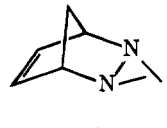
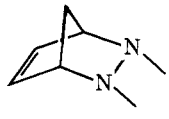


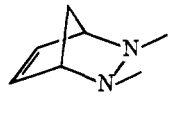
1a



1a′

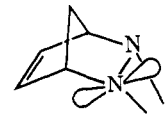


1s$_1$

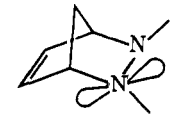


1s$_2$

forms **1a** and **1a′** are the only ones stable enough to be directly observed by NMR spectroscopy, that consecutive N inversion is obviously more favorable energetically than simultaneous double nitrogen inversion, and that the syn methyl forms **1s$_1$** and/or **1s$_2$** should be unstable intermediates, with the half-planar forms **1p$_1$** and/or **1p$_2$** being the



1p$_1$



1p$_2$

transition states. They estimated that the half-planar forms should lie about 10 kcal/mol above the stablest form (**1a**/**1a′**) and that the syn forms **1s$_1$** and **1s$_2$** would be destabilized by the methyl–methyl interaction, which they expected to be 5 kcal/mol, producing the potential curve redrawn as Figure 1A. The same sort of curve was stated to be present for saturated and unsaturated bicyclic hydrazines.[4c]

The double barrier potential curve A will not be correct for all cyclic hydrazines since the activation energy for nitrogen inversion will decrease with increasing ring size,[1] and alkyl–alkyl strain for an eclipsed syn form will increase as the alkyl groups get larger. Jones, Katritzky, and coworkers[7a-d] have asserted that alkyl–alkyl repulsion, not flattening at nitrogen, is the highest barrier to be surmounted in several cyclic hydrazines. The large increase in the $\Delta G^{\ddagger}$ required for "double nitrogen inversion" in 3,4-dialkyl oxadiazolidines **2**(R) as R is changed from methyl to *tert*-butyl[15] indicates that alkyl–alkyl repulsion in the eclipsed form **2**-ecl is the highest barrier to be overcome, at least for **2**(iPr).

An important difference in the conformations of **1** and **2**