

Figure 1. Fourth-order plot of two reduction runs (eq. 1) at -34° in ammonia containing initially *ca.* 0.15 *M* LiOEt: O, reactant concentrations initially in stoichiometric ratio; □, same except initial Li concentration doubled.

mental kinetic attributes of reduction 1 are revealed by our data: the rate of this reaction is profoundly affected by the concentration of a product, lithium ethoxide, and the rate law is fourth order in reactants, not third.

Plotted in Figure 1 are kinetic data for runs involving reaction solutions which were initially saturated with lithium ethoxide (*ca.* 0.15 *M*); the final points plotted for each run represent about 80% reaction. The two are plotted as fourth-order integrals vs. time so that if the reaction is first order each in alcohol and benzene and second order in lithium, coincidental plots of slope k_4 (eq. 3) should result. In one of the depicted runs the three reactants were in stoichiometric ratio (*ca.* 0.07, 0.14, and 0.14 *M*, respectively) while in the other the lithium concentration was doubled. The k_4 value calculated (linear least-squares slope) from the former run is 8.2 ± 0.4 , and from the latter run, 8.0 ± 0.4 (concn.⁻³ sec.⁻¹). Data from these two runs plotted as third order-integrals are not coincidental, nor do they show the same slope.

$$-d(\text{C}_6\text{H}_6)/dt = k_4(\text{C}_6\text{H}_6)(\text{EtOH})(\text{Li})^2 \quad (3)$$

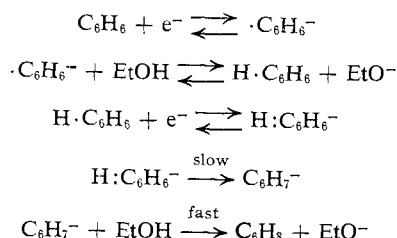
Satisfactory linear fourth-order plots (average $k_4 = 8.0$) were obtained from eight runs involving other variations in the concentrations of reactants (in the range *ca.* 0.03–0.3 *M*), in which the concentration of a product, lithium ethoxide, was initially sufficient for saturation. From runs with less or no initial lithium

Table I

Initial rate constant, k_4	LiOEt added, ^a <i>M</i>
71.2 ± 1.7	0.0
17.0 ± 1.9	0.05
8.2 ± 0.4	0.15 ^b
7.8 ± 0.3	0.60 ^c

^a Sufficient initial LiOEt to give this concentration if all were in solution. ^b Solution initially slightly turbid. ^c Considerable obvious precipitate.

ethoxide, much higher rate constants were apparent from initial slopes of fourth-order plots; deviation from linearity of these plots was also apparent, due both to buildup of ethoxide and to formation of some hydrogen before significant ethoxide was present.¹⁰ The effect of this base on the rate constant is shown in Table I. This effect and fourth-order kinetics can obviously be rationalized with hypothesis B above; indeed, it would seem inconsistent with fourth-order kinetics if there were no effect by base. The details of mechanism we will discuss subsequently.¹¹



Thus we conclude that the frequently cited^{13b-d,12a-d} statement that the rate “of metal-ammonia-alcohol reduction of benzene and some substituted benzenes . . . is governed by the law $d(\text{ArH})/dt = k(\text{ArH})(\text{M})\cdot(\text{ROH})^{2.5}$ is in error, at least in being too general. We wish to emphasize that the new findings reported here concern just the system in eq. 1. Currently we are studying other systems, *e.g.*, the use of *t*-butyl alcohol as proton source.^{12c}

(11) Briefly, by hypothesis B, as outlined below, after reversible addition of the first electron protonation occurs in an equilibrium. Increasing ethoxide (until saturation) would obviously so influence this equilibrium as to decrease the over-all reaction rate. We suggest that addition of the second electron could also involve an equilibrium and that the intermediate ($\text{H}:\text{C}_6\text{H}_6^-$) at that stage of reduction is a π -complex. The complex rearranges in a rate-determining step to the cyclohexadienyl anion (C_6H_7^-), which is rapidly protonated to product (C_6H_8).

