12 ml. of gas was adsorbed within 1.5 days. The yields of amine salt, unsaturated ketone and aminoketone mixture were similar as reported above. For control purposes 3.0 g. of morpholine was allowed to stand in the described apparatus under air, but no change in gas volume was observed within 6 days.

In Boiling Benzene.—Bromoketone VIII (0.0095 mole) and 0.03 mole of morpholine were dissolved in 15 ml. of benzene, the air swept out with nitrogen and the solution heated under reflux for 24 hours. The work-up as above gave 73% of amine hydrobromide salt and 1.05 g. (43%) of a white solid, m.p. 94–96°. Mixed with XII it melted at 108–122°. Recrystallization from petroleum ether or from methanol-water gave a white solid, m.p. 97–98°. Infrared analysis in CCl_4 showed it to be still a mixture of saturated and unsaturated aminoketones: $\gamma_{\text{satd ketone C=O}}$, 1690 cm.$^{-1}$ (rel. abs. 98%); $\gamma_{\text{unsatd ketone C=O}}$, 1662 cm.$^{-1}$ (82%), $\gamma_{\text{C=C}}$ 1620 cm.$^{-1}$ (42%).

Standing of a solution of 0.3 g. of this mixed aminoketone product in 1.5 ml. of morpholine in a gasometer under air for 1.5 days caused an 11-ml. decrease in gas volume. A white solid, m.p. 115–116°, was isolated. Mixed with unsaturated aminoketone XII it melted at 118–124°.

Attempts to hydrogenate 2-morpholino-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (XII) in ethanol in the presence of platinum at 50° were unsuccessful. Only unreacted starting material and lower melting impure fractions were isolated.

2,2-Dibromo-4,4-dimethyl-1-tetralone (IX).—To 1.26 g. of VIII in 3 ml. of chloroform was added a solution of 1.0 g. (1.25 molar equiv.) of bromine in the same solvent at room temperature. Initially it was necessary to apply heat to cause decoloration of the solution, then the rest of the bromine was added. Upon evaporation of the solvent, the solid residue was triturated with petroleum ether–benzene, then with dilute solutions of sodium bisulfite, sodium bicarbonate and water. The solid was dried (1.3 g.) and recrystallized from methanol, m.p. 102–103°. The absorption spectra[3] revealed the presence of an axial and an equatorial bromine.

Anal. Calcd. for $C_{12}H_{12}OBr_2$: C, 43.45; H, 3.65. Found: C, 43.80; H, 3.51.

When 0.3 g. of the dibromoketone IX was allowed to stand with 0.3 g. of morpholine in 0.5 ml. of benzene, 0.15 g. of amine salt was isolated. The acid-soluble portion gave a white solid (0.05 g.), m.p. 124–125°, the melting point and infrared spectrum of which was identical with that of the known **2-morpholino-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (XII).**[6] Some impure starting material was also isolated.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CANTERBURY]

Steric Strains in Methylnaphthalenes

BY J. PACKER, J. VAUGHAN AND E. WONG

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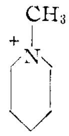
Rates of reaction in nitrobenzene solution of methyl iodide with pyridine, quinoline, isoquinoline, 2-methylquinoline and 8-methylquinoline have been followed over the temperature range 10–50°, using a precise conductimetric method. Relative heats of activation have been taken as quantitative measures of steric strains present in the activated complexes of these reactions. From these results, an estimate is made of the steric strains existing in the homomorphic structures 1-methylnaphthalene, 1,2-dimethylnaphthalene and 1,8-dimethylnaphthalene. Strains associated with these structures are found to be greater than those of comparable alkylbenzenes and the differences are attributed to the rigidity of a fused ring system as compared with an alkyl group.

In naphthalene derivatives, some measure of the magnitude of steric strains associated with the *peri*-CH group in its interaction with functional groups in the 1-position is of primary interest in any attempt to compare reactivities of 1- and 2-derivatives. Any such strain will be enhanced by further substitution in the 2- or 8-position. In the work now reported, estimates of the steric strains in simple examples of such systems were obtained. The method employed was based directly on the "strained homomorph" concept of Brown.[1] Following Brown, values of steric strain obtained by studying the Menschutkin reaction involving quinoline derivatives should also be measures of the strains existing in naphthalene compounds of similar geometry.

