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.

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
$k_2 = 4.250 \times 10^{-3}$	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.

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 $E_{\text{exp}} = (\ln k_2 - \ln k_1)RT_1T_2/(T_2 - T_1)$.

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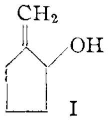
[1] The generous financial support of the Eli Lilly Co., Indianapolis, Ind., and of the National Science Foundation is gratefully acknowledged.

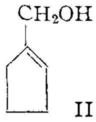
[2] H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, 76, 467 (1954).

proceed in such a manner as to favor the formation or retention of an exo double bond in the 5-ring and to avoid the formation or retention of the exo double bond in the 6-ring systems."[3]

On the basis of this proposal, Wheeler[4] predicted that at equilibrium methylenecyclopentanol (I) should be strongly favored over cyclopentenylcarbinol (II), whereas the reverse relationship should hold for the corresponding 6-membered ring derivatives.



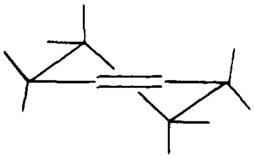
I

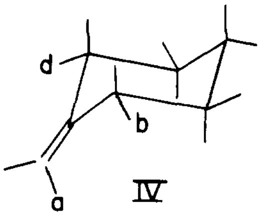


II

The fact that 1-alkylcyclohexenes are thermodynamically more stable than the corresponding alkylidenecyclohexanes is well established. Wallach and his associates[5] have provided a number of examples of the acid-catalyzed isomerization of alkylidenecyclohexanes into 1-alkylcyclohexenes, and a value of −3.1 kcal./mole has been obtained for the heat of isomerization of methylenecyclohexane into 1-methylcyclohexene from the early combustion data of Roth.[6] Further information is available from studies of equilibria between α,β- and β,γ-unsaturated carbonyl compounds possessing exocyclic (cyclohexylidene) and endocyclic (cyclohexenyl) double bonds, which indicate greater stability for the unconjugated, endocyclic forms.[7]

The stability differences between exo and endo isomers of the 6-ring series have been attributed to differences in the conformational properties assigned to these structures by Barton, Cookson, Klyne and Shoppee[8] and by Corey and Sneen.[9] Although quantitative estimation of the relative energies of the cyclohexenyl and cyclohexylidene systems on such a basis is not possible, it is clear that structure III possesses fewer ring interactions than does IV, and that the additional repulsions a → b and c → d in the exocyclic olefin IV may be expected to contribute to the lesser stability of this form.


III



IV

In comparing the relative stabilities of 1-methylcyclohexene and methylenecyclohexane a further effect must be considered. In connection with their investigation of the heats of hydrogenation of substituted ethylenes in the gas phase, Kistiakowsky and his collaborators[10] observed that the heat of hydrogenation of trimethylethylene (−26.9 kcal./mole) is 1.5 kcal./mole lower than that of isobutene (−28.4 kcal./mole). The reduction in the heat of hydrogenation that accompanies increased substitution of the double bond has been variously ascribed to hyperconjugation,[11] to a combination of polar and hyperconjugative effects,[12] and to adjacent bond interactions involving C–C as well as C–H bonds.[13] Irrespective of the details of the interpretation, it would appear that approximately half of the heat of isomerization calculated for the process methylenecyclohexane → 1-methylcyclohexene from the combustion data[6] must be attributed to the substitution effect. A further discussion of this point will be found in a subsequent section of this paper.

Evidence relating to the exo–endo stability relationship in 5-membered rings is not extensive. Wallach and Fleischer[14] have reported that treatment of an impure sample of isopropylidenecyclopentane with ethanolic sulfuric acid affords (in unspecified yield) an olefin fraction from which a crystalline derivative can be obtained by the action of nitrosyl chloride. However, the yield of the latter product was not indicated, and no analyses, melting points, boiling points or other physical data were recorded. The nature of the olefinic material, as well as its origin, is therefore in doubt. Apart from these inconclusive experiments, no studies concerned directly with equilibration of alkylidenecyclopentanes and 1-alkylcyclopentenes appear to have been undertaken, and pertinent thermochemical data for these substances are not available. The observation of Kon and his collaborators[15] that cyclopentylideneacetone and ethyl cyclopentylideneacetate are energetically favored over the corresponding cyclopentenyl derivatives, in contrast to the behavior of the related 6-ring compounds, is not relevant to the present discussion in view of resonance stabilization present in the conjugated, exocyclic isomers.[16]

A survey of the literature reveals scattered observations which suggest that 1-alkylcyclopentenes are more stable than the corresponding alkylidenecyclopentanes. The evidence is not decisive, however, and the available data suffer materially from lack of information on yields and on kinetic as opposed to equilibrium control of the reactions in question, from inadequate characterization of product composition, and from mechanistic ambiguities. Thus, although 1-alkylcyclopentenes of authenticated structure have been obtained by acid-catalyzed dehydration of the corresponding 1-

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(3) The italics are those of Brown, Brewster and Shechter.

(4) O. H. Wheeler, *Chemistry & Industry*, 900 (1954).

(5) (a) O. Wallach, *Ber.*, **39**, 2504 (1906); (b) O. Wallach, E. Evans, J. B. Churchill, M. Rentschler and H. Mallison, *Ann.*, **360**, 26 (1908).

