Kinetics in 2,2,2-Trifluoroethanol. Kinetic studies in 2,2,2-trifluoroethanol were almost identical to those in 80% aqueous acetone. As an example, 0.0709 g (2.16×10^{-4} mol) of indan-1-yl 3,5-dinitrobenzoate was dissolved in 27 mL of anhydrous 2,2,2-trifluoroethanol, and five equivalent portions were sealed in ampules. The ampules were placed in an oil bath at 39.9 °C and removed at convenient intervals. After cooling in ice water followed by equilibration to room temperature, a 5-mL aliquot was taken with a calibrated automatic pipet. This sample was added to 30 mL of ice-cold 5:1 acetone–water and titrated to a bromothymol blue end point using 0.0107 N sodium methoxide in methanol.

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Registry No.—Inden-1-ol, 61463-21-6; 3,5-dinitrobenzoyl chloride, 99-33-2; fluoren-9-one, 486-25-9; fluoren-9-ol, 1689-64-1; 1-methylindene, 767-59-9; methylindenyllithium, 55563-47-8; 1-methylinden-1-ol, 64666-41-7; 9-methylfluoren-9-ol, 6311-22-4; indan-1-one, 83-33-0; 1-methylindan-1-ol, 64666-42-8; cyclopenten-3-ol, 3212-60-0; inden-1-yl cation, 42949-14-4; fluoren-9-yl cation, 19873-39-3; cycloprop[2,3]inden-1-yl cation, 56377-03-8.

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Persistent Cyclic Diacylhydrazyl Radicals from Urazoles and Pyrazolidine-3,5-diones

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Lead dioxide oxidation of 1,4-disubstituted urazoles 4 or 1,4,4-trisubstituted pyrazolidine-3,5-diones 6 affords the corresponding cyclic diacylhydrazyl radicals. A number of these radicals are quite persistent. For example, 1-α-cumyl- and 1-*tert*-butylurazole radicals **4g·–4k·** and 1-phenylpyrazolidinedione radicals **6e·** and **6f·** are in mobile equilibrium with and can be isolated as their tetrazane dimers. As solid dimers, these radicals are indefinitely persistent. Solution lifetimes of pyrazolidinedione radicals **6g·** and **6h·**, 1-phenylurazole radicals **4d·** and **4f·**, and 1-α-cumylurazole radical **4i·** are less than 1 week, whereas solution lifetimes of 1-α-cumylurazole radicals **4g·** and **4h·** and 1-*tert*-butylurazole radicals **4j·** and **4k·** are extremely long and comparable to that of DPPH. The extent of dimerization of several of the radicals has been measured in carbon tetrachloride, benzene, and acetonitrile and shows that 1-α-cumyl- and 1-*tert*-butylurazole radicals are more polar than their tetrazane dimers and that 1-phenylpyrazolidinedione radicals are more than 90% dimerized at concentrations greater than 5×10^{-2} M. Infrared carbonyl stretching frequencies of isolable radicals and their solid tetrazane dimers are compared with those of the corresponding urazole and pyrazolidinedione precursors. These data are also used to exclude the possible existence of dimeric structures in which the carbonyl oxygen is involved in the dimeric linkage. Visible spectral data are reported for highly colored urazole and pyrazolidinedione radicals. EPR spectra of these cyclic diacylhydrazyl radicals are indicative of π radicals and show delocalization of unpaired spin density over the entire heterocycle for the urazole radicals. For the pyrazolidinedione radicals delocalization is restricted primarily to the nitrogens. Additional hyperfine splitting occurs when a phenyl group is bonded to N-1 (but not N-4) in urazole radicals. No splitting is observed for the aromatic ring of a cumyl group bonded to N-1. Persistence of 1-α-cumyl- and 1-*tert*-butylurazole radicals is described as a consequence of steric crowding of the site formally bearing the unpaired electron, substitution by other groups or atoms for hydrogen at sites where disrpoportionation could occur, and delocalization of unpaired spin density. The imide nitrogen of the urazoles reduces the ability of the carbonyl groups to delocalize hydrazyl nitrogen lone pairs. This effect increases delocalization of unpaired spin density in and persistence of 1-α-cumyl- and 1-*tert*-butylurazole radicals relative to α-cumylpyrazolidinedione radicals which lack an imide nitrogen.

Although organic free radicals are typically transient and unisolable, there are notable exceptions. Arylhydrazyl radicals, including the exceptionally persistent[3] diphenylpicrylhydrazyl (DPPH), are among the most extensively studied free radicals known.[4] Recently, interest has been focused on hydrazyl radicals which lack directly bonded aromatic groups,[5–15] and one of these non-arylhydrazyl radicals has been isolated as its dimeric tetrazane.[1] Although cyclic diacylhydrazines have long been known,[16,17] their potential as precursors of hydrazyl radicals has remained unexploited until now. We herein report studies of cyclic diacylhydrazyl radicals derived from urazoles and pyrazolidinediones.

Results

Preparation of Urazoles and Pyrazolidine-3,5-diones. 1,4-Disubstituted urazoles (1,2,4-triazolidine-3,5-diones) were prepared *via* a modified Zinner and Deucker[16] procedure (Scheme I). Treatment of carbazates **2**, formed by the reaction of hydrazines **1** and ethyl chloroformate, with substituted isocyanates furnishes semicarbazides **3**. Cyclization of **3** with potassium hydroxide provides the desired urazoles **4** in good yields. Pyrazolidine-3,5-diones **6** were prepared by sodium ethoxide induced reaction of hydrazines **1** with disubstituted malonates **5** according to the method of Conrad and Zart[17]

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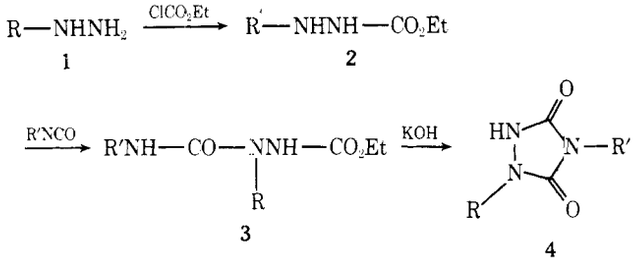
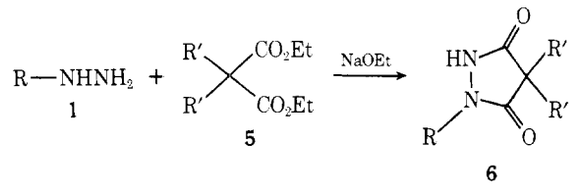
Scheme I



a: R = Ph
b: R = $PhCMe_2$
c: R = *t*-Bu
d: R = R′ = Ph
e: R = Ph, R′ = Me
f: R = Ph, R′ = *t*-Bu
g: R = $PhCMe_2$, R′ = Ph
h: R = $PhCMe_2$, R′ = Me
i: R = $PhCMe_2$, R′ = *t*-Bu
j: R = *t*-Bu, R′ = Ph
k: R = *t*-Bu, R′ = Me
l: R = C_6H_{11}, R′ = Me

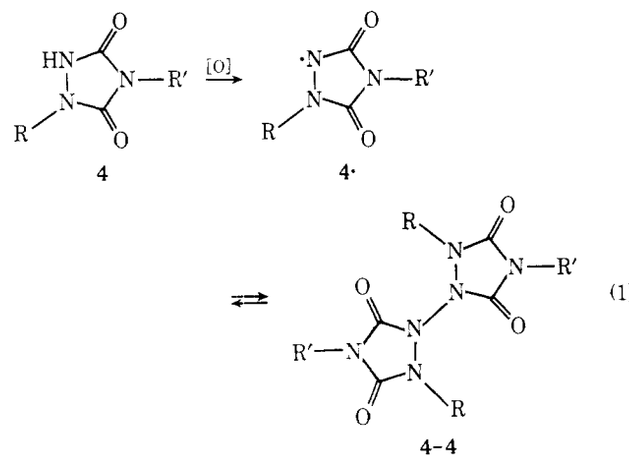
Scheme II



a: R = Ph
b: R = $PhCMe_2$
c: R′ = Et
d: R′ = Me
e: R = Ph, R′ = Et
f: R = Ph, R′ = Me
g: R = $PhCMe_3$, R′ = Et
h: R = $PhCMe_2$, R′ = Me

(Scheme II).

