gen atmosphere with 0.12 g. of 10% palladium-on-charcoal catalyst for 30 minutes at 275–295°. Sublimation *in vacuo* yielded 0.65 g. of semi-crystalline product. From a solution of this material in 15 cc. of ethanol to which was added 13 cc. of saturated ethanolic picric acid, there separated 0.70 g. (31%) of the picrate of the desired hydrocarbon XXI, m.p. 179–181° (with previous softening). Recrystallization from benzene gave dark red needles, m.p. 180–181°.

Anal. Calcd. for $C_{24}H_{19}N_3O_7$: N, 9.11. Found: N, 8.89.

The hydrocarbon was recovered from the picrate by passage through a column of activated alumina, and was purified by sublimation *in vacuo*, followed by recrystallization from acetonitrile and from methanol. **4,5-Dihydro-7,10-dimethylacephenanthrylene (XXI)** took the form of thin colorless blades, m.p. 116.5–117.5°.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.95; H, 6.80.

Los Angeles, California

[Contribution from the Department of General Chemistry of the University of Rome]

Electronic Transmission through Condensed-ring Systems. II. The Kinetics of Methoxydechlorination of Some 6- and 7-Substituted 1-Aza-4-chloronaphthalenes[1,2]

By Gabriello Illuminati and Gianlorenzo Marino

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The influence of a number of 6- and 7-substituents ranging from dimethylamino to nitro on the bimolecular rate constant for the methoxydechlorination of 4-chloroquinoline has been established. The total range in reactivity at 75° corresponds to a change in rate by a factor of 1.5 × 10^4. The compounds studied belong to a non-constant entropy of activation series even though the reaction does not suffer from proximity effects by the substituents. There is noted a definite trend of increasing energies of activation with increasing entropies of activation with a maximum scatter in the cases of the nitro and dimethylamino groups. Reactivity is well accounted for by the expected electronic effects of the substituents.

The relative intensity of transmission of the main electronic effects of substituents through fused aromatic rings has been scarcely treated in the literature in contrast with the well known similar effects in benzene derivatives.[3] In the naphthalene system, heteronuclear[4] positions are of several different kinds[5] which are all non-equivalent to the familiar homonuclear positions and may arise from positions relative to α- or β-reacting centers. A good deal of what is known about the effects of heteronuclear substituents on reactivity is due to a paper by Price and Michel,[6] who determined the dissociation and hydrolysis rate constants of a number of substituted β-naphthoic acids and their esters, respectively. Other studies, restricted to the consideration of the nitro and sulfonic groups, have been concerned with the dissociation of naphthols[7,8] and naphthylamines,[9] and with the piperidinodebromination of α- and β-bromonaphthalenes.[10] Data on the effects of aza-substitution on the reactivity of naphthalene derivatives are found in studies on the hydrolysis of quinolinecarboxylic esters[11] and on the piperidinodebromination of bromoquinolines.[12]

Since quinoline is an aza-substituted naphthalene, there are several advantages in considering this system to approach the problem of electronic transmission through fused rings. In the first place, quinoline contains positions (2 and 4) of low electron density from which attached halogens can be displaced easily on nucleophilic attack. Secondly, it contains another reactive center, the basic ring nitrogen, so that nucleophilic rate data can be compared with dissociation constants. Thirdly, reactions at ring carbon or nitrogen are highly susceptible to changes in electron density,[13-17] a condition particularly desirable in a study of the substituent effects at heteronuclear positions[4] from which the electric transmission is expectedly weaker than at *o*-, *m*- and *p*-positions. Finally, the synthesis of many substituted 2- and 4-haloquinolines is at present more accessible than that of nitro- activated naphthalenes.

Studies of the dissociation constants of monosubstituted quinolines have been reported by several authors[18] and those of 6-substituted 4-chloroquinolines by us in Part I.[1] We now wish to report the kinetics of methoxydechlorination[19] of a number of 6- and 7-substituted 4-chloroquinolines.

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[1] Part I, E. Baciocchi and G. Illuminati, *Gazz. chim. ital.*, **87**, 981 (1957).

[2] Presented to the XVIth International Congress of Pure and Applied Chemistry, Paris, July, 1957.