(6) W. A. Roth and K. von Auwers, *ibid.*, **407**, 145 (1915); W. A. Roth and Ellinger, "Landolt-Börnstein," Hauptw., Vol. II, pp. 1587–1611.

(7) R. P. Linstead, *J. Chem. Soc.*, 2579 (1927); G. A. R. Kon and R. P. Linstead, *ibid.*, 1269 (1929).

(8) D. H. R. Barton, R. C. Cookson, W. Klyne and C. W. Shoppee, *Chemistry & Industry*, 21 (1954); see also C. W. Beckett, N. K. Freeman and K. S. Pitzer, THIS JOURNAL, **70**, 4227 (1948).

(9) E. J. Corey and R. A. Sneen, *ibid.*, **77**, 2505 (1955).

(10) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **57**, 876 (1935).

(11) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 149–152.

(12) R. W. Taft and M. M. Kreevoy, THIS JOURNAL, **79**, 4011 (1957).

(13) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 1625 (1954).

(14) O. Wallach and K. Fleischer, *Ann.*, **353**, 304 (1907).

(15) A. H. Dickins, W. E. Hugh and G. A. R. Kon, *J. Chem. Soc.*, 572 (1929); G. A. R. Kon, R. P. Linstead and G. W. G. Maclennan, *ibid.*, 2454 (1932).

(16) *Cf.* J. Weinstock, R. G. Pearson and F. G. Bordwell, THIS JOURNAL, **78**, 3468 (1956).

alkylcyclopentanols,[17] the yields are either unreported or are too low to permit a reliable assessment of the stability problem. The formation of 1-methylcyclopentene as the sole product of the dehydration of cyclobutylmethylcarbinol by anhydrous oxalic acid has also been noted,[18] but the problem of whether or not equilibration of the 1-methylcyclopentene initially formed on rearrangement can occur under these conditions has not been examined. A special case of the dehydration of a substituted 1-alkylcyclopentanol under non-equilibrium conditions ($POCl_3$–pyridine) to give 71% of the exo-olefin is available in the steroid literature.[19] Of greater interest in the present connection are the more recent observations that acid hydrolysis of 1-methylcyclopentyl chloride furnishes 1-methylcyclopentene in 75% yield,[20] and that methylenecyclopentane and vinylcyclopentane are completely isomerized into the corresponding 1-alkylcyclopentenes by passage over an alumina-supported chromium oxide catalyst at 250°.[21]

In order to establish unequivocally the stability relationship of exocyclic and endocyclic olefins in the 5-ring series, and to provide reliable thermochemical data for these and other related substances, we have undertaken an investigation of this problem by the hydrogenation method. Supplementary information has been derived from an examination of the behavior of certain of these derivatives in the presence of acid.

The results obtained in the hydrogenation work are listed in Table I. Data given for samples 1 of methylenecyclopentane, methylenecyclohexane and 1-methylcyclohexene, and for 1-methylcyclopentene, were reported previously.[22] We have since had occasion to re-examine the heats of hydrogenation of the first three substances mentioned with special regard for the question of peroxide contamination. The figures listed for sample 2 in each instance refer to the more recent measurements, which were carried out on specimens showing a negative peroxide test. The largest variation, 0.3 kcal./mole, was observed in the case of 1-methylcyclohexene, for which the values of the first and second determinations were −25.70 ± 0.10 and −25.41 ± 0.11 kcal./mole, respectively. Since a discrepancy of this magnitude lies only slightly outside the limits of experimental error, it is assumed that peroxide contamination of the original samples, if any, was insignificant. The results of the second determinations are employed in the following discussion.

TABLE I

HEATS OF HYDROGENATION IN ACETIC ACID SOLUTION

Compound	Mmoles	PtO_2, mg.	$-\Delta H$, kcal./mole, 25°
Methylenecyclopentane	3.986	99.31	26.92
Sample 1	3.061	99.97	26.78
	4.402	99.96	26.76
Average, $-\Delta H$ = 26.82 ± 0.08[a]			
Sample 2	3.872	99.06	26.88
	3.539	98.61	26.87
Average, $-\Delta H$ = 26.88 ± 0.02			
1-Methylcyclopentene	3.480	99.67	22.99
	3.620	99.69	23.06
	3.181	99.90	22.98
Average, $-\Delta H$ = 23.01 ± 0.04			
Methylenecyclohexane	3.602	99.35	27.75
Sample 1	3.543	99.47	27.89
Average, $-\Delta H$ = 27.82 ± 0.07			
Sample 2	3.096	98.09	27.62
	2.942	99.44	27.87
Average, $-\Delta H$ = 27.75 ± 0.13			
1-Methylcyclohexene	3.961	99.44	25.60
Sample 1	3.648	99.75	25.79
Average, $-\Delta H$ = 25.70 ± 0.10			
Sample 2	3.506	98.24	25.47
	4.054	97.59	25.50
	3.804	98.36	25.26
Average, $-\Delta H$ = 25.41 ± 0.11			
Methylenecycloheptane	2.535	100.20	26.47
	3.230	98.90	26.23
	2.500	98.40	26.11
Average, $-\Delta H$ = 26.27 ± 0.14			
1-Methylcycloheptene	2.913	99.75	23.93
	2.898	99.82	24.11
Average, $-\Delta H$ = −24.02 ± 0.10			
Ethylidenecyclopentane	3.835	99.63	25.00
	3.762	99.88	24.76
Average, $-\Delta H$ = 24.88 ± 0.12			
1-Ethylcyclopentene	4.837	100.51	23.66
	4.602	101.11	23.46
Average, $-\Delta H$ = 23.56 ± 0.11			
Ethylidenecyclohexane	3.209	99.40	26.33
	3.339	99.65	26.31
Average, $-\Delta H$ = 26.32 ± 0.04			
1-Ethylcyclohexene	3.612	100.43	24.96
	3.756	100.58	25.20
Average, $-\Delta H$ = 25.08 ± 0.13			

