

$Mn^{II}(GH_3)_2^{2-}$ with GH_3^{2-} representing the dianion of gluconic acid which results from the removal of the carboxylate proton and one of the secondary alcoholic protons.

- (13) A study of the reactivity of III and IV with various organic functional groups is in progress to test this proposition. However, the 60% decrease of III in 2 hr from Ar purging for a 0.6 mF solution in contrast to a 20% decrease in 4 hr for a 5 mF solution indicates that reversible O_2 binding is the dominant process at lower concentrations of III.
- (14) W. M. Latimer, "Oxidation Potentials", 2nd ed, Prentice-Hall, New York, N.Y., 1952, p 39.

Donald T. Sawyer,* Mario E. Bodini

Department of Chemistry, University of California
Riverside, California 92502

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Preparation of 1,3-Oxazin-6-one. A Potential Precursor to Azacyclobutadiene

Sir:

Despite divers reports concerning derivatives of 1,*n*-oxazin-6-ones ("aza- α -pyrones"), in no case has the synthesis of the parent species been realized.¹ These systems (which are potential precursors to the unknown azacyclobutadiene^{2,3} by analogy with the chemistry of α -pyrone,⁴ hold the promise of entry to the dihydropyridine manifold. They are also substantial curiosities in and of themselves, because of the presence of imine and ester functionality in a unique cyclic array.

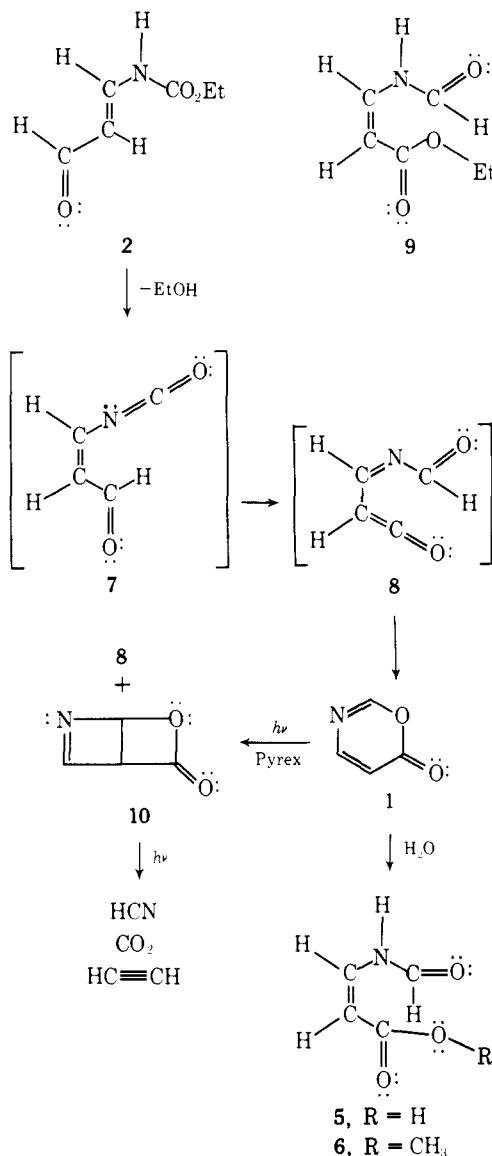
The preparation of 1,3-oxazin-6-one (**1**) has now been achieved via a novel route involving pyrolysis of *trans*-3-ethoxycarbonylamino-prop-2-enal (**2**) (Scheme I). The carbamate **2** was prepared by dropwise addition of ethyl chloroformate (**3**) to a (0°) cooled solution of equivalent amounts (0.05 mol) of β -aminoacrolein⁵ (**4**) and triethylamine in 30 ml of acetonitrile. After being stirred at 25° for 10 hr, 50 ml of ether was added to the mixture, which was, in turn, refrigerated overnight, filtered, and concentrated. Purification of the residue by silica gel chromatography (ether-pentane, 1:10) followed by recrystallization from ether-pentane, gave the colorless solid **2**: mp 67–68° (lit.⁶ mp 66–67°); 86%; NMR ($CDCl_3$), δ 1.34 (3 H, t, $J = 7.5$ Hz), 4.39 (2 H, q, $J = 7.5$ Hz), 5.94 (1 H, dd, $J = 14.5$ Hz, $J = 8.5$ Hz), 7.91 (1 H, dd, $J = 14.5$ Hz, $J = 12.5$ Hz), 9.41 (1 H, br d, $J = 12.5$ Hz), 9.65 ppm (1 H, d, $J = 8.5$ Hz); $\nu_{max}^{CCl_4}$ 3417 m, 1744 s, 1662 m, 1638 vs, and 1140 (s) cm^{-1} . λ_{max}^{ether} 257 nm ($\epsilon \sim 3.6 \times 10^4$); $M^+ 143$.