[3] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[4] Throughout this work we call heteronuclear positions those at a ring other than the one carrying the reacting center. In the reaction herein dealt with the heteronuclear positions happen to be in the *benzenoid* ring of quinoline.

[5] According to Erdmann's nomenclature for disubstituted naphthalenes, these positions are denoted as *ana*, *epi*, *cata*, *peri*, *amphi* and *pros* (see, for example, V. Grignard, "Traité de Chimie Organique," Vol. XVII (I), Masson et Cie, Paris, 1949, p. 8). In the present paper such a nomenclature has been applied to disubstituted 1-azanaphthalenes.

[6] C. C. Price and R. H. Michel, This Journal, **74**, 3652 (1952).

[7] H. Zollinger and W. Büchler, *Helv. Chim. Acta*, **33**, 2002 (1950).

[8] K. C. Schreiber and M. C. Kennedy, This Journal, **78**, 153 (1956).

[9] A. Bryson, *Trans. Faraday Soc.*, **45**, 257 (1949); **47**, 522 (1951).

[10] P. Van Berk, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **76**, 286 (1957).

[11] R. C. Elderfield and M. Siegel, This Journal, **73**, 5622 (1951).

[12] K. R. Brower, W. P. Samuels, J. W. Way and E. D. Amstutz, *J. Org. Chem.*, **18**, 1648 (1953).

[13] E. Berliner and L. C. Monack, This Journal, **74**, 1574 (1952).

[14] C. W. Bevan, *J. Chem. Soc.*, 655 (1953).

[15] J. F. Bunnett, F. Draper, P. R. Ryason, P. Noble, R. G. Tonkyn and R. E. Zahler, This Journal, **75**, 642 (1953).

[16] H. H. Jaffé and G. O. Doak, *ibid.*, **77**, 4441 (1955).

[17] J. Miller, *Austr. J. Chem.*, **9**, 61 (1956).

[18] See references in ref. 1.

[19] In this paper we adopt systematic names for nucleophilic substitutions as suggested by J. F. Bunnett, *Chem. Eng. News*, **40**, 4019 (1954).

TABLE I

KINETIC DATA FOR THE METHOXYDECHLORINATION OF 6- AND 7-SUBSTITUTED 4-CHLOROQUINOLINES IN METHYL ALCOHOL

	$10^4 k_2$, l. mole^{-1} sec.$^{-1}$, at various temperatures (°C.)							$E_{\text{exp.}}$	$-\Delta S^\ddagger$
Substituent	30.0	51.9	63.3	67.9	75.2	86.5	99.2	kcal./mole	e.u.
6-$N(CH_3)_2$					0.0721	0.2055^a	0.619	23.09	18.13
6-OC_2H_5					0.472	1.27	4.25	23.61	12.94
6-OCH_3					0.529	1.477	4.459	22.89	14.74
7-OCH_3					1.44	3.76	10.81	21.65	16.32
6-CH_3					0.957	2.573	7.91	22.68	14.18
H					2.47^a	6.305^a	17.81^a	21.22	16.49
6-SCH_3					3.048	9.51	24.11	22.18	13.20
6-F					5.25^a	12.39^a	39.51^a	21.69	13.70
7-F			4.47		12.36^a	27.58^a		18.88	19.97
6-Cl				8.52^a	16.80^a	42.49		21.01	13.23
7-Cl				11.64^a	21.44^a	46.68^a		18.12	21.07
6-Br			6.66		21.41	52.28		21.39	11.72
7-Br			8.26		21.77	59.59		20.45	14.18
6-NO_2	26.80	155.0^a	451.2^a		(1058)^b			16.95	16.57

^{a} Run in duplicate. ^{b} Value calculated from the activation energy and the velocity constants at 30.0 and 63.3°.