Urazole Radicals. When treated with a variety of oxidizing agents (*tert*-butyl hypochlorite, *N*-bromosuccinimide, lead dioxide) solutions of urazoles **4** provide highly colored paramagnetic solutions of urazole radicals **4·** (eq 1). Though af-



(1)

fording radicals in only mediocre yields, reactions utilizing lead dioxide are particularly clean. Hence, this reagent is preferred for preparative purposes and is especially useful for preparing solutions of transient radicals. 1-α-Cumyl- and 1-*tert*-butylurazoles **4g–k** provide highly colored solutions of radicals **4g–k·**, from which crystalline tetrazane dimers **4-4** can be isolated. Radicals **4g–k·** can be stored indefinitely in the form of these tetrazane dimers. In solution, a mobile equilibrium exists between radical and dimer. In benzene, the lifetimes of urazole radicals **4g·**, **4h·**, **4j·**, and **4k·** appear to be comparable to that of DPPH. However, α-cumyl-*tert*-butylurazole radical **4i·** is less persistent, decomposing within 3 days.

In contrast to the persistence of 1-α-cumyl- and 1-*tert*-butylurazole radicals, 1-phenyl- and 1-cyclohexylurazole radicals **4d–f·** and **4l·**, respectively, are transient. Benzene

Table I. Visible Absorption Maxima for Urazole and Pyrazolidinedione Radicals in Benzene Solution

Radical	Registry no.	λ_{max}, nm	ϵ^a	Concn, M[b]
4d·	64739-49-7	500, 570[c]		
4e·	64739-50-0	331,[c] 337		
		437, 561		
4f·	64739-51-1	330,[c] 338		
		435, 550		
4g·	64739-52-2	316	2400	3.10×10^{-4}
		480	260	2.58×10^{-2}
4h·	52809-14-0	300	2900	3.04×10^{-4}
		380	1200	6.07×10^{-4}
4i·	64754-32-1	297	2500	3.02×10^{-4}
		370[c]	980	3.02×10^{-4}
		410[c]	600	3.02×10^{-4}
4j·	64739-53-3	313	2800	3.10×10^{-4}
		440	270	3.10×10^{-3}
4k·	64739-54-4	303	3100	3.14×10^{-4}
		413	590	1.57×10^{-3}
4l·	64739-55-5	415,[c] 507		
		521, 537		
		547,[c] 506		
6e·	64739-56-6	355	43	1.89×10^{-2}
		487	15	5.05×10^{-2}
6f·	64739-57-7	370[c]	76	5.06×10^{-3}
		480	16	5.06×10^{-2}
6g·	64739-58-8	646		

[a] Extinction coefficients are concentration dependent. [b] Concentration of radical assuming no dimerization. [c] Shoulder.

solutions of urazole radicals **4d·** and **4l·** decompose within 12 hr, **4e·** within 24 hr, and **4f·** within *ca.* 3 days. Upon decomposition, colored radicals **4d–f·** and **4l·** provide colorless (yellow for **4l·**), uncharacterized precipitates that are difficulty soluble even in polar solvents such as acetone or DMSO. Attempts to chromatographically purify or isolate radicals **4d–f·** and **4l·** have resulted in their decomposition.

Solutions of α-cumyl radicals **4h·** and **4i·**, *tert*-butyl radical **4k·**, and cyclohexyl radical **4l·** are orange colored because of broad absorption bands centered near 300 nm and extending out to 600–650 nm. Superimposed on these bands are smaller absorption maxima, the data for which are summarized in Table I. Replacement of the alkyl group on N-4 with an aromatic group as in 4-phenyl radicals **4g·** and **4j·** causes the radical to take on a reddish color that results from an increased absorption in the 450–630 nm region. Replacement of the alkyl group on N-1 with phenyl affords radicals that are purple-brown or purple-gray in color. Purple-brown 1-phenylurazole radicals **4e·** and **4f·** have visible absorption maxima at *ca.* 337 nm which tail into other absorption peaks and on past 700 nm. Diphenylurazole radical **4d·** has an absorption maximum at 500 nm superimposed on the tail of a UV peak which also continues on past 700 nm.

Observing that the color of solutions of either 1-α-cumyl- or 1-*tert*-butylurazole radicals reversibly fades upon cooling and noting that these radicals fail to obey Beer's Law, it was inferred that the radicals are in equilibrium with the dimeric

Table II. Equilibrium Constants for the Association of Urazole Radicals in Solution at 25 °C

Urazole Radical	$K_{Assoc.}$		
	CCl_4	C_6H_6	CH_3CN
4g·	6.0 ± 0.8	1.8 ± 0.7	0.16 ± 0.01
4h·	12 ± 2	4.5 ± 0.4	0.58 ± 0.30
4i·	6.1 ± 2.1	1.4 ± 0.2	0.36 ± 0.10
4j·	1.5 ± 0.4	0.66 ± 0.06	0.33 ± 0.22
4k·	5.6 ± 1.2	3.2 ± 1.1	1.6 ± 0.6

Table III. Infrared Carbonyl Stretching Frequencies of Urazoles, Urazole Radicals, Pyrazolidinediones, and Pyrazolidinedione Radicals[a]

Dione ($CHCl_3$)	Registry no.	$\nu_{C=O}$ (cm^{-1})	Radical ($CHCl_3$)	$\nu_{C=O}$ (cm^{-1})	Tetrazane (KBr)	Registry no.	$\nu_{C=O}$ (cm^{-1})	Dione (KBr)	$\nu_{C=O}$ (cm^{-1})
4g	64739-59-9	1775 (m) 1712 (s)	**4g·**	1761 (m) 1743 (m), 1705 (s)	**4g–4g**	64739-35-1	1792 (m), 1744 (s), 1706 (m)	**4g**	1773 (m) 1697 (s)
4h	52809-13-9	1770 (m) 1710 (s)	**4h·**	1806 (w), 1777 (m) 1739 (m), 1707 (s)	**4h–4h**	52809-05-9	1805 (m), 1792 (m) 1732 (s), 1706 (m)	**4h**	1763 (m) 1693 (s)
4i	64739-60-2	1762 (m) 1702 (s)	**4i·**	1763 (m) 1728 (m), 1693 (s)	**4i–4i**	64739-36-2	1800 (w), 1785 (w) 1734 (s), 1696 (s)	**4i**	1764 (m) 1692 (s)
4j	64739-61-3	1770 (m) 1691 (s)	**4j·**	1764 (m) 1701 (s)	**4j–4j**	64739-37-3	1808 (m), 1792 (m) 1742 (s), 1709 (m)	**4j**	1769 (m) 1704 (s)
4k	64739-62-4	1760 (m) 1689 (s)	**4k·**	1766 (m), 1740 (m), 1706 (s)	**4k–4k**	64739-38-4	1807 (m), 1793 (m) 1732 (s), 1708[b] (m)	**4k**	1760 (m) 1702 (s)
6e	1732-61-2	1742 (m) 1694 (s)	**6e–6e**	1790 (m), 1763 (m), 1729 (s)	**6e–6e**	64739-39-5	1800 (m), 1773 (m), 1732 (s)	**6e**	1746 (s) 1678 (s)
6f	57186-07-9	1760 (m) 1742 (m), 1695 (s)	**6f–6f**	1790 (m) 1777 (m), 1732 (s)	**6f–6f**	64739-40-8	1798 (m), 1776 (m), 1731 (s)	**6f**	1748 (s) 1685 (s)
6g	64739-63-5	1740 (m) 1691 (s)	**6g·**	1756 (m) 1693 (s)					

[a] w = weak, m = medium, s = strong. [b] Shoulder.