[a] Deviations include uncertainty in the heat of hydrogenation of the platinum oxide catalyst.

The values derived for the heats of hydrogenation of methylenecyclohexane (−27.8 kcal./mole) and of 1-methylcyclohexene (−25.4 kcal./mole) are consistent with the established greater stability of the endocyclic isomer in this series, and the heat of isomerization calculated for the hydrogenation data (−2.4 kcal./mole) does not differ appreciably from that obtained by the combustion method (−3.1 kcal./mole).[6] The results for methylenecycloheptane (−26.3 kcal./mole) and for 1-methylcycloheptene (−24.0 kcal./mole) closely parallel those for the 6-membered ring derivatives, the heat

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(17) (a) O. Wallach and K. von Martius, *Ann.*, **365**, 272 (1909); (b) H. Meerwein and H. Probst, *ibid.*, **405**, 142 (1914); (c) G. Chavanne and L. de Vogel, *Bull. soc. chim. Belg.*, **37**, 141 (1928); (d) J. R. van der Bij and E. C. Kooyman, *Rec. trav. chim.*, **71**, 837 (1952).

(18) G. T. Tatevosyan, M. O. Melikyan and A. T. Terzyan, *Zhur. Obshcheĭ Khim.*, **17**, 981 (1947).

(19) A. Butenandt, J. Schmidt-Thomé and H. Paul, *Ber.*, **72**, 1112 (1939).

(20) G. A. Lutz, A. E. Bearse, J. E. Leonard and F. C. Croxton, THIS JOURNAL, **70**, 4135 (1948).

(21) R. Y. Levina, N. N. Mezentsova and P. A. Akishin, *Zhur. Obshcheĭ Khim.*, **23**, 562 (1953).

(22) R. B. Turner and R. H. Garner, THIS JOURNAL, **79**, 253 (1957).

of isomerization (*exo* → *endo*) in this case being −2.3 kcal./mole.

Of somewhat greater interest are the values obtained for methylenecyclopentane (−26.9 kcal./mole) and for 1-methylcyclopentene (−23.0 kcal./mole). It is clear from these results that, in terms of the enthalpy criterion, methylenecyclopentane is *less* stable than 1-methylcyclopentene. The data demonstrate further that the heat of isomerization (−3.9 kcal./mole) is in this instance considerably larger than that observed in the analogous 6-ring system.

In view of the fact that the double bonds in the exocyclic compounds thus far discussed are disubstituted, whereas those of the endocyclic isomers are trisubstituted, the exo-endo stability relationships derived above include a factor for the substitution effect. The investigation of *exo-endo* pairs possessing the same degree of substitution was therefore a matter of considerable interest. Ethylidenecyclopentane, 1-ethylcyclopentene and the corresponding 6-ring derivatives were accordingly prepared, and the heats of hydrogenation of these substances were also measured. In both series the substitution effect is clearly discernible. Thus, the heats of hydrogenation of methylenecyclohexane (−27.8 kcal./mole) and of ethylidenecyclohexane (−26.3 kcal./mole) differ by 1.5 kcal./mole, a figure that is identical with that obtained by Kistiakowsky[10] for the substitution factor in a structurally analogous open-chain system. A slightly larger value (2.0 kcal./mole) is obtained for the methylene–ethylidene difference in the 5-ring case.

Comparison of the result for ethylidenecyclopentane (−24.9 kcal./mole) with that for 1-ethylcyclopentene (−23.6 kcal./mole) indicates that, although greater stability is still retained in the endocyclic olefin, the enthalpy difference between exo and endo isomers, which now possess the same degree of double bond substitution, is reduced from 3.9 to 1.3 kcal./mole. The *exo–endo* difference for the analogous members of the 6-ring series is similarly reduced from 2.4 to 1.2 kcal./mole. It will be noted further that the heat of hydrogenation of 1-ethylcyclopentene is 0.6 kcal./mole *higher* than that of 1-methylcyclopentene (−23.0 kcal./mole), whereas the 1-ethylcyclohexene value (−25.1 kcal./mole) is slightly *lower* (0.3 kcal./mole) than the figure for 1-methylcyclohexene (−25.4 kcal./mole), although the olefins involved do not differ in degree of substitution. Since the heats of hydrogenation of simple alkyl-substituted ethylenes are relatively insensitive to changes in the nature of the alkyl group (*e.g.*, methyl to ethyl),[23] it is probable that the enthalpy variations observed in the cyclic olefins in question are of steric rather than of electronic origin. Some justification for this view can be drawn from examination of the conformational properties of these compounds and of the corresponding reduction products. However, inasmuch as the differences in the heats of hydrogenation are small, a detailed discussion of this problem is hardly warranted.

