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Registry No. $CH_3CHO{\cdot}BF_3$, 306-73-0; $PhCHO{\cdot}BF_3$, 456-30-4; $(CH_3)_2CO{\cdot}BF_3$, 661-27-8; CH_3CHO, 75-07-0; PhCHO, 100-52-7; CH_3COCH_3, 67-64-1; BF_3, 7637-07-2.

Supplementary Material Available: Table of selected structural parameters and Z-matrix of complexes 1–12 (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Electrooxidative Cyclization of *N*-Acylhydrazones of Aldehydes and Ketones to Δ^3-1,3,4-Oxadiazolines and 1,3,4-Oxadiazoles

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The electrolytic oxidation of ketone *N*-acylhydrazones (1) in methanolic sodium acetate induced their intramolecular cyclization to the corresponding 2-methoxy-Δ^3-1,3,4-oxadiazolines **3**. The thermal stability of a given oxadiazoline and what products were formed by its thermal decomposition was found to depend on the natures of the substituents at C-2. Thus, 2-methoxy-2-phenyloxadiazolines preferentially yielded oxiranes **5**, whereas 2-alkyl-2-methoxyoxadiazolines preferentially gave enol ethers **6**. 2,2-Dimethoxyoxadiazolines decomposed to the parent ketones and many unidentified products. The electrolytic oxidation of aldehyde *N*-acylhydrazones **2** gave 2,5-disubstituted 1,3,4-oxadiazoles **4**. The oxidative cyclization of the *N*-benzoylhydrazones of aliphatic aldehydes gave especially high yields of the corresponding heterocycles.

Introduction

The oxidative cyclization of such hydrazine derivatives of aldehydes and ketones as carbohydrazones, thiocarbohydrazones, semicarbazones, and thiosemicarbazones to nitrogen-containing heterocycles can be induced by a number of oxidizing agents.[1] However, to induce such cyclizations electrolytically has certain merits. Electrochemical oxidations obviously do not require oxidizing chemicals and, furthermore, can be performed under mild conditions, e.g., at room temperature. Indeed, many reports[2] of the electrochemically induced intra- and intermolecular cyclization of hydrazine derivatives of aldehydes and ketones have appeared. Most, however, describe the electrolysis of solutions of such compounds in aprotic solvents like acetonitrile.

Previously, we reported[3] that the electrochemical oxidation of ketone *N*-acylhydrazones **1** in methanolic sodium cyanide gives nitrogen and the corresponding nitriles (R_1R_2CHCN) and methyl esters ($MeOCOR_3$). Here, we report that the electrochemical oxidation of **1** and aldehyde *N*-acylhydrazones **2** in methanolic sodium acetate affords oxadiazolines **3** and oxadiazoles **4**, respectively. We also describe the products of the thermal decomposition of compounds **3**.

Results and Discussion

Preparative-scale constant-current electrolyses were performed at room temperature in a divided cell equipped with a carbon rod anode. The results of the electrooxidation of aliphatic ketone *N*-acylhydrazones **1** are summarized in Table I. In all cases, the starting hydrazone **1** was almost wholly consumed by the time 3 F/mol of electricity had passed through the solution and was converted into the corresponding 2-methoxy-Δ^3-1,3,4-oxadiazoline **3** in a yield of between 30 and 77%. The yield of

Scheme I

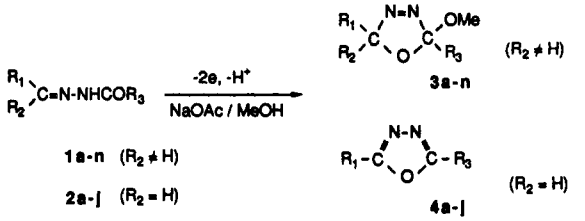

Table I. Synthesis of 2-Methoxy-Δ^3-1,3,4-oxadiazolines by the Electrooxidative Cyclization of Ketone *N*-Acylhydrazones[a]

	hydrazone 1			oxadiazoline 3 (yield, %)[b]
	R_1	R_2	R_3	
1a	Me	Me	Ph	**3a** (70)
1b	*n*-Pr	*n*-Pr	Ph	**3b** (65)
1c	*i*-Pr	*i*-Pr	Ph	**3c** (67)
1d	$-(CH_2)_5-$		Ph	**3d** (77)
1e	Me	Me	Me	**3e** (61)
1f	*n*-Pr	*n*-Pr	Me	**3f** (67)
1g	$-(CH_2)_5-$		Me	**3g** (70)
1h	$-(CH_2)_5-$		*n*-Pr	**3h** (73)
1i	$-(CH_2)_5-$		*i*-Pr	**3i** (73)
1j	$-(CH_2)_4-$		*n*-Pr	**3j** (71)
1k	*n*-Pr	*n*-Pr	*n*-Pr	**3k** (66)
1l	Me	Me	OMe	**3l** (30)
1m	*n*-Pr	*n*-Pr	OMe	**3m** (43)
1n	$-(CH_2)_5-$		OMe	**3n** (50)

[a] Analyte: hydrazone (30 mmol), NaOAc (15 mmol), and MeOH (80 mL). Strength of constant current: 0.5 A. Quantity of electricity: 3 F/mol. Temperature: ca. 15 °C. [b] Isolated yield.