When a 9% solution of **2** in benzene was passed through a quartz tube⁷ heated to 650°, a 27% yield⁸ was attained of a colorless oil, **1**: $\nu_{max}^{CCl_4}$ 1801 m, 1777 s, 1619 s, 1549 m, 1219 s, and 1111 (s) cm^{-1} ; NMR (CCl_4), δ 6.38 (1 H, dd, $J = 7.2$ Hz, $J = 1.8$ Hz), 7.78 (1 H, d, $J = 7.2$ Hz), and 8.09 (1 H, br s); $M^+ 97$; $M^+ - CO$, 69; $M^+ - (CO + HCN)$, 42; λ_{max}^{ether} 262.5 ($\epsilon \sim 10^4$).⁹ Compound **1** is very sensitive to moisture and undergoes ready hydrolysis to *cis*-2-(formylamino)acrylic acid (**5**), characterized as its methyl ester **6**: mp 42°; NMR ($CDCl_3$), δ 3.78 (3 H, s), 5.27 (1 H, d, $J = 9.3$ Hz), 7.60 (1 H, dd, $J = 11.5$ Hz, $J = 9.3$ Hz), 8.43 (1 H, br s), and 10.44 (1 H, broad); $\nu_{max}^{CCl_4}$ 3320 m, 1719 m, 1690 s, 1638 s, 1205 (s) cm^{-1} ; λ_{max}^{ether} 264 nm ($\epsilon \sim 1.7 \times 10^4$); $M^+ 130$.

Preliminary studies of the thermal behavior of **2** in chloroform indicate that **2** is labile at even 75°, and gives rise to a mixture whose infrared spectrum shows a band at 2250 cm^{-1} , typical of isocyanate functionality.¹¹ Possibly this observation provides a clue to the remarkable conversion of **2** to **1** which may be mediated by the β -isocyanatoacrolein (**7**).¹⁰⁻¹²

Irradiation of argon matrix-isolated **1** ($M/R \sim 300$) with Pyrex-filtered mercury lamp light produces a species with

Scheme I



intense bands centered at 2140 cm^{-1} ($=C=O$), as well as a substance(s) possessing absorption at 1878 s and 1840 s (β -lactone carbonyl), 1243 m, 1058 s, 928 w, 917 w, 881 s, and 870 (s) cm^{-1} . Destruction of these species (*tentatively* formulated as **8** and **11**, respectively), is accomplished by irradiation through a water filter leading to hydrogen cyanide, acetylene, and carbon dioxide. From the preliminary results, the photochemical behavior of **1** appears to be similar to that of α -pyrone,¹³ and is the object of further study in our laboratories.¹⁴

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research. Special thanks are due Mr. Joe Laureni for preliminary experiments on the photochemistry of **1**.

References and Notes

- (1) For reports bearing on the 1,3-oxazin-6-one system: (a) C. C. Barker, *J. Chem. Soc.*, 317 (1954); (b) F. Eiden and B. S. Nagar, *Naturwissenschaften*, **50**, 403 (1963); (c) V. Sprio, *Gazz. Chim. Ital.*, **85**, 569 (1956); (d) T. T. Yee, W. E. McEwen, and A. P. Wolf, *Tetrahedron Lett.*, 3115 (1965); (e) H. B. Kagan and Y.-H. Suen, *Bull. Soc. Chim. Fr.*, 1819 (1966); (f) D. R. Eckroth and R. H. Squire, *Chem. Commun.*, 312 (1969); (g) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **36**, 2451 (1971); (h) A. J. Barker and R. K. Smalley, *Tetrahedron Lett.*, 4629 (1971); (i) H. R. Kricheldorf, *Angew. Chem., Int. Ed. Engl.*, **11**, 128 (1972); (j) J. W. Lown and K. Matsumoto, *Can. J. Chem.*, **50**, 584