Stability relationships derived in the present investigation for isomers possessing *exo* and *endo* unsaturation are based upon enthalpy data. Since "stability" is more properly defined in terms of free energies, further evidence supporting the conclusions of the hydrogenation work seemed desirable. A qualitative study of the behavior of methylenecyclopentane, methylenecyclohexane, ethylidenecyclopentane and of ethylidenecyclohexane in the presence of acid was therefore undertaken. These olefins undergo extensive polymerization when undiluted, and the isomerization experiments were therefore carried out in acetic acid solution with *p*-toluenesulfonic acid as the catalyst. The resulting products were analyzed by vapor phase chromatography or by infrared absorption measurements. Both methylenecyclopentane (ΔH_{isom} −3.9 kcal./mole) and methylenecyclohexane (ΔH_{isom} −2.4 kcal./mole) appeared to be quantitatively isomerized into the corresponding 1-methylcycloalkenes. The infrared spectrum of the 1-methylcyclopentene obtained in this way indicated trace contamination by acetate ester, but no residual methylenecyclopentane could be detected. Ethylidenecyclopentane (ΔH_{isom} −1.3 kcal./mole) and ethylidenecyclohexane (ΔH_{isom} −1.2 kcal./mole) both furnish mixtures of exocyclic and endocyclic products in which the endocyclic compounds very largely predominate. The enthalpy criterion therefore provides a valid basis for the estimation of stability relationships in cyclic systems of this type where entropy differences are expected to be small.

In a preliminary report[22] of a portion of the work described in the present paper, mention was made of the fact that the *exo–endo* stability difference obtained for the alkylidenecyclopentane–1-alkylcyclopentene system is incompatible with the generalization (ref. 2.) of Brown, Brewster and Shechter.[2] We have since been informed by Prof. Brown that it was not his intention to include among the reactions covered by the rule any that might involve loss of a double bond exocyclic to a 5-ring by isomerization to an *endo* position. This being the case the wording of the generalization was unfortunate. In view of the considerable confusion that has arisen with regard to interpretation of the 1954 statement, Brown has recently offered the following revision.[24] "*Double bonds which are exo to a 5-ring are less reactive and more stable* (*relative to the saturated derivatives*) *than related double bonds which are exo to a 6-ring. Reactions which involve the formation or retention of an exo double bond in a 5-ring derivative will be favored over corresponding reactions which involve formation or retention of an exo double bond in a 6-ring derivative. Reactions*

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[23] J. B. Conant and G. B. Kistiakowsky, *Chem. Revs.*, **20**, 181 (1937); see also references 12 and 13.

[24] H. C. Brown, *J. Org. Chem.*, **22**, 439 (1957). In seeking to clarify the postulate as it was originally presented, attention is directed to the fact that the paragraph immediately following the original statement of the generalization (reference 2) reads:

"In the simple hydrocarbons, endocyclic are far more stable than exocyclic double bonds. Thus Wallach demonstrated in a number of investigations that alkylidene cyclanes (*e.g.*, methylenecyclohexane) are readily isomerized under the influence of acids to 1-alkylcyclenes (*e.g.*, 1-methylcyclohexene)." The inference that this assertion specifically exempted the alkylidenecyclopentane–1-alkylcyclopentene case from consideration under the rule seems hardly justified, since the work of Wallach to which reference was made provides evidence for 6-membered ring derivatives only, and not for alkylidenecycloparaffins in general. For further discussion see R. Fleck, *ibid.*, **22**, 439 (1957).

which involve the loss of an exo double bond will be favored in the 6-ring as compared to the 5-ring derivative." Although this statement appears to provide a valuable means for correlating a large body of information concerned with 5- and 6-membered ring systems containing carbonyl groups, its applicability to compounds possessing olefinic unsaturation is questionable. In particular, the suggestion[2,24] that the *exo–endo* difference for 5-ring olefins should be less than that for the corresponding 6-ring compounds is not in accord with the present evidence.

In order to avoid any misunderstanding of our own position, we wish to state that in our opinion the angular strain involved in placing a double bond *exocyclic or endocyclic* with respect to a 5-membered ring will make such a double bond less stable than a similarly situated olefinic linkage in a 6-membered ring system. The stability of molecules possessing unsaturation of this type may, of course, involve other factors as well. The following argument will serve to illustrate the point. The heats of hydrogenation (acetic acid solution, 25°) of the isomeric compounds ethylidenecyclopentane and methylenecyclohexane are -24.9 and -27.8 kcal./mole, respectively. The heats of formation (liquid state, 25°) of the corresponding reduction products are, for ethylcyclopentane, -39.1 kcal./mole, and for methylcyclohexane, -45.5 kcal./mole.[25] If the heats of solution of ethylcyclopentane and methylcyclohexane are assumed to be substantially identical, the heat of isomerization of ethylidenecyclopentane into methylenecyclohexane can be calculated and is found to be -3.5 kcal./mole. It follows that methylenecyclohexane is energetically favored over ethylidenecyclopentane, despite the stabilizing effect of the methyl substituent in the latter compound. Similar calculations for 1-ethylcyclopentene and for 1-methylcyclohexene give a heat of isomerization of -4.6 kcal./mole for the endocyclic pair. The point that requires special emphasis is the fact that replacement of a trigonal by a tetrahedral carbon atom in this series results in the introduction of non-bonded interactions that are eclipsed in the 5- and staggered in the 6-ring compounds. Cyclopentane derivatives are therefore less stable than the isomeric cyclohexanes, the difference in general being greater than that between the unsaturated substances. Thus, the heat of isomerization of ethylcyclopentane into methylcyclohexane is -6.4 kcal./mole as compared with the value of -3.5 kcal./mole for the exocyclic, and -4.6 kcal./mole for the endocyclic olefins.