(1) For reviews of the oxidative cyclization of hydrazine derivatives of aldehydes and ketones, see, for example: (a) Butler, R. N.; Scott, F. L.; O'Mahony, T. A. F. *Chem. Rev.* **1973**, *73*, 93. (b) Warkentin, J. *Synthesis* **1970**, 279. (c) Butler, R. N. *Chem. and Ind. (London)* **1968**, 437.

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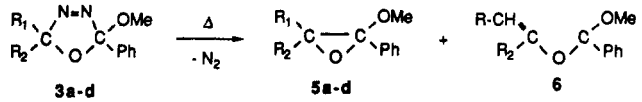
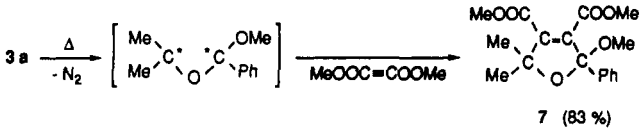
Scheme II



3, 5

a, R_1, R_2 = Me — 5a (90 %)
b, R_1, R_2 = n-Pr — 5b (77 %) + 6b: R = Et, R_2 = n-Pr (22 %)
c, R_1, R_2 = i-Pr — 5c (92 %)
d, R_1, R_2 = -$(CH_2)_5$- — 5d (71 %) + 6d: R, R_2 = -$(CH_2)_4$- (18 %)

Scheme III



7 (83 %)

3 as a function of the *N*-acyl group was benzoyl ≥ aliphatic acyl > carbomethoxy. Increasing the bulkiness of the alkyl groups on the azomethinyl carbon did not significantly affect the yield of the cyclic product.

Most oxadiazolines are unstable at room temperature. They are known to decompose readily, affording the corresponding carbonyl ylides and N_2.[4] Hence, methods for their synthesis are few. Thus, Hoffmann and Luthardt[5] succeeded in preparing a number of 2-acetoxy-Δ^3-1,3,4-oxadiazolines by the low-temperature oxidation of ketone *N*-benzoylhydrazones with lead tetraacetate in methylene chloride. If, however, an alcohol was used as the solvent instead of methylene chloride, a 2-alkoxyoxadiazoline was obtained along with the corresponding 2-acetoxyoxadiazolines.[6] Furthermore, Shimizu and Bartlett[7] found that diaryl- and (arylmethyl)diazomethanes cycloadd to penta- and hexafluoroacetone to give the corresponding difluoromethyl- and trifluoromethyl-substituted aryloxadiazolines.

However, the 2-methoxyoxadiazolines **3** that are obtained by the electrolytic oxidation of ketone *N*-acylhydrazones are sufficiently stable to be isolated by column chromatography. A number of them can also be distilled under reduced pressure. However, some, especially the phenyloxadiazolines **3a–d**, very slowly eliminate nitrogen even on standing at room temperature. Consequently, combustion analysis gave unsatisfactory results. Therefore, the structures of these compounds were inferred from their spectra and from the structures of the products of their thermal decomposition.

The thermal stability of a given 2-methoxyoxadiazoline and what products were formed by its thermal decomposition were highly dependent on the nature of the substituent R_3. For example, the 2-phenyloxadiazolines **3a–d** vigorously evolved nitrogen when heated at ca. 95 °C and gave the oxiranes **5a–d**, respectively, in good yields. The enol ethers **6b** and **6d** were also formed, as byproducts, from **3b** and **3d**, respectively. Methoxyoxiranes like compounds **5** can be used to prepare α-hydroxy ketones and

Scheme IV

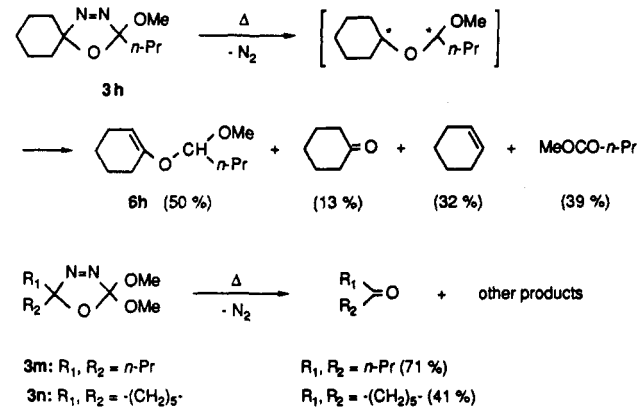


Table II. Synthesis of 2,5-Disubstituted 1,3,4-Oxadiazoles by the Electrooxidative Cyclization of Aldehyde *N*-Acylhydrazones[a]

	hydrazone 2		
	R_1	R_3	oxadiazole 4 (yield, %)[b]
2a	Me	*n*-Pr	**4a** (50)
2b	*n*-Pr	Me	**4b** = **4a** (47)
2c	*n*-Pr	*n*-Pr	**4c** (57)
2d	*i*-Pr	*n*-Pr	**4d** (58)
2e	*n*-Pr	*i*-Pr	**4e** = **4d** (58)
2f	Me	Ph	**4f** (81)
2g	*n*-Pr	Ph	**4g** (86)
2h	*i*-Pr	Ph	**4h** (89)
2i	Ph	*n*-Pr	**4i** = **4g** (22)
2j	Ph	Ph	**4j** (36)