(12) (a) W. L. Jolly in “Solvated Electron,” *Advances in Chemistry Series*, No. 50, American Chemical Society, Washington, D. C., 1965, pp. 27–35; (b) A. P. Krapcho and M. E. Nadel, *J. Am. Chem. Soc.*, **86**, 1096 (1964); (c) A. P. Krapcho and A. A. Bothner-By, *ibid.*, **82**, 751 (1960); (d) H. E. Zimmerman, *Tetrahedron*, **16**, 169 (1961).

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1,3,4-Oxadiazole

Sir:

The first of four possible isomeric unsubstituted oxadiazoles A–D was reported by the Belgian workers,¹

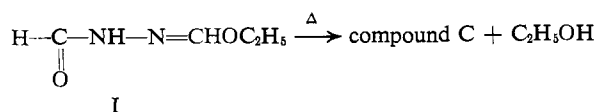


who made the thermally unstable 1,2,4-oxadiazole (A). Recently, Olofson and Michelman² prepared the thermally stable 1,2,5-oxadiazole parent nucleus B. We wish to record the preparation of the thermally stable 1,3,4-oxadiazole (C), the only isomer not containing an oxygen–nitrogen bond.

(1) C. Moussebois, R. Lenaers, and F. Eloy, *Helv. Chim. Acta*, **45**, 446 (1962).

(2) R. A. Olofson and J. S. Michelman, *J. Org. Chem.*, **30**, 1854 (1965).

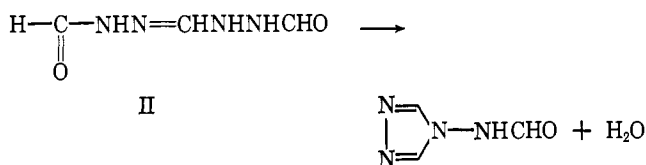
The thermolysis of ethyl formate formylhydrazone (I)



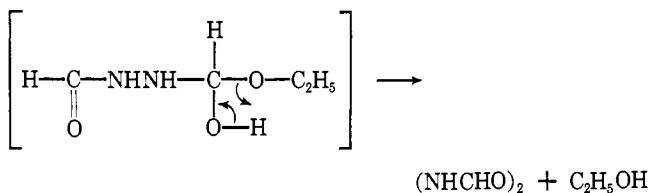
at atmospheric pressure gave 1,3,4-oxadiazole, a liquid at room temperature, b.p. 150°. *Anal.* Calcd.: C, 34.29; H, 2.88; N, 40.00. Found: C, 34.56; H, 3.19; N, 39.71; mol. wt., 70 (mass spectrometry); *m/e* (relative intensity, %) 13 (3.0), 14 (3.7), 18 (2.3), 27 (5.0), 28 (2.5), 29 (23.0), 31 (1.4), 41 (14.0), 42 (69.0), 43 (3.4), 55 (1.6), 70 (100.0), and 71 (3.2); n_{D}^{25} 1.4300; n.m.r. τ 0.60 (neat), 1.27 (CDCl₃); no ultraviolet maximum above 200 m μ ; infrared λ_{max} 3.17, 6.50, 6.67, 7.83, 9.17, 10.46, 10.82, and 11.57 μ (CHCl₃).

Ethyl formate formylhydrazone (I) was formed by heating an ethanol solution of formic acid hydrazide and excess triethyl orthoformate. Compound I showed unusual n.m.r. spectral data, which will be the subject of a separate communication.

Reaction, under anhydrous conditions, of very pure formic acid hydrazide and (a) excess triethyl orthoformate heated under reflux, or (b) an equimolar quantity of compound I heated at 100°, or in ethanol at reflux, gave the same two products. These products are N,N'-diformylhydrazine and 4-formylamino-1,2,4-triazole. Seemingly, N,N'-di(formamido)formamidine (II), formed from the reaction of compound I and formic



acid hydrazide by the elimination of 1 mole of ethanol, readily lost a molecule of water to give the triazole. The water so formed reacted with compound I to give



N,N'-diformylhydrazine and ethanol.

