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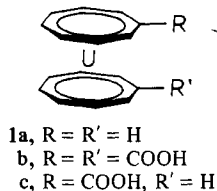
Preparation and Properties of Uranocenecarboxylic Esters

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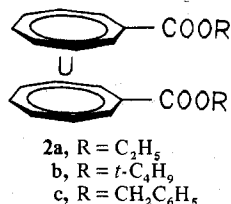
Several esters of uranocenoic acid and 1,1'-uranocenedioic acid were prepared from the corresponding cyclooctatetraene esters by reduction with potassium naphthalide followed by reaction with UCl_4 . The esters are hydrolyzed immediately by hydroxylic solvents. The visible spectra show the hypsochromic shifts expected for electron-withdrawing groups. Infrared and NMR spectra are also reported together with the magnetic susceptibility. These compounds appear to have substantially more ionic metal-ligand bonding than alkyluranocenes, but such bonding is still substantial.

Since the discovery of uranocene **1a** in 1968,² several attempts have

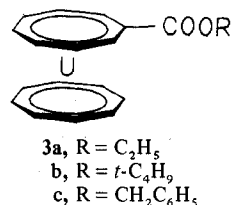


been made to modify the parent uranocene system directly. Electrophilic substitution and metalation reactions do not succeed with uranocene itself; hence most substituted uranocenes have been prepared from the corresponding substituted cyclooctatetraenes (COTs).^{3,4} Several side-chain reactions occur normally^{3,4} and suggest the potential usefulness of carbonyl functions; however, since electron-donating groups such as alkyl substituents appear to stabilize the uranocene ring system and induce lower reactivity, electron-attracting carbonyl groups may have the opposite effect. We now report the preparation and characterization of several uranocenoic esters. Another goal was the synthesis of the uranocenoic acid **1b** or **1c**. Earlier attempts to obtain these acids by metalation of uranocene and subsequent quenching with carbon dioxide failed.^{2b}

The starting (alkoxycarbonyl)cyclooctatetraenes were prepared by the method of Corey and Hegedus⁵ from bromocyclooctatetraene using nickel tetracarbonyl and alkoxide. The uranocenoic esters were prepared by following the usual procedure of reducing the substituted COT and subsequent treatment of the dianion with uranium tetrachloride. The use of potassium sand as a reducing agent leads to decomposition of the COT esters, undoubtedly because of the long contact time in this heterogeneous system. Excellent results were obtained by reaction at $-78^\circ C$ of the COT with a solution of naphthalene radical anion prepared from naphthalene and potassium, followed quickly by a solution of UCl_4 . This method gave the 1,1'-uranocenedicarboxylic esters **2**. When a 1:1 mixture of cyclo-



octatetraene and (alkoxycarbonyl)cyclooctatetraene was employed, the reaction yielded the mixed sandwich **3** together with uranocene and diester **2**. We were not able to obtain the pure compounds **3a-c** although we succeeded in reducing the byproduct level to less than 5%. Using this method, we were able to synthesize and characterize both the mono- and the disubstituted uranocenes.



Results and Discussion

The uranocenoic esters are dark green solids which like most uranocenes are sensitive to oxygen. Controlled air oxidation of **2a** generated ethyl cyclooctatetraenecarboxylate in common with other uranocenes. Uranocene and alkyluranocenes hydrolyze slowly in aqueous solutions;² in contrast, the uranocenoic esters hydrolyze immediately with protic solvents, even benzyl alcohol. We were unable to obtain satisfactory combustion analyses for these compounds, undoubtedly because of this sensitivity. Nevertheless, the compounds were completely characterized by their IR, visible, and NMR spectra and by mass spectroscopy. As discussed below, these spectra leave no doubt as to their structure and also provide interesting conclusions as to electronic structure.

