Cyclic Diacylhydrazyl Radicals from 1,3,4-Oxadiazolidine-2,5-diones, Pyridazine-3,6-diones, and Phthalazine-1,4-diones[1,2]

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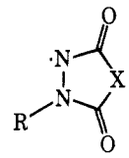
When treated with lead dioxide, α-cumyl and *tert*-butyl substituted oxadiazolidinediones (**3b, 3c**), phenyl and α-cumyl substituted tetrahydrophthalazinediones (**4a, 4b**) and tetrahydropyridazinediones (**5a, 5b**), and α-cumylperhydropyridazinedione (**6b**) afford the corresponding hydrazyl radicals. These radicals are transient and unisolable, decomposing within 48 h. Attempts to degas solutions of pyridazinedione radical **5a•** result in excessive effervescence and no observable EPR signal; radical **5a•** can be detected when a mixture of **5a** and lead dioxide in benzene is observed directly in the cavity of an EPR spectrometer. Phenyloxadiazolidinedione **3a**, when treated with lead dioxide, fails to provide an EPR signal; however, when treated with *tert*-butyl hypochlorite or *N*-bromosuccinimide, **3a** affords a radical which gives rise to a three-line pattern from the relatively strong coupling of the unpaired electron to one nitrogen. Treatment of phenylperhydropyridazinedione **6a** with any of the above oxidizing agents does not provide a detectable EPR signal.

The exceptionally persistent[3] triarylhydrazyl radicals [e.g., diphenylpicrylhydrazyl (DPPH)] are well known and have been extensively studied.[4] Only recently, however, has the chemistry of hydrazyl radicals lacking a directly bonded aromatic group been explored.[5-16] We have reported urazole (**1•**) and pyrazolidinedione (**2•**) radicals that are isolable as

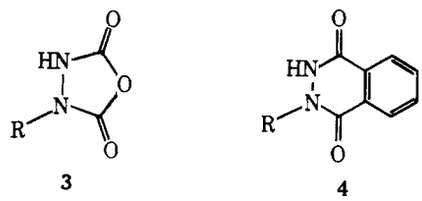


1•, X = NR′
2•, X = CR'_2

their tetrazane dimers.[1] We now report three new types of cyclic diacylhydrazyl radicals, one in which the disubstituted carbon of the pyrazolidinedione has been replaced by an ethano group and two in which the urazole imide nitrogen has been replaced by an oxygen or a carbon–carbon double bond. The persistence of these radicals is compared to that of type **1•** and **2•** radicals.

Results

Preparation of Cyclic Diacylhydrazines. 1,3,4-Oxadiazolidine-2,5-diones **3**,[17] 1-phenyltetrahydropyridazine-3,6-dione **5a**,[18] and 1-α-cumyltetrahydropyridazinedione **5b**[19]



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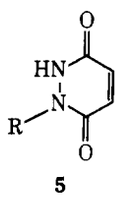

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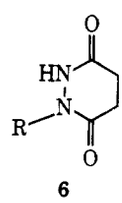

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a, R = Ph
b, R = $PhCMe_2$
c, R = *t*-Bu

were prepared by literature methods. 2-Phenyltetrahydrophthalazine-1,4-dione was prepared (34%) from phthalic anhydride and phenylhydrazine by a literature method[18] or, in higher yield (52%), by sodium ethoxide treatment of diethyl phthalate and phenylhydrazine, a method similar to that used to prepare pyrazolidinediones **2**.[1,20] Attempts to prepare 2-α-cumyltetrahydrophthalazinedione **4b** by reaction of α-cumylhydrazine[21] with either phthalic anhydride or with diethyl phthalate and sodium ethoxide provided a mixture of products. Heating a toluene solution of α-cumylhydrazine and phthalic anhydride at reflux gives only *N*-α-cumylaminophthalimide. When treated with sodium ethoxide, the imide affords the desired α-cumylphthalazinedione **4b** in high yield.[22] Perhydropyridazine-3,6-diones **6** were prepared by hydrogenation of the corresponding tetrahydropyridazinediones **5** at 50 psi and 80 °C with platinum–carbon catalyst[23] in the case of **6a** or, for **6b**, at 30 psi and 25 °C with the more active rhodium–carbon catalyst.

