Comparisons of the Inden-1-yl, Fluoren-9-yl, and Cycloprop[2,3]inden-1-yl Cations

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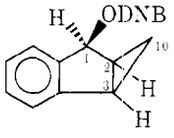
The first-order rate constants for hydrolysis of the inden-1-yl and fluoren-9-yl 3,5-dinitrobenzoates in 80% aqueous acetone at 80 °C have been indirectly determined. By comparison with kinetic data for hydrolysis of suitable model compounds under similar conditions, these can be estimated to be approximately 10^{11}- and 10^{8}-fold, respectively, retarded in rate by the presence of destabilizing antiaromatic effects in their rate-determining activated complexes for ionization. Comparisons with the much smaller corresponding antihomoaromatic rate retardations of about 10^{3}-fold for hydrolyses of the cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates under the same reaction conditions have also been made. A possible explanation for the differing magnitudes of the rate-retarding effects is offered.

Introduction

We recently reported[1] a detailed investigation of the rates and products of hydrolysis of the *endo*- and *exo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates (**1** and **2**, respectively) in 80% aqueous acetone. Kinetic comparisons with model compounds clearly showed the presence of moderate rate-retarding antihomoaromatic effects in the reactions of these systems. Also, from the effects on rate of introducing methyl substituents at C-3 and C-10, it could be concluded that delocalization of positive charge to C-3 in the activated complexes for ionization of both **1** and **2** is prohibited. However, considerable positive charge is delocalized to C-10 in these species.



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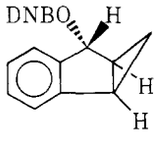

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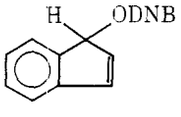
In connection with the above study and with the interesting question of the comparative behaviors of cyclopropane rings, carbon–carbon double bonds, and benzene rings in delocalization of positive charge, we became interested in obtaining quantitative information in the indene system concerning the relative effectiveness of cyclopropane rings in transmitting rate-retarding antihomoaromatic effects vs. carbon–carbon double bonds and benzene rings in transmitting rate-retarding antiaromatic effects. Thus, we wished to determine the rates of hydrolysis of the inden-1-yl and fluoren-9-yl 3,5-dinitrobenzoates (**3** and **4**, respectively) in 80% aqueous acetone for comparison with the rates of hydrolysis of suitable model systems in which antiaromatic interactions are precluded, and with the rate data obtained earlier[1] with the cycloprop[2,3]-inden-1-yl 3,5-dinitrobenzoates **1** and **2**. The results of these studies are described below.



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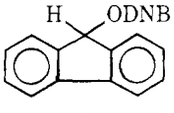

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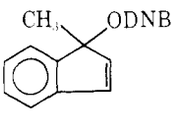
Results and Discussion

Initial solvolytic studies in 80% aqueous acetone at 100 °C with both the inden-1-yl and fluoren-9-yl 3,5-dinitrobenzoates (**3** and **4**, respectively) revealed very slow rates of acid production which were almost identical for both compounds (k_1 = $\sim 10^{-7}$ s^{-1} at 100 °C). Also, the acid production continued well beyond the expected theoretical infinities. These results suggest that the primary source of acid was not from hydrolysis of the esters, but from a different process such as slow oxidation of the solvent.[2] Thus, the maximum rate constants for hydrolysis of both **3** and **4** in 80% aqueous acetone at 100 °C must be 10^{-7} s^{-1}, but the actual values may be several powers of ten smaller. Isolation of unreacted **3** showed that its apparent low solvolytic reactivity was not the result of a 1,3-proton shift[3] to give the isomeric vinylic inden-3-yl ester.