As expected from the above discussion, one cannot hydrolyze the ester group with acid or base without destroying the uranocene complex at the same time. We did not find any evidence for a decomposition mechanism in which the ester group is hydrolyzed in the first step followed by decomposition of the intermediate uranocenoic acid. Most reactions of uranocenes are thought to involve direct attack at the metal;^{2b,6} nevertheless, the present observations show that such reactions are remarkably sensitive to ring substituents.

Several attempts to prepare the acid from its esters failed. The mass spectra of the esters show fragment peaks that can be formulated as uranium bound to cyclooctatetraenecarboxylic acid or the protonated analogue; however, we were not able to obtain the acid by pyrolysis of the *tert*-butyl ester **2b**. The hydrogenolysis of the benzyl ester **3c** yielded only cyclooctane, cyclooctanecarboxylic ester and acid, and toluene, as identified by 1H NMR and mass spectroscopy but no uranocene derivative was found. Since we found that the esters **2** and **3** are not stable to even very weak acids, it is doubtful that the uranocenoic acid is stable to itself. The infrared spectra (Table I) of the uranocenoic esters have one feature of particular interest. The ester carbonyl stretching frequency of $1690-1695\text{ cm}^{-1}$ is relatively low; for comparison, benzoate esters absorb at 1720 cm^{-1} . In fact, the uranocenoate esters show the same carbonyl absorption as (ethoxycarbonyl)ferrocene (1690 cm^{-1}).⁷ The general correlation of the carbonyl stretching frequency of ketones with the relative

(1) NATO Fellow, 1977-1978.

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Table I. IR Data (Nujol Mull) of Uranocenoic Esters

uranocene	frequency, cm ⁻¹
2a ^a	1690 s, 1332 w, 1242 s, 1210 s, 1060 m, 950 m, 930 m, 722 s
2b	1690 s, 1335 w, 1250 s, 1210 w, 1155 s, 1060 m, 955 m, 930 w, 720 s
2c	1695 s, 1330 w, 1245 s, 1210 s, 1060 m, 1045 m, 760 s, 755 s, 720 s
3a	1690 m, 1245 s, 1210 s, 1060 w, 700 s
3b	1690 m, 1260 s, 1250 s, 1220 m, 1160 s, 705 s
3c	1695 m, 1240 s, 1205 s, 1045 m, 720 s, 700 s

^a 3005 w in Fluorolube.

Table II. Visible Spectra (in THF)

uranocene	wavelength, nm (ext coeff)
2a	600 (2020), 626 (580), 643 (330)
2b	600 (2210), 627 (615), 645 (345)
2c	600 (2010), 626 (570), 644 (300)
3a	607 (1850), 635 (590), 655 (345)
3b ^a	607, 635, 654
3c	607 (1890), 635 (645), 654 (365)
1a ^b	616 (1800), 643 (720), 661 (410), 681 (120)

^a The extinction coefficient could not be determined because of contamination by 2b. ^b Reference 2b.

stability of the corresponding alkyl cations⁸ implies that uranocenylmethyl cations should have stabilities comparable to ferrocenylmethyl cations. This anticipated reactivity in carbocationic reactions contrasts with the absence of demonstrated electrophilic substitution reactions on uranocene rings^{2b} and points up again that the reactions with electrophilic reagents apparently involve prior attack at uranium.

The visible spectra (Table II) of the uranocenoic esters show the cascade of bands typical of uranocenes but markedly shifted to shorter wavelengths. These shifts follow the generalization established by other substituted uranocenes in which electron-donating groups produce shifts to longer wavelengths.^{3,4} Of additional significance is the observation that the shifts in the disubstituted uranocenes **2** are twice as large as those for the monosubstituted systems, **3**. This fact establishes that the transition involves both ligand rings acting together. If the transition had involved each ring separately, we could have expected to see two sets of bands corresponding to each ligand and having half the intensity.