[a] Analyte: hydrazone (20 mmol), NaOAc (40 mmol), and MeOH (80 mL). Strength of constant current: 0.5 A. Quantity of electricity: 4–5 F/mol. [b] Isolated yield.

derivatives thereof.[8] The latter are usually prepared by the treatment of α-halo ketones with sodium methoxide[9] or by the oxygenation of enol ethers by peracids in methanol.[10] Thus, with the method described here, which makes use of an intramolecular coupling reaction, it may be possible to prepare α-hydroxy ketones that are otherwise inaccessible by the usual methods. An attempt was made to trap the intermediate carbonyl ylide that is produced by the thermal decomposition of **3a**. Thus, refluxing a benzene solution of **3a** and dimethyl acetylenedicarboxylate gave the expected dihydrofuran **7** in a yield of 83%.[11]

The 2-alkyl-2-methoxyoxadiazolines **3e–k** decomposed at ca. 120 °C. Their thermal decomposition, unlike that of the 2-methoxy-2-phenyloxadiazolines, did not afford oxiranes. For example, the pyrolysis of **3h** derived from cyclohexanone *N*-butyrylhydrazone gave the enol ether **6h** (50%), methyl propionate (39%), cyclohexene (32%), and cyclohexanone (13%). That a relatively large amount of **6h** was produced indicated that, rather than cyclizing to an oxirane, the intermediate carbonyl ylide preferentially underwent a 1,4-H transfer. It was also clear that another process, fragmentation of the ylide to carbonyl compounds

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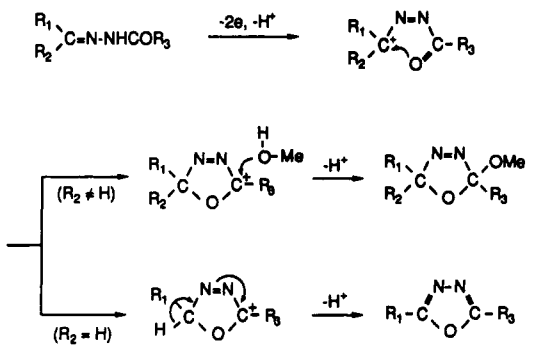
Scheme V



and carbenes, competed with the 1,4-H transfer.[4a,g,7] Although the 2,2-dimethoxyoxadiazolines **31–n** are appreciably more stable than 2-alkyl- or 2-phenyl-2-methoxyoxadiazolines, they also slowly decompose, when heated above 130 °C, to yield the parent ketone and small amounts of many unidentified products.

The electrolytic oxidation of aldehyde *N*-acylhydrazones **2** gave the corresponding 1,3,4-oxadiazoles **4** (Table II). 1,3,4-Oxadiazoles can also be obtained by the chemical oxidation of compounds **2** by lead tetraacetate[12] or by the dehydration of 1,2-diacylhydrazines.[13] As the *N*-benzoylhydrazones of aliphatic ketones gave relatively high yields of oxadiazolines, so also did the *N*-benzoylhydrazones of aliphatic aldehydes give relatively high yields of oxadiazoles. Thus, the *N*-acylhydrazones of aliphatic aldehydes gave the corresponding oxadiazoles in yields of 50–60%. The yields did not depend on the nature of the substituents R_1 and R_3. However, it appears that the *N*-acylhydrazones of aromatic aldehydes can be expected to give only low yields of compounds **4**. For example, both the *N*-benzoylhydrazone of butyraldehyde (**2g**) and the *N*-butyrylhydrazone of benzaldehyde (**2i**) gave the identical product, 2-*n*-propyl-5-phenyl-1,3,4-oxadiazole (**4g**). However, the yield of **4g** from **2g** was 86%, whereas that from **2i** was only 22%. The electrolytic oxidation of **2i** also produced methyl butyrate (60%), benzaldehyde dimethyl acetal (22%), methyl benzoate (18%), benzyl alcohol (12%), and benzaldehyde (10%).

The electrochemically induced cyclizations described here appear to involve a cationic intermediate generated from **1** or **2** by the loss of two electrons and one proton.[3] In the absence of a strong nucleophile like cyanide ion, the cationic center at the azomethinyl carbon of the intermediate would be attacked intramolecularly by the carbonyl oxygen (Scheme V). In the case of aldehyde *N*-acylhydrazones, the product of such an attack can lose a proton and rearrange to form a stable oxadiazole. However, in the case of ketone *N*-acylhydrazones, which do not bear a hydrogen atom on the azomethinyl carbon, such a pathway is not open. One way the cationic intermediate can then form a stable product is by combining with a Lewis base, e.g., methanol, to form a 2-methoxyoxadiazoline.

An attempt to convert acetophenone *N*-benzoylhydrazone to the corresponding 2-methoxyoxadiazoline was unsuccessful. During electrolysis, evolution of N_2 from the anolyte was observed. This suggested that either a different sort of reaction was occurring or that the product 2-methoxyoxadiazoline decomposed as soon as it formed.

