

As can be seen by comparison with the limited amount of experimental data available, the agreement for dimerization energies, heavy-atom separations, and X-H stretching force constants, K_{XH} , is moderately good. It appears that simultaneous optimization of both the proton and heavy-atom positions is only necessary for $\text{ClH} \cdots \text{NH}_3$, and, when this was carried out, the heavy atoms become 0.1 Å closer together, the proton moves 0.1 Å from its monomer position toward the nitrogen lone pair, and E_D becomes 12.8 kcal/mol. Dimer dipole moments are overestimated to the same degree traditionally found for separated monomers.

The results reported here parallel those for the second-row dimers found by Kollman and Allen² using a Hartree-Fock atomic orbital basis set, and comparison with other earlier work can be found in the review by these authors.³ The water dimer has been studied more extensively than any other, and, since publication of the review noted above, two important new calculations have been reported. Curtiss and Pople⁴ employed the 6-31G* basis (which includes d polarization functions) and obtained $E_D = 5.6$ kcal/mol, $R = 2.97$ Å, $\theta = 57^\circ$, and $K_{OH} = 8.66$ mdyn/Å. Popkie, Kistenmacher, and Clementi⁵ used a very large basis set, including s, p, d, and f functions on oxygen and s, p, and d on hydrogens, and they obtained $E_D = 3.90$ kcal/mol, $R = 3.0$ Å, and $\theta = 30^\circ$. Two interesting and pertinent papers by Sabin⁶ on $(\text{H}_2\text{S})_2$ and Kollman, *et al.*,⁷ on $(\text{HF})_2$, H_2OHF , H_3NHF , HClHF , $(\text{HCl})_2$, HFHCl , H_2OHCl , and H_3NHCl employ wave functions of higher total energies than 4-31G. The STO-3G basis used by Kollman, *et al.*, yields an erratic ordering of the six monomer dipole moments relative to the experimental values while 4-31G gives the correct order. R values from STO-3G are also appreciably shorter than with 4-31G. Comparing our 4-31G basis set results with the available experimental data shows that our E_D values are poorest when oxygen acts as a proton donor and suggests that our E_D estimates for these systems are approximately 25% too large. Other E_D estimates may be reliable to $\pm 15\%$. Experiment and the most accurate theoretical work on $(\text{HF})_2$ and $(\text{H}_2\text{O})_2$ suggest that our R values are 5% too small. In a similar manner, dipole moments should be multiplied by 0.6 and force constants, K_{XH} , by 0.85. Some of the K_{XH} are in error (*e.g.*, some show a blue shift) because we have used experimental rather than theoretically determined monomer geometries.

An analysis of hydrogen bonding using the wave functions for the dimers presented here and a more extended comparison with other work will be reported shortly. During the course of this research we learned that P. Kollman, J. McKelvey, A. Johansson, and S. Rothenberg have been carrying out similar computations. E_D , R , and θ values have been compared and we have agreement within 0.1 kcal, 0.05 Å, and 10° . We have enjoyed numerous useful and stimulating conversations with Peter Kollman. We also acknowledge

(2) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **52**, 5085 (1970); *J. Amer. Chem. Soc.*, **92**, 753 (1970).

(3) P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 283 (1972).

(4) L. A. Curtiss and J. A. Pople, to be submitted for publication.

(5) H. Popkie, H. Kistenmacher, and E. Clementi, *J. Chem. Phys.*, **59**, 1325 (1973).

(6) J. R. Sabin, *J. Amer. Chem. Soc.*, **93**, 3613 (1971).

(7) P. A. Kollman, A. Johansson, and S. Rothenberg, *Chem. Phys. Lett.*, **24**, 199 (1974).

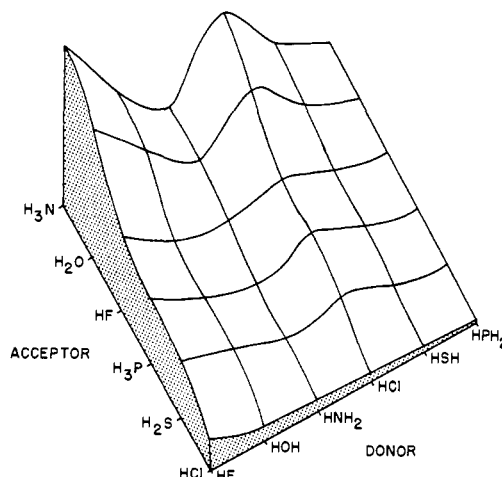


Figure 1. Dimerization energies, E_D , for the hydrides of the electronegative atoms in the second and third rows.