Table IV. Hyperfine Splitting for Urazole and Pyrazolidinedione Radicals at 25 °C[a,b]

Radical	$a_{N\text{-}2(1)}$(G)	$a_{N\text{-}1(2)}$(G)	$a_{N\text{-}2(1)}/a_{N\text{-}1(2)}$	$a_{N\text{-}4}$(G)	a_H(G)
4d·	7.7[c]	5.7[c]	0.74	1.45	1.35 (3H), 0.60 (2H)
4e·	7.7[c]	5.7[c]	0.74	1.45	1.35 (3H), 0.60 (5H)
4f·	7.7[c]	5.7[c]	0.74	1.40	1.40 (3H), 0.60 (2H)
4g·[e]	7.75	6.30	0.81	1.50	
4h·	7.70	6.25	0.81	1.47	0.56 (3H)
4i·[e]	7.70	6.25	0.81	1.45	
4j·	7.50	6.05	0.81	1.45	
4k·	7.55	6.15	0.81	1.50	0.65 (3H), 0.13[d] (9H)
6e·	7.75	5.60	0.72		1.40 (3H), 0.60 (2H)
6f·	7.85	5.60	0.71		1.40 (3H), 0.60 (2H) 0.15[d]
6g·	8.05	6.35	0.79		
6h·	8.10	6.40	0.78		

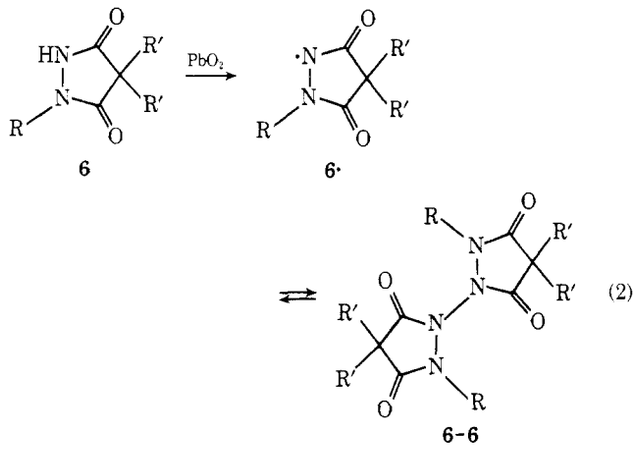
[a] 0.05 G, unless otherwise stated. [b] In benzene solution, unless otherwise stated. [c] ±0.10 G. [d] ±0.02 G. [e] In carbon disulfide solution.

tetrazanes. Equilibrium constants for the association of these radicals (Table II) were determined by vapor pressure osmometry for carbon tetrachloride, benzene, and acetonitrile solution. Though these data are not of high precision, it is evident that the tendency of the radicals to associate decreases as solvent polarity increases.

Urazoles **4g–k,** whether as solids or in solution, have two infrared carbonyl absorptions, 1775–1760 (m) and 1715–1690 (s) cm^{-1}. In the solid state, the corresponding tetrazane dimers exhibit four absorption peaks, 1810–1800 (m), 1795–1785 (m), 1745–1730 (s), and 1710–1695 (m–s) cm^{-1}. In solution, the urazole radicals have three carbonyl absorptions, 1780–1760 (m), 1745–1725 (m–s), and 1710–1695 (s) cm^{-1}. Detailed infrared carbonyl data for diacylhydrazines, radicals, and dimers appear in Table III.

In urazole radicals, the hyperfine splitting constants (hfsc) for each of the three types of nitrogen are relatively insensitive to structural variation (Table IV). The EPR spectra of 4-phenylurazole radicals **4d·** and **4g·** are virtually identical to those of 4-*tert*-butyl analogs **4f·** and **4i·,** indicating that unpaired spin density is not appreciably delocalized into the N-4 phenyl since splitting by the aromatic hydrogens is too small to be observed.[18] Urazole radicals **4g·, 48·,** and **4j·** have almost identical EPR spectra and clearly show the unequal splitting of the three urazole nitrogens. *tert*-Butylmethylurazole radical **4k·** gives rise to an EPR spectrum similar to that of α-cumylmethyl radical **4h·**[1] but has an additional hfsc due to the coupling of the *tert*-butyl hydrogens. The EPR spectra of 1-phenylurazole radicals **4d·** and **4f·** are almost identical and show that the splitting caused by the N-1 phenyl arises from the unequal coupling of the two equivalent *meta* hydrogens and the three equivalent *ortho* and *para* hydrogens. The EPR spectrum of phenylmethyl radical **4e·** is similar to those for other 1-phenylurazole radicals, but has an additional splitting arising from the N-4 methyl group. Cyclohexylurazole radical **4l·,** the only radical studied in which a carbon α to the hydrazyl nitrogens bears a hydrogen, gives rise to a complex EPR spectrum that has frustrated interpretation.

Pyrazolidine-3,5-dione Radicals. Solutions of colorless pyrazolidinediones **6** afford highly colored solutions of pyrazolidinedione radicals **6·** (eq 2) when treated with lead dioxide. Solutions of α-cumylpyrazolidinedione radicals **6g·** and **6h·** are emerald green whereas the related phenyl radicals **6e·** and **6f·** are brownish-red. Solutions containing dimethyl radical **6h·** become colorless within 2 hr. Diethyl radical **6g·,** however, can be chromatographically purified, but decomposed to uncharacterized yellow gum when attempts were made to isolate it or its dimer. A green solution of unchromatographed **6g·** decomposes over a period of several days at 25 °C. Evaporation of solutions of chromatographically purified 1-phen-



6 6· 6-6 (2)

ylpyrazolidinedione radicals **6e·** and **6f·** provide the dimers **6–6** as tan solids that appear to be indefinitely stable. However, in benzene solution, these radicals decompose within 2 weeks at 25 °C to give orange-red diamagnetic solutions.

The visible spectrum of α-cumylpyrazolidinedione radical **6g·** (Table I) has a tail from the UV region extending into the visible, a minimum at 529 nm, and a maximum at 646 nm that continues on past 700 nm. Diethylphenyl radical **6e·** also has a visible tail of a UV absorption and several discrete visible absorption maxima. Although basically similar to that of **6e·**, the visible spectrum of dimethyl radical **6f·** has a shoulder rather than a discrete maximum in the 370 nm region.

The color of solutions of 1-phenylpyrazolidinedione radicals **6e·** and **6f·** also fades reversibly upon cooling, but to a smaller degree than for 1-α-cumyl- or 1-*tert*-butylurazole radicals. Vapor pressure osmometric studies indicate that at concentrations greater than 5×10^{-2} *M* in either carbon tetrachloride, benzene, or acetonitrile, radicals **6e·** and **6f·** are greater than 90% dimerized. Similarly, the green color of 1-α-cumylpyrazolidinedione radicals **6g·** and **6h·** fades reversibly upon cooling. By analogy with urazole radicals, the presence of an equilibrium between **6g·** and **6h·** and their tetrazane dimers is inferred. The inability to isolate **6g·** or **6h·** prevented the determination of their association constants by vapor pressure osmometry.

As solids, pyrazolidinediones have two strong infrared carbonyl absorptions at 1750–1745 and 1685–1675 cm^{-1} (Table III); in chloroform solution there are typically two absorptions, 1745–1740 (m) and 1695–1690 (s) cm^{-1}. In solution, the tetrazane dimers of 1-phenylpyrazolidinedione radicals exhibit three carbonyl absorptions 1790 (m), 1771–1763 (m), and 1729 (s) cm^{-1}. α-Cumyl radical **6g·**, however, exhibits only two carbonyl absorptions. As solids, the carbonyl absorption of tetrazane dimers **6e–6e** and **6f–6f** occur at 1800–1795 (m), 1780–1770 (m), and 1735–1730 (s) cm^{-1}.

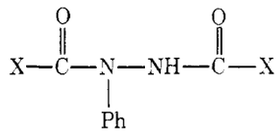
The EPR spectra of 1-α-cumylpyrazolidinedione radicals **6g·** and **6h·** are virtually identical and have nine lines owing to unequal splitting by the hydrazyl nitrogens (Table IV). Phenyldiethyl radical **6e·** gives rise to an EPR spectrum that shows coupling of the hydrazyl nitrogens and the aromatic hydrogens. Phenyldimethyl radical **6f·** has the same basic EPR spectrum as **6e·** but contains an additional hyperfine splitting of *ca.* 0.15 G.