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Experimental Section

^{1}H NMR spectra of $CDCl_3$ solutions were recorded at 200 MHz. Chemical shifts are reported in ppm downfield (δ) from internal Me_4Si. GC/MS analyses were performed with a 1-m glass column packed with 2% FFAP on Diasolid. The spectrometer was operated at an ionization potential of 20 eV. GLC analyses were performed with stainless steel columns packed with 10% FFAP on Chromosorb W AW. N_2 served as the carrier gas. The gas chromatograph was equipped with a flame ionization detector. A 2-m glass column packed with 10% FFAP on Uniport B was used for preparative GLC. He served as the carrier gas.

Materials. *N*-Acylhydrazones were prepared by the reaction of an appropriate *N*-acylhydrazine and a ketone or aldehyde.[3] The physical properties, including spectra, of previously unknown compounds are described in the supplementary material. Of previously known compounds, the following were used: **1a**, mp 145–146 °C (lit.[14] mp 142 °C); **1e**, mp 139 °C (lit.[15] mp 140 °C); **2b**, mp 78–79 °C (lit.[16] mp 75.5–76.5 °C); **2f**, mp 161–163 °C (lit.[17] mp 162 °C); **2i**, mp 102–103 °C (lit.[18] mp 98 °C); **2j**, mp 205–207 °C (lit.[17] mp 206 °C).

Preparative-Scale Electrolyses. The electrolysis apparatus that was used was similar to that described previously. All electrolyses were performed in a 100-mL divided cell. A fine-frit glass cup served as the cathodic compartment. Four carbon rods (8-mm dia × 100 mm) served as the anode, and a Pt coil served as the cathode. Throughout an electrolysis, the cell was cooled with running water and the anolyte was stirred magnetically. The progress of the reaction was monitored by either TLC or GLC.

Electrolysis of Ketone *N*-Acylhydrazones. General Procedure. A solution of **1** (50 mmol), MeOH (80 mL), and NaOAc (15 mmol) was electrooxidized by passing a constant current of 0.5 A. After 3.0 F/mol of electricity had been passed, the solvent was evaporated at rt in vacuo. Water was added to the residue. The two liquid layers that formed were separated. The oily organic layer was extracted with Et_2O (20 mL × 3). The combined extracts were washed with water (30 mL), dried (Na_2SO_4), and concentrated in vacuo at rt. The residue was purified by column chromatography on silica gel (Merck Kieselgel 60, 70–230 mesh; column: 4 cm i.d. × 30 cm glass; eluant: benzene). The fraction of **3a–d** usually contained about 10% of methyl benzoate. The ester was removed by evaporation in vacuo (ca. 0.2 mmHg) at rt.

2,2-Dimethyl-5-methoxy-5-phenyl-1,3,4-Δ^3-oxadiazoline (3a). Its ^{1}H NMR spectrum was consistent with that described in the literature:[7b] IR (neat) ν 1280, 1235, 1105, 1060 cm^{-1}; ^{1}H NMR δ 1.52 (s, 3 H, CH_3–), 1.69 (s, 3 H, CH_3–), 3.22 (s, 3 H, CH_3O–), 7.3–7.7 (m, 5 H, *Ph*).

A solution of **3a** (2.06 g, 10.0 mmol) and benzene (40 mL) was refluxed for 5 h. Subsequent distillation of the solution under reduced pressure gave the oxirane **5a** (1.60 g, 90%): bp 92–94 °C (20 mm) [lit.[9a] bp 68–70 °C (3 mm)]; IR (neat) ν 2960, 1265, 1230, 1130, 1110, 760, 700 cm^{-1}; ^{1}H NMR δ 1.00 (s, 3 H, CH_3–), 1.54 (s, 3 H, CH_3–), 3.20 (s, 3 H, CH_3O–), 7.14–7.55 (m, 5 H, *Ph*); MS *m/e* (relative intensity) 43 (28), 77 (40), 105 (100), 109 (17), 135 (44), 178 (M^+, 2). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.13; H, 8.11.

Thermal Decomposition of 2a in the Presence of Dimethyl Acetylenedicarboxylate. A solution of **2a** (2.0 g, 9.7 mmol), dimethyl acetylenedicarboxylate (1.70 g, 12 mmol), and benzene (40 mL) was refluxed for 4 h. The benzene was then evapolated. The residue was distilled in vacuo to give the dihydrofuran **7** (2.52 g, 83%): bp 125 °C (0.15 mm); IR (neat) ν 2960, 1265, 1230, 1130, 1110, 760, 700 cm^{-1}; ^{1}H NMR δ 1.66 (s, 3 H, CH_3–), 1.68 (s, 3 H, CH_3–), 3.33 (s, 3 H, CH_3O–), 3.69 (s, 3 H, CH_3OCO), 3.79 (s, 3 H, CH_3OCO), 7.3–7.5 (m, 5 H, *Ph*); MS *m/e* (relative intensity) 43 (12), 77 (10), 105 (36), 213 (14), 230 (16), 243 (13), 289 (100), 290 (19), 305 (M^+ – 15, 6). Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.92; H, 6.33.