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William C. Topp, Leland C. Allen*
Department of Chemistry, Princeton University
Princeton, New Jersey 08540
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Stereochemistry of Nitrosylmetalloporphyrins. Nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(1-methylimidazole)iron and Nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(4-methylpiperidine)manganese

Sir:

There is much current interest in the structure and bonding of the small molecules, dioxygen, nitric oxide, and carbon monoxide, with metalloporphyrins and in their relationship to the corresponding hemoprotein complexes.¹ We wish to report the structures of two six-coordinate nitrosylmetalloporphyrins, nitrosyltetraphenylporphinato(1-methylimidazole)iron, $\text{ONFeTPP}(\text{NMeIm})$, and nitrosyltetraphenylporphinato(4-methylpiperidine)manganese, $\text{ONMnTPP}(\text{MPip})$. These compounds represent models of the coordination group in the respective nitrosylmetalloproteins.^{1f,1g}

The compounds were prepared by reductive nitrosylation^{1a,2} and recrystallized, under an argon-nitric oxide atmosphere, from chloroform solutions containing a large excess of the nitrogen base. The structures of the two molecules have been determined by X-ray diffraction techniques. Both crystallize in the ortho-

(1) (a) W. R. Scheidt and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8281 (1973); (b) J. P. Collman, R. R. Gagne, T. R. Halbert, J.-C. Marchon, and C. A. Reed, *ibid.*, **95**, 7868 (1973); (c) B. B. Wayland and L. W. Olson, *J. Chem. Soc., Chem. Commun.*, 897 (1973); (d) D. V. Stynes and B. R. James, *ibid.*, 325 (1973); (e) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 4087 (1973); (f) J. C. W. Chien, *ibid.*, **91**, 2166 (1969); L. C. Dickinson and J. C. W. Chien, *ibid.*, **93**, 5036 (1971); (g) T. Yonetani, H. Yamamoto, J. E. Erman, J. S. Leigh, Jr., and G. H. Reed, *J. Biol. Chem.*, **247**, 2447 (1972).

(2) (a) D. Gwost and K. G. Caulton, *Inorg. Chem.*, **12**, 2095 (1973). (b) The nitrosyl manganese complex is readily prepared by treatment of a chloroform solution of ClMnTPP with nitric oxide in the presence of an excess of 4-methylpiperidine. The complex is easily isolated by the addition of methanol. The general nature of the reaction is being investigated, P. L. Piccolo and W. R. Scheidt, to be submitted.

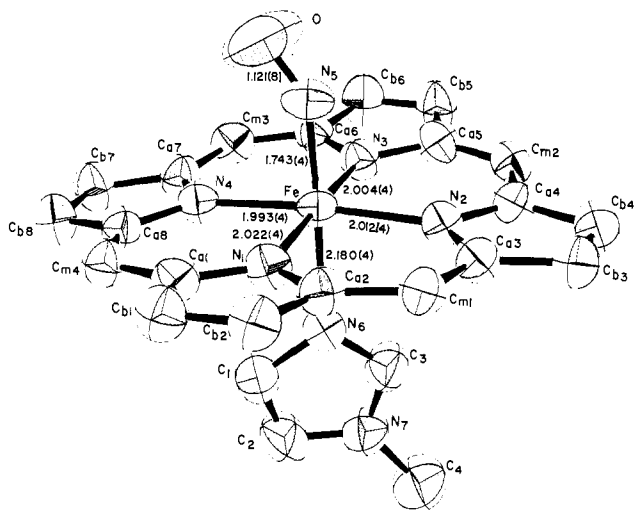


Figure 1. Model in perspective of the ONFeTPP(NMeIm) molecule. Atoms are represented by their vibrational ellipsoids, contoured to enclose 50% of the electron density. The $N_3\text{Fe}N_4$ angle is 176.3° . The phenyl groups have been omitted for clarity.

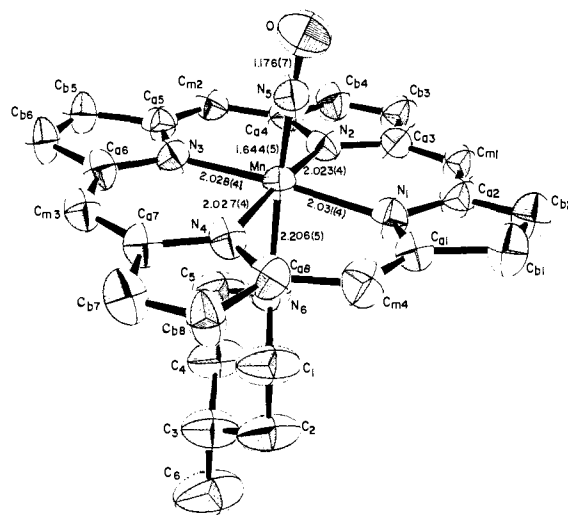


Figure 2. Model in perspective of the ONMnTPP(MPip) molecule. Atoms are represented by their vibrational ellipsoids, contoured to enclose 50% of the electron density. The $N_3\text{Mn}N_4$ angle is 177.2° . The phenyl groups have been omitted for clarity.

