that the present version of the apparatus is suitable for those dihalides that yield the desired products after abstraction of the first halogen atom by spontaneous loss of the second halogen atom (2.1). Thus, suitable future target molecules are strained olefins and small-ring propellanes. For other targets, a better mixing system is needed.

Acknowledgment. This work was supported by the National Science Foundation (CHE 81-21122).

Registry No. **1a**, 627-31-6; **2a**, 628-21-7; **3a**, 628-77-3; **4**, 75-19-4; **5**, 74-85-1; **6**, 115-07-1; K, 7440-09-7; Na, 7440-23-5; *n*-butane, 106-97-8; cyclopentane, 287-92-3; 1-pentene, 109-67-1; *n*-pentane, 109-66-0; *o*-diiodobenzene, 615-42-9; *o*-benzyne, 462-80-6; *p*-diiodobenzene, 624-38-4; *m*-diiodobenzene, 626-00-6; *o*-dibromobenzene, 583-53-9; *m*-dibromobenzene, 108-36-1; iodobenzene, 591-50-4.

Studies in Lipid Mimics. Synthesis and Carbon-13 Relaxation Time Measurements (T_1 Values) of Methyl Esters of ω-(2-Anthryl)alkanoic Acids

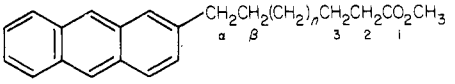
Kristy M. Waugh[1] and K. Darrell Berlin*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

Received July 19, 1983

The syntheses of methyl 12-(2-anthryl)dodecanoate, methyl 14-(2-anthryl)tetradecanoate, and methyl 17-(2-anthryl)heptadecanoate have been achieved. Both ^1H and ^{13}C chemical shifts and T_1 values for carbons in the systems have been recorded. By using selected heteronuclear decoupling and performing heteronuclear correlated 2-dimensional (HETCOR-2-D) experiments, it was possible to assign protons to specific carbons in most cases.

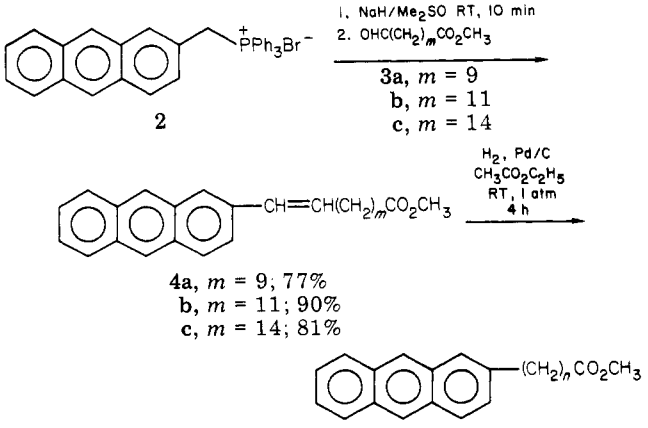
Structure and functions of biological membranes continue to be major areas of interest.[2] Diagnostic evaluation of the two variables via the use of fluorescent probes[3] has generated a lively stimulus to synthesize artificial lipid mimics. A preliminary report[4] disclosed an approach to certain ϵ-(2- and 9-anthryl)alkanoic acids and a few esters. However, these esters have relatively short chains, and, since natural membranes have longer carbon chains, we report herein the preparations and NMR spectral properties of three members of **1**. The strategy to obtain **1** is

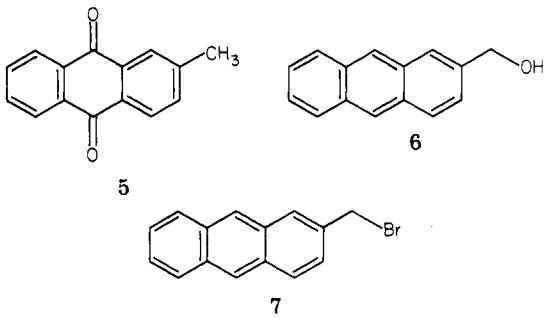


1a, $n = 7$
b, $n = 9$
c, $n = 12$

outlined in Scheme I and involved intermediates **2**–**4**. Phosphonium salt **2** was prepared starting from available

Scheme I





5 6 7

2-methylanthraquinone (**5**). With known procedures,[5] the latter was converted to 2-(hydroxymethyl)anthracene (**6**) (45% overall). Treatment of the alcohol with triphenylphosphine dibromide in DMF at room temperature gave **7** (84%). Alkylation of phosphorus in triphenylphosphine with **7** in boiling benzene gave salt **2**.

