other than minor shifts in peak positions. Consistent with the results in the tropane salts,[1] the axial methyl groups appear at lower field than the equatorial methyls.

If the factors that determine the steric preference in the tropanes and the tropidines are similar (as is suggested by the similar results in both series), it is unlikely that interference with the axial approach of the quaternizing reagent is the dominant factor. If this is so, the interaction of the nitrogen substituent with two of the hydrogens of the ethane bridge must be greater than the interaction it suffers when being fixed in the axial position in the transition state. This is a reasonable interpretation in the tropidine series.

In view of the flattened nature[10-13] of the six-membered ring in tropanes, the interpretation may be reasonable there as well. The flattening of the ring should cause the axial hydrogens to twist away from one another, thus reducing their steric influence. Substantial axial quaternization in the piperidine series[14] further establishes the importance of the rigid ethane bridge in giving an equatorial bias to the reaction. Further work on the nature and extent of these interactions is in progress.

Acknowledgments. One of us (J.H.S.) is grateful to the National Science Foundation for a Science Faculty Fellowship, to Professor A. R. Katritzky for helpful discussions, to the University of East Anglia for the use of facilities, and to the Research Foundation of the State University of New York for partial financial support.

(10) H. Schenk, C. H. MacGillavry, S. Skolnik, and J. Laan, *Acta Crystallogr.*, **23**, 423 (1967).

(11) R. J. Bishop, G. Fodor, A. R. Katritzky, F. Soti, L. E. Sutton, and F. J. Swinbourne, *J. Chem. Soc. C*, 74 (1966).

(12) J. H. Supple, L. N. Pridgen, and J. J. Kaminski, *Tetrahedron Lett.*, 1829 (1969).

(13) M. Ohashi, I. Morishima, K. Okada, T. Yonezawa, and T. Nishida, *Chem. Commun.*, 34 (1971).

(14) See, for example, D. R. Brown, R. Lygo, J. McKenna, J. M. McKenna, and B. G. Hutley, *J. Chem. Soc. B*, 1184 (1967).

Jerome H. Supple,* Eric Eklum
Department of Chemistry, State University College
Fredonia, New York 14063

Received July 19, 1971

Protonation of Cyclopropane

Sir:

There has been much interest in the species formed by protonation of cyclopropane and in the fate of *n*-propyl cation;[1] we have studied these problems using the MINDO/2 method.[2]

As a preliminary we calculated the energies of several carbonium ions which are believed to have classical structures and are predicted to do so by MINDO/2. The geometries were optimized by the SIMPLEX method,[3] using a program written by Dr. A. Brown, and should correspond to true minima on the potential surface. The calculated heats of atomization were converted to heats of formation using experimental values for heats of atomization. The results are compared with experiment in Table I.

Table I. Heats of Formation of Carbonium Ions

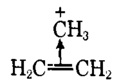
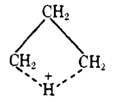
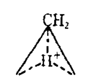
Ion	Heat of formation, kcal/mol, at 25°: Calcd	Obsd[a]
CH_3^+	275.9	260
$CH_3CH_2^+$	225.2	219
$CH_3\overset{+}{C}HCH_3$	191.5	190
$CH_3CH_2\overset{+}{C}HCH_3$	183.4	183,[b] 192[c]
$(CH_3)_3C^+$	171.3	171.5,[d] 176[c]

[a] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. J. Herron, K. Draxl, and F. M. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," National Bureau of Standards, Washington, D. C., 1969. [b] From photoionization studies of F. A. Elder, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **36**, 3292 (1962). [c] Electron impact value. [d] From photoionization studies of B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961).

The agreement is good, except for CH_3^+, for heats of formation calculated from photoionization data. The electron impact value for *sec*-Bu^+ is clearly too high, given that the corresponding values (Table I, footnote *a*) for *i*-Pr^+ and *n*-$BuCH^+CH_3$ are 190 and 173 kcal/mol, respectively.