The rates of reaction in nitrobenzene of methyl iodide with quinoline, isoquinoline, 2-methylquinoline, 8-methylquinoline and pyridine were measured at four temperatures over the range 10–50°. The strain in the activated complex of the Menschutkin reaction has been estimated[2] to be *ca.* two-thirds of the strain in the final product and thus the activation energies connected with the formation of the ions should lead to measures of the steric strains associated with the corresponding hydrocarbons



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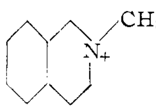

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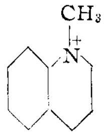

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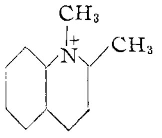

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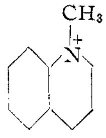

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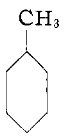

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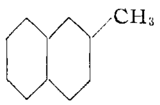

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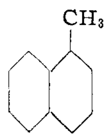

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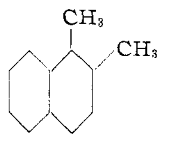
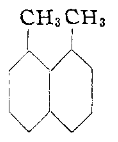


XI



X

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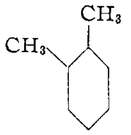
(1) H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson and K. L. Nelson, THIS JOURNAL, **75**, 1 (1953).

(2) H. C. Brown and A. Cahn, *ibid.*, **77**, 1715 (1955).

Apart from internal comparisons within the naphthalene series, the results also allow, for example, comparison of the steric strain associated with the fused benzene ring of a naphthalene compound with the strain associated with an *o*-methyl group in a comparable benzene derivative. Thus structures VIII, IX and X may be compared with structures XI, XII and XIII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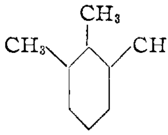
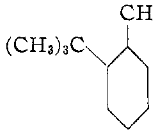

XII


XIII

Strain energies for these benzene structures have already been estimated by Brown and his co-workers.[1]

Experimental

Method.—In following the Menschutkin reactions, the conductimetric method of Larsen and Kraus[3] was used, with only slight modifications. Conductance of the pure quaternary ammonium salt solution was first measured over a concentration range which included salt concentrations developed during actual runs. In general, the concentration of the reactants in kinetic work was *ca.* 0.01 M and the extent of reaction covered during a run was $<0.5\%$. With such low concentrations of ionic products (*ca.* 10^{-5} M) conductivity cells of small cell constants were required and were of the type described by Nichol and Fuoss.[4] The high precision a.c. conductivity bridge used in this work has been described previously.[5] Bath temperatures were accurate to ±0.02°.

Since the percentage of reaction followed was so small, the reaction rate was essentially constant and the unintegrated form of the second-order equation $dx/dt = kc_ac_b$ could be used to evaluate the rate constant k. The rate dx/dt was determined indirectly from the relationship

$$\frac{dx}{dt} = \frac{dx}{d\frac{1}{R}} \times \frac{d\frac{1}{R}}{dt}$$

Under the favorable experimental condition of low ionic concentration, the conductance $1/R$ was found to be a linear function of concentration x. Over the small reaction range the conductance was also a linear function of the time t so that both $dx/(d1/R)$ and $d(1/R)/dt$ were constants for a given reaction. These factors were determined experimentally and rate constants were obtained from the equation

$$k = \frac{dx}{d\frac{1}{R}} \times \frac{d\frac{1}{R}}{dt} \times \frac{1}{c_{\text{amine}}} \times \frac{1}{c_{\text{MeI}}}$$

With some of the faster reactions (pyridine, quinoline and isoquinoline at 40°) kinetic measurements were also made by volumetric analysis, using the Volhard method for iodide ion determination. Results from both methods were in good agreement.

Materials. Amines.—Fractionation of the commercial samples after drying was generally inadequate for satisfactory purification. All amines except pyridine were converted into solid derivatives, chiefly the phosphate and/or picrate, which were purified by recrystallization and reconverted to amines. This process was repeated when necessary until no change in the rate constant was observed. Because the reaction rate in the method employed is so sensitive to impurities, constancy of rate constant, determined after each purification procedure, proved to be the best criterion of purity for these liquid amines. Physical constants are: pyridine, b.p. 115.0°, $n^{20}\text{D}$ 1.5100; quinoline, b.p. 111.5° (16 mm.), $n^{20}\text{D}$ 1.6251, phosphate m.p. 159°, picrate m.p. 201°; isoquinoline, b.p. 120° (18 mm.), phosphate m.p. 135°, picrate m.p. 223°; 2-methylquinoline, b.p. 115° (14 mm.), $n^{20}\text{D}$ 1.6125, phosphate m.p. 220°; picrate m.p. 192°; 8-methylquinoline, b.p. 122.5° (16 mm.), $n^{20}\text{D}$ 1.6170, phosphate m.p. 158°, picrate m.p. 201°.