Since ω-oxo esters **3a**–**c** were not available, methods to obtain these materials have been developed and are outlined in Scheme II [$^8 \rightarrow {}^9 \rightarrow {}^3$a, **10** → **11** → **12** → **3b**, **13** → **14** → **3c**]. In general, members of **3a**–**c** were used shortly after preparation. Treatment of the anion of **2** with **3a**–**c** were used shortly after preparation. Treatment of the anion of **2** with **3a**–**c** gave the unsaturated esters **4**–**c**, which could be hydrogenated in ethyl acetate over 10% Pd/C (without reduction of the 9,10-positions of the an-

(1) Taken in part from the Ph.D. Dissertation, Oklahoma State University, May, 1983. Phillips Fellow, summer, 1982; Skinner Fellow 1982–83.

(2) Harrison, R.; Lunt, G. G. "Biological Membranes—Their Structure and Function"; Wiley: New York, 1975.
(3) Beddard, G. S.; West, M. A. "Fluorescent Probes", Academic Press: New York, 1981.
(4) Arjunan, P.; Shymasundar, N.; Berlin, K. D.; Najjar, D.; Rockley, M. G. *J. Org. Chem.* **1981**, *46*, 626.
(5) (a) Berstein, E. *Ber.* **1883**, *16*, 2609. (b) Carlack, E. A.; Mossetig, E. *J. Am. Chem. Soc.* **1945**, *67*, 2255. (c) Golden, R.; Stock, L. M. *Ibid.* **1972**, *94*, 3081. (d) Iljinsky, M. A., Ginden, L. G.; Kasakova, V. A. *Dokl. Akad. Nauk. SSSR* **1983**, *20*, 555. (e) Stewart, F. H. C. *Aust. J. Chem.* **1960**, *13*, 478.