Because of the problems described above, an indirect approach was required to obtain estimates of the desired rates of hydrolysis of **3** and **4** in 80% aqueous acetone via first-order nucleophilic substitution mechanisms. Thus, studies of the rates of hydrolysis of the 1-methylinden-1-yl (**5**) and 9-methylfluoren-9-yl (**6**) 3,5-dinitrobenzoates and of the model compounds **7** and **8** were carried out in 80% aqueous acetone. The tertiary derivatives **5** and **6** are considerably more reactive than the corresponding secondary esters **3** and **4** and are also able to react only via an ionization mechanism. Then, to enable prediction of the expected α-CH_3/H rate ratios for the inden-1-yl and fluoren-9-yl systems in 80% aqueous acetone, the rates of solvolysis of **3** and **5** and of the model compound **7** in the strongly ionizing but poorly nucleophilic[4] 2,2,2-trifluoroethanol solvent were determined. The results of these studies are summarized in Tables I and II.



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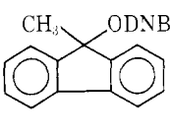

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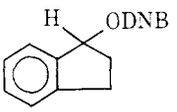

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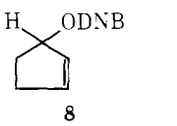

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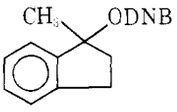

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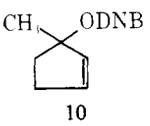

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For the purpose of the rate comparisons, solvolytic data for **4**, **6**, and **9** in 2,2,2-trifluoroethanol and for **9** and **10** in 80% aqueous acetone would ideally also have been desirable. However, we were unable to carry out a kinetic study with the fluorenyl derivatives **4** and **6** in 2,2,2-trifluoroethanol owing to their low solubilities. Also, we were unsuccessful in attempts to prepare **9** owing to its high reactivity. Several attempts to prepare **9** from the corresponding tertiary alcohol resulted only in isolation of 3-methylindene. It is presumed that **10** should be even more reactive than **9**.

Included among the attempts to prepare **9** were low-temperature reactions of 1-methylindan-1-ol with 3,5-dinitrobenzoyl chloride in pyridine followed by low temperature

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Table I. Rates of Hydrolysis of Some 3,5-Dinitrobenzoates in 80% Aqueous Acetone

Compd	Registry no.	Concn, 10^3 M	Temp, °C	$10^5 k_1$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
3	53820-88-5	7.7	100.0	<0.01		
4	64666-55-3	1.2	100.0	<0.01		
5	64666-56-4	4.8	100.0	10.5 ± 0.4		
		6.1	80.0	1.31 ± 0.05	26.6 ± 1.0	−5.9 ± 2.9
6	64666-57-5	7.9	80.0	105 ± 1		
		9.2	60.0	13.5 ± 0.2	23.3 ± 0.2	−11.2 ± 0.6
7	61463-15-8	7.8	100.0	30.6 ± 0.4		
		11.5	80.0	4.53 ± 0.04	24.3 ± 0.4	−9.9 ± 1.1
8	64666-40-6	10.6	80.0	116 ± 5		
		12.1	60.0	13.7 ± 0.7	24.3 ± 1.1	−8.2 ± 3.4

Table II. Rates of Solvolysis of Some 3,5-Dinitrobenzoates in 2,2,2-Trifluoroethanol

Compd	Concn, 10^3 M	Temp, °C	$10^5 k_1$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
3	4.1	125.0	0.110 ± 0.005		
	5.4	100.0	0.0104 ± 0.0003	27.1 ± 0.9	−14.1 ± 2.6
		80.0	(0.00124)		
5		80.0	(91.2)		
	4.5	60.0	11.3 ± 0.1		
	4.9	39.9	1.07 ± 0.4	23.7 ± 1.3	−5.9 ± 4.2
7		80.0	(343)		
	5.4	60.0	49.6 ± 1.1		
	6.9	39.9	5.59 ± 0.28	21.9 ± 0.7	−8.4 ± 2.3

aqueous as well as nonaqueous workups. Also, reactions of the tertiary alcohol were carried out with sodium hydride or with methyllithium in ether followed by addition of 3,5-dinitrobenzoyl chloride at −20 °C. In the latter case, a white solid presumed to be **9** was obtained on evaporation of the ether solvent at lower than 0 °C. However, on warming to room temperature, this liquified to a mixture shown by NMR examination to consist of 3-methylindene and 3,5-dinitrobenzoic acid.

