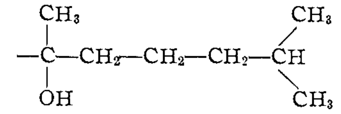
$H_{32}O_5$, m.p. 59.5–60.5°. The tertiary hydroxyl was eliminated by thionyl chloride–pyridine, to yield a mixture of unsaturated compounds, separated by chromatography on alumina. The major product, anhydrotetrahydroalcohol-I ab acetate A ("anhydro-A"), $C_{18}H_{30}O_4$, contained a trisubstituted double bond (813 cm.$^{-1}$) which when hydroxylated with osmium tetroxide (LAH workup of osmate ester) yielded a viscous triol, $C_{16}H_{30}O_5$. This afforded isocapraldehyde on cleavage with sodium periodate. The isomeric dehydration product, "anhydro-B," showed terminal methylene absorption (1640, 895 cm.$^{-1}$) and yielded formaldehyde (methone derivative) upon ozonization. This evidence indicates that the side chain in tetrahydroalcohol-I ab is II.



II

The possibility of rearrangement during dehydration of tetrahydroalcohol-I ab acetate was ruled out by treating anhydro-A and anhydro-B with monoperphthalic acid and reducing each epoxide with LAH; both isomeric epoxides yielded crystalline tetrahydroalcohol-I ab as the main product. The compound obtained from the epoxidation of anhydro-B (terminally unsaturated) was identical (based on rotation and infrared) with the acetate of dihydroalcohol-Ia (side chain double bond reduced), demonstrating the correctness of I for the side chain of alcohol-I.

The n.m.r. spectra of alcohol-I and some derivatives support these conclusions. Alcohol-I shows a doublet centered at 7.65 τ[9] assigned to the epoxide protons, whereas tetrahydroalcohol-I ab lacks this doublet and exhibits a new peak at 8.65 τ due to a methyl group attached to a carbon atom also bearing an oxygen atom.

Anhydro-A shows a peak at 8.30 τ characteristic of an allylic methyl group. This peak is not present in tetrahydroalcohol-I ab.

(9) G. Van Dyke Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(10) To whom inquiries should be addressed.

(11) Abbott Laboratories Fellow, 1957–1958.

(12) Abbott Laboratories Fellow, 1958–1959.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, N. Y.

R. M. CARMAN
D. D. CHAPMAN
N. J. MCCORKINDALE
D. S. TARBELL[10]
F. H. L. VARINO[11]
R. L. WEST[12]
D. J. WILSON

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THE PROTON AFFINITY OF BENZENE

Sir:

The proton affinity of benzene long has been a matter of interest due to the importance of the $C_6H_7^+$ ion and its homologs in electrophilic aromatic substitution reactions. The $C_6H_7^+$ ion is prominent in the mass spectrum of both 1,3-cyclohexadiene and 5-methyl-1,3-cyclohexadiene; consequently the appearance potentials of $C_6H_7^+$ ion from these compounds have been determined and the proton affinity of benzene calculated from these results.

Measurements with 1,3-cyclohexadiene were made with a 180° direction focusing mass spectrometer (Consolidated Electrodynamics Corporation, Model 21-103C). The mass 84 krypton isotope was employed as a standard, equalizing the partial pressures of the gases so that the intensities of the peaks of interest (79 and 84) agreed within 10% at 70 v. electron energy. Ionizing voltage was reduced in steps and the portion of the spectrum of interest scanned after each step. Near onset the size of the steps was reduced to 0.05 v. Several years ago a single determination of $Ap(C_6H_7^+)$ from a sample of 5-methyl-1,3-cyclohexadiene, of unknown purity, was made employing a 90° direction focusing instrument with a sector magnet (Westinghouse Type LV), the same calibrating gas and identical methods of measurement. The 1,3-cyclohexadiene was obtained from Farchan Research Laboratory and had a purity of about 96%; this was entirely satisfactory, the maximum possible contribution from any conceivable impurity being only 0.2%.