0022-3263/84/1949-0873$01.50/0

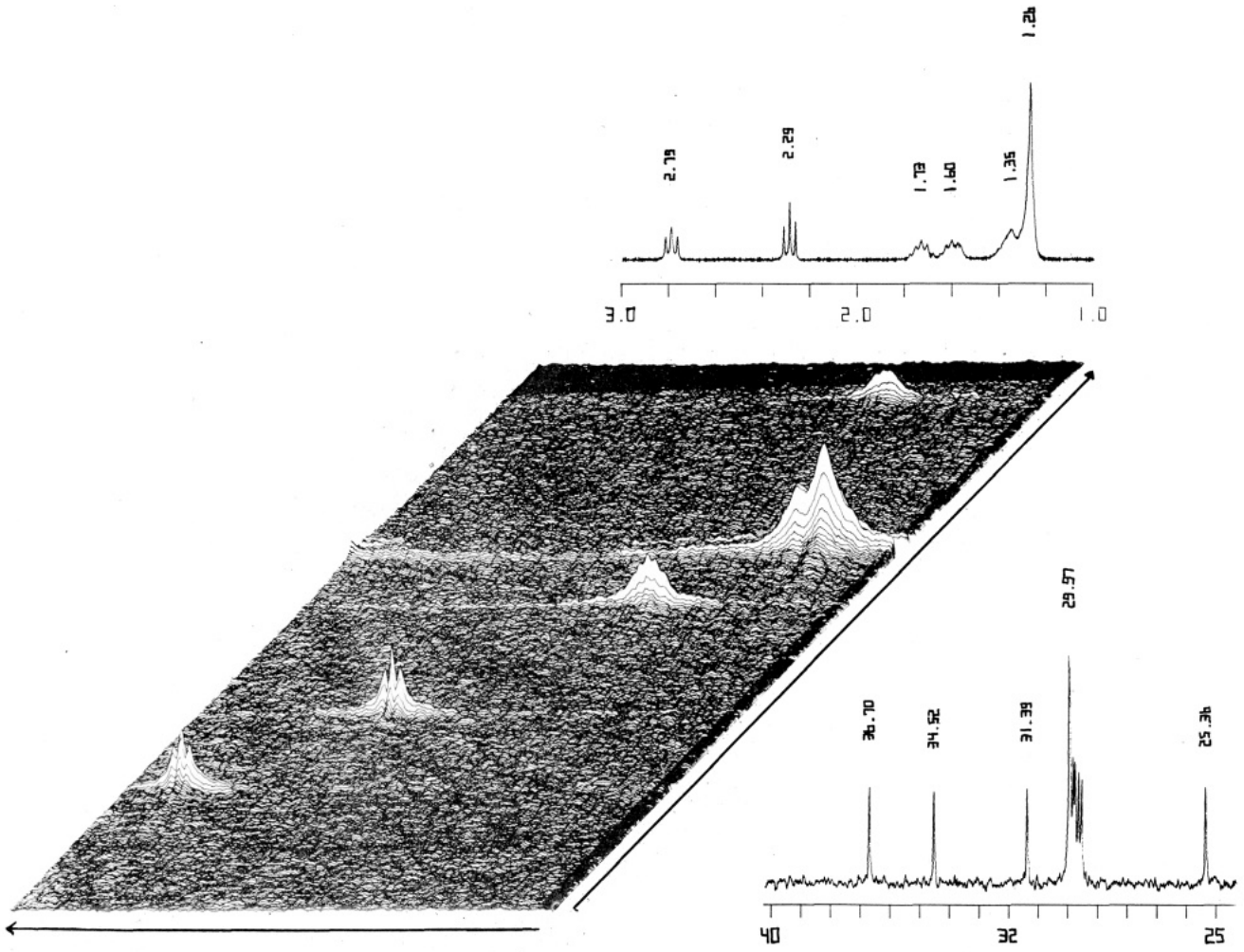


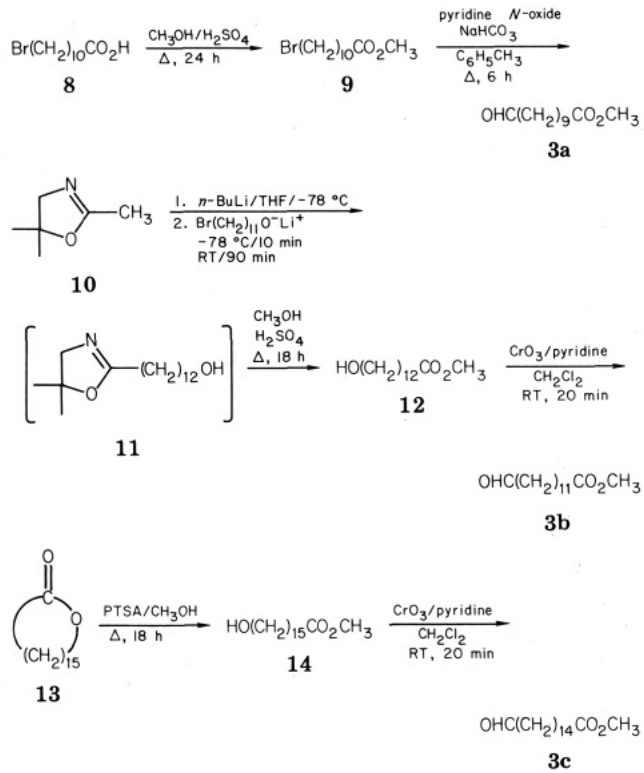
Figure 1. Contour plot of a HETCOR-2-D experiment in the aliphatic region of **1a**.

thracene ring) to yield **1a–c**.

The ^{1}H NMR spectra are recorded for **1a–c** in the Experimental Section and are somewhat complex. However, signals occurred at δ 3.64, 3.63, and 3.65, respectively, for the methyl protons. Triplets appeared for H(2) at δ 2.28, 2.27, and 2.29, respectively, and for H(α) (H(12), H(14), and H(17), respectively, in **1a–c**) at δ 2.78, 2.78, and 2.79. When **1a** was treated with $NaOCH_3$ in CH_3OD for 1 h, some incorporation of deuterium occurred at H(2) as reflected in a reduction of the intensity of the triplet at δ 2.28. This confirmed the assignment of the triplet at δ 2.78 to H(α) (H(12) in **1a**). Irradiation of the triplet at δ 2.28 caused collapse of the multiplet at δ 1.48–1.62 to the expected triplet. Thus, the signal for H(3) must occur in the multiplet cited. Irradiation of the triplet at δ 2.78 caused collapse of the multiplet at δ 1.62–1.74 to an expected triplet, which confirmed the range of δ 1.62–1.74 as that for H(β) (H(11) in **1a**).