Course of Reaction and Results

Mainly because of the presence of a basic ring nitrogen, halogen displacements by neutral nucleophiles, such as piperidine and molecular thiols, have been shown to be complicated by autocatalysis in some cases[20] or generally[21] depending on reagent, substrate and conditions. Indeed, reactivity orders have been shown to be altered by autocatalysis in the displacement by thiols.[22] Alkoxydechlorination of heterocyclic compounds is free from such a complexity and was therefore preferred as a first structural investigation of the present type. The nature of the products for this reaction in the series of monosubstituted 4-chloroquinolines has been ascertained in many instances by several workers in preparative work.[23] That the reaction goes to completion was evident from the values of reaction percentages at the infinity readings as determined by us for nearly all the kinetic experiments herein reported. The occurrence of reactions other than a "straight" S_N2 process, whatever the detailed mechanism for the latter may be, has been considered very unlikely.[20c]

Methoxydechlorination of 4-chloroquinolines with sodium methoxide in absolute methanol was found to be second order in accordance with previously investigated similar reactions[20c] and to obey the Arrhenius law in a rigorous manner. Although a systematic redetermination of the order of the reaction with the chloro compounds examined here was not considered necessary, whenever duplicate experiments were carried out with different concentrations of the sodium methoxide reagent (in the range of 50% increases) there were noticed changes in the velocity constant values only within the probable error region. Also, second order plots showed no drifts from linearity in all cases examined. Our results are reported in Table I and include the bimolecular rate constants at various temperatures and the energies and entropies of activation. The probable errors in k and E_{exp} were found to be 1.6% and 0.34 kcal./mole, respectively, except for the nitro derivative for which, because of difficulties arising from the low availability of the substance, probable errors of 10% in k and 1.37 kcal./mole were estimated. In the case of the dimethylamino derivative the reliability of the data is somewhat limited by some uncertainty in the degree of purity of the sample used (see Experimental).

Discussion

The substituents investigated were chosen with sufficiently different electronic character, ranging from dimethylamino to nitro groups, to illustrate how intense electrical effects from heteronuclear positions can be.[4] The total range in reactivity at 75° corresponds to a change in rate by a factor of about 1.5 × 10^4. This is a considerably smaller range than that found in similar reactions[17,24] with *m*- and *p*-substituents, but is still large enough to justify a search for the degree of selectivity among the various positions in the ring other than the one carrying the reactive center. For this reason we included a comparison of two adjacent positions, 6 and 7, which are *cata* and *epi*[5] to the site of the chlorine displacement, respectively. It must be noted that we can draw more important resonance structures for a *cata*-substituted than for an *epi*-substituted derivative and that the situation for such pairs of isomerides resembles that well known for *para, meta* pairs. Accordingly, the analogy has often been used as a base of discussion by previous investigators in the field of the naphthalene system.[6,9,10]

The entropies of activation vary in the relatively wide range of 9.3 e.u. even though the energies of activation vary in the range of only 6.7 kcal./mole. If one plots these two quantities, one finds a definite, linear trend of the activation energies to increase with increasing activation entropies. The best fit to this trend is observed for seven of the

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(20) (a) R. R. Bishop, E. A. S. Cavell and N. B. Chapman, *J. Chem. Soc.*, 437 (1952); (b) N. B. Chapman and C. W. Rees, *ibid.*, 1190 (1954); (c) N. B. Chapman and D. Q. Russell-Hill, *ibid.*, 1563 (1956).

(21) G. Illuminati and L. Santucci, *Gazz. chim. ital.*, **83**, 1106 (1953); G. Grassini and G. Illuminati, *ibid.*, **86**, 437 (1956).

(22) G. Illuminati and G. Marino, *Rend. acc. naz. Lincei, Classe Sci. fis. mat. e nat.*, **21**, 318 (1956).

(23) H. Meyer, *Monatsh.*, **27**, 255 (1906); L. Knorr and E. Fertig, *Ber.*, **30**, 937 (1897); H. John, *J. prakt. Chem.*, **119**, 43 (1928); F. J. Buchmann and C. S. Hamilton, THIS JOURNAL, **64**, 1357 (1942); R. H. Baker, *et al.*, *ibid.*, **68**, 1532 (1946); G. Illuminati and H. Gilman, *ibid.*, **71**, 3349 (1949).

(24) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953. p. 804.

fourteen investigated groups (H, 7-F, 7-Cl, 6-CH_3, 6-CH_3O, 7-CH_3O and 6-C_2H_5O), whereas the highest scatter is observed for the most strongly polar dimethylamino and nitro groups. Since the energies of activation for the latter groups are quite far apart as would be predicted from their electronic character, the entropy of activation is probably mainly responsible for the scatter. It should be noted that the series investigated is free from proximity effects by the substituents.