In three replicate determinations $Ap(C_6H_7^+)$ from 1,3-cyclohexadiene was found to be 11.32 ± 0.05 e.v. Several measurements using such diverse calibrating gases as propane and ethylbenzene confirmed these results within 0.2–0.3 e.v. Previously we had found $Ap(C_6H_7^+)$ from 5-methyl 1,3-cyclohexadiene to be 10.6 e.v. The confirmation of our recent measurements by the older one is striking; assuming the neutral fragments to be H and CH_3, respectively, we obtain values for $\Delta H_f(C_6H_7^+)$ of 235 and 233 kcal./mole. The heats of formation of 1,3-cyclohexadiene and 5-methyl-1,3-cyclohexadiene were obtained by assumption of the equality of heats of hydrogenation of the cyclodiolefins and combination of the heat of hydrogenation of 1,3-cyclohexadiene[1] with heats of formation of cyclohexane and methylcyclohexane.[2]

Taking 235 kcal./mole as the most reliable value of $\Delta H_f(C_6H_7^+)$, 20 kcal./mole for $\Delta H_f(C_6H_6^+)$,[2] and 365 kcal./mole for $\Delta H_f(H^+g)$,[3] we obtain a value for the proton affinity of benzene of 150 kcal./mole.

Barker, Williams, and Hamill[4] have reported the formation of $C_6H_7^+$ by the ion molecule reaction $C_4H_6^+ + C_4H_6 \rightarrow C_6H_7^+ + C_2H_5$. Such reactions are not endothermic. Assuming zero heat of reaction and assuming $C_6H_7^+$ to be cyclic, we calculate the lower limit of the proton affinity of benzene to be 145 kcal./mole. In this same connection their observation of the formation of the ion $C_7H_9^+$, *viz.*, $C_4H_6^+ + C_4H_4 \rightarrow C_7H_9^+ + CH_3$, permits calculation of a lower limit for the proton affinity of toluene of 143 kcal./mole. Equivalently this

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(2) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Press, Pittsburgh, Pa., 1953.

(3) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

(4) R. Barker, R. R. Williams, Jr., and W. H. Hamill, paper presented at meeting of A.S.T.M. Committee E-14 on Mass Spectrometry, New Orleans, Louisiana, June 2-6, 1958.

observation leads to a lower limit to the methyl ion affinity of benzene of 48 kcal./mole.

RESEARCH AND DEVELOPMENT DIVISION
HUMBLE OIL & REFINING COMPANY
BAYTOWN, TEXAS
J. L. FRANKLIN
F. W. LAMPE
H. E. LUMPKIN

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RELATIVE STABILITIES OF *cis*- AND *trans*-CYCLONONENE, CYCLODECENE, CYCLOUNDECENE AND CYCLODODECENE

Sir:

Several qualitative investigations[1] have indicated the greater stabilities of the *cis* isomers of cyclononene and cyclodecene compared to the *trans* isomers. Recently, it has been reported that the sulfuric acid catalyzed equilibration of the cyclododecenes at room temperature gives a *cis*/*trans* ratio of 40/60.[2]

We have determined the position of *cis–trans* equilibrium for the nine-, ten-, eleven- and twelve-membered cycloalkenes in acetic acid solution employing *p*-toluenesulfonic acid as catalyst. The *cis*/*trans* ratios at equilibrium were determined by gas–liquid chromatography. In each case equilibrium was approached from both the *cis* and *trans* isomers at three temperatures. Plots of the logarithm of the equilibrium constants *versus* the reciprocal of the absolute temperatures were linear. The equilibrium constants and derived thermodynamic quantities are summarized in Table I.

TABLE I

EQUILIBRATION OF CYCLOALKENES IN ACETIC ACID

Ring size	Equilibrium constant (*cis*)/(*trans*) 79.9°	100.4°	130.0°
9	298	232	178
10	16.2	12.2	8.60
11	0.402	0.406	0.411
12	0.534	0.517	0.497

Free energies, enthalpies and entropies of isomerization at 100.4° (373.6°K.)

Ring size	ΔF^0 (kcal./mole)	ΔH^0 (kcal./mole)	ΔS^0 (cal./mole °K.)
9	−4.04	−2.9(−2.9)[a]	3.0
10	−1.86	−3.6(−3.3)[a]	−4.7
11	0.67	0.12	−1.5
12	0.49	−0.41	−2.4

[a] From heats of hydrogenation (ref. 3).