The ^{13}C NMR assignments and spin–lattice relaxation times (T_1 values) are recorded in Table I. Assignments for C(1′), C(1)8 C(2), and C(3) and C(α) (C(12)) and C(β) (C(11)) in **1a** were made initially by using model compounds.[6,7] A comparison was also made with short-chain homologues **15a–c** and is included in Table I. Signals for

Scheme II

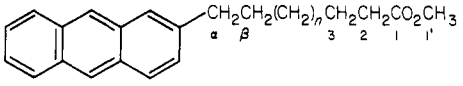


C(2,3) in **15a**, for C(2,4,5) in **15b**, and C(2,6,7) in **15c** are correct in Table I and differ from those reported.[1] Se-

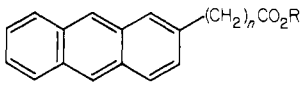
(6) (a) "Sadtler Standard C-13 Nuclear Magnetic Resonance Spectra", Sadtler Research Labs: Philadelphia, PA. (b) Hansen, P. E. *Org. Magn. Reson.* **1979**, *12*, 109.

(7) (a) Stothers, J. B. "Carbon-13 NMR Spectroscopy", Academic Press: New York, 1982; p 98. (b) Doddrell, D.; Allerhand, A. *J. Am. Chem. Soc.* **1971**, *93*, 1558. (c) Chachaty, C.; Wolkowski, Z.; Piriou, F.; Lukcus, G. *J. Chem. Soc., Chem. Commun.* **1973**, 951.

Table I. ^{13}C NMR Chemical Shifts (T_1 Values) for the Carbons in the Side Chain of 1a-c, 15a-c



1a, n = 7
b, n = 9
c, n = 12



15a, n = 2; R = C_2H_5
b, n = 4; R = CH_3
c, n = 6; R = CH_3

carbon number	chemical shift[a] (T_1 value, s)					
	1a	1b	1c	15a	15b	15c
1	174.0 (44.5)	173.9 (45.3)	174.0 (44.1)	172.6	173.6 (37.2)	173.8 (38.5)
2	34.1 (1.96)	34.0 (1.92)	34.0 (2.07)	31.3	38.8 (1.7)	33.9 (1.9)
3	24.9 (1.61)	24.9 (1.56)	24.9 (1.83)	35.5	24.6 (1.4)	24.8 (1.4)
4	29.1 (1.27)	29.1 (1.31)	29.1 (1.42)		30.2 (1.4)	28.8 (1.1)
5	29.2 (1.18)	29.2 (1.14)	29.2 (1.25)		35.8 (1.1)	28.8 (1.1)
6	29.4 (1.12)	19.4 (0.98)	29.4 (1.09)			30.6 (1.0)
7	29.5 (0.96)	29.5 (0.90)	29.6 (0.96)			36.0 (1.0)
8	29.5 (0.96)	29.5 (0.90)	29.6 (0.96)			
9	29.5 (0.96)	29.5 (0.90)	29.6 (0.96)			
10	29.3 (0.93)	29.5 (0.90)	29.6 (0.96)			
11	30.9 (0.85)	29.5 (0.90)	29.6 (0.96)			
12	36.2 (0.78)	29.3 (0.79)	29.6 (0.96)			
13		30.9 (0.78)	29.6 (0.96)			
14		36.2 (0.69)	29.6 (0.96)			
15			29.36 (0.92)			
16			31.0 (0.89)			
17			36.2 (0.80)			
1'	51.3 (6.3)	51.2 (5.9)	51.3 (6.3)	60.3	51.3 (6.1)	51.2 (6.2)
2'				14.2[b]		

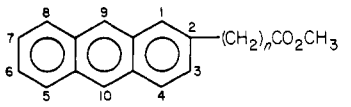
[a] Measured in ppm downfield from Me_4Si. [b] The CH_2 group of the ethyl function.

lective heteronuclear decoupling experiments and a heteronuclear correlated 2-dimensional (HETCOR-2-D)[8] NMR experiment were performed on **1a**. The latter type of experiment was done on a Varian XL-300 spectrometer to correlate ^1H signals for a particular proton with the ^{13}C signal for the carbon(s) to which the proton(s) was attached. Figure 1 shows the HETCOR-2-D spectrum of **1a**. Signal correlations previously made for H(2)–C(2)8 H-(3)–C(3), H(11)–C(11), and H(12)–C(12) were confirmed by analysis of the spectrum as can be seen by inspection of Figure 1. The remaining signals at δ 1.1–1.4 for H-(4)–H(10) are attached to carbons giving signals between 29.1–29.5 ppm. By analogy, assignments were given for **1b** and **1c** (Table I) and permitted correction for those carbons cited previously[4] and which were in error in **15a–c**.