Discussion

1-α-Cumyl- and 1-*tert*-butylurazole radicals are unique as they are the first hydrazyl radicals to be isolated in which the hydrazyl nitrogens lack a directly bonded aromatic group. Both urazole and pyrazolidinedione radicals are true hydrazyl radicals as evidenced by the magnitude of the hyperfine splitting constants.[19]

Three conditions are generally considered prerequisite for persistence of hydrazyl radicals: (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.[4,20,21] All of these conditions are fulfilled in the 1-α-cumyl- and 1-*tert*-butylurazole radicals. The steric bulk necessary to retard reactions at the divalent nitrogen is provided by the α-cumyl and *tert*-butyl groups. The nearly identical behavior and properties (similarity of visible spectra, EPR spectra, IR spectra, association constants, and persistence) of the radicals bearing these substituents indicate that the aromatic ring of the cumyl group is not involved in delocalization of unpaired spin density. Such delocalization, however, does occur in hydrazyl radicals bearing directly bonded aromatic groups. Like DPPH, 1-α-cumyl- or 1-*tert*-butylurazole radicals do not react with molecular oxygen but are capable of reacting with compounds having abstractable hydrogen atoms. Neither 1-α-cumyl- nor 1-*tert*-butylurazole radicals have hydrogens on carbons α to the hydrazyl nitrogens and hence do not undergo disproportonation. 1-Cyclohexylurazole radical **4l·**, however, has an α hydrogen and is observed to rapidly decompose.

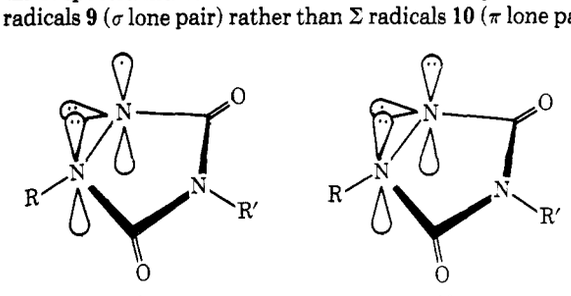
The EPR spectra of urazole radicals show that the unpaired electron is delocalized over the entire heterocycle. When treated with lead dioxide, solutions of acyclic diacylhydrazines **7** and **8** give rise to weak EPR spectra that exhibit strong coupling of the unpaired electron to only one nitrogen (Table IV), a characteristic of hydrazoxyl radicals.[9,22] The contrasting behavior of cyclic and acyclic diacylhydrazines presumably results from conformational preferences. At 44 °C, the 60 MHz NMR spectra of **7** and **8** each exhibit two equally intense peaks



7: X = OEt
8: X = NHMe

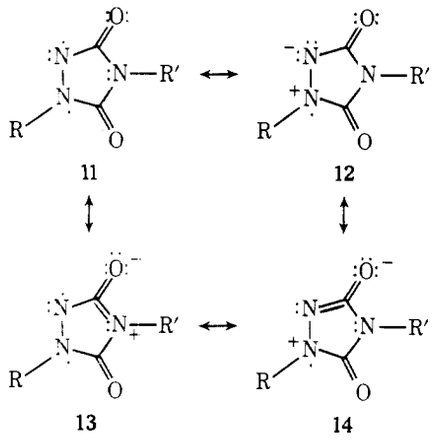
for the α-cumyl methyls, indicative of restricted N-N rotation[23–26] and an orthogonal relationship between the two acyl groups. The rotational barrier for **7** is calculated[26,27] from the coalesence temperature of these diastereotopic signals (T_c = 85–90 °C, $\Delta\nu$ = 9 Hz) to be *ca.* 19 kcal/mole. This orthogonal geometry prevents overlapping of the p orbitals of the adjacent nitrogens. In the cyclic urazoles and pyrazolidinediones, the two acyl groups are forced into a coplanar relationship that, consequently, allows efficient overlap of the hydrazyl nitrogen p orbitals. Thus, delocalization of the unpaired electron over the two hydrazyl nitrogens is facilitated in the urazole and pyrazolidinedione radicals (because of the parallel orbital alignment) relative to the acyclic diacylhydrazines.

EPR spectra indicate that urazole radicals are ground state π radicals **9** (σ lone pair) rather than Σ radicals **10** (π lone pair).



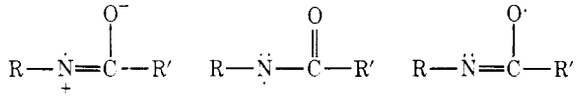
9 **10**

Although resonance structure **11** is used to represent urazole radicals, the a_{N-1}/a_{N-2} ratios for urazole radicals (0.74–0.81) and pyrazolidinedione radicals (0.71–0.79) are similar to that of DPPH (0.83)[28] and indicates significant unpaired spin



11 12 13 14

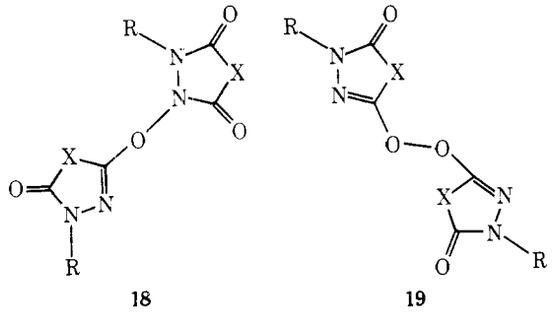
density on the trivalent nitrogen as represented by canonical form **12**. Charge separation thus induced can be further delocalized as in **14**.[39] The nearly equal $a_{CH3}/a_{N\text{-}4}$ values of 4-methylurazole radicals **4e**· (0.41), **4h**· (0.38), and the phthalimide radical anion (0.35)[30] suggest a similar geometry about the imide nitrogen in these systems. The importance of this imide nitrogen toward the persistence of 1-α-cumyl and 1-*tert*-butylurazole radicals is strongly suggested by the lesser persistence of the α-cumylpyrazolidinedione radicals. Simple amido radicals **16** have been observed by EPR spectroscopy but are transient.[31] The preferred delocalization of a lone pair of electrons (**15**) over the delocalization of the unpaired electron[32] (**17**) has the effect of localizing unpaired electron spin



15 16 17

density on the amide nitrogen and renders the radical more reactive. Delocalization of the imide nitrogen lone pair onto the carbonyl oxygen (shown in **13**) reduces the ability of this carbonyl group to delocalize the lone pair of electrons on the divalent nitrogen. Similar reasoning leads to the expectation that α-cumylpyrazolidinedione radicals should be less persistent than the analogous urazole radicals. This proves to be the case.

The well known[4] reversible dimerization of hydrazyl radicals to tetrazanes was first observed by Goldschmidt[33] and later studied by Wilmarth and Schwartz[34] for 1,1-diaryl-2-acylhydrazyl radicals. In the case of urazole and pyrazolidinedione radicals, three different dimeric linkages are conceivable: N–N (*e.g.*, **4–4** or **6–6**), O–N (**18**), or 0–0 (**19**). Strucutres such as **18** and **19** that include carbonyl oxygen in the linkage are ruled out on the basis of infrared spectral data. Dimers **18** and **19** would be expected to have strong absorp-



18 19

tions at *ca.* 1605 and *ca.* 1513 cm^{-1}, characteristic of the O–C=N functionality in these structures.[35] No such absorptions are noted in the infrared spectra of the dimers.[36]

The decreasing tendency for urazole radicals to associate in solution as solvent polarity increases demonstrates greater polarity for the radicals than for the dimers as might be expected on the basis of dipolar canonical structures such as **12–14**.

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. Visible spectra were recorded with a Cary 14 spectrophotometer. NMR spectra were obtained with Varian A-60A or HA-100 spectrometers. Chemical shifts, δ, are expressed in ppm relative to internal tetramethylsilane. EPR spectra were recorded with a Varian E-9 X-Band spectrometer. Mass spectra were obtained with Varian MAT CH-5 or 731 mass spectrometers. 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. Vapor pressure osmometry data were obtained with a Mechrolab 301A vapor pressure osometer operating at 25.0 ± 0.2 °C.

All hydrazines, isocyanates, and chloroformates were distilled prior to use. Other commercially available reagents and reagent grade solvents were used without further purification, unless otherwise stated. Column chromatography was carried out on Brinkmann 0.05–0.2 mm silica gel. Analytical thin layer chromatography (tlc) was performed on Merck 0.25 mm precoated fluorescent silica gel plates.