The reaction has been extended by the use of appropriate starting materials to include the preparation of the unreported monoalkyl and unsymmetrical 2,5-dialkyl-1,3,4-oxadiazoles. A detailed report of the study is in preparation.

Acknowledgment. The microanalyses were performed by W. L. Brown and associates. The physical measurements were made by L. G. Tensmeyer, W. Hargrove, and associates.

(3) The CEC 21-110 mass spectrometer was used: reservoir temperature 250°, ionization voltage 70 v., acceleration voltage 8 kv., and block temperature 200°.

(4) Determined with a Varian HA-60 spectrometer.

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Deuteron Magnetic Resonance Spectroscopy of Large Molecules. Spectrum of Chlorophyll a-d₇₂¹

Sir:

By comparison to proton magnetic resonance spectroscopy, deuteron magnetic resonance (d.m.r.) is as yet little explored, and its scope remains to be defined. Diehl and Liepert² have made the most extensive investigation of d.m.r. so far reported and have shown its applicability to compounds of low molecular weight. For large, unsymmetrical molecules, the increase in correlation time combined with the deuterium electric quadrupole relaxation³ could conceivably broaden the resonance lines sufficiently to obliterate the d.m.r. spectrum. The successful culture of fully deuterated microorganisms makes available a great variety of fully deuterated compounds,⁴ many of the more interesting of which have molecular weights in the range 300 to 1000. We can now report the first d.m.r. data that have been obtained for a large and complex natural product and are able to show that useful d.m.r. spectra can be obtained with highly anisotropic large molecules.

Table I lists the principal lines in a 15.4-Mc. spectrum⁵ of methyl (CH₃) deutero pheophorbide a. The observed line widths of 2 to 7 c.p.s. are considerably

Table I. Chemical Shifts (δ , p.p.m.) in Methyl Pheophorbide^a

Position ^b	D.m.r. Methyl deutero-pheophorbide a (0.12 M)	P.m.r. ^c Methyl pheophorbide a (0.12 M)	Δ , (d.m.r.) - (p.m.r.)
11	3.33	3.38	-0.05
5	3.64	3.65	-0.01
1	3.96	4.00	-0.04
3	4.31	4.35	-0.04
4	5.71	5.67	+0.04

^a Chemical shifts are given in p.p.m. from internal CDCl₃ and CHCl₃; high-field values are positive. The d.m.r. chemical shifts represent the average of ten measurements with standard deviations not greater than ± 0.03 p.p.m. ^b See ref. 6 for chlorophyll position numbering. Protons no. 1, 3, and 5 are methyl groups attached directly to the macrocycle; no. 4 is the CH₃ of the ethyl group at position 4; and no. 11 is the methyl group of the carbomethoxy group at carbon 10 in the isocyclic ring V of chlorin. ^c Reference 6.

larger than those commonly observed in p.m.r., but they are quite comparable to the d.m.r. line widths for low molecular weight alcohols observed by Diehl and Liepert.² The deuteron chemical shifts (p.p.m. from CDCl₃ as solvent and internal standard) for deutero pheophorbide a are directly comparable to the proton chemical shifts for the same groups in ordinary methyl pheophorbide a⁶ at the same concentration. The

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) P. Diehl and Th. Liepert, *Helv. Chim. Acta*, **47**, 545 (1964).

(3) A. Abragam, "The Principles of Nuclear Magnetism," The Clarendon Press, Oxford, 1961, p. 313 ff.

(4) J. J. Katz, 39th Annual Priestley Lectures, The Pennsylvania State University, University Park, Pa., 1965.

(5) The d.m.r. spectra reported here were recorded at a magnetic field of about 23.4 kgauss by the use of a slow sweep unit with a Varian V-4311 n.m.r. spectrometer, operated in the high-resolution mode. A conventional side-band technique (with high modulation indexes) was used for the calibrations. The samples were contained in standard 5-mm. tubes.

(6) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85**, 3809 (1963).