- (1972); (k) H. Matsukubo and H. Kato, *J. Chem. Soc., Chem. Commun.*, 412 (1974); (l) W. Steglich, E. Buschmann, and O. Hollitzer, *Angew. Chem., Int. Ed. Engl.*, **13**, 533 (1974). For examples of 1,2-oxazin-6-ones: (m) E. P. Kohler and R. C. Goodwin, *J. Am. Chem. Soc.*, **49**, 219 (1927); (n) T. Ajello and S. Cusmano, *Gazz. Chim. Ital.*, **70**, 512 (1940); (o) C. Armengaud, *C. R. Acad. Sci.*, **254**, 3696 (1962); (p) M. Prasad and C.-G. Wermuth, *ibid.*, **264**, 405 (1967); (q) T. Severin, P. Adhikary, and I. Schnabel, *Chem. Ber.*, **102**, 1325 (1969). For 1,4-oxazin-2-ones: (r) E. Biekert and J. Sonnenbichler, *Chem. Ber.*, **95**, 1460 (1962); (s) K. Dickoré, K. Sasse, and K.-D. Bode, *Justus Liebig's Ann. Chem.*, **733**, 70 (1970); (t) W. Gauss and H. Heitzer, *ibid.*, 59 (1970).
- (2) Derivatives of this system have been prepared by G. Seybold, U. Jersak, and R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **12**, 847 (1973); B. M. Adger, M. Keating, C. W. Rees, and R. C. Storr, *J. Chem. Soc., Chem. Commun.*, 19 (1973).
- (3) G. Maier, *Angew. Chem., Int. Ed. Engl.*, **13**, 425 (1974), has described preliminary experiments with 1,3-oxazin-6-ones directed toward the synthesis of azacyclobutadiene.
- (4) Condensation of α -pyrone with dienophiles leads to cyclohexa-1,3-diene intermediates, see H. Behringer and P. Heckmaier, *Chem. Ber.*, **102**, 2835 (1969); J. A. Reed, C. L. Schilling, Jr., R. F. Tarvin, T. A. Rettig, and J. K. Stille, *J. Org. Chem.*, **34**, 2188 (1969), and references cited therein.
- (5) J. Terpinski and J. Dabrowski, *J. Mol. Struct.*, **4**, 285 (1969).
- (6) A. V. Stavrovskaya, T. V. Protopopova, and A. P. Skoldinov, *Zh. Org. Khim.*, **9**, 699 (1973), report only a melting point for **2**.
- (7) In a typical experiment, 1 ml of a 9% solution of **2** in benzene was injected (0.5 drop/sec) into a quartz tube (55 \times 0.9 cm) with a nitrogen flow (30 cm³/min). **1** was separated from the pyrolysate (which contained undecomposed **2**, 1–2% ethyl carbamate, and an as yet unidentified component), by gas chromatography (5 ft \times 0.25 in., 15% SE-30 on 80/100 Chromosorb W at 80°).
- (8) The yield, which has not been optimized, was based on unrecovered **2** and was sensitive to the surface of the pyrolysis tube.
- (9) The iminolactone **2** is very sensitive to moisture and did not consistently give reproducible values of the ultraviolet spectral parameters. The extinction coefficient is an average of several experiments ($\pm 20\%$).
- (10) In support of this hypothesis, Kricheldorf¹¹ has reported the facile isomerization of a β -isocyanatoacrylate to an alkoxy-1,3-oxazin-6-one.
- (11) Steglich et al.¹¹ have furnished examples of thermal conversions of derivatives of **9** to 1,3-oxazin-6-ones.
- (12) Hydrogen shifts, as formulated for **7** to **8**, have been proposed by W. H. Pirkle, H. Seto, and W. V. Turner, *J. Am. Chem. Soc.*, **92**, 6984 (1970); W. H. Pirkle and W. V. Turner, *J. Org. Chem.*, **40**, 1617 (1975).
- (13) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972); O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 244 (1973); R. G. S. Pong and J. S. Shirk, *ibid.*, **95**, 248 (1973).
- (14) These results parallel an earlier report by Maier³ of a derivative of **1**.

A. Krantz,* B. Hoppe

Department of Chemistry, State University of New York
Stony Brook, New York 11794

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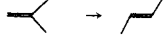

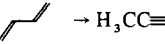
Concerning Criticisms of MINDO/3 by Pople¹ and Hehre²

Sir:

Pople¹ bases his criticisms of MINDO/3³ on calculated heats of reaction for 16 processes, mostly artificial, in 11 of which the errors in the MINDO/3 values are large. This is not surprising since they involve three compounds (CH₄, C(CH₃)₄, CH₃C \equiv CCH₃) for which the errors in the MINDO/3 heats of formation are unusually great. Since we not only tabulated the errors in our papers but also drew specific attention to them in the text,⁴ it is not clear to us what further point Pople is trying to make.