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2,2-Di-*n*-propyl-5-methoxy-5-phenyl-1,3,4-Δ³-oxadiazoline (3b): IR (neat) ν 2940, 1450, 1090, 985, 900, 755 cm^{-1}; ^{1}H NMR δ 0.89, 0.95 (t, t, J = 7.3 Hz each, total 6 H, 2 CH_3–), 1.1–2.1 (m, total 8 H, 2 $CH_3CH_2CH_2$–), 3.20 (s, 3 H, CH_3O–), 7.3–7.8 (m, 5 H, *Ph*).

A solution of **3b** (2.37 g, 9.05 mmol) and benzene (50 mL) was refluxed for 5 h. Subsequent vacuum distillation of the solution gave 2.06 g of a colorless oil, bp 110–118 °C (4 mm). GLC analysis (0.5 m FFAP; column temperature: 110 °C; flow rate = 40 mL/min) showed two compounds to be present. The two were isolated by preparative GLC, and their structures were inferred from their spectra. The more abundant of the two (t_R = 3.4 min) was the oxirane **5b**, whereas the other (t_R = 6.1 min) was the enol ether **6b**. The yields of **5b** and **6b** were estimated, by GLC, to be 77% and 22%, respectively. **5b**: IR (neat) ν 2930, 1445, 1260, 1120, 1070, 985, 960, 765, 700 cm^{-1}; ^{1}H NMR δ 0.72 (t, J = 7 Hz, 3 H, CH_3CH_2–), 1.01 (t, J = 7 Hz, 3 H, CH_3CH_2–), 1.1–2.0 (m, 8 H, 2 $CH_3CH_2CH_2$–), 3.18 (s, 3 H, CH_3O–), 7.3–7.5 (m, 5 H, *Ph*); MS m/e (relative intensity) 43 (36), 77 (34), 105 (100), 163 (43), 135 (44), 234 (M^+, 1). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.97; H, 9.63. **6b**: IR (neat) ν 2920, 1660, 1445, 1270, 1180, 1065, 740, 700 cm^{-1}; ^{1}H NMR δ 0.93 (t, J = 7 Hz, 6 H, 2 CH_3CH_2–), 1.5–1.7 (m, 2 H, $CH_3CH_2CH_2$–), 1.99 (pent, J = 7 Hz, 2 H, CH_3CH_2CH=), 2.21 (t, J = 7 Hz, 2 H, CH_2CH_2C) 3.30 (s, 3 H, CH_3O–), 4.67 (t, J = 7 Hz, 1 H, OC*H*), 7.3–7.5 (m, 5 H, *Ph*); MS m/e (relative intensity) 77 (22), 105 (22), 121 (100), 163 (9), 234 (M^+, <1).

2,2-Diisopropyl-5-methoxy-5-phenyl-1,3,4-Δ³-oxadiazoline (3c): IR (neat) ν 2970, 1450, 1090, 1055, 980, 760 cm^{-1}; ^{1}H NMR δ 0.74, 0.80 (d, d, J = 6.6 and 7.3 Hz, total 6 H, 2 CH_3CH–), 1.03, 1.05 (d, d, J = 7.3 and 6.6 Hz, total 6 H, 2 CH_3CH–), 2.35–2.55 (m, 2 H, CH_3CH–), 3.18 (s, 3 H, CH_3O–), 7.3–7.8 (m, 5 H, *Ph*).

Refluxing a solution of **3c** (3.70 g, 14.1 mmol) and benzene (40 mL) for 5 h gave oxirane **5c** (3.05 g, 92%): bp 103–104 °C (5 mm): IR (neat) ν 2940, 1450, 1275, 1240, 1100, 1070, 980, 705 cm^{-1}; ^{1}H NMR δ 0.73 (d, J = 6.6 Hz, 3 H, CH_3CH–), 0.88 (d, J = 7.3 Hz, 3 H, CH_3CH–), 1.03 (d, 3 H, J = 7.3 Hz, CH_3CH–), 1.15–1.30, 1.23 (m, d, J = 6.6 Hz, total 4 H, CH_3CH–, CH_3CH–), 2.25–2.45 (m, 1 H, CH_3CH–), 3.12 (s, 3 H, CH_3O–), 7.3–7.5 (m, 5 H, *Ph*); MS m/e (relative intensity) 77 (29), 83 (36), 105 (100), 163 (39), 234 (M^+, <1). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.60; H, 9.67.

2,2-Pentamethylene-5-methoxy-5-phenyl-1,3,4-Δ³-oxadiazoline (3d): IR (neat) ν 2930, 1440, 1270, 1090, 890 cm^{-1}; ^{1}H NMR δ 1.4–2.2 (br m, 10 H, cyclo C_6H_{10}), 3.23 (s, 3 H, CH_3O–), 7.3–7.8 (m, 5 H, *Ph*).