Another significant, though qualitative, regularity should be pointed out. In all pairs of isomerides examined involving halogens and the methoxy group, both the activation energy and entropy for the 6-isomeride are higher than the corresponding quantities for the 7-isomeride. This is probably influenced by the higher, deactivating conjugation of the *cata* groups as compared with the corresponding *epi* groups. If this interpretation is correct, the reverse order of activation quantities should be observed with the nitro group for which conjugation is activating. Unfortunately, the 7-nitro isomeride was not available for this study and we hope to make a test with it in the future.

The lack of constancy in $\Delta S^{\ddagger}$ is not a surprising result and provides additional material to the problem of the interrelations concerning the "thermodynamic" activation quantities and electronic structure.[25] In the field of nucleophilic aromatic substitutions of chloroheterocyclic compounds it has been observed previously that the entropies of activation for the displacement of chlorine by ethoxide ions vary over wide ranges in contrast to the displacement by piperidine.[20c] Our results clearly indicate that changes in entropy of activation may be at least as important functions of electronic structure as changes in energy of activation. Reactivity data have long been considered as more simply related to structural changes than Arrhenius parameters.[26] On inspection of the rate constants listed in Table I the operation of well known electronic effects of the substituents examined can be in fact recognized readily. Such effects will be discussed in some detail in a subsequent paper[27] by use of free energy relationships in conjunction with the dissociation reaction. The application of the Hammett equation will then enable a concise interpretation of the reactivity data for two interrelated reactions in terms of substituent constants.

Experimental

Materials. (a) **Preparation of 4-Chloroquinolines** (Work done with the collaboration of Drs. F. Tarli and C. Veneziani).—Data concerning the preparation and the properties of some of the compounds examined in this work are collected in Table II. For the five remaining compounds, which were not included in this table, pertinent data were given in Part I.[1] The crude products were purified first by adsorption through an alumina column and then by crystallization from either ethanol or petroleum ether. Further details are recorded in the table.

TABLE II

PREPARATION AND PROPERTIES OF SOME SUBSTITUTED 4-CHLOROQUINOLINES

Substituent	Synthetic method [a]	M.p., °C.[b]	References and other details
7-F	A	72–72.5	[c]
7-Cl	..	84.5–85	[d]
7-Br	A	105–105.5	[e]
7-OCH_3	A	84.5–86	[f]
6-Br	B	112.5–113	[g]
6-OC_2H_5	A	87.5–88.5	[h]
6-SCH_3	A	65–67	[i]
6-NO_2	C	142–142.5	[l]
6-Me_2N	A	*ca.* 40	[m]

[a] Method A is in essential accordance with C. C. Price and R. M. Roberts "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p. 272. Method B consists in the use of sodioethyl oxalacetate as a condensing agent (L. Musajo, *Gazz. chim. ital.*, **67**, 222 (1937); G. F. Lisk and G. W. Stacy, THIS JOURNAL, **68**, 2686 (1946)). Method C involves a modification in the decarboxylation procedure (R. H. Baker, G. R. Lappin, C. J. Albisetti and B. Riegel, *ibid.*, **68**, 1267 (1946)). [b] All melting points are uncorrected. [c] H. R. Snyder, *et al.*, THIS JOURNAL, **69**, 371 (1947). The starting *m*-fluoroaniline was prepared according to G. Schiemann and R. Pillarsky, *Ber.*, **62**, 3041 (1929). [d] C. C. Price and R. M. Roberts, THIS JOURNAL, **68**, 1206 (1946); the sample used here was obtained through the courtesy of Parke, Davis & Co. [e] A. E. Conroy, H. S. Mosher and F. C. Whitmore, THIS JOURNAL, **71**, 3236 (1949). [f] W. M. Lauer, R. T. Arnold, B. Tiffany and J. Tinker, *ibid.*, **68**, 1268 (1946). [g] Not reported previously. *Anal.* Calcd. for C_9H_5NClBr: N, 5.77. Found: N, 5.75. [h] Not reported previously. *Anal.* Calcd. for $C_{11}H_{10}ONCl$: N, 6.74. Found: N, 6.57. [i] Not reported previously. The starting *p*-methylthioaniline was prepared according to the method of W. R. Waldron and E. E. Reid, THIS JOURNAL, **45**, 2399 (1923). *Anal.* Calcd. for $C_{10}H_8NClS$: N, 6.68; S, 15.29. Found: N, 6.59; S, 14.52. [l] See paper by Baker, *et al.*, in note *a*. [m] Reported as an oil by B. Riegel, *et al.*, THIS JOURNAL, **68**, 1264 (1946). The sample used here was obtained in several batches starting from a freshly distilled *p*-dimethylaminoaniline, but the final crude product could not be further purified by recrystallization from any common solvent after the chromatographic treatment. *Anal.* Calcd. for $C_{11}H_{11}N_2Cl$: N, 13.55. Found: N, 12.21. Infinity readings in the kinetic experiments were found to correspond to 98% reaction. Also, from the kinetic experiments, which provided good second order plots and reproducible results, it appeared that the sample used did not contain any fast-reacting impurities. It was concluded that impurities would be responsible for some lowering in the *k* values, if any. No anomaly was observed in the Arrhenius plots.