In a previous section of this paper mention was made of the fact that at equilibrium cyclopentylideneacetone and ethyl cyclopentylideneacetate are favored over the corresponding cyclopentenyl derivatives. The stability order in the analogous 6-membered ring compounds is reversed, and it has been shown further that cyclopentylideneacetic acid, in contrast to the ethyl ester, furnishes cyclopentenylacetic acid as the major product of base-catalyzed equilibration.[26] These observations may now be clarified in the light of the present data. The heat of isomerization of ethylidenecyclopentane into 1-ethylcyclopentene is 1.3 kcal./mole. Assuming a similar value for the heat of isomerization of a hypothetical, resonance-free cyclopentylideneacetone into cyclopentenylacetone[27] and a stabilization energy of the order of 2 kcal./mole for the resonance-stabilized molecule,[28] a difference of roughly 1 kcal./mole is obtained in favor of the conjugated, exocyclic form. Since resonance interaction between the carbonyl group and double bond should decrease somewhat in the series ketone, ester, carboxylate anion,[29] the amount of exocyclic isomer present at equilibrium is expected to diminish in the same order. The experimental results are in accord with this prediction.[30] In the 6-ring compounds the planar arrangement required for maximum resonance in the unsaturated carbonyl system is subject to repulsive strains involving the interaction of an equatorial ring hydrogen atom and the carbonyl substituent. Resonance stabilization of the exo (conjugated) modification is thereby reduced and hence also the amount of this substance present at equilibrium.

Mention should finally be made of a problem that arises in connection with comparison of the heats of hydrogenation of cyclopentanone (-12.5 kcal./mole) and cyclohexanone (-15.4 kcal./mole)[31] with those of methylenecyclopentane (-26.9 kcal./mole) and methylenecyclohexane (-27.8 kcal./mole). On the basis of steric considerations Brown, Brewster and Shechter[2] were led to the conclusion that the difference between the heats of hydrogenation of the methylene compounds should be larger than the corresponding difference (2.9 kcal./mole) for the ketones. The fact that the experimental results are at variance with this prediction constitutes a discrepancy for which we see no ready explanation. Although it is possible that the carbonyl and methylene groups may differ in their abilities to accommodate the angular distortion required in the 5-ring compounds, no data are available which would permit estimation of the magnitude, or even the direction, of such an effect. An alternative suggestion is based on the assumption that cyclopentanone derives special stability from hyperconjugation, since its geometry is presumably more favorable for such a process than is that of cyclohexanone,[32] while the electron demand of the carbonyl function is greater than that of the methylene group. The validity of this argument is difficult to evaluate in the present unsettled state

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[25] "Selected Values of Properties of Hydrocarbons," Circular C461 of the National Bureau of Standards, U. S. Printing Office, Washington, D. C., 1952.

[26] A. A. Goldberg and R. P. Linstead, *J. Chem. Soc.*, 2343 (1928).

[27] From the point of view of hyperconjugative and inductive effects (reference 12) ethylidenecyclopentane does not constitute an entirely satisfactory model for the cyclopentylideneacetone system. Its choice in this instance was dictated by steric considerations.

[28] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, THIS JOURNAL, **60**, 440 (1938), report a value of 2.4 kcal./mole for the resonance energy of crotonaldehyde.

[29] *Cf.* M. M. Kreevoy and R. W. Taft, *ibid.*, **79**, 4016 (1957).

[30] See Table I of reference 2.

[31] Gas phase data of J. B. Conn, G. B. Kistiakowsky and E. A. Smith, THIS JOURNAL, **61**, 1868 (1939).

