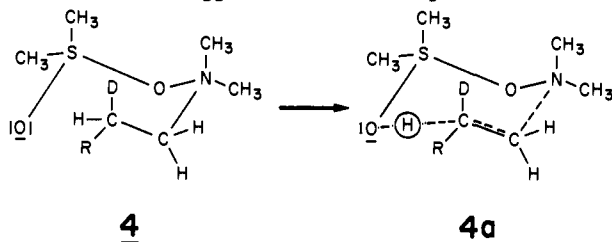


X = ONMe<sub>2</sub>), containing approximately 1.6 mol of H<sub>2</sub>O per mole of **1**, was run in dilute Me<sub>2</sub>SO solution at each of six temperatures over a 70 °C temperature interval. The data gathered in Table I clearly show a regular variation of  $k_H/k_D$  with temperature, in distinction to the temperature invariant values realized in the earlier studies<sup>5</sup> in diglyme solvent. The activation parameters calculated<sup>11a,14</sup> from these data,  $[\Delta E_a]_D^H = 0.695$  kcal/mol and  $A_H/A_D = 1.14$ , reflect the fact that the change to the coordinating solvent Me<sub>2</sub>SO has indeed effected a change in the transition-state structure. Under these altered circumstances, the H transfer takes place linearly between carbon and oxyanion centers of the solvent-coordinated substrate. An attractive representation of this, shown in **4**, would suggest that 1 mol of Me<sub>2</sub>SO has coordinated



the oxyanion center of the original amine oxide **1** (X = ONMe<sub>2</sub>) and thereby created a seven-membered cyclic arrangement which makes possible the geometry required for linear H transfer. One

(14) Drenth, W.; Kwart, H. "Kinetics Applied to Organic Reactions"; Marcel Dekker: New York, 1980; Chapter 5.

possible TS<sup>\*</sup> conformation is the chair shown as **4a**, wherein the greater length of the S–O bonds has served to accommodate the reaction barrier width, i.e., the distance of separation of the centers between which H transfer must occur in the TS<sup>\*</sup>, which permits linear H transfer without tunneling.

The fact that  $[\Delta E_a]_D^H$  is little more than half as great as the zero-point energy difference,  $[\Delta E_0]_D^H$ , is in keeping with the premise that the Me<sub>2</sub>SO-coordinated reaction is not a pericyclic process<sup>14</sup> as was identified for the thermolysis of sulfoxides;<sup>5</sup> nor is it a pseudopericyclic reaction<sup>15</sup> similar to that proposed for the uncoordinated amine oxide in diglyme solvent. We have here, instead, an example of an unsymmetrical TS<sup>\*</sup>, i.e., a product-like or reactant-like TS<sup>\*</sup> of linear H transfer,<sup>16</sup> probably the former in view of the extraordinary capability of Me<sub>2</sub>SO for stabilization of the anionic character developing in accompaniment to the proton transfer.

Finally, these results make it clear that the lower activation energy observed for sulfoxide and amine oxide thermolysis in Me<sub>2</sub>SO compared to inert, noncoordinating solvents is due to a change in mechanism, rather than to the mere sequestering of water as has been alleged.<sup>6</sup>

(15) Ross, J. A.; Seiders, R. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 4325.

(16) For a full discussion, see: (a) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265. (b) Bigeleisen, J. *Pure Appl. Chem.* **1964**, *8*, 217.

(17) (a) Kwart, H.; Stanulonis, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 4009. (b) Kwart, H.; Barnette, W. E. *Ibid.* **1977**, *99*, 614. (c) Kwart, H.; Benko, D. A. *Ibid.* **1979**, *101*, 1277.

## Additions and Corrections

**Isolation and Characterization of the First Host Recognition Substance for Parasitic Angiosperms** [*J. Am. Chem. Soc.* **1981**, *103*, 1868–1870]. DAVID G. LYNN,\* JOHN C. STEFFENS, VINAYAK S. KAMAT, DAVID W. GRADEN, JEFFREY SHABANOWITZ, and JAMES L. RIOPEL,\* Departments of Chemistry and Biology, University of Virginia, Charlottesville, Virginia 22901.

The third author's name should read Vinayak S. Kamat (not Kamut).

**Competitive Condensation and Proton-Transfer Processes in the Reaction of *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> Ions with Ammonia in Gaseous Systems at Atmospheric Pressure** [*J. Am. Chem. Soc.* **1980**, *102*, 6896–6898]. M. ATTINA, FULVIO CACACE,\* P. GIACOMELLO, and M. SPERANZA, University of Rome, 00100 Rome, Italy, and Istituto di Chimica Nucleare del C.N.R., 00016 Monterotondo Stazione, Rome, Italy

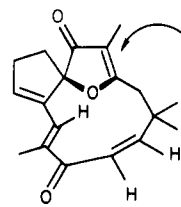
Page 6897, lines 18 and 31, right column: In both lines 2-butene should be isobutene.

**A Strategy for the Total Synthesis of Jatrophone: Synthesis of Normethyljatrophone** [*J. Am. Chem. Soc.*, **1981**, *103*, 219]. A. B. SMITH, III,\* M. A. GUACIARO, S. R. SCHOW, P. M. WOVKULICH, B. H. TODER, and T. W. HALL, The Department of Chemistry, The Laboratory for Research on the Structure of Matter and the Monell Chemical Senses Center, The University of Pennsylvania, Philadelphia, Pennsylvania 19104

In the note added in proof the minus sign was inadvertently deleted by the production editor from both jatrophone and epijatrophone. It should read: Since acceptance of the manuscript,

we have successfully completed the first stereocontrolled total synthesis of both (±)-jatrophone (**1**) and that of its epimer (±)-epijatrophone, exploiting the synthetic strategy outlined above; **5a** its epimer served, respectively, as starting materials. A complete account of this effort will be forthcoming in the near future.

In ref 15 the 3(2*H*)-furanone ring of structure **15** should contain a double bond as indicated below.



**15**

**Interaction of Pyruvate–Thiamin Diphosphate Adducts with Pyruvate Decarboxylase. Catalysis through "Closed" Transition States** [*J. Am. Chem. Soc.* **1981**, *103*, 1214–1216]. RONALD KLUGER\* and TIMOTHY SMYTH, Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

The Michaelis–Menten expression on p 1216 should read:  $1/v = (K_m/V_{max})(1/s) + 1/V_{max}$ .  $K_m$  is  $[k_3(k_{-1} + k_2)]/k_1k_2$ . If  $k_2 \gg k_{-1}$ ,  $K_m = k_3/k_1$ .

The discussion and analysis that follow were based on the correct equations ( $K_m$  inversely proportional to  $k_1$ ).