Carbon designation for those atoms at the center of the side chains of **1a–c** were made by using the corresponding ^{13}C spin–lattice relaxation times (T_1 value in Table I). Since the anthracene ring is bulky and acts as an anchor, the mobility of carbons attached to this ring should be restricted. Relative mobility should increase for carbons further removed along the chain up to C(2). This change is reflected in the T_1 values for each distinguishable carbon. Such values should be the smallest for C(12), C(14), and C(17) in **1a**, **1b**, and **1c**, respectively, and should increase progressively to C(2) which is found.[4] Although the exact value for each T_1 is estimated to have less than a 5% standard deviation, the same trend was always observed in many different experiments with **1a–c**. The consistency observed lends credence to the assignments.

Unequivocal ^{13}C assignment for all aromatic carbons (Table II) in **1a–c** was not possible. Assignments for protonated aromatic carbons were made by using an HETCOR-2-D experiment (Figure 2). The experiment was performed between δ 6.9–8.7 in the ^1H domain and between 114–134 ppm in the ^{13}C domain. Although

Table II. ^{13}C NMR Assignments (T_1 Values) of Aromatic Carbons of 1a-c



1a, n = 11
b, n = 13
c, n = 16

carbon number	chemical shift[a] (T_1 values, s)		
	1a	1b	1c
1[b]	125.5 (1.30)	125.5 (1.43)	125.5 (1.48)
2	139.6 (14.3)	139.5 (14.0)	139.6 (13.9)
3	127.3 (1.05)	127.3 (1.16)	127.3 (1.21)
4	127.8 (1.28)	127.8 (1.46)	127.8 (1.43)
5[c]	127.9 (1.30)	127.9 (1.48)	128.0 (1.40)
6	124.6 (0.71)	124.6 (0.58)	124.7 (0.71)
7	124.9 (1.11)	124.9 (1.33)	125.0 (1.25)
8[c]	127.8 (1.28)	127.8 (1.46)	127.8 (1.43)
9[b]	125.1 (1.34)	125.1 (1.38)	125.1 (1.44)
10[b]	125.7 (1.46)	125.6 (1.43)	125.7 (1.38)
4a[d]	131.6 (25.1)	131.6 (25.4)	131.6 (23.7)
8a[d]	130.4 (24.3)	130.3 (22.7)	130.4 (23.9)
9a[d]	131.0 (23.8)	131.0 (26.4)	131.0 (23.9)
10a[d]	131.8 (23.5)	131.7 (26.8)	131.8 (22.8)

[a] Measured in ppm downfield from Me_4Si. [b] May be interchanged. [c] May be interchanged. [d] May be interchanged.

splitting patterns for certain ^1H signals (Table III) allowed diagnosis of a few individual protons in **1a** (which in turn was correlated with certain carbons), some of the assignments for the ^{13}C atoms must be viewed with caution. Models[4,6,7] suggest that H(3) and H(4) are distinguished in the ^1H spectrum by the splitting patterns and permit assignments for C(3) and C(4) using the HETCOR-2-D spectrum. Although the ^1H spectrum did not provide a resolved pattern for H(6) and H(7), the HETCOR-2-D experiment revealed that C(6) and C(7) gave signals at 124.6 and 124.9 ppm, assignments which were further

(8) (a) Gray, G. R. VIAs *Varian Instrum. Appl.* **1982**, *16*, 11. (b) Gray, G. A. *Org. Magn. Reson.* **1983**, *21*, 111 and references therein.