EPR Samples. Solutions of transient radicals were prepared by stirring a solution of the urazole or pyrazolidinedione with lead dioxide and anhydrous sodium sulfate. After 30 sec–5 min, these mixtures were filtered, the filtrates placed in 4 mm o.d. quartz tubes, and the samples stored at −196 °C. Solutions of persistent radicals were prepared as described above or by dissolving the appropriate amount of the isolated tetrazane dimer in the desired solvent. All samples were vacuum degassed by at least 3 freeze-pump-thaw cycles and sealed while frozen under high vacuum. Samples of transient radicals were stored at −196 °C when not being observed.

Syntheses. The preparation of a typical urazole is outlined below. Experimental procedures for the preparation of the remaining urazoles are provided in the supplementary material.

Ethyl 3-α-Cumylcarbazate (2b). To a mechanically stirred solution of α-cumylhydrazine[37] (**1b**, 30.05 g, 0.20 mol) and triethylamine (20.24 g, 0.20 mol) in anhydrous ether (400 ml), which was cooled to below 0 °C in an ice-acetone bath, was added a solution of ethyl chloroformate (21.60 g, 0.20 mol) in anhydrous ether (200 ml) at a rate that maintained the temp below 5 °C. After the addition was completed, the resulting mixture was allowed to warm to room temperature, and filtered. Removal of the solvent from the filtrate at reduced pressure and vacuum distillation afforded 40.16 g (0.181 mol, 90%) of carbazate **2b** as a viscous, yellow oil: bp 120 °C (0.05 Torr); IR ($CHCl_3$) 3435, 3375, and 3325 (NH), 3015, 2990, and 2945 (CH), 1724 (C=O), 1532, 1497, 1471, 1446, 1383 (CMe_w), 1368 (CMe_2), 1256 (C–CO), 1177, 1154, 1048, and 707 cm^{-1}; NMR ($CDCl_3$) 1.18 (t, 3, J = 7 Hz, OCH_2CH_3), 1.43 (s, 6, $C(CH_3)_2$), 4.05 (s, 1, CN*H*N), and 4.08 (q, 2, J = 7 Hz, $CO_2CH_2CH_3$), 6.05 (s, 1, CON*H*N), and 7.1–7.6 (m, 5, C_6H_5); mass spectrum (70 eV) m/e (rel intensity) 222 (weak, M^+), 120 (11), 119 (100), 104 (14), 91 (53), 79 (11), 77 (10), 41 (19), and 29 (10).

Anal. Calcd for ($C_{12}H_{18}N_2O_2$) C, H, N.

1-Carbethoxy-2-α-cumyl-4-methylsemicarbazide (3h). A solution of α-cumyl carbazate **2b** (91.36 g, 0.41 mol) and methyl isocyanate (33.5 g, 0.587 mol) in benzene (600 ml) was heated at reflux for 4 hr. Removal of the solvent under reduced pressure followed by vacuum drying of the resultant viscous, slightly yellow liquid afforded a foam-like solid. Washing of the solid with benzene (3X) and vacuum drying furnished 94.09 g (0.337 mol, 82%) of semicarbazide **3h** as a white solid: mp 144–145.5 °C; IR ($CHCl_3$) 3485, 3445, 3380, and 3265 (NH), 3015, 3995, and 2950 (CH), 1750 (carbamate C=O), 1679 (urea C=O), 1522, 1496, 1387 (CMe_2), 1240 (C–O), 1060, and 707 cm^{-1}; NMR ($CDCl_3$) 1.25 (t, 3, J = 7 Hz, OCH_2CH_3), 1.60 (s, 6, $C(CH_3)_2$), 2.52 (d, 3, J = 5 Hz, $NHCH_3$), 4.18 (q, 2, J = 7 Hz, $CO_2CH_2CH_3$), 5.92 (q, 1, CON*H*CH_3), 7.0–7.7 (m, 5, C_6H_5), and 8.47 (s, 1, CON*H*); mass spectrum (70 eV) m/e (rel intensity) 279 (weak, M^+), 161 (14), 120 (11), 119 (100), 104 (27), 41 (14), and 28 (10).

Anal. Calcd for ($C_{14}H_{21}N_3O_3$) C, H, N.

1-α-Cumyl-4-methylurazole (4h). A solution of semicarbazide **3h** (96.90 g, 0.347 mol) in aq 25% potassium hydroxide (200 ml) was heated on a steam bath for 2 hr. After diluting with water (200 ml) and

cooling to 0 °C, the solution was acidified with concentrated hydrochloric acid causing a solid to form. Filtration, washing the isolated solid with water until the washings were neutral, and recrystallization from ethanol afforded 72.27 g (0.310 mol, 89%) of urazole **4h**: mp 129.5–130.5 °C [EtOH; lit.[38] mp 126.5–127 °C (sublimation)]; IR ($CHCl_3$) 3365 (NH), 3015 and 2985 (CH), 1770 and 1710 (C=O), 1477, 1390 (CMe_2), and 1371 (CMe_2) cm^{-1}; IR (KBr) 3265 (NH), 2995 and 2940 (CH), 1763 and 1693 (C=O), 1482, 1452, 1383 (CMe_2), 1366 (CMe_2), 1232, 770, and 702 cm^{-1}; NMR ($CDCl_3$) 1.80 (s, 6, $C(CH_3)_2$), 2.95 (s, 3, NCH_3), 7.3–7.5 (m, 5, C_6H_5), and 8.82 (s, 1, CONH); mass spectrum (70 eV) *m/e* (rel intensity) 233 (weak, M^+), 120 (11), 119 (100), 91 (38), 79 (6), 77 (7), and 41 (8).

Anal. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.73; H, 6.44; N, 18.13.

1-α-Cumyl-4-phenylurazole (4g). Mp 159.5–161 °C; IR ($CHCl_3$) 3370 (NH), 3025 and 2990 (CH), 1775 and 1712 (C=O), 1507, 1430, 1390 (CMe_2), and 1370 (CMe_2) cm^{-1}; IR (KBr) 3170 (NH), 3070, 2995, and 2980 (CH), 1773 and 1697 (C=O), 1495, 1427, 1383 (CMe_2), 1364 (CMe_2), 866, 775, and 700 cm^{-1}; NMR ($CDCl_3$) 1.82 (s, 6, $C(CH_3)_2$), 7.1–7.5 (m, 10, C_6H_5), and 8.38 (s, 1, CONH); mass spectrum (70 eV) *m/e* (rel intensity) 295 (weak, M^+), 120 (11), 119 (100), 91 (32), 77 (7), and 41 (12).

Anal. Calcd for $C_{17}H_{17}N_3O_2$: C, 69.14; H, 5.80; N, 14.23. Found: C, 69.26; H, 5.86; N, 14.22.

1-α-Cumyl-4-*tert*-butylurazole (4i). Mp 149.5–150.5 °C; IR ($CHCl_3$) 3365 (NH), 3020, 2990, and 2940 (CH), 1762 and 1702 (C=O), 1400, and 1373 cm^{-1}; IR (KBr) 3430, 3180 (NH), 3070, 3040, 3010, 2985, and 2950 (CH), 1764 and 1692 (C=O), 1467, 1412, 1385, 1378, 1370, 1270, 1177, 778, 768, and 702 cm^{-1}; NMR ($CDCl_3$) 1.53 (s, 9, $C(CH_3)_3$), 1.75 (s, 6, $C(CH_3)_2$), 7.1–7.5 (m, 5, C_6H_5), and 8.42 (s, 1, CONH); mass spectrum (70 eV) *m/e* (rel intensity) 275 (weak, M^+), 120 (10), 119 (100), 91 (37), 79 (5), 77 (6), 57 (9), 41 (20), 29 (5), and 29 (5).

Anal. Calcd for $C_{15}H_{21}N_3O_2$: C, 65.45; H, 7.69; N, 15.26. Found: C, 65.30; H, 7.61; N, 15.57.