Like other uranocenes⁹ the esters are paramagnetic. The magnetic susceptibility of **2b** shows normal Curie-Weiss behavior with $\mu_{\text{eff}} = 2.65 \pm 0.2 \mu_{\text{B}}$ from 30 to 90 K and temperature independent paramagnetism below 20 K with $\chi_{\text{M}} = 0.029$ emu. Similarly, **2a** shows linear Curie-Weiss behavior from 5 to 43 K with $\mu_{\text{eff}} = 2.53 \mu_{\text{B}}$.

The ¹H NMR spectra of **2** and **3** are summarized in Table III. The spectra were run on the Berkeley 180-MHz TR NMR spectrometer equipped with a variable temperature probe. The temperature of the probe was monitored by a precalibrated thermocouple 5 mm from the sample tube and could be held to ± 0.3 °C. Spectra were run in toluene-*d*₈, and shifts were measured relative to the methyl group of the toluene. The shifts are reported relative to Me₄Si by assigning the toluene methyl resonance as 2.09 ppm. This resonance differs from that in undeuterated toluene (2.31 ppm).

The ¹H NMR spectra of **2** and **3** are completely consistent with the assigned structures and are interpreted in terms of

Table III. ¹H NMR Data

compd	δ , from Me ₄ Si (toluene- <i>d</i> ₈ , 30 °C)
1a	-36.63
2a	-29.93, -32.69, -35.78 (H5), -42.14, -6.05 (t, $J = 7.0$ Hz, 3 H, CH ₃), -4.23 (q, $J = 7.0$ Hz, 2 H, CH ₂)
3a	-28.84, -32.93, -36.14 (H5), -40.27, -6.57 (CH ₃), -4.45 (CH ₂), -37.07 (8 H, unsubst ring)
2b	A, -33.43; B, -33.80; C, -37.30; D, -40.54 (H5), -11.49 (CH ₃)
3b	A, -33.41; B, -34.74; C, -39.51; D, -43.37 (H5), -10.82 (CH ₃), -36.02 (8 H, unsubst ring)
2c	-29.81, -32.08, -36.23 (H5), -43.16, -2.98 (CH ₂), -0.56 (d, $J = 7.2$ Hz, ortho), 4.09 (t, $J = 7.3$ Hz, meta), 5.20 (t, $J = 7.3$ Hz, para)
3c	-28.51, -32.40, -32.98 (H5), -40.63, -2.99 (CH ₂), -36.06 (8 H, unsubst ring), -1.16 (2 H, d, $J = 7$ Hz, ortho), 3.94 (2 H, t, $J = 7.1$ Hz, meta), 5.30 (1 H, t, $J = 7.1$ Hz, para)

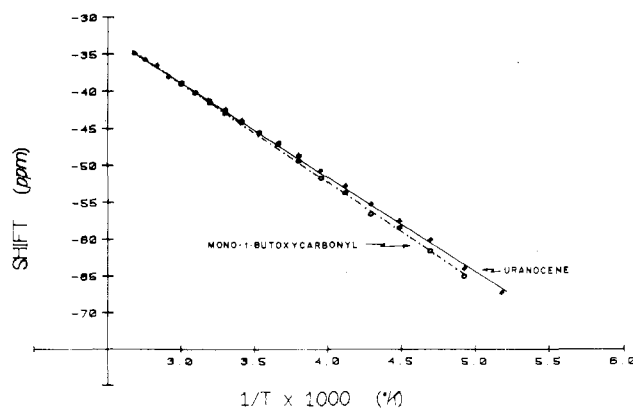


Figure 1. Unsubstituted ring proton isotropic shifts as a function of temperature for uranocene **1a** and the mono-*tert*-butyl ester, **3b**. The cyclooctatetraene dianion (δ 5.7) was taken as the diamagnetic reference.

both pseudocontact and contact shifts arising in the paramagnetic system.^{9,10} The signals for the ring protons of the substituted rings could not be assigned with the exception of the proton in the 5-position. In this case the signal can be assigned unambiguously by comparison of the integral ratios in the ring region of the ¹H NMR.