Methyl Iodide.—Commercial "pure" methyl iodide was washed successively with water, dilute sodium carbonate, water, dilute sodium thiosulfate, and water. After drying over calcium chloride and subsequent distillation, a fraction b.p. 42.7-43.3° was collected and stored over mercury.

Nitrobenzene.—Extraction with 2 N sodium hydroxide was followed by washes with water, dilute hydrochloric acid and water. After drying ($CaCl_2$) the nitrobenzene was fractionated under reduced pressure, b.p. 96–98° (18–19 mm.), $n^{20}\text{D}$ 1.5526, d^{40}_4 1.1842, d^{20}_4 1.2032. Calcium chloride was an adequate drying agent, as was shown when use of nitrobenzene dried over phosphorus pentoxide before fractionation led to unchanged rate constants.

Quaternary Ammonium Iodides.—Standard solutions of the salts were prepared (by weight) and checked by Volhard's method. Pyridine methiodide was hygroscopic and the standard solution was made in this case by allowing pyridine and methyl iodide (in slight excess) to react in nitrobenzene solution. Excess methyl iodide was removed by evaporation under reduced pressure, the solution was diluted to the required strength and the exact concentration then determined. Calibrations were carried out on nitrobenzene solutions of the salts and checks were made on solutions containing also either the relevant amine or methyl iodide. Amine additions, resembling the quantities present during an actual run, had no effect on the conductance of the salt. The presence of methyl iodide appeared to increase the conductance slightly, but the increase was unimportant and was also constant so that the rate of change of conductance was not affected.

Results

Rate constants (l.mole^{-1} sec.$^{-1}$) are listed below, together with the parameters of the Arrhenius equation $\log k = \log A - E_a/RT$. The uncertainty in both E_a and $\log A$ values is < 0.1. The reaction with pyridine has been studied recently by Brown and Cahn.[2] The two sets of results are in excellent agreement.

Pyridine, $k \times 10^4$

10°	20°	30°	40°
1.025	2.42	5.05	10.43
1.009	2.42	5.12	10.32
0.995	2.39	5.03	10.45
0.993	2.39	5.08	10.19

E_a = 13.68 kcal./mole; log A = 6.57

Isoquinoline, $k \times 10^4$

10°	20°	30°	40°
1.427	3.18	6.88	14.37
1.439	3.18	6.90	14.43
1.430	3.22	6.85	14.44
1.462	3.16	6.90	
	3.18	6.86	
	3.15	6.99	

E_a = 13.54; log A = 6.60

Quinoline, $k \times 10^5$

25°	30°	35°	40°
5.27	7.99	11.71	17.55
5.31	8.02	11.75	17.53
5.33		11.83	17.36

E_a = 14.79; log A = 6.57

2-Methylquinoline, $k \times 10^6$

25°	30°	40°	50°
4.35	6.62	15.72	34.6
4.41	6.72	15.87	34.7
4.33	6.98	15.63	
4.29		16.07	
		16.17	
		16.12	

E_a = 16.02; log A = 6.38

8-Methylquinoline, $k \times 10^8$

25°	30°	40°	50°
5.38	8.78	23.9	62.6
5.38	8.76	23.7	62.3
5.36		24.2	62.8
5.33		24.2	61.8
			61.7

E_a = 18.80; log A = 6.51

Further relevant data are included in Table I, where $\Delta\Delta H^{\ddagger} = \Delta E_a$ and $\Delta\Delta S^{\ddagger} = 2.303\ \Delta \log A$.

Discussion

The data in Table I show that of the two factors, $\Delta\Delta H^{\ddagger}$ and $T\Delta\Delta S^{\ddagger}$, the first appears to play the

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(3) R. P. Larsen and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S.*, **40**, 70 (1954).

(4) J. C. Nichol and R. M. Fuoss, *J. Phys. Chem.*, **58**, 696 (1954).

(5) A. Fischer, J. D. Murdoch, J. Packer, R. D. Topsom and J. Vaughan, *J. Chem. Soc.*, in press (1958).