rhombic system, space group $P2_12_12_1$. Unit cell dimensions for ONFeTPP(NMeIm) are $a = 17.733$ (13), $b = 25.339$ (22), and $c = 9.752$ (10) Å and $Z = 4$ and for ONMnTPP(MPip) $a = 17.561$ (6), $b = 25.580$ (13), and $c = 10.175$ (6) Å and $Z = 4$. Using Mo $K\alpha$ radiation, 4148 reflections with $F_o > 3\sigma(F_o)$ and in the range $3^\circ < 2\theta < 55^\circ$ were collected for ONFeTPP(NMeIm) and 3440 reflections with $F_o > 3\sigma(F_o)$ and in the range $3^\circ < 2\theta < 53^\circ$ were collected for ONMnTPP(MPip). (See paragraph at end of paper regarding supplementary material.) An automated diffractometer employing ω -scans was used for data collection. The structures have been refined anisotropically to $R_1 = 0.052$ and $R_2 = 0.074$ for the iron complex and $R_1 = 0.053$ and $R_2 = 0.078$ for the manganese complex. From the X-ray structure analysis, both crystals were shown to have a chloroform molecule of crystallization in the asymmetric unit of structure.³

The molecular stereochemistry and bond parameters for the coordination group of the two complexes are displayed in Figures 1 and 2. Bond parameters of the core are similar to those of other porphyrins. The average $\text{Fe}-N_p$ (N_p = porphine nitrogen) distance of 2.008 Å can be compared to the 2.004 Å found in low-spin bis(piperidine)tetraphenylporphyratoiron(II)⁴ and the 1.989 Å found for low-spin bis(imidazole)tetraphenylporphyratoiron(III).⁵ The average $\text{Mn}-N_p$ distance is somewhat longer at 2.028 Å.

The axial $\text{Mn}-N_{\text{NO}}$ distance of 1.644 (5) Å is comparable to the 1.66 Å distance found for $\text{K}_3\text{Mn}(\text{CN})_5\text{NO}$.⁶ The corresponding $\text{Fe}-N_{\text{NO}}$ distance of 1.743 (4) Å is substantially longer. The $\text{Fe}-N_{\text{NO}}$ distance is shorter than the $\text{Co}-N_{\text{NO}}$ distance of 1.833 Å in ONCoTPP^{1a} and longer than the 1.63 Å in the nitroprusside ion, $[\text{Fe}(\text{CN})_5\text{NO}]$.²⁻⁷ The $\text{M}-N_{\text{NO}}$ distances

in the metalloporphyrins follow the order $\text{Mn}-\text{N} < \text{Fe}-\text{N} < \text{Co}-\text{N}$ and suggest an ordering for decreased π interaction in the bonding system (*vide infra*).

The iron atom in ONFeTPP(NMeIm) is not in the plane of the four porphyrinato nitrogen atoms but rather is displaced out-of-plane toward the coordinated nitric oxide by 0.07 Å. The manganese atom is also displaced out-of-plane toward the coordinated nitrosyl by 0.10 Å. The displacement of the metal atoms toward the axial nitrosyl groups reflects the tight $N_p \cdots N_{\text{NO}}$ separation in these complexes.⁸

The complexing bond to 1-methylimidazole in ONFeTPP(NMeIm) is quite long with $\text{Fe}-N_b = 2.180$ (4) Å. The $\text{Fe}-N_b$ distance for a six-coordinate imidazoleiron(II) porphyrin is not known, but the $\text{Fe}-N_b$ distances of 1.957 and 1.991 Å in bis(imidazole)tetraphenylporphyratoiron(III),⁵ 2.127 Å in bis(piperidine)tetraphenylporphyratoiron(II),⁴ and 1.985 Å in bis(dimethylglyoximate)diimidazoleiron(II)⁹ suggest that a value of ~ 2.0 Å is reasonable. Hence, the nitric oxide ligand exerts a structural trans effect of ~ 0.20 Å in ONFeTPP(NMeIm). Similar effects are observed in six-coordinate cobalt nitrosyl complexes with a structural trans effect of 0.33 Å observed¹⁰ in *trans*-chloronitrosylbis(ethylenediamine)cobalt(III) perchlorate and 0.24 Å in nitrosylpentaamminecobalt(III).¹¹ Although the $\text{Mn}-N_b$ bond to 4-methylpiperidine is also quite long at 2.206 (5) Å, the distance to the center of the porphine nitrogens is 2.10 Å, a distance that engenders difficult steric interactions between the axial ligand and atoms of the porphyrinato core.¹² Hence, the long bond

(7) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).