[32] Evidence relating to the stereochemical requirements of hyperconjugation has been provided by V. J. Shiner, *ibid.*, **78**, 2653 (1956); see also A. Streitwieser, R. H. Jagow and S. Suzuki, *ibid.*, **77**, 6713 (1955).

of the hyperconjugation problem, and it may be noted that Kreevoy and Taft have recently proposed that hyperconjugation is relatively insensitive to electron demand.[12]

Experimental

The procedure employed for the measurement of heats of hydrogenation in acetic acid solution was that described in Paper I of this series.[33]

Preparation of Methylenecyclopentane, Sample 1.—Cyclopentylmethylamine (6 g.), prepared from cyclopentylacetic acid by the method of von Braun,[34] was heated under reflux for 8 hours with 100 ml. of 38% aqueous formaldehyde, 100 ml. of 98% formic acid and 200 ml. of water. The mixture was then cooled, made basic with sodium hydroxide solution, saturated with sodium chloride, and extracted with ether. The resulting ethereal solution was dried over anhydrous magnesium sulfate, and the **N,N-dimethylcyclopentylmethylamine** was isolated by distillation through a 30-cm., 75-plate center-rod column, b.p. 150–151°, $n^{29.5}\mathrm{D}$ 1.4355. The material proved to be rather hygroscopic, and analysis was therefore carried out on the picrate, m.p. 143–143.4° (from ethanol).[35]

Anal. Calcd. for $C_{14}H_{20}N_4O_7$: C, 47.16; H, 5.66; N, 15.73. Found: C, 47.34; H, 5.91; N, 15.70.

The product was further characterized as the crystalline methiodide, m.p. 206.2–206.4° (from ethanol).

Anal. Calcd. for $C_9H_{20}IN$: C, 40.12; H, 7.49; N, 5.20. Found: C, 40.19; H, 7.53; N, 5.33.

Hofmann degradation of N,N-dimethylcyclopentylmethylamine proved unsatisfactory as a preparative route to methylenecyclopentane, since pyrolysis furnished a mixture containing about 25% of olefin and 75% of regenerated amine as compared with an olefin:tertiary amine ratio of approximately 55:45 in the analogous 6-ring case. An acceptable procedure was found in the amine oxide degradation.[36] A solution of 7 g. of N,N-dimethylcyclopentylmethylamine in 30 ml. of methanol was accordingly treated with 30 g. of 30% hydrogen peroxide. After standing at room temperature for 40 hours, the excess hydrogen peroxide was destroyed by stirring with 0.5 g. of platinum black. The catalyst was removed by filtration, and the solution was concentrated under reduced pressure to a viscous oil. Treatment of a small sample of this material with an ethanol solution of picric acid furnished the **picrate of N,N-dimethylcyclopentylmethylamine oxide**, which was recrystallized from ethanol, m.p. 126–126.5°.

Anal. Calcd. for $C_{14}H_{20}N_4O_8$: C, 45.16; H, 5.41; N, 15.05. Found: C, 45.21; H, 5.48; N, 14.86.

Pyrolysis of the remaining amine oxide (180°, 3 mm.) gave volatile material which was collected as two layers in a Dry Ice trap. After thorough washing with water, the olefin layer was distilled, yielding 2.5 g. of methylenecyclopentane, b.p. 76.0°, $n^{25}\mathrm{D}$ 1.4332 (literature[17d] values b.p. 75.7°, $n^{20}\mathrm{D}$ 1.4355).

Comparison of the infrared spectrum of this material with that of 1-methylcyclopentene (see below) revealed no detectable contamination by the latter substance, the distinctive absorption bands of 1-methylcyclopentene at 1382, 1335, 1298, 1000 and at 787 cm.$^{-1}$ being completely missing from the spectrum of methylenecyclopentane. It was determined by the examination of known mixtures that the method is capable of detecting 2% of 1-methylcyclopentene in methylenecyclopentane.

Sample 2.—Material for a second determination of the heat of hydrogenation of methylenecyclopentane was prepared by the procedure described above. Twenty-nine grams of tertiary amine afforded 13 g. of olefin which was distilled through a 75-plate center-rod column. The material boiled flat at 76.2° (761 mm.) and was arbitrarily divided into three fractions: fraction 1, $n^{25}\mathrm{D}$ 1.4333; fraction 2, $n^{25}\mathrm{D}$ 1.4332; fraction 3, $n^{25}\mathrm{D}$ 1.4333. The infrared spectra of the three fractions were identical. The center cut (fraction 2) was employed for the hydrogenation runs. A sample was tested for peroxide by the sodium iodide–starch technique.[37] No iodine was liberated under conditions which would have detected 0.05 mole % of peroxide. Infrared analysis of material that had been allowed to stand in acetic acid solution at room temperature for 3 days indicated that no isomerization into 1-methylcyclopentene occurs under these conditions.

1-Methylcyclopentene.—The 1-methylcyclopentene employed in this investigation was obtained from the American Petroleum Institute, Sample No. 1046-5S, impurity 0.14 ± 0.08 mole %.

Preparation of Methylenecyclohexane. Sample 1.—Iodomethylcyclohexane (85 g., b.p. 175–178°)[38] was added to a solution of 40 g. of trimethylamine in 150 ml. of acetone. The reaction mixture was allowed to stand at room temperature for 6 days, at the end of which time 90 g. of **N,N-dimethylcyclohexylmethylamine methiodide**, m.p. 225–226° (literature[39] value 225°), had separated. This product was dissolved in water, and freshly prepared silver oxide was added until no further silver iodide was formed. The solution was then filtered, and the water was removed under reduced pressure with gentle warming. The residue was finally pyrolyzed at atmospheric pressure (bath temperature, 180°) and the volatile product was collected and washed with dilute acetic acid to remove trimethylamine and N,N-dimethylcyclohexylmethylamine. After thorough washing with water, the methylenecyclohexane was dried and distilled, b.p. 102.5°, $n^{25}\mathrm{D}$ 1.4461 (literature[17d] values b.p. 103.3°, $n^{20}\mathrm{D}$ 1.4497).

