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

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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.

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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).

fact that an endocyclic double bond in a medium-sized ring will partially relieve the strain due to crowding of hydrogen atoms.

During the equilibration of methylenecyclodecane, *trans*-1-methylcyclodecene was formed initially at a rate only slightly slower than the *cis* isomer. This result indicates that the presumed carbonium ion precursor can lose a proton to give *cis* and *trans* endocyclic olefins with approximately equal ease. After the concentration of the *trans* isomer had reached a maximum value of 37% of the total olefin mixture, it decreased slowly to the equilibrium value of 0.5%.

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RECEIVED APRIL 27, 1959

SOLVATION EFFECTS AND THE BAKER-NATHAN SEQUENCE

Sir:

In view of current interest in reëxamining the origin of the Baker–Nathan effect,[1] we are prompted to report some kinetic and thermodynamic measurements we have made at 25.06° with *p*-methylbenzyl chloride and *p*-*t*-butylbenzyl chloride, as solutions in methanol and as pure liquids.

First-order specific rate constants (k, in sec.$^{-1}$) for the production of acid from solutions of the benzyl chlorides have been established as $3.06 \pm 0.01 \times 10^{-7}$ and $2.76 \pm 0.01 \times 10^{-7}$ for the *p*-methyl and *p*-*t*-butyl compounds, respectively. Thus, in this system, the Baker–Nathan sequence of substituent effects is followed with $k_{p\text{-methyl}} > k_{p\text{-}t\text{-butyl}}$.

By application of the dynamic vapor pressure technique,[2] and ultraviolet spectroscopic analysis, partial pressures (p_0, in mm.) of the pure benzyl chlorides have been measured, the values being 0.18 ± 0.01 and 0.017 ± 0.001 for the *p*-methyl and *p*-*t*-butyl compounds, respectively. Application of the same techniques to solutions of the benzyl chlorides has yielded Henry's law constants (H, in mm./mole/kg. solvent) of 0.19 ± 0.01 and 0.026 ± 0.002 for the *p*-methyl and *p*-*t*-butyl compounds, respectively, invariant with concentration over the range 0.100–0.00100 molal.

If one defines solvation energy as the free energy of the transformation, pure compound → hypothetical 1 molal solution (as $2.303\ RT \log H/p_0$),[3] the solvation energies (in cal./mole) of the benzyl chlorides are +30 ± 30 and +250 ± 50 for the *p*-methyl and *p*-*t*-butyl compounds, respectively. Alternatively, solvation effects may be expressed in terms of the ratio of the experimental vapor pressure to that calculated from Raoult's law; values less than unity indicate enhanced interactions between solute and solvent over those in the pure components, and values greater than unity indicate reduced interactions.[4] This ratio ($H/0.0310\ p_0$), for the hypothetical 1 molal solutions of benzyl chlorides, is 34 ± 2 and 49 ± 4 for the *p*-methyl and *p*-*t*-butyl compounds, respectively. By either criterion, it is apparent that, in this system, *p*-*t*-butylbenzyl chloride is less strongly solvated than *p*-methylbenzyl chloride.

To our knowledge, these are the first measurements of solvation effects in a system which undergoes chemical reaction according to the Baker–Nathan sequence. The results support the contention[5] that the Baker–Nathan sequence is associated with differential solvation effects rather than C–H hyperconjugation.

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(1) Conference on Hyperconjugation, Indiana University, June 2–4, 1958; *Tetrahedron*, **5**, 105 (1959).

(2) A. L. Bacarella, A. Finch and E. Grunwald, *J. Phys. Chem.*, **60**, 573 (1956).

(3) This definition of *solvation* energy, although arbitrary, is analogous to that for the Gibbs free energy of mixing (E. A. Guggenheim, "Thermodynamics," Interscience Publishers, Inc., New York, N. Y., 1957, p. 242) which is a measure of the *total* change in free energy associated with a solution phenomenon. Like the latter, it has the advantage of yielding values for solvation effects which are insensitive to absolute volatilities, and hence significant for comparisons involving different compounds. Thus, for all substances which form ideal solutions, regardless of the vapor pressures of the pure substances, this definition yields identical solvation energies of $2.303\ RT \log X$, where X is the mole fraction of the solute in the hypothetical 1 molal solution.

(4) W. J. Moore, "Physical Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1955, p. 135.

(5) W. M. Schubert, J. M. Craven, R. G. Minton and R. B. Murphy, *Tetrahedron*, **5**, 194 (1959), and earlier papers by W. M. Schubert.

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A NEW HYPOTENSIVE STEROID ALKALOID FROM CONOPHARYNGIA PACHYSIPHON

Sir:

In the course of our plant screening program we had occasion to prepare an extract of the roots of *Conopharyngia pachysiphon* (Apocynaceae) obtained from Trinidad.[1] This extract was found by our Macrobiology Division to exert considerable hypotensive activity when tested intravenously in dogs. However, this action was accompanied by a marked respiratory depressant effect. Chromatography of the crude extract on a silicic acid column effected a complete separation of these actions and permitted the crystallization of the pure hypotensive factor, m.p. 259–260°. Microanalysis indicated the formula $C_{27}H_{45}NO_6{\cdot}HCl$. Treatment of the hydrochloride with ammonia yielded the free base, m.p. 285–288°, infrared absorption bands (Nujol) at 3528 cm.$^{-1}$ (OH); 3404, 3270 cm.$^{-1}$ (bonded OH, NH); 1595 cm.$^{-1}$ (NH of NH_2); multiple strong bands in 1000–1100 cm.$^{-1}$ region (C–O–C). Acetylation with acetic anhydride in pyridine formed a pentaacetate, $C_{37}H_{55}NO_{11}$, m.p. 202–203°, infrared bands at 1750 cm.$^{-1}$ (O-acetyl); 1650 cm.$^{-1}$ (N-acetyl). Mild alkaline hydrolysis of the pentaacetate yielded a product, m.p. 269–271°, $C_{29}H_{47}NO_7$, which still showed an infrared band indicative of N-acetyl, whereas the 1750 cm.$^{-1}$ band had disappeared completely. Therefore, it seemed evident that the pentaacetate contained four O-acetyl and one N-acetyl, a fact confirmed by acetyl determination. That a primary amine was origi-

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(1) This material was very kindly collected and identified by Prof. F. J. Simmonds, Imperial College of Tropical Agriculture, St. Augustine, Trinidad, B.W.I., to whom we are most grateful.