Refluxing a solution of **3d** (3.27 g, 13.3 mmol) and benzene (40 mL) gave 2.58 g of a colorless oil, bp 149–158 °C (17 mm). GLC analysis (0.5 m FFAP; column temperature: 110 °C; flow rate: 80 mL/min) indicated that the oil contained two compounds. The two were isolated by preparative GLC, and their structures were inferred from their spectra. The more abundant of the two (t_R = 3.2 min) was the oxirane **5d**, whereas the other (t_R = 6.9 min) was the enol ether **6d**. The yields of **5d** and **6d** were estimated, by GLC, to be 71% and 18%, respectively. **5d**: [lit.[9b] bp 97–100 °C (0.4 mm)]; IR (neat) ν 2930, 1445, 1270, 1210, 1130, 1075, 985, 950, 770, 700 cm^{-1}; ^{1}H NMR δ 1.1–2.1 (m, 10 H, cyclo C_6H_{10}), 3.20 (s, 3 H, CH_3O–), 7.3–7.5 (m, 5 H, *Ph*); MS m/e (relative intensity) 77 (28), 105 (100), 106 (9), 147 (8), 218 (M^+, 1). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.84; H, 8.52. **6d**: IR (neat) ν 2920, 1715, 1670, 1445, 1270, 1155, 1070, 1015, 745, 700 cm^{-1}; ^{1}H NMR δ 1.4–2.2 (m, 8 H, cyclo C_6H_8), 3.33 (s, 3 H, CH_3O–), 4.87 (distorted t, 1 H, cyclo CH_2CH=C), 5.83 (s, 1 H, OC*H*), 7.3–7.5 (m, 5 H, *Ph*); MS m/e (relative intensity) 77 (40), 91 (39), 105 (100), 123 (55), 218 (M^+, 3).

2-Methoxy-2,5,5-trimethyl-1,3,4-Δ³-oxadiazoline (3e). Its ^{1}H NMR spectrum was consistent with that described in the literature:[7c] bp 36–37 °C (7 mm); IR (neat) ν 2980, 1460, 1380, 1190, 1055, 990, 910 cm^{-1}; ^{1}H NMR δ 1.48 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 3.13 (s, 3 H, OCH_3); MS m/e (relative intensity) 15 (24), 28 (29), 43 (100), 116 (M^+ – 28, 2). Anal. Calcd for $C_6H_{12}N_2O_2$: C, 49.98; H, 8.39; N, 19.43. Found: C, 49.89; H, 8.33; N, 19.57.

2-Methoxy-2-methyl-5,5-di-*n*-propyl-1,3,4-Δ³-oxadiazoline (3f): bp 84–85 °C (4 mm); IR (neat) ν 2940, 1230, 1145, 1055, 990, 920 cm^{-1}; ^{1}H NMR δ 0.92, 0.95 (t, t?, J = 7.3 and 6.8 Hz, 6 H, 2 CH_3CH_2), 1.1–1.9, 1.68 (m, s, total 11 H, 2 $CH_3CH_2CH_2$, CH_3), 3.25 (s, 3 H, OCH_3); MS m/e (relative intensity) 43 (35), 55, (23), 59 (100), 71 (19), 114 (13), 141 (2), 172 (M^+ – 28, 2). Anal. Calcd for $C_{10}H_{20}N_2O_2$: C, 59.97; H, 10.07; N, 13.99. Found: C, 60.04; H, 10.09; N, 13.92.

2-Methoxy-2-*n*-propyl-5,5-pentamethylene-1,3,4-Δ³-oxadiazoline (3h): bp 93–94 °C (3 mm); IR (neat) ν 2930, 1190, 1065, 995, 895 cm^{-1}; ^{1}H NMR δ 0.95 (t, J = 7 Hz, 3 H, CH_3CH_2), 1.3–2.1 (m, total 14 H, cyclo-C_6H_{10}, $CH_3CH_2CH_2$), 3.13 (s, 3 H, OCH_3); MS m/e (relative intensity) 43 (55), 45 (100), 55 (32), 71 (69), 87 (89), 153 (4), 184 (M^+ – 28, 2). Anal. Calcd for $C_{11}H_{20}N_2O_2$: C, 62.23; H, 9.50; N, 13.20. Found: C, 62.13; H, 9.62; N, 13.14.

Neat **3h** (3.68 g, 17.4 mmol) was heated in an oil bath (140–150 °C) for 1 h. At that point, GLC analysis indicated that the reaction mixture contained at least four compounds (t_R = 2.3 and 5.5 min on 2-m FFAP, column temperature: 70 °C; flow rate: 20 mL/min, and t_R = 1.4 and 3.3 min on 1-m FFAP, column temperature: 120 °C; flow rate: 25 mL/min, respectively). Analysis of the mixture by GC/MS showed that the first three were cyclohexene, cyclohexanone, and methyl butyrate, respectively. The identity of each was confirmed by comparing its mass spectrum with that of an authentic sample. The yields were estimated, by GLC, to be 32, 13, and 39%, respectively. The main product (t_R = 3.3 min) was isolated by distillation. It was shown to be the enol ether **6h** (1.61 g, 50%): bp 118–119 °C (24 mm); IR (neat) ν 2930, 1670, 1445, 1380, 1170 cm^{-1}; ^{1}H NMR δ 0.93 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 1.3–1.8 (m, total 8 H, 2 $CH_3CH_2CH_2$, cyclo CH_2CH_2), 1.95–2.15 (m, 4 H, 2 cyclo CH_2), 3.33 (s, 3 H, CH_3O–), 4.83 (distorted t, 1 H, cyclo CH_2CH=C), 4.91 (t, J = 5.4 Hz, 1 H, OC*H*); MS m/e (relative intensity) 45 (100), 55 (28), 81 (17), 87 (90), 184 (M^+, 1).