Sample 2.—A second sample was prepared by the procedure described above except that pyrolysis was carried out under reduced pressure with a nitrogen purge. Distillation through a 75-plate center-rod column gave material boiling flat at 102.8° (756 mm.) which was collected in three fractions: fraction 1, $n^{25}\mathrm{D}$ 1.4469; fraction 2, $n^{25}\mathrm{D}$ 1.4470; fraction 3, $n^{25}\mathrm{D}$ 1.4463. The infrared spectra of the three fractions were identical. Fraction 2, which was employed for the hydrogenation studies, was tested for the presence of peroxide with negative results. The material further showed a single symmetrical peak on passage through a Perkin–Elmer vapor fractometer. Examination of known mixtures established that 0.2% contamination by 1-methylcyclohexene was easily detectable by this procedure. The fact that methylenecyclohexane is stable in acetic acid solution was established by vapor chromatography of a sample that had remained in contact with acetic acid for 3 days at room temperature. No trace of 1-methylcyclohexene could be detected after this treatment.

Preparation of 1-Methylcyclohexene. Sample 1.—1-Methylcyclohexene was prepared as described by Mosher,[40] b.p. 110.2°, $n^{25}\mathrm{D}$ 1.4478 (literature values[41] b.p. 110°, $n^{20}\mathrm{D}$ 1.45067).

Sample 2.—American Petroleum Institute Sample No. 1040-5S, impurity 0.18 ± 0.08 mole %, was employed in the second determination. The peroxide test on this material was negative.

Preparation of Methylenecycloheptane.[42]—Cycloheptane carboxamide[43] (29.8 g.) was added in portions over a period of 1.5 hours to a suspension of 13 g. of lithium aluminum hydride in 350 ml. of ether. The reaction mixture was heated under reflux for 9 hours, cooled, and treated with 110 ml. of water. The ether layer was decanted, and the residual salts were washed twice with ether. The ethereal solution was then dried over anhydrous magnesium sulfate and concentrated to small volume. Some unreduced amide separated during the latter operation and was removed by filtration. Distillation of the residual material furnished cycloheptylmethylamine, 13.6 g., b.p. 73–75°.[39]

A mixture of 13.6 g. of cycloheptylmethylamine, 90 g. of methyl iodide, 45 g. of potassium carbonate and 200 ml. of

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[33] R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

[34] J. von Braun, E. Anton and C. Kemeny, *Ber.*, **66**, 1373 (1933).

[35] M. Mousseron, R. Jacquier and R. Zagdoun, *Bull. soc. chim.*, **19**, 197 (1952), report a melting point of 168–169° for a substance of this presumed structure. No analytical data were given.

[36] *Cf.* A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, **71**, 3929 (1949).

[37] W. Dasler and C. D. Bauer, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 52 (1946).

[38] J. Gutt, *Ber.*, **40**, 2067 (1907).

[39] O. Wallach, A. Fels and W. Lange, *Ann.*, **353**, 284 (1907).

[40] W. A. Mosher, THIS JOURNAL, **62**, 552 (1940).

[41] A. I. Vogel, *J. Chem. Soc.*, 1323 (1938).

[42] The methylenecycloheptane employed in the calorimetric experiments was prepared by D. W. Wiley, Department of Chemistry, Yale University.

[43] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

methanol was allowed to stand at room temperature for 48 hours with frequent shaking. The clear solution was then decanted, and the solid residue was extracted with chloroform in a Soxhlet extractor for 4 hours. Evaporation of the methanol solution gave solid material which was similarly extracted with chloroform. The chloroform extracts were finally combined and concentrated yielding 32.5 g. of **N,N-dimethylcycloheptylmethylamine methiodide**, which was purified by recrystallization from ethyl acetate containing 3% of ethanol. The product separated as large colorless prisms, m.p. 235.7° dec. (literature[39] value 223°).

A solution of 30.2 g. of the quaternary iodide in 150 ml. of water was treated with a slight excess of freshly prepared silver oxide, and the mixture was stirred rapidly for 30 min. and filtered. The residue was washed with water, and the filtrate and washings were then concentrated to small volume under reduced pressure and finally heated to 160–180°. The distillate was collected and washed with 5 portions of water to remove trimethylamine, and, after drying, was refluxed for 3 hours with sodium. Distillation afforded 5.6 g. of methylenecycloheptane, b.p. 130–135°, which was purified by redistillation through a 120-plate concentric tube column, b.p. 135°, n^{25}D 1.4600.

Preparation of 1-Methylcycloheptene.—1-Methylcycloheptanol, prepared from cycloheptanone and methylmagnesium iodide, was dehydrated by distillation in the presence of a small amount of iodine. The olefin in the distillate was separated and, after washing with water and drying over anhydrous sodium sulfate, was distilled through a 75-plate center-rod column. 1-Methylcycloheptene, b.p. 136°, n^{25}D 1.4563 (literature[44] values b.p. 137.5–138.5°, $n^{19.5}$D 1.4581) was obtained by this procedure.