Since the MINDO/2 method thus seems applicable to carbonium ions,[4] we calculated the various species that might be formed by protonation of cyclopropane. Only edge-protonated cyclopropane III was found to be stable, the other isomers, I, II, and IV, rearranging to III without activation. The values for I, II, and IV listed in Table II were calculated by assuming the CCC bond

Table II

Ion	Heat of formation, kcal/mol, at 25°
$CH_3CH_2\overset{+}{C}H_2$ I	216.0
 II	195.0
 III	187.6
 IV	247.5

---

(1) (a) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); (b) C. C. Lee and J. E. Kruger, *Tetrahedron*, **23**, 2539 (1967); (c) J. D. Petke and J. L. Whitten, *J. Amer. Chem. Soc.*, **90**, 3338 (1968); (d) H. Fischer, H. Kollmar, and H. O. Smith, *Tetrahedron Lett.*, 5821 (1968); (e) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 1813 (1971).

(2) (a) M. J. S. Dewar and E. Haselbach, *ibid.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

(3) J. A. Nelder and R. Mead, *Comput. J.*, 7, 308 (1964).

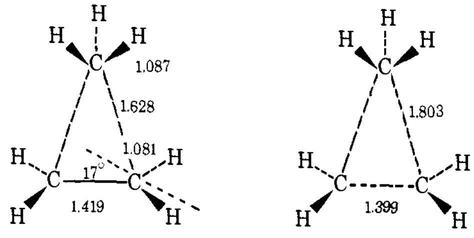
(4) It had already been shown that MINDO/2 gives good estimates of heats of formation of cation radicals formed by ionization of neutral molecules; see ref 2b and N. Bodor, M. J. S. Dewar, W. B. Jennings, and S. D. Worley, *Tetrahedron*, 26, 4109 (1970).

angle in I to be the same as in propane (110.5°), by assuming the methyl carbon in II to lie midway between the methylene carbons, and by assuming the central hydrogen in IV to lie midway between the carbon atoms. Apart from these restrictions, all the values reported in this communication correspond to structures optimized with respect to all geometrical parameters.

These results differ in several respects from those reported by Pople, *et al.*,[1e] using an *ab initio* SCF method. They concluded that the most stable form should be a somewhat distorted *n*-propyl cation, I, with a CCC bond angle of 101.5°, and that i-Pr$^+$ should be more stable than I by 20 kcal/mol. The predicted order of stability of the other isomers was I > II > III > IV.

The chemical evidence suggests that I can isomerize easily to II or III in solution, that II and III are stable in solution, and that III is probably more stable than II.[5] Since the solvation energies of the classical ions I and i-Pr$^+$ must be greater than those of the "nonclassical" ions II and III, our results seem to be in better agreement with the available evidence than those of Pople, *et al.*[1e] Our geometry for the π complex II also seems more reasonable than theirs (see Chart I). It is difficult to believe that the apical–basal CC bonds could be so much longer than the bonds in cyclopropane.

Chart I. Calculated Geometries for II[a]



a b

[a] Bond lengths in ångströms: a, MINDO/2; b, *ab initio* SCF.[1e]

Our calculations lead to the prediction that III should be more stable than i-Pr$^+$ in the gas phase though the difference in heat of formation (4 kcal/mol) is too small for this conclusion to be reliable. The fact that i-Pr$^+$ is the stable form of $C_3H_7^+$ in solution is of course irrelevant in this connection since, as pointed out above, the energy of solvation of i-Pr$^+$ must be much greater than that of III.

Since *ab initio* SCF methods give very poor estimates of heats of atomization, they can be used to calculate energies only on an empirical basis. While some justification exists for their use in comparing systems with equal numbers of similar bonds,[6] this does not extend to comparisons of dissimilar species such as I–IV. Since MINDO/2 has been shown to give good estimates of heats of atomization for a wide variety of molecules, including (see above) carbonium ions, and also activation energies for several reactions,[2,7] we feel that the results reported here may give reasonably reliable results in situations of the type considered here.