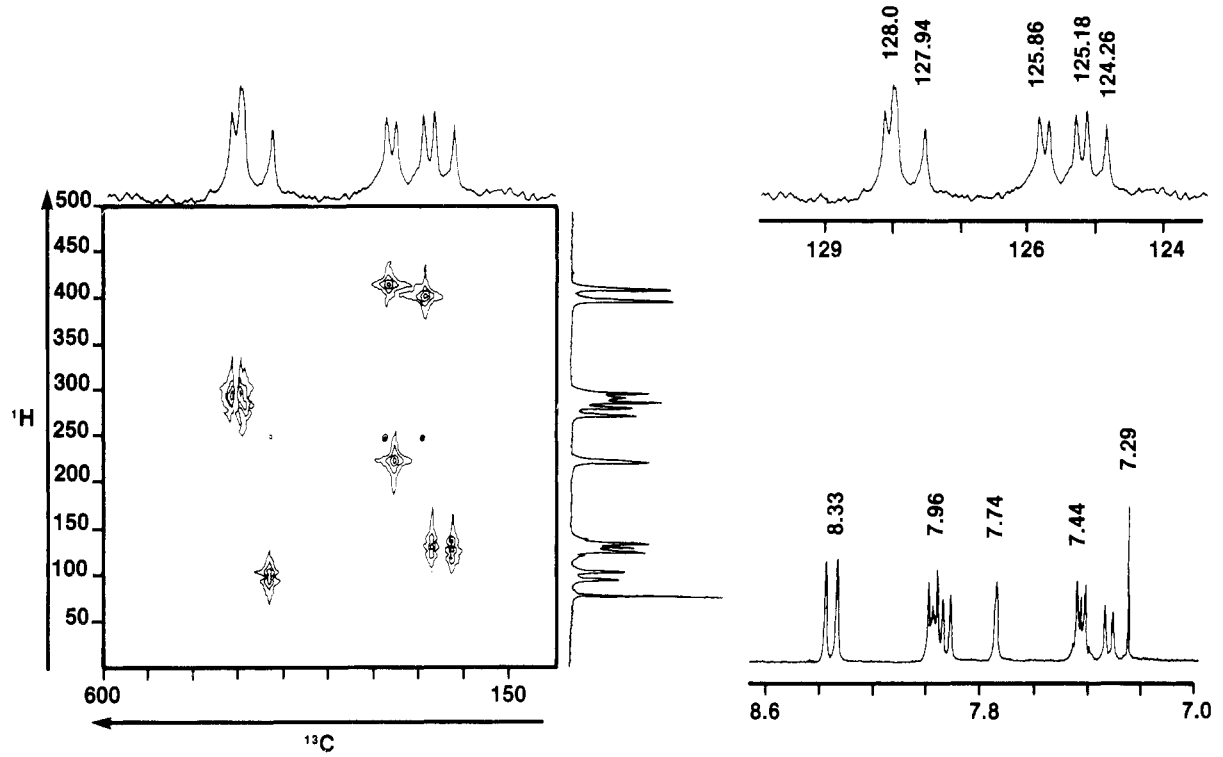
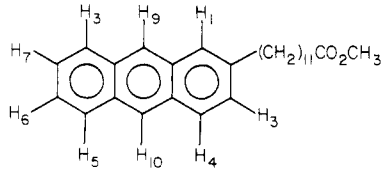


Figure 2. HETCOR-2-D contour plot of the aromatic regions of the ^1H and ^{13}C NMR spectra of **1a**.

Table III. ^1H NMR Assignments for the Aromatic Protons of 1a



1a

proton number	expected splitting pattern[c]	observed chemical shift, ppm	observed splitting pattern
1[a]	d	7.68	br s
3	dd	7.27	dd
4	d	7.87	d
5[b]	dd	7.89-7.96	m
6	ddd or ps t	7.35-7.42	ps t
7	ddd or ps t	7.35-7.42	ps t
8[b]	dd	7.89-7.96	m
9[a]	s	8.27	s
10[a]	s	8.31	s

[a] Assignments may be interchanged. [b] Assignments may be interchanged. [c] s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, ps t = pseudotriplet.

supported by T_1 measurements. The basis for the latter rests upon the known tendency for protonated carbons along an axis of symmetry in an aromatic ring to have a short T_1.[9] Assuming an axis of symmetry through C(2) and C(6) in **1a** produces anisotropic tumbling, C(6) should have the smallest T_1 value of any aromatic carbons. This is indeed the case and leaves the signal at 124.9 ppm assignable to C(7). Assignments for analogous carbons in **1b** and **1c** were made by comparison. To the best of our knowledge, **1a–c** are the only examples in the literature of this type of 2-substituted anthracene with a long side chain.

As can be seen from examination of the T_1 data in Table I, the T_1 values decrease in going from the carbonyl atom of the ester to a near constant value in the middle of the chain. The values increase as expected[4] for the α and β carbons attached to the anthracene ring. Thus, the motional characteristics of the chain are reasonable. The capabilities of such molecules as fluorescent probes awaits further study.