1-*tert*-Butyl-4-phenylurazole (4j). Mp 150–153.5 °C (EtOAc); IR ($CHCl_3$) 3370 and 3180 (NH), 3030 and 2980 (CH), 1770 and 1691 (C=O), 1498, 1425, 1393 (CMe_3), and 1364 (CMe_3) cm^{-1}; IR (KBr) 3450 and 3180 (NH), 3075 and 2980 (CH), 1769 and 1704 (C=O), 1506, 1433, 1396 (CMe_3), 1369 (CMe_3), 1213, 774, and 716 cm^{-1}; NMR ($CDCl_3$) 1.46 (s, 9, $C(CH_3)_3$), 7.3–7.6 (m, 5, C_6H_5), and 9.37 (s, 1, CONH); mass spectrum (70 eV) *m/e* (rel intensity) 233 (8, M^+), 178 (10), 177 (95), 120 (12), 119 (13), 93 (6), 91 (7), 77 (6), 64 (5), 58 (5), 57 (100), 56 (7), 41 (32), 39 (6), and 29 (27).

Anal. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 62.05; H, 6.58; N, 18.25.

1-*tert*-Butyl-4-methylurazole (4k). Mp 129–130.5 °C (EtOAc); IR ($CHCl_3$) 3380 and 3180 (NH), 3030 and 2985 (CH), 1760 and 1689 (C=O), 1480, 1399 (CMe_3)$_3$ and 1368 (CMe_3) cm^{-1}; IR (KBr) 3450 and 3175 (NH), 2980 (CH), 1760 and 1702 (C=O), 1483, 1396 (CMe_3), 1370 (CMe_3), and 1221 cm^{-1}; NMR ($CDCl_3$) 1.46 (s, 9. $C(CH_3)_3$), 3.02 (s, 3, NCH_3), and 9.24 (s, 1, CONH); mass spectrum (70 eV) *m/e* (rel intensity) 171 (7, M^+), 116 (7), 115 (87), 58 (15), 57 (100), 56 (10), 42 (5), 41 (35), 29 (24), and 28 (5).

Anal. Calcd for $C_7H_{13}N_3O_2$: C, 49.11; H, 7.65; N, 24.54. Found: C, 49.51; H, 7.60; N, 24.80.

1-Phenyl-4,4-diethylpyrazolidine-3,5-dione (6e). Treatment of a solution of diethyl diethylmalonate (**5c,** 21.63 g, 0.100 mol) and phenylhydrazine (**1a,** 11.00 g, 0.102 mol) in absolute ethanol (50 ml) with sodium ethoxide (0.110 mol) according to the method of Conrad and Zart[15a] afforded, after work-up and recrystallization (EtOAc), 7.64 g (33 mmol, 33%) of a colorless solid: mp 110.5–112 °C [lit.[17a] mp 114–115 °C (EtOH)]; IR ($CHCl_3$) 3360 and 3155 (NH), 3015, 2975, 2940, and 2885 (CH), 1742 and 1694 (C=O), 1597, 1498, 1460, and 1308 cm^{-1}; IR (KBr) 3440 and 3135 (NH), 2965, 2930, and 2875 (CH), 1746, and 1678 (C=O), 1502, 1447, 1308, 752, and 723 cm^{-1}; NMR ($CDCl_3$) 0.90 (t, 6, J = 7 Hz, CH_2CH_3), 1.83 (q, 4, J = 7 Hz, CCH_2CH_3), 7.1–7.7 (m, 5, C_6H_5), and 10.13 (s, 1, CONH); mass spectrum (70 eV) *m/e* (rel intensity) 233 (14, m + 1), 232 (90, M^+), 204 (23), 189 (18), 108 (10), 98 (67), 97 (100), 91 (10), 83 (64), 77 (36), 69 (33), 55 (36), 51 (13), 43 (10), 41 (30), 39 (12), 29 (28), 28 (15), and 27 (11).

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.22; H, 7.09; N, 12.12.

1-Phenyl-4,4-dimethylpyrazolidine-3,5-dione (6f). Treatment of a solution of phenylhydrazine (**1a,** 11.00 g, 0.102 mol) and diethyl dimethylmalonate (**5d,** 18.82 g, 0.100 mol) in absolute ethanol (50 ml) with sodium ethoxide (0.117 mol) according to the method of Conrad and Zart[17a] afforded, after work-up and recrystallization (EtOAc), 14.14 g (69 mmol, 69%) of a colorless solid: mp 180–182 °C; IR ($CHCl_3$) 3355 and 3150 (NH), 3020, 2980, 2935, and 2875 (CH), 1760, 1742, and 1695 (C=O), 1595, 1498, 1391, 1247, 1230, and 1199 cm^{-1}; IR (KBr) 3440 and 3135 (NH), 2985, 2975, 2940, and 2880 (CH), 1748 and 1685 (C=O), 1597, 1501, 1440, 1389, 1346, 1336, 1300, 760, and 745 cm^{-1}; NMR ($CDCl_3$) 1.40 (s, 6, $C(CH_3)_2$), 7.1–7.7 (m, 5, C_6H_5), and 10.27 (s, 1, CONH); mass spectrum (70 eV) *m/e* (rel intensity) 205 (14, m + 1), 204 (100, M^+), 148 (19), 107 (23), 105 (14), 91 (10), 77 (41), 70 (74), 69 (22), 51 (16), 43 (19), 42 (31), 41 (26), and 39 (12)

Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.81; H, 5.89; N, 13.99.

1-α-Cumyl-4,4-diethylpyrazolidine-3,5-dione (6g). Treatment of a solution of α-cumylhydrazine[37] (**1b,** 6.00 g, 40 mmol) and diethyl diethylamalonate (**5c,** 9.00 g, 41.7 mmol) in absolute ethanol (30 ml) with sodium ethoxide (48 mmol) according to the method of Conrad and Zart[17a] afforded, after work-up and recrystallization (EtOAc), 3.09 g (11.3 mmol, 28%) of a colorless solid: mp 117.5–118.5 °C; IR ($CHCl_3$) 3370 (NH), 3020, 2975, 2940, and 2885 (CH), 1740 and 1691 (C=O), 1459, 1449, 1443, 1390 (CMe_2), 1369 (CMe_2), 1305, 1188, 1174, and 704 cm^{-1}; NMR ($CDCl_3$) 0.76 (t, 6, J = 7.5 Hz, CH_2CH_3), 1.68 (q, 4, J = 7.5 Hz, CCH_2CH_3), 1.87 (s, 6, $C(CH_3)_2$), 7.1–7.4 (m, 5, C_6H_5), and 8.62 (s, 1, CONH); mass spectrum (70 eV) *m/e* (rel intensity) 274 (1, M^+), 120 (10), 119 (100), 118 (4), 91 (25), 79 (4), and 41 (10).

Anal. Calcd for $C_{16}H_{22}N_2O_2$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.23; H, 8.04; N, 10.15.

1-α-Cumyl-4,4-dimethylpyrazolidine-3,5-dione (6h). Treatment of a solution of diethyl dimethylmalonate (**5d,** 7.60 g, 40.3 mmol) and α-cumylhydrazine[37] (**1b,** 6.00 g, 40.0 mmol) in absolute ethanol (30 ml) with sodium ethoxide (48 mmol) according to the method of Conrad and Zart[17a] afforded, after work-up and recrystallization (EtOAc), 3.29 g (13.4 mmol, 33%) of a colorless solid: mp 145–146.5 °C; IR (KBr) 3435 and 3235 (NH), 2995, 2980, 2935, and 2875 (CH), 1740 and 1682 (C=O), 1467, 1447, 1419, 1392 (CMe_2), 1368 (CMe_2), 1360 (CMe_2), 1344, 775, 766, 706, and 700 cm^{-1}; NMR ($CDCl_3$) 1.20 (s, 6, $(CO)_2C(CH_3)_2$), 1.84 (s, 6, $PhC(CH_3)_2$), 7.1–7.4 (m, 5, C_6H_5), and 8.92 (s, 1, CONH); mass spectrum (70 eV) *m/e* (rel intensity) 246 (weak, M^+), 120 (10), 119 (100), 118 (4), 91 (31), 79 (5), 77 (4), and 41 (12).

Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.42; H, 7.23; N, 11.43.