Cyclic Diacylhydrazyl Radicals. When treated with lead dioxide, α-cumyl- and *tert*-butyloxadiazolidinediones **3b** and **3c** afford, after centrifugation and decantation, orange or yellow solutions of radicals **3b•** and **3c•**, respectively. Sealed, degassed toluene solutions of radical **3c•** change from light yellow to bright orange when frozen at −196 °C, reverting to light yellow on warming above −100 °C. α-Cumyloxadiazolidinedione radical **3b•** gives rise to an EPR spectrum consisting of nine lines owing to the unequal splitting of the hydrazyl nitrogens. The hyperfine splitting (hfs) constants of this and other radicals described in this paper are summarized in Table I. *tert*-Butyl radical **3c•** has not only the same basic EPR spectrum as α-cumyl radical **3b•**, but also an additional splitting arising from the coupling of the unpaired electron to the *tert*-butyl hydrogens. Oxadiazolidinedione radicals **3b•** and **3c•** decompose within 24 h affording colorless, diamagnetic solutions containing colorless solids. Treatment of phenyloxadiazolidinedione **3a** with lead dioxide does not provide a radical detectable by EPR. However, when treated with either *tert*-butyl hypochlorite or *N*-bromosuccinimide, **3a** gives rise to a very weak EPR signal consisting of three equally intense lines as a consequence of the relatively strong coupling of the unpaired electron to one nitrogen.

When treated with lead dioxide, phthalazinediones **4a** and **4b** and α-cumylpyridazinedione **5b** afford light yellow, paramagnetic solutions of the corresponding radicals. Sealed, degassed toluene solutions of α-cumyl radicals **4b•** and **5b•** become intensely purple when frozen at −196 °C. Upon warming above −100 °C, the color returns to light yellow. α-Cumylphthalazinedione radical **4b•** gives rise to an EPR spectrum that has nine lines from the unequal coupling of the unpaired electron to the hydrazyl nitrogens. α-Cumylpyridazinedione radical **5b•** has an EPR spectrum similar to that of its phthalazinedione analogue **4b•**, but also contains an

Table I. Hyperfine Splitting Constants of Cyclic Diacylhydrazyl Radicals [a,b]

Radical	$a_{N\text{-}2(1)}$	$a_{N\text{-}1(2)}$	$a_{N\text{-}1(2)}/a_{N\text{-}2(1)}$	a_H
3a•[c]	9.50[d]			
3b•	7.50	6.50	0.87	
3c•[e,f]	7.60	6.50	0.86	0.15[g] (9 H)
4a•[e]	7.30	4.50	0.62	0.55 (5 H)
4b•	7.05	5.05	0.72	
5a•	6.75[d]	4.25[d]	0.63	
5b•	6.35	4.50	0.71	0.55 (1 H)
6b•	9.00	5.80	0.64	0.80 (2 H)

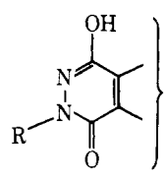
[a] ±0.05 G, unless otherwise stated. [b] In benzene solution at room temperature, unless otherwise stated. [c] This radical most probably is not a hydrazyl type radical. [d] ±015 G. [e] In toluene solution. [f] At 0 °C. [g] ±0.02 G.

additional splitting arising from the coupling of one hydrogen. The EPR spectrum of phenylphthalazinedione radical **4a**• shows, in addition to the unequal splitting of the hydrazyl nitrogens, a splitting due to the five equivalent hydrogens of the phenyl substituent. After treatment with lead dioxide, solutions of phenylpyridazinedione **5a** effervesce excessively when vacuum degassed and do not give rise to any detectable EPR signal. However, when an undegassed, unsealed mixture of **5a** and lead dioxide in benzene is observed by EPR, a weak signal consisting of nine lines appears. Within 36 h, the EPR signals of phthalazinedione radicals **4**• and pyridazinedione radicals **5**• disappear.

When treated with lead dioxide, α-cumylperhydropyridazinedione **6b** affords a light yellow solution of the corresponding radical. In addition to the basic nine-line pattern from the splitting of the hydrazyl nitrogens, the EPR spectrum of radical **6b**• reveals the coupling of two equivalent hydrogens, and a smaller unresolved splitting. The EPR signals of **6b**• disappear within 48 h. Treatment of phenylperhydropyradazinedione **6a** with lead dioxide, *tert*-butyl hypochlorite, or *N*-bromosuccinimide fails to produce any detectable EPR signal.