To obtain information regarding just how reactive is the tertiary 1-methylindan-1-yl system as compared to the secondary indan-1-yl system, we carried out a brief NMR study of the reactions of the alcohols corresponding to **7** and **9** in dry acetic acid at 40 °C. It was found that the 1-methylindan-1-ol reacted to give 3-methylindene 1000 times faster than indan-1-ol reacted to give indan-1-yl acetate. No evidence could be found for even transient formation of 1-methylindan-1-yl acetate from the 1-methylindan-1-ol. The 1000-fold rate difference would not appear alone to suffice to explain our inability to isolate **9**. Thus, other factors such as the pronounced tendency of the 1-methylindan-1-yl system to undergo elimination may also be responsible.

In considering the data in Table II for the reactions run in the 2,2,2-trifluoroethanol solvent, it is seen that inden-1-yl 3,5-dinitrobenzoate (**3**) is approximately 10^5 less reactive than 1-methylinden-1-yl 3,5-dinitrobenzoate (**5**). This 10^5 α-CH_3/H rate ratio in the inden-1-yl system is in the same range as that expected[5] for limiting solvolyses of simple alkyl systems in which no charge delocalization is possible. However, it differs significantly from the smaller values of about 10^2–10^3 commonly observed[5] for systems in which benzylic-type charge delocalization is possible.

Using the approximately 10^5 rate ratios between **3** and **5** or **7** in 2,2,2-trifluoroethanol reported in Table II, one can then estimate for 80% aqueous acetone, where **5** and **7** also exhibit similar relative reactivities, that the first-order rate constant for ionization of inden-1-yl 3,5-dinitrobenzoate (**3**) should be approximately 1×10^{-10} s^{-1} at 80 °C. Furthermore, assuming a similar 10^5 α-CH_3/H rate ratio for the fluoren-9-yl system, a first-order rate constant for the ionization of **4** in 80% aqueous acetone at 80 °C of approximately 1×10^{-9} s^{-1} can be obtained. This estimated value for **4** appears quite reasonable and also in accord with literature kinetic data for other fluoren-9-yl derivatives which have appeared earlier. Thus, both Ledwith and Morris,[6] in their studies of the relative rates of hydrolysis of the fluoren-9-yl and benzhydryl *p*-toluenesulfonates in 90% aqueous tetrahydrofuran at 25 and 0 °C, and Lovins, Andrews, and Keefer,[7] in their studies of the relative rates of reaction of the corresponding bromides in 80% aqueous ethanol at about 70 °C, found fluoren-9-yl to benzhydryl rate ratios of about 10^{-3}. From Goering and Hopf's data[8] for the hydrolysis of benzhydryl *p*-nitrobenzoate in 90% aqueous acetone, one can estimate that in 80% aqueous acetone at 80 °C k_1 for the 3,5-dinitrobenzoate should be approximately 1×10^{-6} s^{-1}. Thus, using this value and a 10^{-3} fluoren-9-yl to benzhydryl rate ratio, k_1 for hydrolysis of fluoren-9-yl 3,5-dinitrobenzoate in 80% aqueous acetone at 80 °C can be estimated to be about 1×10^{-9} s^{-1}.

Finally, using the above derived rate constants for **3** and **4** and other data reported in Table I or from the literature, the relative rates of reaction summarized in Table III can be obtained. Based on the information in Table III, simple additive substituent effects in the cyclopentyl system point to the inden-1-yl (**3**), fluoren-9-yl (**4**), and cycloprop[2,3]inden-1-yl (**1** and **2**) 3,5-dinitrobenzoates being about 10^{12}, 10^9, and 10^4, respectively, less reactive than would be expected in the absence of antiaromatic or antihomoaromatic effects. However, it should be noted that these rate-retardation factors based on simple additive substituent effects are likely to be somewhat high. Our earlier work[1] on the cycloprop[2,3]inden-1-yl systems **1** and **2** involving a more detailed study of cumulative conjugating substituent effects showed that a realistic antihomoaromatic rate-retardation factor for this system is about 10^3. Thus, one can conclude that antiaromatic destabilizing effects in the activated complexes for the ionization of **3** and **4** actually produce rate retardations of approximately 10^{11} and 10^8, respectively.