(8) The average $N_p \cdots N_{\text{NO}}$ separation in ONFeTPP(NMeIm) is 2.705 Å and in ONMnTPP(MPip) is 2.673 Å. These nonbonded contacts would be shorter still if the metal atom were centered in the porphyrinato plane. The normal separation is ~ 3.0 Å; *cf.* L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(9) K. Bowman, A. P. Gaughan, and Z. Dori, *J. Amer. Chem. Soc.*, **94**, 727 (1972).

(10) D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, **9**, 2760 (1970).

(11) C. S. Pratt, B. A. Coyle, and J. A. Ibers, *J. Chem. Soc. A*, 2146 (1971).

(3) The chloroform molecules are well separated in the crystal and are not associated with the complex.

(4) L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2073 (1972).

(5) D. M. Collins, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2066 (1972).

(6) A. Tullberg and N. Vannerberg, *Acta Chem. Scand.*, **21**, 1462 (1967).

in ONMnTPP(MPip) is not necessarily a result of a structural trans effect of the NO ligand but rather a stretch resulting from steric interaction.

The most significant difference in the two structures is the manner in which NO coordinates to the metal. Nitric oxide coordinates to manganese in a linear fashion with a MnN₂O angle of 176.2 (5)°; the FeN₂O system is bent with the angle equal to 142.1 (6)°. The manganese complex is isoelectronic with the corresponding carbonyl heme derivative which is expected to have a linear FeCO bond system;¹³ the iron nitrosyl complex has one additional electron. These results are most readily understood in terms of a general bonding model for metal nitrosyl complexes discussed by Mingos.¹⁴ In addition, a molecular orbital model which is compatible with all data on CO, NO, and O₂ complexes of cobalt(II) and iron(II) porphyrins leads to similar predictions.¹⁵

In this bonding scheme, a linear geometry is expected to be more stable for d¹-d⁶ complexes and a bent geometry with a bond angle of ~120° for d⁸ complexes. A bending of the MNO grouping is associated with an energetically more stable bonding ($\pi^*(\text{NO})$, d_{z²}) and a less bonding (d_{z²}, $\pi^*(\text{NO})$) pair of orbitals of σ symmetry; concomitant with the distortion is a destabilization of the (d_{z²}, $\pi^*(\text{NO})$) π -type molecular orbital. The stabilization of ($\pi^*(\text{NO})$, d_{z²}) and the destabilization of (d_{z²}, $\pi^*(\text{NO})$) are both proportional to the MNO angle or distortion. In this d⁷ iron complex, the FeNO angle of ~140° is consistent with a smaller stabilization of the half-filled ($\pi^*(\text{NO})$, d_{z²}) molecular orbital and a correspondingly smaller destabilization of the filled (d_{z²}, $\pi^*(\text{NO})$) molecular orbital compared to the d⁸ complexes.¹⁶ As noted above, the M-N_{NO} bond lengths are consistent with a decreased π interaction in the order Mn > Fe > Co. The structural trans effect is also consistent with this bonding model. Further work on the apparent interrelationship of the MNO angle and the M-N_{NO} π -type interaction is underway.

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Supplementary Material Available. A listing of structure factor amplitudes for ONMTPP(MPip) and ONFeTPP(NMeIm) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-5293.

(12) See ref 4 and W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8289 (1973), for quantitative discussion of the difficult steric interactions. No such steric interactions (at these distances) are required when 1-methylimidazole is the axial ligand.

(13) V. L. Goedken, J. Molin-Case, and Y.-A. Whang, *J. Chem. Soc., Chem. Commun.*, 337 (1973).

(14) D. M. P. Mingos, *Inorg. Chem.*, **12**, 1209 (1973).

(15) B. B. Wayland, J. V. Minkiewicz, and M. E. Abd-Elmageed, *J. Amer. Chem. Soc.*, **96**, 2795 (1974).

(16) This is also consistent with the structure¹⁷ of the five-coordinate complex ONFeTPP wherein the FeNO bond angle is ~150°.

(17) W. R. Scheidt and M. E. Frisse, to be submitted for publication.