1-α-Cumyl-4-phenylurazole Radical (4g·). A solution of urazole **4g** (1.48 g, 5.01 mmol) in benzene (75 ml) was stirred with lead dioxide (2.39 g) and anhydrous sodium sulfate (2.14 g) for 2.5 hr at room temperature. Filtration and concentration of the filtrate afforded a brown oil, which was chromatographed on silica gel with chloroform. Collection of the mobile colored band, and evaporation at reduced pressure afforded, after vacuum drying, 0.69 g (2.34 mmol, 47%) of an off-white solid: mp 113.5–115.5 °C; IR ($CHCl_3$) 3075, 3045, 3000, and 2955 (CH), 1761, 1743, and 1705 (C=O), 1505, 1399, 1372 (CMe_2), and 1127 cm^{-1}; IR (KBr) 3070, 2990, and 2940 (CH), 1792, 1744, and 1706 (C=O), 1500, 1402, 1372 (CMe_2), 1240, 1187, 1147, 769, 731, 714, 701, and 689 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 294 (weak, M^+), 120 (10), 119 (100), 118 (8), 91 (30), and 41 (11).

Anal. Calcd for $C_{17}H_{16}N_3O_2$: C, 69.37; H, 5.48; N, 14.28; mol wt, 294.1242. Found: C, 68.86; H, 5.60; N, 14.00; mol wt, 294.1239 (mass spectrum).

1-α-Cumyl-4-methylurazole Radical (4h·). A solution of urazole **4h** (1.17 g, 5.0 mmol) in benzene (25 ml) was treated with lead dioxide (2.39 g, 10 mmol) and anhydrous sodium sulfate (2.14 g) as described for radical **4g·**. After chromatographic purification (SiO_2/$CHCl_3$), 0.70 g (3.05 mmol, 61%) of a beige solid was obtained: mp 108–109 °C; IR ($CHCl_3$) 3040, 3000, and 2960 (CH), 1806, 1777, 1739, and 1707 (C=O), 1452, 1396, 1373 (CMe_2), and 706 cm^{-1}; IR (KBr) 3015, 3995, 2975, and 2950 (CH), 1805, 1792, 1732, and 1706 (C=O), 1465, 1455, 1395, 1379 (CMe_2), 1140, 781, 775, 739, and 709 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 232 (5, $M^·$), 120 (11), 119 (100), 118 (9), 117 (7), 103 (9), 91 (41), 79 (7), 77 (8), 51 (5), and 41 (13).

Anal. Calcd for $C_{12}H_{14}N_3O_2$: C, 62.06; H, 6.08; N, 18.09; mol wt, 232.1086. Found: C, 62.04; H, 5.98; N, 18.01; mol wt, 232.1080 (mass spec).

1-α-Cumyl-4-*tert*-butylurazole Radical (4i·). Treatment of a solution of urazole **4i** (1.38 g, 5.01 mmol) in benzene (75 ml) with lead dioxide (2.39 g, 10 mmol) and anhydrous sodium sulfate (2.14 g) as described for radical **4g·** afforded, after chromatographic purification (SiO_2/$CHCl_3$), 1.07 g (3.90 mmol, 78%) of a beige solid: mp 83.5–85.5 °C; IR ($CHCl_3$) 2990 and 2945 (CH), 1763, 1728, and 1693 (C=O), 1393, 1360, and 703 cm^{-1}; IR (KBr) 2985 and 2940 (CH), 1800, 1785, 1734, and 1696 (C=O), 1371, 1267, 1151, 769, 750, and 705 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 274 (weak, M^+), 217 (6), 120 (10), 119 (100), 118 (7), 91 (22), 57 (9), and 41 (13).

Anal. Calcd for $C_{15}H_{20}N_3O_2$: C, 65.67; H, 7.35; N, 15.32; mol wt,

274.1555. Found: C, 65.65; H, 7.46; N, 15.08; mol wt, 274.1557 (mass spectrum).

1-*tert*-Butyl-4-phenylurazole Radical (4j·). Treatment of a solution of urazole **4j** (1.16 g, 4.97 mmol) in benzene (75 ml) with lead dioxide (2.39 g, 10.0 mmol) and anhydrous sodium sulfate as described for radical **4g·** afforded, after chromatographic purification (SiO_2/$CHCl_3$), 0.58 g (2.50 mmol, 50%) of a light wine red solid: mp 74.5–76.5 °C; IR ($CHCl_3$) 2995 and 2945 (CH), 1764 and 1701 (C=O), 1504, 1403, and 1373 (CMe_3) cm^{-1}; IR (KBr) 3015, 2995, and 2950 (CH), 1808, 1792, 1742, and 1709 (C=O), 1509, 1498, 1421, 1403, 1371 (CMe_3), 1207, 1191, 752, 746, 735, and 717 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 232 (4, M^+), 177 (7), 120 (5), 119 (28), 91 (4), 58 (5), 57 (100), 41 (9), and 29 (5).

Anal. Calcd for $C_{12}H_{14}N_3O_2$: C, 62.06; H, 6.08; N, 18.09; mol wt, 232.1086. Found: C, 62.03; H, 6.21; N, 17.85: mol wt, 232.1087 (mass spectrum).

1-*tert*-Butyl-4-methylurazole Radical (4k·). A solution of urazole **4k** (0.86 g, 5.02 mmol) in benzene (75 ml) was treated with lead dioxide (2.39 g, 10.0 mmol) and anhydrous sodium sulfate (2.14 g) as described for radical **4g·**. After chromatrographic purification (SiO_2/$CHCl_3$), 0.23 g (1.35 mmol, 27%) of a beige solid was obtained: mp 94–96 °C; IR ($CHCl_3$) 3025, 2980, and 2930 (CH), 1766, 1740, and 1706 (C=O), 1455, 1399 (CMe_3), 1375 (CMe_3), 1271, 1139, and 1004 cm^{-1}; IR (KBr) 2965 and 2940 (CH), 1807, 1793, and 1732 (C=O), 1463, 1398 (CMe_3), 1371 (CMe_3), 1289, 1166, and 1118 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 170 (3, M^+), 116 (10), 115 (34), 98 (10), 58 (8), 57 (100), 56 (14), 42 (8), 41 (36), 39 (6), and 29 (18).

Anal. Calcd for $C_7H_{12}N_3O_2$: C, 49.40; H, 7.11; N, 24.69; mol wt, 170.0930. Found: C, 49.57; H, 7.28; N, 24,48; mol wt, 170.0933 (mass spectrum).

1-Phenyl-4,4-diethylpyrazolidine-3,5-dione Radical (6e·). Treatment of a solution of pyrazolidinedione **6e** (1.16 g, 4.99 mmol) with lead dioxide (2.39 g, 10 mmol) and anhydrous sodium sulfate (2.14 g) as described for radical **4g·** afforded, after chromatographic purification (SiO_2/$CHCl_3$), 0.44 g (2.17 mmol, 44%) of a brown solid: mp 106–108 °C; IR ($CHCl_3$) 3040, 2995, 2945, and 2880 (CH), 1799, 1777, and 1732 (C=O), 1499, 1390, 1336, and 1308 cm^{-1}; IR (KBr) 3070, 2990, 2945, and 2880 (CH), 1798, 1776, and 1731 (C=O), 1498, 1392, 1346, 1313, 1296, 779, 752, 724, and 695 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 205 (10, m + 2), 204 (76, m + 1), 203 (15, M^+), 154 (21), 148 (15), 112 (12), 107 (19), 105 (15), 91 (13), 85 (52), 83 (80), 78 (80), 77 (86), 74 (10), 71 (11), 70 (100), 69 (21), 64 (11), 57 (11), 52 (19), 51 (40), 50 (21), 48 (12), 47 (26), 44 (15), 43 (38), 42 (48), 41 (48), 39 (38), 36 (12), and 35 (10).

Anal. Calcd for $C_{11}H_{11}N_2O_2$: C, 65.01; H, 5.46; N, 13.78; mol wt, 203.0820. Found: C, 65.08; H, 5.54; N, 13.08; mol wt, 203.0823 (mass spectrum).