The observation that the rate-retarding antiaromatic effects

Table III. Estimated Relative Rates for Limiting S_N1 Hydrolyses of Some 3,5-Dinitrobenzoates in 80% Aqueous Acetone at 80 °C

System	k_1, s^{-1}	k_{rel}
Inden-1-yl (3)	1×10^{-10}	1
Fluoren-9-yl (4)	1×10^{-9}	10
Cycloprop[2,3]inden-1-yl (1 or 2)	3×10^{-5} [a]	10^5
Indan-1-yl (7)	5×10^{-5}	10^5
Cyclopenten-3-yl (8)	1×10^{-3}	10^7
Bicyclo[3.1.0]hexan-2-yl (11)	2×10^{-6} [b]	10^4
Cyclopentyl (12)	1×10^{-10} [c]	(1)

[a] Estimated from the data of E. C. Friedrich and D. B. Taggart, *J. Org. Chem.*, **42**, 1437 (1977). [b] Estimated from the data of E. C. Friedrich and M. A. Saleh, *J. Am. Chem. Soc.*, **95**, 2617 (1973). [c] Estimated from the data of H. C. Brown and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 5008 (1964); and K. B. Wiberg and W.-F. Chen, *J. Am. Chem. Soc*, **96**, 3900 (1974).

upon the reactions of 3 and 4 are of considerably greater magnitude than are the rate-retarding antihomoaromatic effects upon the reactions of 1 and 2 requires some comment. This may be due in part to a carbon–carbon π bond in a benzocyclopenten-3-yl or cyclopenten-3-yl type cation being better for charge delocalization due to stereoelectronic reasons than is a cyclopropane ring in a bicyclo[3.1.0]hexan-2-yl type cation. Thus, it is seen from the results in Table III that 7 and 8 are 10^1 and 10^3 more reactive than 11. However, the major reason is most likely related to the observation[1] that in the cycloprop[2,3]inden-1-yl system a stabilizing interaction involving delocalization of charge to the C-10 cyclopropyl methylene is present which can at least partially counteract any destabilizing antihomoaromatic interactions. Such a type of counteracting stabilization is not available to the antiaromatic inden-1-yl and fluoren-9-yl systems.

Experimental Section

General. Melting and boiling points are uncorrected. Infrared spectra were run on a Perkin-Elmer 237B grating infrared spectrophotometer either as mineral oil mulls or in potassium bromide pellets. NMR spectra were run on a Varian Associates A-60A instrument, and chemical shifts are reported in ppm (δ) downfield from a Me_4Si internal standard. Mass spectra were run by Mr. John Voth or Mr. Paulus Bruins of the University of California, Davis, on a CEC Model 21-104 single-focusing instrument. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Inden-1-yl 3,5-Dinitrobenzoate. This dinitrobenzoate was prepared employing a slight modification of our earlier reported[3] procedure. After cooling the pyridine solvent to −25 °C, 1.7 g (0.013 mol) of inden-1-ol[3] was added followed by the addition in portions of 3.5 g (0.015 mol) of 3,5-dinitrobenzoyl chloride. The reaction mixture was maintained at −20 to −25 °C for 2 h and then poured into 160 mL of ice-cold 1 M hydrochloric acid. The precipitate collected was recrystallized from 150 mL of 1:1 chloroform–petroleum ether (30–60 °C) to yield 3.35 g of crude inden-1-yl 3,5-dinitrobenzoate, mp 136–145 °C. Further recrystallization of 2.3 g of this material from acetone yielded 1.7 g (61%) of pure inden-1-yl 3,5-dinitrobenzoate: mp 145.5–146.5 °C [lit.[3] mp 142–145 °C]; NMR ($CDCl_3$) 6.5 (m, 2 H, CHODNB and CHCHODNB), 6.9 (dd, J = 2 and 6 Hz, 1 H, CH-arom), 7.3 (m, 4 H, arom), and 9.2 ppm (s, 3 H, arom).