Discussion

Although the results of various studies[24] demonstrate that phthalazinediones **4** and pyridazinediones **5** exist predominantly in the monoketo, monoenol form **7**, when treated with



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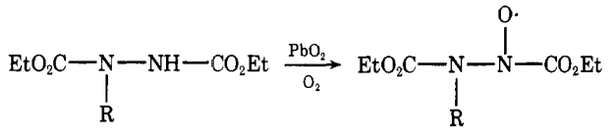
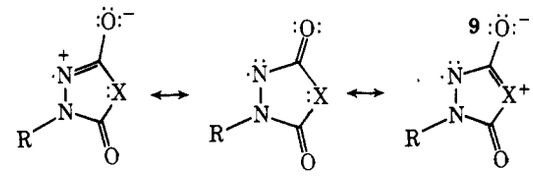
lead dioxide, these cyclic diacylhydrazines, along with perhydropyridazinedione **6b** and oxadiazolidinediones **3b** and **3c**, afford free radicals, the EPR spectra of which are characteristic of nitrogen centered, hydrazyl radicals.[25] Oxidation of phenyloxadiazolidinedione **3a** affords a free radical that has an EPR spectrum not dissimilar to those obtained from the oxidation of acyclic diacylhydrazines **8** (R = CH_3,[8] $PhCMe_2$[1]). These acyclic radicals have been shown[8] to be hydrazoxyls **9**



8 **9**

rather than the hydrazyl radicals. However, it is also possible that this radical is a nitroxide-type radical.[25]

The hydrazyl radicals described in this paper most probably have π ground states, this being the simplest rationale for the extensive spin delocalization observed. Danen et al.[26] have previously addressed themselves to the question of π vs. Σ ground states for a somewhat similar situation (i.e., *N*-alkoxy-*N*-carbethoxyamine radicals). Using essentially their argument, one infers that delocalization of the lone pair of electrons on the divalent nitrogen into the carbonyl group as in canonical form **10** has the effect of localizing the unpaired electron on that nitrogen. In urazole radicals (**11**, X = N–R′) delocalization of the lone pair on the imide nitrogen as in resonance structure **12** reduces the ability of the carbonyl group to delocalize the divalent nitrogen lone pair and thus allows delocalization of the unpaired electron.



10 **11** **12**

To the extent that both hydrazyl nitrogens are similarly hybridized, the ratio of their hyperfine splitting (hfs) constants, $a_{N\text{-}1(2)}/a_{N\text{-}2(1)}$, is suggestive of the distribution of the unpaired electron spin density over these nitrogens. The ratios for oxadiazolidinedione radicals **3b**• and **3c**• are slightly greater than for DPPH (0.83)[4] or the corresponding urazole radicals (0.81).[1] Delocalization of the unpaired electron over the hydrazyl nitrogens in α-cumylphthalazinedione and pyridazinedione radicals **4b**• and **5b**• is similar to that of the 1-phenylurazole and pyrazolidinedione radicals (0.71–0.74).[1] The distribution of spin density between the hydrazyl nitrogens in phenylphthalazinedione and pyridazinedione radicals **4a**• and **5a**• and α-cumylperhydropyridazinedione **6b**• is more disparate than in any of the other cyclic diacylhydrazyl radicals studied.

That the cyclic diacylhydrazyl radicals studied in this paper are less persistent than the analogous urazole radicals is not surprising. Three conditions are generally required for organic free radicals to be persistent: (a) steric congestion of the site formally bearing the unpaired electron, (b) substitution of hydrogen by other groups or atoms at sites where disproportionation may occur, and (c) delocalization of unpaired electron spin density.[4,10,27] In the case of urazole radicals, all these conditions are met. However, for the radicals described here, removal of the urazole imide nitrogen alters the delocalization of spin density. Because an oxygen or a carbon–carbon double bond is not as effective as a nitrogen in delocalizing its pair of electrons, resonance structure **12** does not play as significant a role in the electronic structure of oxadiazolidinedione radicals (**11**, X = O), phthalazinedione or pyridazinedione radicals (**11**, X = C=C), as it does in the urazole radicals. The resultant localization of the unpaired electron in radicals **3**•, **4**•, **5**•, and **6**• renders them less persistent. In view of the fact that phenyl substituted pyrazolidinedione radicals (**11**, R = Ph; X = CR'_2) can be isolated, it is surprising that, even when treated with a variety of oxidizing agents, phenyl-substituted perhydropyridazinedione **6a** does not form a free radical.