Paul L. Piciulo, Gregory Rupprecht, W. Robert Scheidt*
Department of Chemistry, University of Notre Dame
Notre Dame, Indiana 46556

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Effect of the Cyclopropyl Substituent on the Rates of Electrophilic Additions to Alkenes

Sir:

The interaction of the cyclopropyl group with an adjacent electron-deficient center continues to be a topic of extreme interest.^{1,2} Conspicuously absent among these studies has been a systematic examination of the effect of a cyclopropyl group on the rates of electrophilic addition to alkenes.³⁻⁶

We report herein an investigation of the influence of cyclopropyl on the rates of representative electrophilic additions to ethylenes. The results show accelerations by large factors (*ca.* 1000) for cyclopropyl relative to phenyl when the transition state for addition leads to a relatively open positive charge on the adjacent carbon susceptible to resonance stabilization by the substituent. We find minimal rate differences (factors between one and four) when the substrate contains another strongly stabilizing substituent which preempts the effect of the cyclopropyl or when there is formation of a bridged intermediate which precludes resonance stabilization. Thus the magnitude of the acceleration provides a useful criterion of the transition state structure.

The reaction of vinylcyclopropane with bromine in acetic acid, aqueous sulfuric acid, and *p*-chlorobenzene-sulfonyl chloride in acetic acid and of diethyl α -cyclopropylvinyl phosphate with aqueous HCl were found to proceed as shown in eq 1-4.

The rates are presented in Table I, along with data for the reactions of the corresponding phenyl and *n*-alkyl substituted derivatives for comparison.^{7,9,10} The

(1) (a) D. F. Eaton and T. G. Traylor, *J. Amer. Chem. Soc.*, **96**, 1226 (1974); (b) R. S. Brown and T. G. Traylor, *ibid.*, **95**, 8025 (1973); (c) C. F. Wilcox, L. M. Loew, and R. Hoffmann, *ibid.*, **95**, 8192 (1973); (d) W. J. Hehre and P. C. Hiberty, *ibid.*, **96**, 302 (1974); (e) G. A. Olah and P. W. Westerman, *ibid.*, **95**, 7530 (1973); (f) G. A. Olah and G. Liang, *ibid.*, **95**, 3792 (1973); (g) E. N. Peters and H. C. Brown, *ibid.*, **95**, 2397, 2400 (1973).

(2) (a) G. A. Olah, C. L. Jewell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 146 (1971); (b) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965); (c) G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973); (d) H. G. Richey in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley Interscience, New York, N. Y., 1972, p 1295; (e) K. B. Wiberg and A. J. Ashe, *ibid.*, p 1201; (f) M. Charton in "Chemistry of Alkenes," J. Zabicky, Ed., Wiley Interscience, New York, N. Y., 1970, p 511.

(3) For reviews on electrophilic additions to alkenes see (a) R. Bolton in "Comprehensive Chemical Kinetics," Vol. 9, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, London, 1973, p 1; (b) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, London, 1966; (c) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

(4) There are several cases where the products of electrophilic addition to various cyclopropylalkenes have been studied, but there has been no systematic study of the kinetics of these reactions: (a) R. T. Gray and H. E. Smith, *Tetrahedron*, **25**, 3161 (1969); (b) P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, **32**, 24 (1967); (c) J. B. Hendrickson and R. K. Boeckman, Jr., *J. Amer. Chem. Soc.*, **93**, 4491 (1971).

(5) The cleavage of cyclopropanes by electrophiles has been extensively examined: (a) R. J. Ouellette, R. D. Robins, and A. South, Jr., *J. Amer. Chem. Soc.*, **90**, 1619 (1968); (b) C. H. DePuy and R. H. McGirk, *ibid.*, **95**, 2366 (1973); **96**, 1121 (1974); (c) C. H. DePuy, A. H. Andrist, and P. C. Fünfschilling, *ibid.*, **96**, 948 (1974); (d) R. T. LaLonde and A. D. Debboli, Jr., *J. Org. Chem.*, **38**, 4228 (1973); (e) P. E. Peterson and G. Thompson, *ibid.*, **33**, 968 (1968).

(6) For the rate of electrophilic hydration of *p*-cyclopropylstyrene see L. B. Jones and S. S. Eng, *Tetrahedron Lett.*, 1431 (1968).

(7) The presence of ring-opened product from the bromination of cyclopropylethylene as determined by Slobodin and coworkers⁸ could result from competitive electrophilic attack on the ring and double bond so that the rate of electrophilic attack on the double bond would be only 60% of the rate of disappearance of olefin. This rate would still be within the limits specified in Table I.

(8) Ya. M. Slobodin and I. Z. Egenburg, *Zh. Org. Khim.*, **5**, 1315