2,2-Dimethoxy-5,5-dimethyl-1,3,4-Δ³-oxadiazoline (31): bp 51–52 °C (7 mm); IR (neat) ν 2940, 1455, 1180, 1145, 1065, 915 cm^{-1}; ^{1}H NMR δ 1.55 (s, 6 H, 2 CH_3), 3.48 (s, 6 H, 2 OCH_3); MS m/e (relative intensity) 15 (97), 28 (28), 43 (100), 59 (49), 128 (trace). Anal. Calcd for $C_6H_{12}N_2O_3$: C, 44.99; H, 7.55; N, 17.49. Found: C, 44.79; H, 7.72.

2,2-Dimethoxy-5,5-di-*n*-propyl-1,3,4-Δ³-oxadiazoline (3m): bp 103–104 °C (10 mm); IR (neat) ν 2950, 1440, 1360, 1130, 900 cm^{-1}; ^{1}H NMR δ 0.92 (t, J = 7.3 Hz, 6 H, 2 CH_3CH_2), 1.1–1.6 (m, 4 H, 2 $CH_3CH_2CH_2$), 1.7–1.9 (m, 4 H, 2 $CH_3CH_2CH_2$), 3.54 (s, 6 H, 2 OCH_3); MS m/e (relative intensity) 15 (38), 41 (25), 43 (100), 71 (72), 188 (M^+ – 28, <1). Anal. Calcd for $C_{10}H_{20}N_2O_3$: C, 55.35; H, 9.32; N, 12.95. Found: C, 55.57; H, 9.38; N, 12.88.

2,2-Dimethoxy-5,5-pentamethylene-1,3,4-Δ³-oxadiazoline (3n): bp 98–100 °C (5 mm); IR (neat) ν 2930, 1435, 1130, 1090, 895 cm^{-1}; ^{1}H NMR δ 1.4–2.4 (m, 10 H, cyclo-C_6H_{10}), 3.48 (s, 6 H, 2 OCH_3); MS m/e (relative intensity) 28 (46), 42 (84), 55 (100), 75 (91), 172 (M^+ – 28, <1). Anal. Calcd for $C_9H_{16}N_2O_3$: C, 53.98; H, 8.06; N, 13.99. Found: C, 54.30; H, 8.09; N, 13.92.

The thermal decomposition of 3m and 3n at 160–170 °C for 1 h gave the respective parent ketones and many other, unidentified, products. The yields of 4-heptanone and cyclohexanone were estimated by GLC (2 m FFAP, column temperature: 110 °C, flow rate: 20 mL/min) to be 71% and 41%, respectively.

Electrolysis of Aldehyde *N*-Acylhydrazones. General Procedure. A solution of **2** (20 mmol), MeOH (80 mL), and NaOAc (40 mmol) was electrooxidized by passing a constant current of 0.5 A. After 4–5 F/mol of electricity had been passed, the solvent was evaporated. The residue was treated with brine. The two liquid layers that formed were separated. The oily organic layer was extracted with Et_2O (25 mL × 4). The combined extracts were dried (Na_2SO_4) and concentrated. The oily residue was then distilled in vacuo. In the case of **4j**, white crystals precipitated out and were filtered and washed with a small amount of cold Et_2O.

2-Methyl-5-*n*-propyl-1,3,4-oxadiazole (4a): bp 92–94 °C (17 mm); IR (neat) ν 2950, 2860, 1585, 1560, 1450, 1225, 1180, 960 cm^{-1}; ^{1}H NMR δ 1.02 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 1.82 (sext, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 2.51 (s, 3 H, CH_3), 2.79 (t, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2$); MS m/e (relative intensity) 41 (33), 43 (76), 55 (29), 56 (24), 99 (100), 126 (M^+, 1), 127 (M^+ + 1, 3). Anal. Calcd for $C_5H_{10}N_2O$: C, 57.11; H, 7.99; N, 22.21. Found: C, 57.12; H, 7.98; N, 22.15.

2,5-Di-*n*-propyl-1,3,4-oxadiazole (4c): bp 110–111 °C (17 mm) [lit.[18] bp 123 °C (19 mm)]; IR (neat) ν 2950, 2855, 1580, 1560,

1450, 1175, 965 cm^{-1}; ^{1}H NMR δ 1.02 (t, J = 7.3 Hz, 6 H, 2 CH_3CH_2), 1.81 (sext, J = 7.3 Hz, 4 H, 2 $CH_3CH_2CH_2$), 2.81 (t, J = 7.3 Hz, 4 H, 2 $CH_3CH_2CH_2$); MS m/e (relative intensity) 43 (42), 55 (22), 71 (20), 127 (100), 140 (19), 154 (M^+, 2), 155 (M^+ + 1, 3). Anal. Calcd for $C_8H_{14}N_2O$: C, 62.30; H, 9.15; N, 18.17. Found: C, 62.27; H, 9.12; N, 18.09.