Preparation of Ethylidenecyclopentane.—Ethylidenecyclopentane, b.p. 110–111°, was prepared by the procedure of Wallach and von Martius.[17a] Vapor phase chromatography of the product indicated contamination by 1-ethylcyclopentene, and the specimen that was employed for the hydrogenation work was purified chromatographically.

Preparation of 1-Ethylcyclopentene.—1-Ethylcyclopentanol (31 g.), prepared by the action of ethylmagnesium bromide on cyclopentanone, and 0.6 g. of iodine were heated in a distillation flask at atmospheric pressure. The olefin fraction that distilled was washed with water, dried over anhydrous magnesium sulfate and fractionated. The crude product (12 g.) was redistilled through a 75-plate center-rod column and furnished 9 g. of 1-ethylcyclopentene, b.p. 106.2–106.9° (literature value[17d] 107.3°). The product gave a single peak on vapor phase chromatography.

Preparation of Ethylidenecyclohexane.—Ethylidenecyclohexane was prepared as described by Wallach and his associates.[5b] Distillation of the product through a Podbielniak column furnished material boiling at 134.5°, n^{27}D 1.4656 (literature[17d] values b.p. 136.8°, n^{20}D 1.4623). The infrared spectrum of the product revealed no detectable amounts of 1-ethylcyclohexene.

Preparation of 1-Ethylcyclohexene.—1-Ethylcyclohexene was obtained by the iodine-catalyzed dehydration of 1-ethylcyclohexanol according to the method of Mosher.[40] Fractionation of the crude product in a 75-plate center-rod column gave material boiling at 136.2° (literature value[45] 135.7–136.6°).

Isomerization Experiments.—Samples (0.5 ml.) of methylenecyclopentane, methylenecyclohexane, ethylidenecyclopentane and ethylidenecyclohexane were dissolved in 1.0-ml. portions of glacial acetic acid containing catalytic amounts of *p*-toluenesulfonic acid. The mixtures were sealed under vacuum in bent tubes arranged in such a manner that total reflux could be obtained during the reaction period. The solutions were then heated to 100° for 6 hours, at the end of which time the tubes were tilted, and the contents were distilled into the second limb which was cooled in liquid nitrogen. In the cases of methylenecyclohexane and ethylidenecyclopentane the distillate was analyzed directly by vapor phase chromatography. Since methylenecyclopentane and and 1-methylcyclopentene, as well as ethylidenecyclohexane and 1-ethylcyclohexene, were not separable under the chromatographic conditions employed, the products obtained in these experiments were separated from the acetic acid by water dilution, and, after thorough washing with water and drying, were analyzed in the infrared.

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(44) O. Wallach and H. Kohler, *Ann.*, **345**, 139 (1906).

(45) F. K. Signaigo and P. L. Cramer, THIS JOURNAL, **55**, 3326 (1933).

HOUSTON, TEXAS

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

Heats of Hydrogenation. VI. Heats of Hydrogenation of Some Substituted Ethylenes[1]

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The heats of hydrogenation of several substituted ethylenes have been measured in acetic acid solution at 25°. The compounds included in this investigation and the ΔH values (kcal./mole) obtained are as follows: 2,4-dimethyl-1-pentene (−26.7), 2,4-dimethyl-2-pentene (−25.2); 2,4,4-trimethyl-1-pentene (−25.5), 2,4,4-trimethyl-2-pentene (−26.8); 4-methyl-*cis*-2-pentene (−27.3), 4-methyl-*trans*-2-pentene (−26.4); 4,4-dimethyl-*cis*-2-pentene (−30.8), 4,4-dimethyl-*trans*-2-pentene (−26.5); 2,2,5,5-tetramethyl-*cis*-3-hexene (−36.2), 2,2,5,5-tetramethyl-*trans*-3-hexene (−26.9).

The nature of the directive forces responsible for elimination in the senses of the Hofmann and Saytzeff rules has long been a matter of concern to organic chemists. In recent years considerable attention has been devoted to Hofmann-type eliminations that occur under certain circumstances in alkyl halides and in related compounds that customarily undergo elimination with Saytzeff orientation.[2] In particular, the observation that solvolysis of 2-halo-2,4,4-trimethylpentanes (I) furnishes olefin mixtures in which 2,4,4-trimethyl-1-pentene (II) largely predominates over the isomeric 2,4,4-trimethyl-2-pentene (III) has been extensively discussed.[3,4] This result is contradictory to normal expectations based upon the Saytzeff rule, and to the fact that under similar conditions 2-bromo-2,4-dimethylpentane yields larger amounts of 2,4-dimethyl-2-pentene (IV) than of 2,4-dimethyl-1-pentene (V).[5]

First order eliminations (E1) in I have been carried out under a wide variety of conditions, and a decision as to whether the ratio of olefinic products

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(2) For leading references see H. C. Brown and I. Moritani, THIS JOURNAL, **78**, 2203 (1956).

(3) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953); H. C. Brown and I. Moritani, *ibid.*, **77**, 3607 (1955).

(4) E. D. Hughes, C. K. Ingold and V. J. Shiner, *J. Chem. Soc.*, 3827 (1953).

(5) H. C. Brown and M. Nakagawa, THIS JOURNAL, **77**, 3610 (1955).