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.

We wish to thank the National Science Foundation for its support of this work under grant number G-5116.

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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.