Table I

Base	10^5k (30°)	$\Delta \log A$	$\Delta\Delta H^{\ddagger}$, kcal./mole	$T\Delta\Delta S^{\ddagger}$ (30°), kcal./mole
Pyridine	50.7	(0.00)	(0.00)	(0.00)
Isoquinoline	69.0	.03	−0.14	.04
Quinoline	8.00	.00	1.11	.00
2-Methyl-	0.677	− .19	2.34	− .26
8-Methyl-	0.00877	− .06	5.12	− .08

dominant role in accounting for the observed decrease in rate going from isoquinoline to 8-methylquinoline. Discussion may thus deal mainly with activation energies. Results are in accord with the assumption that, as for the alkylpyridine series,[2] rate is determined chiefly by the steric factor; k-values decrease sharply in the present series, with corresponding increases in E_a as the steric requirement of the base is increased. The $\Delta\Delta H^{\ddagger}$ values are not accounted for on the basis of polar effects and there is no apparent correlation between pK_a values and heats of activation. In view of the similarity between E_a values for the unhindered amines isoquinoline and pyridine (*cf.* also Brown and Cahn's figures for 3-methylpyridine, $E_a = 13.59$, and 4-methylpyridine, $E_a = 13.62$), the relative heats of activation with respect to pyridine ($\Delta\Delta H^{\ddagger}$) are here used as quantitative measures of steric strains in the transition states of reactions involving the other bases.

The steric strain energies ($\Delta\Delta H^{\ddagger}$) in Table I, together with the data of Brown and Cahn, afford several interesting comparisons. The strain associated with the fused ring of quinoline (1.11 kcal./mole) is seen to be appreciably greater than that for the *o*-methyl group in α-picoline (0.30 kcal./mole) and this also is evident from the $\Delta\Delta H^{\ddagger}$ values for 2-methylquinoline (2.3 kcal./mole) and 2,6-lutidine (1.2 kcal./mole). Similarly, the strain energy in the transition state for 8-methylquinoline (5.1 kcal./mole) is appreciably larger than that for *o*-*t*-butylpyridine (3.8 kcal./mole).

From the observation of Brown, *et al.*,[6] that the steric strains in the corresponding alkylpyridine–borine addition compounds are larger than the strains in the corresponding activated complexes in the displacement reaction it follows that the strains present in the structures 1-methylnaphthalene (VIII), 1,2-dimethylnaphthalene (IX) and 1,8-dimethylnaphthalene (X) must be higher still than the corresponding $\Delta\Delta H^{\ddagger}$ values for the activated complexes in the quinoline series. Using the factor $3/2^2$ the strain in these structures is estimated to be 1.6, 3.4 and 7.6 kcal./mole, respectively. These structures are likewise more strained than the corresponding benzene structures: *o*-xylene (XI) (0.5 kcal./mole), hemimellitene (XII) (2 kcal./mole), *o*-*t*-butyltoluene (XIII) (6 kcal./mole). The larger strain values associated with the naphthalene structures may be attributed to the rigidity of the fused ring as compared with an aliphatic side-chain of an *o*-benzene derivative. One consequence of this rigidity is that the *peri*-CH group lacks freedom of rotation. An *o*-alkyl group may adopt different conformations and it was on an assumption of such freedom that Brown and Cahn were able to explain, in their 2-alkylpyridine studies, small increases in strain when going from methyl to ethyl to isopropyl as compared with the much larger increase from isopropyl to *t*-butyl. Furthermore, because of the rigidity in bond angles of the fused ring of naphthalene, relief of strain by bending of the 8–9-bond cannot be of importance.

Finally, it is to be noted that, as distinct from the $\Delta\Delta H^{\ddagger}$ values, the entropy of activation changes ($T\Delta\Delta S^{\ddagger}$) in the quinoline series are all very much smaller than those for the corresponding 2-alkylpyridines. In the pyridine series there is a parallel decrease in $T\Delta\Delta S^{\ddagger}$ with increase in $\Delta\Delta H^{\ddagger}$, but in the quinolines the decreases in $T\Delta\Delta S^{\ddagger}$ are almost insignificant compared with the large increases in heats of activation. The loss of more degrees of freedom by the alkyl substituents in the pyridine series may account for the greater decrease in entropy on the formation of the sterically hindered transition state.

The authors are grateful to the Research Fund Committee of the University of New Zealand for a grant and for the award of a Research Fund Fellowship to E.W.

CHRISTCHURCH, NEW ZEALAND

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[6] H. C. Brown, Centenary Lecture, *J. Chem. Soc.*, 1248 (1956).