The ¹H NMR of **2c** and **3c** were also determined as a function of temperature. Spectra were run at 10 °C intervals in at least the range -80 to +70 °C. The unsubstituted rings in **3a-c** show up as clear singlets but shifted by <1 ppm from **1a** itself. The temperature dependence of the unsubstituted ring of **3c** was compared with uranocene itself. For conversion of the shifts relative to Me₄Si to the corresponding isotropic shifts, suitable diamagnetic references are required. The thorocenes are probably the best such references, but the ring proton chemical shifts of several thorocenes studied differ from those of the corresponding cyclooctatetraene dianions by less than 1 ppm.^{11,12}

The temperature dependence of the isotropic shift in uranocene itself was measured on two independent samples. At the same nominal temperature slight differences between the two samples are probably due to differences in the true temperatures and provide an estimate of the systematic error in

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Table IV. Least-Squares Regression Analysis of Isotropic Shifts of Uranocenes vs. T^{-1}

compd	slope ^a	intercept ^a	r^2
1a, sample 1	-12.83 ± 0.07	-0.32 ± 0.32	0.9992
1a, sample 2	-12.94 ± 0.06	0.21 ± 0.21	0.9997
1a ¹³	-14.70	6.96	0.9991
3b, unsubstd ring	-13.54 ± 0.12	1.88 ± 0.47	0.9989
3b, A	-11.02 ± 0.08	0.19 ± 0.31	0.9993
3b, B	-12.47 ± 0.12	2.89 ± 0.47	0.9987
3b, C	-13.01 ± 0.08	1.30 ± 0.31	0.9995
3b, D ^b	-14.62 ± 0.09	0.19 ± 0.36	0.9994
3b, <i>t</i> -Bu	-3.47 ± 0.04	3.73 ± 0.16	0.9980
2b, A	-4.63 ± 0.02	1.16 ± 0.08	0.9997
2b, B	-10.52 ± 0.07	-0.37 ± 0.29	0.9993
2b, C	-12.60 ± 0.12	2.36 ± 0.47	0.9987
2b, D ^b	-14.05 ± 0.11	0.73 ± 0.43	0.9991
2b, <i>t</i> -Bu	-3.41 ± 0.04	3.72 ± 0.16	0.9980

^a Error limits given as standard deviations. ^b H5.

Table V. Line Width at Half-Height of ¹H NMR Resonances of Uranocenes (Hz)

compd	temp, °C		
	-70	+30	+70
1a	102	90	76
3b ^a	50	38	32
2a		20-25	

^a Unsubstituted ring.

the temperature measurement. A plot of shift vs. T^{-1} (Figure 1) is strictly linear with an extrapolated intercept at $T^{-1} = 0$ of zero within experimental error (Table IV). The difference between this result and that reported earlier by this group¹³ appears to arise entirely from the higher temperature uncertainty (± 3 °C) in the older work. Given this uncertainty, the older data can be fit to a straight line that intercepts zero at $T^{-1} = 0$.

The isotropic shift of the unsubstituted ring of **3b** is also a linear function of T^{-1} ; the small difference of the intercept from zero probably results from the use of the COT dianion as the diamagnetic reference. A significant feature of this system is that χ_x and χ_y (for the C_8 axis of uranocene taken as the z coordinate) are not constrained to be equal by symmetry. Changes in the line width at half-heights as a function of temperature parallel those of uranocenes (Table V) and undoubtedly result from the known change in paramagnetic relaxation times as a function of temperature rather than the onset of coalescence.¹⁴ This result implies that ring rotation in monosubstituted uranocenes is rapid on the NMR time scale at our temperatures.