2-*n*-Propyl-5-isopropyl-1,3,4-oxadiazole (4d): bp 102–104 °C (17 mm); IR (neat) ν 2950, 2860, 1580, 1555, 1450, 1185, 1140 cm^{-1}; ^{1}H NMR δ 1.02 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 1.38 (d, J = 6.8 Hz, 6 H, 2 CH_3Ch), 1.81 (sext, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 2.81 (t, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 3.17 (m, 1 H, CH_3CH); MS m/e (relative intensity) 43 (60), 55 (32), 71 (25), 127 (100), 140 (26), 154 (M^+, 2), 155 (M^+ + 1, 6). Anal. Calcd for $C_8H_{14}N_2O$: C, 62.30; H, 9.15; N, 18.17. Found: C, 62.14; H, 9.32; N, 18.03.

2-Methyl-5-phenyl-1,3,4-oxadiazole (4f): bp 123–125 °C (3 mm), mp 67–69 °C; IR (KBr) ν 1580, 1480, 1445, 1250, 780, 710, 690 cm^{-1}; ^{1}H NMR δ 2.62 (s, 3 H, CH_3), 7.40–8.09 (m, 5 H, *Ph*); MS m/e (relative intensity) 43 (52), 77 (47), 90 (53), 104 (44), 105 (61), 160 (M^+, 100). Anal. Calcd for $C_9H_8N_2O$: C, 67.48; H, 5.03; N, 17.49. Found: C, 67.49; H, 4.95; N, 17.48.

2-*n*-Propyl-5-phenyl-1,3,4-oxadiazole (4g): bp 141–143 °C (3 mm); IR (neat) ν 2970, 2875, 1570, 1550, 1485, 1445, 1005, 710, 690 cm^{-1}; ^{1}H NMR δ 1.06 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 1.88 (sext, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 2.90 (t, J = 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 7.37–8.09 (m, 5 H, *Ph*); MS m/e (relative intensity) 43 (49), 77 (33), 90 (43), 105 (59), 160 (100), 188 (M^+, 23). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.17; H, 6.50; N, 14.73.

2-Isopropyl-5-phenyl-1,3,4-oxadiazole (4h): bp 130–132 °C (3 mm); IR (neat) ν 2980, 2875, 1565, 1550, 1485, 1450, 1070, 710, 690 cm^{-1}; ^{1}H NMR δ 1.45 (d, J = 6.8 Hz, 6 H, 2 CH_3CH), 3.27 (m, 1 H, CH_3CH), 7.37–8.10 (m, 5 H, *Ph*); MS m/e (relative intensity) 43 (100), 77 (46), 90 (41), 105 (92), 117 (54), 188 (M^+, 79). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.13; H, 6.49; N, 14.67.

2,5-Diphenyl-1,3,4-oxadiazole (4j): mp 139–140 °C (lit.[12] mp 141 °C). The material that was isolated was identical to an authentic sample of **4j** prepared by the dehydration of 1,2-dibenzoylhydrazine by PPA.[19] **4j**: IR (KBr) ν 1550, 1485, 1445, 1070, 785, 710, 685 cm^{-1}; ^{1}H NMR δ 7.48–8.20 (m, 10 H, *Ph*); MS m/e (relative intensity) 77 (49), 90 (41), 105 (100), 165 (71), 166 (39), 222 (M^+, 93).

Supplementary Material Available: Characterization data for **1h–l**, **2a,c–e,g,h**, and **3g,i–k** (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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PPP-MO Calculations Predict Spectra of Quinone and Imide Anion Radicals

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PPP-MO calculations were used to calculate the electronic structure of quinone and imide anion radicals, including diquinones, diimides, and *N*-cyanoimine derivatives of quinones. The results were used to correlate electronic excitation spectra which extend from 400 to 1600 nm, ESR spectra, and electrochemical reduction potentials. Comparison with ab initio calculations is made.

Semiquinones, the anion radicals of quinones, are important species in biology, medicine, and chemistry.[1] It is surprising, therefore, that little attention has been given to molecular orbital calculations on these species. Work from this laboratory has recently explored the unusual properties of radical anions derived from diquinones,[2,3] diimides,[4] and the *N*-cyanoimine derivatives of quinones.[5] Of particular interest were the optical spectra which showed electronic absorption bands in the NIR region, often beyond 1000 nm. We wished to use MO theory to calculate the wavelength of these bands in order to predict which anion radicals would be of interest before they were synthesized. In addition we wished to confirm the origin of these long-wavelength bands, confirm the structure of the anion radicals by ESR spectroscopy, and predict the reduction potentials at which the anion radicals would be formed.

Some time ago extensive MO studies of π-orbital levels and spectra of neutral quinones appeared.[6,7] In principle these levels could be used to predict some of the quantities of interest here. As part of our work on semiquinones we have reported ab initio calculations.[3] These are high-quality calculations with large basis sets, which sometimes included configuration interaction (CI). Even so, the electronic transition energies did not accurately reflect

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