Fluoren-9-ol. This material was prepared by lithium aluminum hydride reduction of 15 g (0.083 mol) of fluoren-9-one in ether. Workup and recrystallization from 1:1 ether–petroleum ether (30–60 °C) afforded 7.9 g (52%) of fluoren-9-ol: mp 154.5–156.5 °C [lit.[9] mp 154–155 °C]; NMR ($CDCl_3$) (external Me_4Si) δ 2.2 (s, 1 H, OH), 5.7 (s, 1 H, CHOH), and 7.7 ppm (m, 8 H, arom).

Fluoren-9-yl 3,5-Dinitrobenzoate. In the usual manner, 1.8 g (0.010 mol) of fluoren-9-ol in pyridine at 0 °C was treated with 3.0 g (0.0130 mol) of 3,5-dinitrobenzoyl chloride. After workup, recrystallization from 1:1 hexane–chloroform afforded 2.4 g (63%) of fluoren-9-yl 3,5-dinitrobenzoate: mp 215.5–217.5 °C; NMR ($CDCl_3$) δ 7.2 (s, 1 H, CHODNB), 7.6 (m, 8 H, arom), and 9.3 ppm (s, 3 H, arom).

Anal. Calcd for $C_{20}H_{12}N_2O_6$: C, 63.83; H, 3.21; N, 7.44. Found: C, 63.77; H, 3.16; N, 7.35.

1-Methylinden-1-ol. Initially, phenyllithium was prepared by the slow addition of an ethereal solution of 25.2 g (0.16 mol) of bromobenzene to 2.2 g (0.32 mol) of small pieces of lithium wire in ether and under a nitrogen atmosphere. This mixture was stirred at room temperature for 12 h, then 17.6 g (0.14 mol) of 1-methylindene[3] in ether was added, and the solution was cooled to −78 °C. Oxygen was bubbled into the resulting solution of methylindenyllithium at a rate of 40 L/h for 1 h. After neutralization by dropwise addition of 80 mL of 1 N hydrochloric acid, 40 g of potassium iodide in 100 mL of 1:1 water–acetic acid was added. The solution was stirred briefly and then transferred to a separatory funnel. Extraction with ether was followed by washing the combined ethereal solution with saturated sodium bicarbonate solution and saturated sodium chloride solution and then drying over anhydrous magnesium sulfate. The solid remaining, after removal of the ether, was recrystallized from 3:1 chloroform–pentane to yield 7.9 g (40%) of 1-methylinden-1-ol: mp 96–98 °C; NMR (CCl_4) δ 1.5 (s, 3 H, CH_3), 1.8 (s, 1 H, OH), 6.2 (d, J = 6 Hz, 1 H, CHC(OH)-CH_3), 6.5 (d, J = 6 Hz, 1 H, CH-arom), and 7.1 ppm (m, 4 H, arom); IR (mineral oil) 3225 (OH), 3145 (OH), and 1100 cm^{-1} (CO); mass spectrum (70 eV) *m/e* (rel intensity) 147 (9), 146 (77), 145 (30), 132 (10), 131 (100), 128 (17), 127 (11), 115 (13), 103 (21), 102 (11), 77 (15).

1-Methylinden-1-yl 3,5-Dinitrobenzoate. Following the usual procedure, 1.06 g (0.0073 mol) of 1-methylinden-1-ol in pyridine at 0 °C was treated with 2.0 g (0.0088 mol) of 3,5-dinitrobenzoyl chloride. Workup was followed by unsuccessful attempts at recrystallization of the resulting gummy solid from ether, ether–pentane, or ether–mixed hexanes. However, removal of all the solvents and drying of the resulting yellow powder under vacuum at room temperature for 24 h provided 1.31 g (55%) of 1-methylinden-1-yl 3,5-dinitrobenzoate: mp 71–73 °C; NMR ($CDCl_3$) δ 1.9 (s, 3 H, CH_3), 6.7 (q, 2 H, CH=CH), 7.3 (m, 4 H, arom), and 9.1 ppm (m, 3 H, arom).