The pseudocontact shift in the point-dipole approximation that is assumed to apply to uranocenes is given by eq 1,¹⁵ in

$$\delta_{\text{pseudocontact}} = \frac{\chi_z - \frac{1}{2}(\chi_x + \chi_y)}{3N} \left[\frac{3 \cos^2 \theta - 1}{R^3} \right] + \frac{\chi_x - \chi_y}{3N} \left[\frac{\sin^2 \theta \cos 2\psi}{R^3} \right] \quad (1)$$

which R , θ , and ψ are polar coordinates centered on uranium for each proton.¹⁰ For $\chi_x = \chi_y = \chi_{\perp}$, either by axial symmetry or by rapid rotation involving equivalent rotomers, the second term vanishes; however, if $\frac{1}{2}(\chi_x + \chi_y)$ differs seriously from χ_{\perp} of uranocene, we would expect a significant change in slope.

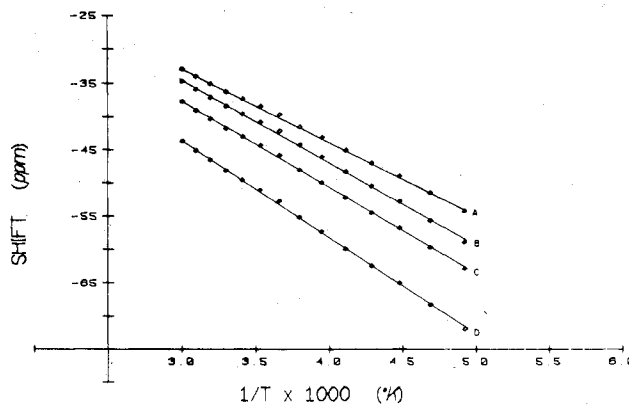


Figure 2. Isotropic shifts of the ring protons of the di-*tert*-butyl ester, **2b**, as a function of temperature. The pattern for **3b** is comparable and is not shown.

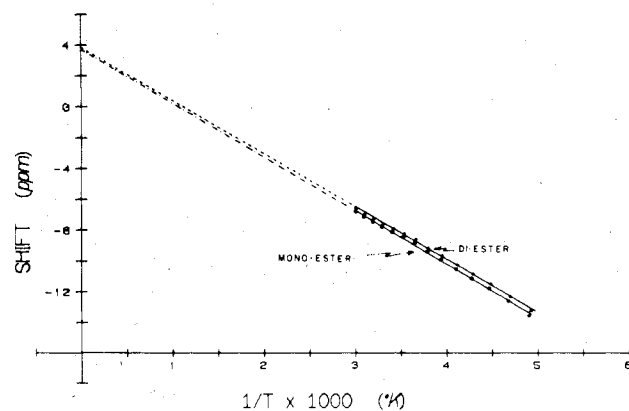


Figure 3. Isotropic shifts for *tert*-butyl protons of **2b** and **3b** as a function of temperature.

The agreement of the slopes in Table IV provides highly suggestive, albeit not rigorous, evidence that $\chi_x \approx \chi_y \approx \chi_{\perp}$ for **3b** and perhaps generally for all uranocenes. Fischer¹⁶ has independently arrived at the same generalization from studies of uranocenes with *t*-Bu₂P and *t*-Bu₃Sn substituents.

The isotropic shifts of the proton ring resonances of the substituted rings of **2b** and **3b** are also linear in T^{-1} (Figure 2 and Table IV). The resonances are identified by letters in order of more negative (upfield) shifts (Table III). For both compounds resonance D corresponds to H5. The order of the resonances in both cases does not change over a normal temperature range. The intercepts at $T^{-1} = 0$ for all of the protons differ but little from zero. No assignment of these resonances other than H5 can be made at this time.