(b) **Solvent and Methoxide Reagent.**—Dry methanol was prepared by refluxing commercially pure methanol with magnesium and iodine[28] and taking the median fraction on distillation through a Fenske column. For the preparation of the methoxide reagent, freshly cut sodium lumps were transferred rapidly in a convenient volume of dry methanol and the resulting solution was filtered by slight suction through a fine-mesh sintered glass funnel in an all-glass system protected from moisture and carbon dioxide. The solvent and the reagent were stored under dry nitrogen; the former could be delivered from the storage bottle by a syphoning system under nitrogen pressure whereas samples of the latter could be simply withdrawn with a pipet sealed to a ground-glass stopper to be interchanged with an ordinary glass stopper under an escaping nitrogen stream. The methoxide reagent was titrated with a 0.1 *N* hydrochloric acid solution, methyl red being the indicator.

Kinetic Procedure.—The reaction mixture for each kinetic experiment was prepared in a 25-ml. volumetric flask by dissolving a weighed sample of the quinoline with about

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(25) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); R. W. Taft in Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 662.

(26) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936); see also ref. 24, p. 255.

(27) E. Baciocchi, G. Illuminati and G. Marino, THIS JOURNAL, **80**, in press (1958).

(28) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1951, p. 168.

20 ml. of methanol, then adding the calculated volume of the methoxide reagent and finally diluting with the solvent to the mark and shaking. The final concentrations used were in the range of 0.025 to 0.050 M in the quinoline compound and 0.060 to 0.145 M in sodium methoxide. From the kinetic solution 2-ml. samples immediately were pipetted into constricted Pyrex tubes which were soon afterwards sealed and simultaneously immersed in an oil-bath with a thermostat regulated to within ±0.05° below 60° and 0.10° or better above this temperature. The equilibrium temperature values reported in the tables include the stem corrections.[29]

The sealed tubes were removed at convenient time intervals, chilled in ice-water if necessary, thoroughly rinsed with distilled water and finally crushed in a heavy Pyrex glass beaker under 20 ml. of a 0.3 N nitric acid solution. The content of the tube was then analyzed for the chloride ion by the Volhard method. Because of the development of interfering colors and/or the high reactivity of the organic chloride, in some cases (6-nitro, 6-dimethylamino and 6-methylthio derivatives) the tubes were crushed under a mixture of 40 ml. of water and 50 ml. of benzene, and the organic material was extracted in a separatory funnel. The aqueous layer together with the washings was then made acid with 1 ml. of 6 N nitric acid and analyzed in the usual manner.

The zero time of the reaction was made to correspond to the removal of the first tube, which was effected 10 minutes after the immersion in the thermostat. A total of 60 independent kinetic experiments was carried out, 18 of which were duplicate runs. Results from two typical experiments are reported in Table III.