(5) G. J. Karabatsos, Ch. Zioudrou, and S. Meyerson, *J. Amer. Chem. Soc.*, **92**, 5996 (1970); C. J. Collins, *Chem. Rev.*, **69**, 543 (1969).

(6) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

(7) M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **91**, 7521 (1969); M. J. S. Dewar, E. Haselbach, and M. Shansal, *ibid.*, **91**, 3506 (1969); A. Brown, M. J. S. Dewar, and W. Schoeller, *ibid.*, **92**, 5516 (1970); M. J. S. Dewar and W. W. Schoeller, *ibid.*, **93**, 1481 (1971); *Tetrahedron*, **27**, 4401 (1971).

Acknowledgment. This work was supported by the Air Force Office of Scientific Research through Contract No. F44620-70-C-0121.

(8) R. A. Welch Postdoctoral Fellow; on leave of absence from the Chemical-Pharmaceutical Research Institute, Cluj, Romania.

Nicolae Bodor,[8] Michael J. S. Dewar*
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Received June 10, 1971

Self-Reactions of Diethylamino and Diisopropylamino Radicals[1]

Sir:

The chemistry of dialkylamino radicals has received little attention, and accurate kinetic and thermodynamic data for such radicals are almost nonexistent. We wish to report the first absolute rate measurements for the self-reactions of diethylamino and diisopropylamino radicals in solution. Both of these radicals (and also the dimethylamino radical) were generated in the cavity of a Varian E-3 epr spectrometer by photolysis of the appropriate tetraalkyltetrazene in a hydrocarbon solvent. The epr spectra of these radicals have been reported previously by Danen and Kensler using the same technique.[3] Decay of the radicals when the light

$$R_2N{-}N{=}N{-}NR_2 \xrightarrow{h\nu} 2R_2N\cdot + N_2$$

was cut off was monitored in the usual way.[4]

The epr signal due to dimethylamino was too weak for kinetic studies. Diethylamino radicals decayed with second-order kinetics at a rate close to the diffusion-controlled limit. In *n*-pentane at −90°, the decay rate constant, $k_{epr}{}^2 = 2k^{Et_2N}$, was $(7 \pm 3) \times 10^9\ M^{-1}\ sec^{-1}$

$$2Et_2N\cdot \xrightarrow{2k^{Et_2N}} \text{nonradical products}$$

Diisopropylamino radicals decay completely with clean second-order kinetics at temperatures below ∼−10°. In *n*-pentane, the measured decay rate constant $k_{epr}{}^2 = (4.5 \pm 1.0) \times 10^6\ M^{-1}\ sec^{-1}$ at all temperatures in the range −13 to −70°. If a sample of the tetrazene which has been photolyzed at these low temperatures is allowed to warm up in the dark after the i-Pr$_2$N· radical has completely decayed, the signal due to this radical reappears at ∼−5° and grows rapidly as the temperature is raised further. In typical experiments, a radical concentration of $\sim 5 \times 10^{-7}\ M$ is obtained at ∼+10°, and this does not decay noticeably in 20 min. In the range −5 to ∼+20°, the radical concentration could be increased and decreased reversibly by raising and lowering the temperature. Presumably, the radical is in equilibrium with its dimer, tetraisopropylhydrazine.

$$2i\text{-}Pr_2N\cdot \rightleftarrows i\text{-}Pr_2NN\text{-}i\text{-}Pr_2$$

The variation in radical concentration with temperature yielded a heat of formation of the dimer, $\Delta H = 25 \pm$

(1) Issued as NRCC No. 12279. Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. IV.[2]

(2) Part III: D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 6555 (1971).

(3) W. C. Danen and T. T. Kensler, *ibid.*, **92**, 5235 (1970).

(4) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *ibid.*, **93**, 902 (1971).