Anal. Calcd for $C_{17}H_{12}N_2O_6$: C, 60.00; H, 3.55. Found: C, 60.15; H, 3.60.

9-Methylfluoren-9-ol. Methylmagnesium bromide was prepared under nitrogen from 1.1 g (0.045 mol) of magnesium turnings in anhydrous ether by adding 6.6 g (0.046 mol) of methyl iodide in ether. After stirring at room temperature for 1 h, 5.5 g (0.031 mol) of fluoren-9-one was added and the resulting mixture was stirred at reflux for 1 h. Neutralization with ice-cold 2 M sulfuric acid was followed by ether extraction. The ethereal solution was washed with saturated sodium bicarbonate and dried over anhydrous magnesium sulfate. Concentration of the ether solution to 100 mL followed by cooling to −25 °C provided 5.0 g (83%) of white plates of 9-methylfluoren-9-ol: mp 173–174 °C [lit.[10] mp 174–175 °C].

9-Methylfluoren-9-yl 3,5-Dinitrobenzoate. In portions, 2.3 g (0.010 mol) of 3,5-dinitrobenzoyl chloride was added to 1.45 g (0.074 mol) of 9-methylfluoren-9-ol in pyridine at 0 °C. Workup followed by recrystallization from 60 mL of ether afforded 2.4 g (83%) of 9-methylfluoren-9-yl 3,5-dinitrobenzoate: mp 107–110 °C dec; NMR ($CDCl_3$) δ 2.0 (s, 3 H, CH_3), 7.4 (m, 8 H, arom), and 9.0 ppm (m, 3 H, arom).

Anal. Calcd for $C_{21}H_{14}N_2O_6$: C, 64.62; H, 3.62. Found: C, 64.49; H, 3.58.

Indan-1-yl 3,5-Dinitrobenzoate. This material was prepared as described[1] by us in an earlier paper.

1-Methylindan-1-ol. The reaction of 2.47 g (0.020 mol) of indan-1-one with methyllithium in ether followed by workup and recrystallization from *n*-pentane produced 1.70 g (52%) of 1-methylindan-1-ol: mp 55–56 °C [lit.[11] mp 56–57 °C]; NMR (CCl_4) δ 1.3 (s, 3 H, CH_3), 2.0 (m, 2 H, $CH_2C(OH)CH_3$), 2.7 (m, 2 H, CH_2-arom), 3.2 (br s, 1 H, OH) and 7.0 ppm (m, 4 H, arom).

Cyclopenten-3-yl 3,5-Dinitrobenzoate. In the usual manner, 2.5 g (0.030 mol) of cyclopenten-3-ol[12] in pyridine was treated with 8.3 g (0.036 mol) of 3,5-dinitrobenzoyl chloride. Workup and recrystallization from chloroform–*n*-pentane produced 4.7 g (57%) of slightly impure product, mp 118–121 °C. A second recrystallization of a portion of this material yielded small white crystals of pure cyclopenten-3-yl 3,5-dinitrobenzoate: mp 122–123 °C; NMR ($CDCl_3$) δ 2.5 (m, 4 H, CH_2CH_2), 6.0 (m, 2 H, CH=CH), 6.2 (m, 1 H, CHODNB), and 9.1 ppm (s, 3 H, arom).

Anal. Calcd for $C_{12}H_{10}N_2O_6$: C, 51.81; H, 3.62. Found: C, 51.72; H, 3.56.

Kinetics in 80% Aqueous Acetone. The equipment, solvents, procedure used for measuring reactions rates, and treatment of the data were as described earlier.[1] All runs were carried out in duplicate.

2,2,2-Trifluoroethanol. This solvent was dried over anhydrous sodium carbonate and redistilled from powdered 4A Linde molecular sieves through a 50-cm Widmer column.

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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