Evaluation of the Kinetic Constants.—The calculation of the rate constants was based upon the equation: $\ln (a - x)/(b - x) = (a - b)kt + C$, in which a and b are the concentrations of the reactants at the zero time of the reaction and x the concentration of the product formed in time t. The slopes of the plots $\log (a - x)/(b - x)$ *vs.* t were calculated by the method of least squares[30] and the k values derived therefrom were corrected for the thermal expansion of methanol[31] at the appropriate temperature. Similarly, the E_{exp} values were obtained from the slopes of the Arrhenius plots $\log k$ *vs.* $1/T$ as calculated by the method of least squares. The entropy of activation was calculated from the equation[32]: $\ln k = 1 + \ln (\mathbf{k}T/\mathrm{h}) - E_{\text{exp}}/RT + \Delta S^{\ddagger}/R$ and the values reported in Table I are averages from those obtained by this equation at all temperatures used for each substance.

The probable errors in the k values given in the general part represent the mean percentage deviation from the mean as based on duplicate runs. The probable errors in the E_{exp} values were estimated by taking into account the probable error in k at the two extreme temperatures under which each compound was investigated and using the equation $E_{\text{exp}} = (\ln k_2 - \ln k_1)RT_1T_2/(T_2 - T_1)$.

TABLE III

TYPICAL KINETIC EXPERIMENTS

Compounds and conditions	Time, min.	NH_4CNS, ml.[a]	Reaction, %[a]	log $(a - x)/(b - x)$
4-Chloro-7-fluoroquinoline	0	3.52	0	0.49786
$a = [CH_3ONa] = 0.14840\ M$	32	3.37	10.41	.53102
	75	3.16	24.99	.58669
$b = 0.04716\ M$	120	3.04	33.32	.62387
$k_2 = 4.47 \times 10^{-4}$	165	2.90	43.03	.67828
temp. 63.3°	215	2.76	52.75	.74356
	265	2.67	59.00	.78453
	315	2.59	64.55	.84864
	375	2.50	70.80	.92177
	∞	(2.08)	(100)	....
4-Chloro-6-ethoxyquinoline	0	3.57	0	0.46660
	37	3.40	11.41	.50166
$a = [CH_3ONa] = 0.14003\ M$	98	3.18	26.04	.55659
	159	3.01	37.58	.61097
$b = 0.04788\ M$	221	2.85	48.99	.67904
$k_2 = 4.250 \times 10^{-4}$	288	2.72	57.04	.72876
temp. 99.2°	343	2.63	63.09	.78344
	410	2.56	67.78	.84336
	482	2.48	73.15	.91199
	∞	(2.08)	(100)	....

[a] The values in parentheses were calculated; in all cases infinity readings were found to coincide, within experimental error, with such calculated values.

ROME, ITALY

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(29) E. L. Skau and H. Wakeham in A. Weissberger's "Physical Methods of Organic Chemistry," Vol. I, first ed., Interscience Publ., Inc., New York, N. Y., 1945, p. 32.

(30) F. Daniels, J. H. Mathews, J. W. Williams and co-workers, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 370.

(31) J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier Press, New York, N. Y., 1950, p. 303.

(32) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

Heats of Hydrogenation. V. Relative Stabilities in Certain Exocyclic–Endocyclic Olefin Pairs[1]

BY RICHARD B. TURNER AND ROBERT H. GARNER

RECEIVED MAY 13, 1957

Stability differences in a number of isomer pairs possessing exocyclic and endocyclic double bonds have been investigated by the hydrogenation method. In all cases that have been examined thus far the endocyclic modification possesses the lower heat of hydrogenation and hence the greater stability. The heats of hydrogenation (kcal./mole) that have been measured in the present study are: methylenecyclopentane (−26.9), 1-methylcyclopentene (−23.0); methylenecyclohexane (−27.8), 1-methylcyclohexene (−25.4); methylenecycloheptane (−26.3), 1-methylcycloheptene (−24.0); ethylidenecyclopentane (−24.9), 1-ethylcyclopentene (−23.6); ethylidenecyclohexane (−26.3), 1-ethylcyclohexene (−25.1). Stability relationships derived from the hydrogenation work have been confirmed in several instances by studies of acid-catalyzed isomerization.

Stability differences that exist between isomers possessing double bonds exocyclic and endocyclic with respect to 5- and 6-membered rings have been discussed by Brown, Brewster and Shechter.[2] The conclusions drawn by these authors from correlations of existing experimental data were expressed in the generalization that *"reactions will*

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(1) The generous financial support of the Eli Lilly Co., Indianapolis, Ind., and of the National Science Foundation is gratefully acknowledged.

(2) H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954).