The *tert*-butyl resonances are similar in both **2b** and **3b** and can be fit to straight lines (Figure 3); however, the extrapolation to $T^{-1} = 0$ is distinctly nonzero and the experimental points do show a slight curvature. (The r^2 values are lowest for these protons in Table IV.) Such curvature would be expected if two or more conformations with varying population and isotropic shift are involved. The *tert*-butyl protons should experience almost wholly a pseudocontact shift that would be sensitive to conformation. The similar situation with alkyl-uranocenes has been analyzed in greater detail.¹⁷

The mass spectra of the uranocenoic esters are also completely consistent with the assigned structures. All showed peaks for the molecular ion. Important fragment peaks usually

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included M^+ – one ligand and peaks associated with the ligands.

These varied spectroscopic results provide characterization for these compounds and indicate structures for the esters that are comparable to other uranocenes. The unsubstituted ring 1H NMR spectra of **3b** are so similar to those of the parent uranocene itself that the structure and electronic structure must also be comparable. The greater hydrolytic reactivity of the esters, however, suggests greater ionic ring–metal bonding, a result which would be consistent with a greater energy gap between ring π MOs and interacting metal f and d orbitals.¹² Nevertheless, ring–metal bonding is still substantial in the esters. A mixture of **2b** and COT in benzene- d_6 showed no change in NMR spectrum in the course of 1 day. Hence, no significant dissociation occurs at least at room temperature.

The present study of several uranocenoic esters provides a consistent and developing pattern for uranocene chemistry, but the hydrolytic sensitivity of the esters limits their usefulness as chemical reagents.

Experimental Section

General Methods. Visible spectra were obtained with a Cary 118 recording spectrometer and IR spectra with a Perkin-Elmer 297 infrared spectrophotometer. 1H NMR spectra were recorded with a Varian T60 and 180-MHz NMR spectrometer. In all reactions reagent-grade solvents were used after being distilled from potassium/benzophenone and subsequent vacuum transfer. Anhydrous uranium tetrachloride was prepared from uranium trioxide and hexachloropropene.¹⁸ Analyses were obtained from the Analytical Laboratory, Department of Chemistry, University of California, Berkeley.

Cyclooctatetraenecarboxylic Esters. (All preparations with nickel tetracarbonyl were performed in a well-ventilated hood.) To a solution of 0.1 mol of potassium alkoxide in 140 mL of the corresponding alcohol was added 19.3 mL of nickel tetracarbonyl (25.5 g, 0.15 mol), followed by the addition of 9.2 g of bromocyclooctatetraene¹⁹ (0.05 mol). The reaction mixture was stirred for 4 h at room temperature. Carbon monoxide was then bubbled through the solution to remove volatile nickel complexes. (Note: In the case of butanol the last step does not apply; the complexes are not volatile.) Ether (500 mL) was added, and the mixture was extracted repeatedly with 1 N hydrochloric acid and several times with water. The organic layer was dried over magnesium sulfate, and the solvent was stripped off. The product was purified by column chromatography over silica gel with hexane/ether (20:1) followed by distillation. (Ethoxycarbonyl)cyclooctatetraene in two preparations: bp 63 °C (0.03 torr), yield 75%; bp 63–65 °C (0.01 torr), yield 92%. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.66, 75.18; H, 6.82, 6.95. (tert-Butoxycarbonyl)cyclooctatetraene: bp 49–50 °C (0.01 torr), yield 78%. Anal. Calcd for $C_{12}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.18; H, 7.83. [(Benzyloxy)carbonyl]cyclooctatetraene: bp 110–115 °C (0.01 torr), yield 56%. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.83; H, 5.94.