The present results confirm the surprising finding of Turner and Meador[3] that in acetic acid the enthalpy decrease in the isomerization (*trans* → *cis*) is greater for the cyclodecenes than for the cyclononenes. However, the corresponding free energy decrease is much greater in the smaller ring ($\Delta F^0 C_9 - \Delta F^0 C_{10} = -2.2$ kcal./mole at 100°) as a result of the large difference in the entropy change ($\Delta S^0 C_9 - \Delta S^0 C_{10} = 7.7$ cal./mole °K., equivalent to 2.9 kcal./mole at 100°). Part of this change may result from solvent effects.

The order of relative thermodynamic stability (as measured by ΔF^0) *reverses* with the eleven- and twelve-membered cycloalkenes, the *trans* isomers being the more stable. However, in both cases the observed stabilities reflect mainly *entropy* differences. Indeed, *trans*-cyclododecene actually has a *higher* enthalpy than its *cis* isomer.[4]

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(1) A. C. Cope, D. C. McLean and N. A. Nelson, THIS JOURNAL, **77**, 1628 (1955); A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *ibid.*, **74**, 3636 (1952); N. L. Allinger, *ibid.*, **79**, 3443 (1957).

(2) M. Svoboda and J. Sicher, *Chemistry and Industry*, 290 (1959).

(3) R. B. Turner and W. R. Meador, THIS JOURNAL, **79**, 4133 (1957).

(4) Svoboda and Sicher (ref. 2) state that ". . . the *trans* isomer has a lower energy content than the *cis* form." Extrapolation of our results to 25° gives $K = 0.59$ in acetic acid compared to *ca.* 0.67 (ref. 2) with no solvent, suggesting that the solvent effects in this case are small and would not result in a reversal of the enthalpy change.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE
OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS
ARTHUR C. COPE
PHYLIS T. MOORE
WILLIAM R. MOORE

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ACID-CATALYZED EQUILIBRATIONS OF ENDOCYCLIC AND EXOCYCLIC OLEFINS

Sir:

The question of the relative stabilities of endocyclic and exocyclic olefins recently has attracted some interest.[1–5] We have determined the positions of the equilibria between methylenecycloalkanes and 1-methylcycloalkenes having five- to eight-membered rings in acetic acid solution at 25°, employing *p*-toluenesulfonic acid as catalyst. Gas chromatography was used to determine the positions of the equilibria, which were approached from both the exocyclic and the endocyclic isomers. The results, summarized in Table I, show that in the five- to seven-membered rings the amount of methylenecycloalkane present at equilibrium increases with increasing ring size. This order of stability is in qualitative agreement with the results obtained by Turner from heats of hydrogenation.[2] The enthalpies of isomerization (ΔH^0, *exo* → *endo*) for the six- and seven-membered ring systems are very similar, and the considerable difference between K *endo*/*exo* for the two ring sizes is due to the much larger value of ΔS^0 for the isomerization in the six-membered ring.

TABLE I

EQUILIBRIA BETWEEN METHYLENECYCLOALKANES AND 1-METHYLCYCLOALKENES IN ACETIC ACID AT 25°

Ring size	$K_{endo/exo}$	ΔF^0 (kcal./mole)	ΔH^0 (kcal./mole)[a]	ΔS^0 (cal./mole °K.)[b]
5	1144	−4.17	−3.9	+0.9
6	240	−3.24	−2.4	+2.8
7	74.4	−2.55	−2.3	+0.8
8	598	−3.79		

[a] Ref. 2. [b] Calculated using the values of ΔH^0 obtained by the hydrogenation method (ref. 2).

Methylenecyclononane and methylenecyclodecane were isomerized to their endocyclic isomers under the conditions employed for the lower homologs. The amount of exocyclic isomer present at equilibrium in both cases was found to be less than 0.1% ($K_{endo\text{-}cis/exo} > 1000$). The amount of *trans*-1-methylcyclononene in equilibrium with the *cis* isomer was found to be less than 0.2%. The increase in equilibrium (*endo*/*exo*) ratios in eight-, nine- and ten-membered rings may be due to the

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(2) R. B. Turner and R. H. Garner, *ibid.*, **80**, 1424 (1958).

(3) R. A. Benkeser and J. J. Hazdra, *ibid.*, **81**, 228 (1959).

(4) W. J. Bailey and W. F. Hale, *ibid.*, **81**, 651 (1959).

(5) B. R. Fleck, *J. Org. Chem.*, **22**, 439 (1957).