The Hartree-Fock values cited by Pople¹ were derived from 6-31 G* or 4-31 G calculations of energies of molecules, using assumed geometries. We might point out that there seems to be no difficulty in getting reasonably accurate estimates of molecular energies by semiempirical methods if one is willing to make such assumptions. This is illustrated in Table I by a comparison of Pople's results for his 16 reactions with those calculated by MINDO/1.⁵ The standard deviations for the nine reactions for which data are available by both methods are 3.22 (HF) and 1.75 (MINDO/1) kcal/mol, respectively. Note that MINDO/1 represented only a preliminary version. We did not pursue this approach further because of the limited scope of a treatment in which geometries are not optimized. With re-

Table I. Comparison of Errors in Heats of Reaction Calculated by ab Initio SCF and MINDO/1 Methods

Reaction	Error in calcd heat of reaction (kcal/mol)	
	"Hartree-Fock"	MINDO/1
CH ₃ CH ₃ + H ₂ \rightarrow 2CH ₄	-6.4	+0.2
CH ₂ =CH ₂ + 2CH ₄ \rightarrow 2CH ₃ CH ₃	-5.3	-1.6
HC \equiv CH + 4CH ₄ \rightarrow 3CH ₃ CH ₃	-12.1	-
CH ₃ CH ₂ CH ₃ + CH ₄ \rightarrow 2CH ₃ CH ₃	-1.2	0.0
CH ₃ (CH ₂) ₂ CH ₃ + 2CH ₄ \rightarrow 3CH ₃ CH ₃	-4.0	-1.1
CH ₃ (CH ₂) ₃ CH ₃ + 3CH ₄ \rightarrow 4CH ₃ CH ₃	-	-1.4
CH ₃ CH=CH ₂ + CH ₄ \rightarrow CH ₃ CH ₂ + CH ₂ =CH ₂	-1.3	+1.0
CH ₃ C \equiv CH + CH ₄ \rightarrow CH ₃ CH ₃ + HC \equiv CH	0.4	-
H ₂ C=C=CH ₂ + CH ₄ \rightarrow 2CH ₂ =CH ₂	-1.2	-
CH ₃ CH=CH ₂ \rightarrow Δ	0.0	+3.3
CH ₃ C \equiv CH \rightarrow Δ	3.5	-
CH(CH ₃) ₃ \rightarrow n-C ₄ H ₁₀	1.5	-0.4
C(CH ₃) ₄ \rightarrow n-C ₅ H ₁₂	-	+1.4
 \rightarrow 	-1.0	+1.6
 \rightarrow H ₃ CC \equiv CCH ₃	-2.1	-
C ₆ H ₆ + 6CH ₄ \rightarrow 3CH ₃ CH ₃ + 3CH ₂ CH ₂	+1.4	+3.0

gard to ref 2, it is surprising that no reference is made to calculations of bond lengths. Moreover the major errors he cites again occur in cases to which we have drawn specific attention in our papers.

Since very extensive tests of MINDO/3 have been published,³ including applications to a wide variety of chemical reactions,⁶ there seems no need for further comment.⁷

References and Notes

- (1) J. A. Pople, *J. Am. Chem. Soc.*, **97**, 5306 (1975).
- (2) W. J. Hehre, *J. Am. Chem. Soc.*, **97**, 5308 (1975).
- (3) (a) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975); (b) *ibid.*, **97**, 1294 (1975); (c) *ibid.*, **97**, 1302 (1975); (d) *ibid.*, **97**, 1307 (1975); (e) M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *ibid.*, **97**, 1311 (1975).
- (4) See in particular Figures 2 and 3 of part XXV,^{3a} Table I of part XXVI,^{3b} Table I of part XXVII,^{3c} Table I of part XXVIII,^{3d} Table I of part XXIX,^{3e} and the discussions on pp 1292,^{3a} 1294,^{3b} 1302,^{3c} 1309–1310,^{3d} and 1313.^{3e}
- (5) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969).
- (6) For a review see M. J. S. Dewar, *Chem. Brit.*, **11**, 97, (1975). Most of the work summarized has now been published or is in press.
- (7) EDITOR'S NOTE: This communication should have appeared concurrently with the communications cited in ref 1 and 2, but was inadvertently delayed in editorial processing.

Michael J. S. Dewar

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

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Catalytic Electrochemical Reduction of Acetylene in the Presence of a Molybdenum-Cysteine Complex

Sir:

A chemical model for nitrogenase enzyme¹ based on the binuclear molybdenum(V)-cysteine complex, Na₂Mo₂O₄(Cys)₂ (**1**),² has been shown to be effective in the catalytic reduction of nitrogenase substrates. A Mo(IV)-cysteine monomer, produced by reduction of **1** with NaBH₄ or Na₂S₂O₄, has been proposed^{1b} as the active species responsible for binding and reducing substrates such as acetylene.