General Preparation of Bis[π -(alkoxycarbonyl)cyclooctatetraene]uranium(IV). All operations were carried out in inert

atmosphere and with degassed solvents. To a solution of 5 g of naphthalene in 200 mL of 2-methyltetrahydrofuran was added 0.79 g of potassium (0.02 mol), and the solution was stirred at room temperature for 4 h. The dark green solution was then cooled to –78 °C, and 0.01 mol of the cyclooctatetraene ester and a solution of 1.9 g of uranium tetrachloride (0.005 mol) in 50 mL of 2-methyltetrahydrofuran were added sequentially. The mixture was stirred for 10 min, the dry ice bath was removed, and the solvent was pumped off. The solid reaction product was then extracted with diethyl ether or hexane. **2a**: yield 54%, 57% (ether); sublimes 150 °C (1.3×10^{-2} torr); mass spectrum (70 eV), m/e 590 (7, M^+), 459 (1), 415 (3, UC_8H_7COOEt, H^+), 176 (19, $C_8H_7COOEt^+$), 131 (17, $C_8H_7CO^+$), 103 (100, $C_8H_7^+$). **2b**: yield 53% (hexane). **2c**: yield 22% (ether); mass spectrum, m/e 714 (0.4, M^+), 623 (0.5, $M^+ - C_6H_5CH_2$), 517 (0.6), 442 (0.3), 358 (0.4, $OUC_8H_8^+$), 356 (0.5), 238 (63, $C_8H_7COOC_7H_7^+$), 91 (100, $C_7H_7^+$).

Despite numerous attempts, we were never able to get satisfactory analyses for these sensitive compounds. The best result was a marginally acceptable analysis for **2a**. Anal. Calcd for $C_{22}H_{24}O_4U$: C, 44.75; H, 4.10. Found: C, 45.32; H, 4.50.

2-Methyltetrahydrofuran was used for many of these preparations because it appeared early in this study that the esters react with THF. With carefully purified THF, however, a sample of **2b** was found to decompose with a half-life of 4 days; we did not determine whether this slow rate was with THF itself or with residual impurities.

General Preparation of [(Alkoxycarbonyl)cyclooctatetraene](cyclooctatetraene)uranium(IV). The procedure was the same as above. Instead of pure COT ester a 1:1 mixture of COT and COT ester was used. The products were always contaminated by uranocene and the diester. The monobenzyl ester could be obtained free of diester by extracting the diester with hexane and extracting the monoester with ether. **3a**: yield 20% (ether); mass spectrum, m/e 518 (18, M^+), 387 (45, $UC_8H_7CO_2H_2^+$), 358 (35, $OUC_8H_8^+$), 342 (64, $UC_8H_8^+$), 104 (84, $C_8H_8^+$), 103 (92, $C_8H_7^+$), 51 (100). **3b**: yield 46% (ether); mass spectrum, m/e 546 (38, M^+), 490 (42, $U(C_8H_8)C_8H_7CO_2H^+$), 358 (33), 342 (23), 104 (56), 103 (55), 41 (100). **3c**: yield 82% (hexane/ether). The mass spectra showed contamination by uranocene and some of the m/e 342 peak comes from this source. For a determination of the extinction coefficients of the monoesters that were contaminated with uranocene, the ester was decomposed with a small amount of benzyl alcohol after the visible spectrum was taken. Benzyl alcohol reacts very slowly with uranocene but rapidly with the uranocenoic esters. After about 1 h, another spectrum was taken which showed the absorption due to the uranocene. The spectrum of the ester was derived by subtracting the two spectra. This subtraction was done with an interactive computer graphics program written by Dr. W. Holloway for a Tektronix 4051.

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Registry No. **1a**, 11079-26-8; **2a**, 73360-49-3; **2b**, 73367-23-4; **2c**, 73367-24-5; **3a**, 73367-25-6; **3b**, 73360-50-6; **3c**, 73360-51-7; bromocyclooctatetraene, 7567-22-8; nickel tetracarbonyl, 13463-39-3; potassium ethoxide, 917-58-8; potassium *tert*-butoxide, 865-47-4; potassium benzyl oxide, 22379-62-0; (ethoxycarbonyl)cyclooctatetraene, 73360-45-9; (*tert*-butoxycarbonyl)cyclooctatetraene, 73347-72-5; [(benzyloxy)carbonyl]cyclooctatetraene, 73347-73-6; uranium tetrachloride, 10026-10-5.

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