1-α-Cumyl-4,4-diethylpyrazolidine-3,5-dione Radical (6g·). A solution of pyrazolidinedione **6g** in chloroform was stirred with lead dioxide and anhydrous sodium sulfate for 20 min. The product was purified by applying the reaction mixture to a short column of silica gel and eluting with chloroform. Collection of the mobile green band and concentration at reduced pressure with a bath temperature below 25 °C afforded an emerald green solution of radical **6g·**: IR ($CHCl_3$) 3000, 2980, 2950, 2890 (CH), 1756, 1793 (C=O), 1463, 1258, 1125, and 706 cm^{-1}.

***tert*-Butylhydrazine (1c).**[39,40] To an etheral solution of *tert*-butylmagnesium chloride prepared from magnesium (31 g, 1.28 mol) and *tert*-butyl chloride (118 g, 1.27 mol) in anhydrous ether (650 ml) was added a solution of diphenyldiazomethane[41] (166 g, 0.855 mol) in anhydrous ether (350 ml). After standing overnight, the reaction mixture was worked-up with saturated ammonium chloride. Recrystallization from ethanol afforded 172.56 g (0.684 mol, 80%) of benzophenone *tert*-butylhydrazone: mp 76–78 °C (lit.[39] mp 73.5–75 °C).

To a slurry of benzophenone *tert*-butylhydrazone (165 g, 0.654 mol) in ethanol (350 ml) was added concentrated hydrochloric acid (235 ml), causing all of the solid to dissolve. While being stirred at room temperature for 2 days. this solution became cloudy. After stirring for an additional day, a solid had formed. This mixture was separated by filtration and the solid (mp 45 °C) was shown to be benzophenone (mp 48 °C). Concentration of the filtrate to about 1/2 of the original volume under reduced pressure caused more solid to precipitate from solution. This solid was also separated by filtration and shown to be benzophenone. The filtrate was extracted with ether (3X). Removal of the liquid from the aqueous phase under reduced pressure afforded an off-white solid, which was dried *in vacuo*. Absolute ethanol was added to the solid, the mixture thoroughly mixed, and the ethanol removed under reduced pressure. This process was repreated a second time. Finally, the solid was thoroughly washed with benzene. After filtration, 48.15 g (0.386 mol, 59%) of *tert*-butylhydrazine hydrochloride was obtained. A small sample was recrystallized from ethanol: mp 190–192 °C (lit.[39] mp 189 °C).

tert-Butylhydrazine was obtained by distilling the hydrochloride from 25% sodium hydroxide. The distillate was dried with sodium hydroxide and then distilled from barium oxide.

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Registry No.—**1a,** 100-63-0; **1b,** 3178-39-0; **1c,** 32064-67-8; **2a,** 6233-02-9; **2b,** 52809-11-7; **2c,** 64739-41-9; **3d,** 64739-42-0; **3e,** 64739-43-1; **3f,** 64739-44-2; **3g,** 64739-45-3; **3h,** 52809-12-8; **3i,** 64739-46-4; **3j,** 64739-47-5; **3k,** 64739-48-6; **4d,** 34874-03-8; **4e,** 4500-23-3; **4f,** 64728-39-8; **4l,** 64728-40-1; **5c,** 77-25-8; **5d,** 1619-62-1; **6h,** 64728-41-2; , **6h·,** 64728-44-5; **7,** 64728-42-3; **8,** 64728-43-4; ethyl chloroformate, 541-41-3; ethyl isocyanate, 624-83-9; phenyl isocyanate, 03-71-9; *tert*-butyl isocyanate, 609-86-5.

Supplementary Material Available: EPR spectra of radicals **4e·, 4f·, 4i·, 4k·, 4l·, 6e·, 6f·, 6g·,** and spectral data (NMR, infrared, mass spectra), elemental analyses, and procedures for preparation of carbazates **2c,** semicarbazides **3d–g, 3i–k,** urazoles **4d–g, 4k–l,** and hydrazines **7** and **8** (17 pages). Ordering information is given on any current masthead page.

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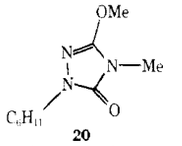

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Ionization and Fragmentation of Tri-*tert*- butylcarbinol. Evidence for a Transient *tert*-Butyl Carbanion in Me_2SO?

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The title compound undergoes immediate fragmentation to di-*tert*-butyl ketone and isobutane when treated with the potassium salt of dimethyl sulfoxide in that solvent at 25 °C. The reaction is highly exothermic, the heat evolved corresponding closely to Schleyer's estimate of the strain energy. Tri-*tert*-butylcarbinol is unassociated in carbon tetrachloride under conditions where neopentyl alcohol and di-*tert*-butylcarbinol show strong intermolecular hydrogen bonding. The latter two alcohols are recovered quantitatively under the conditions where the title compound is cleaved completely. The evidence can be interpreted in terms of mechanisms which involve a *tert*-butyl radical or a *tert*-butyl carbanion. The latter seems much more likely.

In the course of a systematic investigation[1-5] of Brønsted acidity in dimethyl sulfoxide (Me_2SO), we observed a steady decrease in enthalpy of deprotonation (ΔH_D) for aliphatic alcohols as bulky groups were substituted on the α carbon. However, when the limiting member of the series, tri-*tert*-butylcarbinol, was deprotonated a highly exothermic release of heat was observed which far exceeded that expected from the trend of the less crowded members. An excellent correlation had been found previously between the pK_a's of Brønsted acids in Me_2SO and their heats of deprotonation, ΔH_D.[4] On that basis, the ΔH_D of -23.2 kcal/mol for tri-*tert*-butylcarbinol suggests that its pK_a in Me_2SO should be about 22.5, or roughly equivalent to that of phenol. However, it was found that the alcohol did not dissolve in a dilute aqueous solution of sodium hydroxide. Examination of its acidity by Professor Bordwell's group at Northwestern University (using a Steiner-type indicator titration in Me_2SO) showed that the alcohol was not nearly as acidic as the heat of deprotonation suggested.

It was noted that easy fragmentation of the alcohol occurred in the pulsed ion cyclotron resonance spectrometer and that steric hindrance seemed to reduce the rate of the gas-phase proton transfer. Fragmentation in solution was also suggested by spectral evidence. A ^1H NMR spectrum of the deprotonation product showed a sharp singlet at 0.98 ppm, corresponding almost exactly to that of the starting alcohol. However, an infrared spectrum of the product solution showed a strong band in the carbonyl region at 1680 cm^{-1} suggesting the formation of di-*tert*-butyl ketone through a fragmentation reaction similar to those reported by Cram,[6] Zook,[7] and Lomas[8] in which either a *tert*-butyl carbanion or radical was ejected. Preliminary evidence supporting this possibility came when gas evolution was observed concurrently with deprotonation. Clearly, a careful recovery experiment was called for. The details of this investigation and strong evidence in favor of a facile base-catalyzed elimination of a *tert*-butyl carbanion will be described below.

Experimental Section

Synthesis. Tri-*tert*-butylcarbinol was prepared following the procedure of Bartlett and Lefferts.[9] In our hands yields were low (ca. 40%) with some improvement to 60% by addition of tetramethylethylenediamine to activate the reaction of *tert*-butyllithium (Ventron). The product was freed of residual di-*tert*-butyl ketone by steam distillation then recrystallized repeatedly from an ethanol–ice water mixture and vacuum sublimed until it was homogeneous to gas chromatography on a 9-ft column of SF-96 on Chromosorb W. A constant, but not very sharp, melting point between 116 and 117 °C (lit.[9] 117.5 °C) was achieved. The ^1H NMR spectrum in $CHCl_3$ at 250 MHz showed a single absorption at 0.98 ppm integrating for 27 protons and a small spike at 1.08 ppm, integrating for one proton, which disappeared in the presence of added D_2O.

Di-*tert*-butylcarbinol was prepared by reduction of di-*tert*-butyl ketone in ether with $LiAlH_4$. After solvent stripping, a white crystalline solid was left. The crystals were air dried and then dried over phosphorus pentoxide under vacuum. After several vacuum sublimations, the crystals gave a mp of 49–50 °C (lit.[10] 50 °C). Analysis by GLC on a 9-ft column of SF-96 on Chromosorb W revealed only one peak. The ^1H NMR spectrum in $CHCl_3$ at 250 MHz showed a peak at 0.98 ppm integrating for 18 protons, a peak at 2.52 ppm for one

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