Experimental Section

General. Melting points were taken in open Pyrex capillary tubes using a Büchi "Schmelzpunktbestimmungs Apparat" and are uncorrected. Infrared spectra were taken on a Beckman IR-12 grating spectrophotometer. NMR spectra were obtained with Varian A-60A or HA-100 spectrometers. Chemical shifts, δ, are expressed in parts per million relative to internal tetramethylsilane. EPR spectra were

recorded with a Varian E-9 X-Band spectrometer. Mass spectra were obtained with a Varian MAT CH-5 mass spectrometer. Mass spectral data processing equipment employed was provided by NIH Grants CA 11388 and GM 16864 from the National Cancer Institute and the National Institute of General Medical Sciences, respectively. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences, University of Illinois. All hydrazines were distilled prior to use. Other commercially available reagents and reagent grade solvents were used without further purification, unless otherwise stated.

EPR Samples. Solutions of radicals were prepared by stirring solutions of the appropriate cyclic diacylhydrazine with lead dioxide. After 15 s–5 min, the mixtures were centrifuged and the supernatant liquid was put into 4-mm o.d. quartz tubes and frozen at −196 °C. Each sample was vacuum degassed by at least three freeze–pump–thaw cycles and sealed while frozen under high vacuum. All samples were stored at −196°C until used.

2-Phenyl-1,2,3,4-tetrahydrophthalazine-1,4-dione (4a). A solution of sodium ethoxide (prepared from 2.58 g, 112 mmol, of sodium), diethyl phthalate (22.22 g, 100 mmol), and phenylhydrazine (10.81 g, 100 mmol) in absolute ethanol (100 mL) was heated at reflux for 22 h and then concentrated in vacuo. The resultant gum was dissolved in water and extracted with dichloromethane (twice) to remove unreacted starting material. Acidification of the aqueous solution with concentrated hydrochloric acid afforded, after filtration, 19.96 g of a tan solid. Recrystallization (three times) from nitromethane afforded 12.46 g (52.3 mmol, 52%) of slightly off-white needles: mp 214–216 °C [lit.[22a] mp 212 °C (EtOH)]; IR (KBr) 1650, 1602, 1577, 1565, and 1202 cm^{-1}.

Anal. Calcd for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.47; H, 4.19; N, 11.85.

***N*-α-Cumylaminophthalimide.** A solution of α-cumylhydrazine[21] (3.75 g, 25 mmol) and phthalic anhydride (3.70 g, 25 mmol) in toluene (175 mL) was heated at reflux for 20 h, the condensate being collected in a Dean-Stark trap. Removal of the solvent under reduced pressure and recrystallization of the crude solid from ethanol afforded 6.28 g (22.4 mmol, 90%) of the phthalimide as a yellow solid: mp 87–89 °C; IR (KBr) 3460 and 3300 (NH), 3065, 2990, 2975, and 2940 (CH), 1788, 1768, and 1732 (C=O), 1390 (CMe_2), 1377, 1366 ($CMe)_2$, 1112, 888, 767, and 710 cm^{-1}; NMR ($CDCl_3$) δ 1.56 [s, 6, $C(CH_3)_2$], 4.69 (s, 1, NH), 7.1–7.4 and 7.5–7.9 (m, 9, C_6H_5, C_6H_4); mass spectrum (70 eV) *m/e* (rel intensity) 280 (weak, M^+), 162 (28), 120 (10), 119 (100), 118 (24), 104 (11), 103 (6), 91 (43), 79 (9), 77 (15), 76 (10), 51 (5), and 41 (22).

Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.65; H, 5.65; N, 10.03.

2-α-Cumyl-1,2,3,4-tetrahydrophthalazine-1,4-dione (4b). A solution of sodium ethoxide (prepared from 1.24 g, 54 mmol, of sodium), *N*-α-cumylaminophthalimide (5.61 g, 20 mmol), and ethyl acetate (1.00 g, 11.4 mmol) in absolute ethanol (80 mL) was heated at reflux for 20 h and then concentrated to ca. 40 mL. After dilution with water (ca. 50 mL), acidification with concentrated hydrochloric acid, and filtration, a solid was obtained. Recrystallization from ethanol afforded 4.47 g (16.9 mmol, 80%) of phthalazinedione **4b** as a white solid which melts at 218 °C, immediately resolidifies, and does not melt again below 300 °C: IR (KBr) 3445 (OH), 3145 (NH), 3060, 3035, 3005, 2985, and 2935 (CH), 1643 (C=O), 1590, 1574, 1558, 1497, 1387 (CMe_2), 1365 (CMe_2), 1358, 1263, 1195, 1156, and 698 cm^{-1}; NMR (acetone-d_6) δ 1.87 [s, 6, $C(CH_3)]_2$, 2.86 (s, 1, OH), 7.0–7.3 and 7.68 (m, 9, C_6H_5,C_6H_4); mass spectrum (70 eV) *m/e* (rel intensity) 280 (13, M^+), 163 (28), 162 (97), 132 (10), 120 (1), 119 (100), 118 (93), 117 (18), 104 (15), 103 (11), 91 (64), 79 (12), 78 (11), 77 (19), 51 (11), and 41 (30).

Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.83; H, 5.67; N, 10.02.

1-Phenyl-1,2,3,6-tetrahydropyridazine-3,6-dione (5a) was prepared according to the method of Biquard and Grammaticakis[18] by heating a solution of maleic anhydride (9.81 g, 100 mmol) and phenylhydrazine (10.81 g, 100 mmol) in glacial acetic acid (40 mL) at reflux for 1 h. After workup and recrystallization from ethanol, 8.76 g (46.6 mmol, 47%) of pyridazinedione **5a** was obtained as white needles: mp 267.5–268.5 °C [lit.[18] mp 265 °C (EtOH)]; IR (KBr) 1763, 1601, 1573, 1500, 1483, 1456, 1265 cm^{-1}.

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.29; N, 14.89. Found: C, 64.07; H, 4.30; N, 15.09.

1-Phenylperhydropyridazine-3,6-dione (6a). A 200-mL pressure bottle wrapped with heating tape was charged with a solution of pyridazinedione **5a** (1.88 g, 10.0 mmol) in ethanol (100 mL) and platinum–carbon catalyst (100 mg). After attaching the bottle to a Parr apparatus, the hydrogen pressure was set at 50 psi. The bottle was then heated until the pressure had increased another 15 psi. After shaking for 2 days, the reactions mixture was filtered and concentrated in vacuo to afford 1.91 g of an off-white solid. Recrystallization from ethanol afforded 1.15 g (6.05 mmol, 61%) of pyridazinedione **6a** as a white solid: mp 197–198 °C [lit.[28] mp 199 °C (H_2O)]; IR (KBr) 1672 cm^{-1}.

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.72. Found: C, 63.26; H, 5.29; N, 14.94.

1-α-Cumylperhydropyridazine-3,6-dione (6b). A solution of pyridazinedione **5b**[19] (0.12 g, 0.52 mmol) in ethanol (75 mL) was shaken in a Parr apparatus with rhodium–carbon catalyst (50 mg) under an atmosphere of hydrogen (30 psi). After 24 h, the reaction mixture was filtered and concentrated at reduced pressure. Recrystallization of the crude product from ethyl acetate afforded 0.08 g (0.34 mmol, 67%) of pyridazinedione **6b** as a white solid: mp 134–136 °C; IR (KBr) 3450 and 3230 (NH), 2990 (CH), 1675 (C=O), 1400, 1186, 768, and 702 cm^{-1}; NMR (acetone-d_6) δ 1.76 [s, 6, $C(CH_3)_2$], 2.48 (s, 4, $COCH_2$), 2.77 (s, 1, CONH), and 7.1–7.6 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 232 (weak, M^+), 120 (11), 119 (100), 118 (10), 103 (5), 91 (50), 79 (7), 77 (9), 41 (16), and 28 (6).

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.10; H, 6.84; N, 12.10.

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Supplementary Material Available. EPR spectra of radicals **3b•**, **3c•**, **4a•**, **4b•**, **5b•**, and **6b•** (6 pages). Ordering information is given on any current masthead page.

Registry No.—**3a•**, 61446-35-3; **3b•**, 61446-36-4; **3c•**, 61446-37-5; **4a**, 5439-98-5; **4a•**, 61446-38-6; **4b**, 61446-39-7; **4b•**, 61446-40-0; **5a**, 1698-54-0; **5a•**, 61446-41-1; **5b•**, 61446-42-2; **6a**, 61446-43-3; **6b**, 61446-44-4; **6b•**, 61446-45-5; diethyl phthalate, 84-66-2; phenylhydrazine, 100-63-0; *N*-α-cumylaminophthalimide, 61446-46-6; α-cumylhydrazine, 3178-39-0; phthalic anhydride, 85-44-9; ethyl acetate, 141-78-6; maleic anhydride, 108-31-6.

References and Notes

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