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

RESEARCH AND DEVELOPMENT DIVISION J. L. FRANKLIN
HUMBLE OIL & REFINING COMPANY F. W. LAMPE
BAYTOWN, TEXAS 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 ($\Delta F^0\text{C}_9 - \Delta F^0\text{C}_{10} = -2.2$ kcal./mole at 100°) as a result of the large difference in the entropy change ($\Delta S^0\text{C}_9 - \Delta S^0\text{C}_{10} = 7.7$ 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 ARTHUR C. COPE
OF TECHNOLOGY PHYLIS T. MOORE
CAMBRIDGE 39, MASSACHUSETTS 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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[1] H. C. Brown, *J. Org. Chem.*, **22**, 439 (1957); H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954).

[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).