Experimental Section[10]

Preparation of 2-(Hydroxymethyl)anthracene (6). The procedure employed 2-methylanthraquinone (**5**, Aldrich, mp 170–173 °C) as the starting material, and published procedures[5] gave **6** (45% overall); mp 222.5–223.5 °C (lit.[5c] mp 223–224 °C). The HETCOR-2-D technique has been completely described.[8]

2-(Bromoethyl)anthracene (7). Bromine (1.5 mL) was added dropwise under N_2 to a stirred solution of triphenylphosphine (7.0 g, 26.72 mmol) in dry DMF (40 mL). The alcohol **6** (5.0 g, 24.04 mmol) was added as a solid to the resulting orange suspension. After 5 min, a pale yellow solid precipitated. After stirring for an additional 75 min, the yellow solid was filtered (vacuum). A second crop of the solid was obtained by cooling the filtrate to 0 °C for 4 h. The combined solids were recrystallized ($HCCl_3$) to give 5.48 g 84.1%) of **7** as a pale yellow powder: mp 198.5–199 °C (lit.[11] mp 160 °C); ^1H NMR ($DCCl_3$) δ 4.79 (s, 2 H, CH_2Br), 7.24–8.37 (m, 9 H, Ar H). Anal. Calcd for $C_{15}H_{11}Br$: C,

(9) (a) Abraham, R.; Loftus, P. "Proton and ^{13}C NMR Spectroscopy", Heyden: Son, Philadelphia, Pa, 1978. (b) Breitmaier, E.; Spohn, K.; Berger, S. *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 144. (c) Levy, G. C. *Acc. Chem. Res.* **1976**, *6*, 161.

(10) All melting points and boiling points are uncorrected. IR spectra were recorded on a Perkin-Elmer 681 spectrometer. NMR spectral data were gathered on a Varian XL-100(15) unit equipped with a Nicolet TT-100 PFT accessory or on a Varian XL-300 unit. The ^1H data were taken at 100.1 or 299.94 MHz and ^{13}C data at 25.2 or 75.42 MHz. Chemical shifts values are expressed for ^1H in δ values and for ^{13}C in ppm from tetramethylsilane as an internal reference. All T_1 measurements were made on the XL-100(15) spectrometer operating at 25.2 MHz for ^{13}C observation by using the FIRFT method [Canet, D.; Levy, G. C.; Peat, J. R. *J. Magn. Reson.* **1975**, *18*, 199. Ramarajan, K. Ph.D. Dissertation, Oklahoma State University, 1980]. Mass spectral data were recorded on a CEC Model 21-110 B HR unit.

(11) Laarhoven, W. H.; Cuppen, T. J. H. M.; Nivard, R. J. F. *Tetrahedron* **1970**, *26*, 4865.

66.45; H, 4.06; Br, 29.49. Found: C, 66.10; H, 4.15; Br, 29.52.

(2-Anthrylmethyl)triphenylphosphonium Bromide (2).[11] A solution of **7** (1.7 g, 6.27 mmol) and triphenylphosphine (1.7 g, 6.49 mmol) in dry benzene (75 mL) was heated at reflux under N_2 for 24 h. The mixture was cooled and filtered. The resulting solid was reprecipitated from $HCCl_3$ by using anhydrous ether, washed with dry ether (50 mL), and dried under vacuum to give 3.0 g (89.8%) of **2** as an off-white powder: mp >220 °C; ^1H NMR ($DCCl_3$) δ 5.54–5.68 (d, 2 H, CH_2P^+), 7.0–7.2 (m, 24 H, Ar H); ^{31}P NMR ($DCCl_3$) 22.9 ppm (85% H_3PO_4 reference). The salt was used without further purification.

Methyl 11-Bromoundecanoate (9). A solution of 11-bromoundecanoic acid (8), 20.0 g, 0.103 mol) and concentrated H_2SO_4 (2 mL) in methanol (200 mL) was heated at reflux under N_2 through 3-Å molecular sieve for 48 h in a 500-mL, round-bottomed flask equipped with a Soxhlet condenser. The solution was concentrated to a volume of 50 mL, diluted with ether (50 mL), and washed successively with 10% aqueous $NaHCO_3$ (2 × 50 mL), H_2O (25 mL), and saturated aqueous NaCl (25 mL). The solution was dried (Na_2SO_4), and the solvent was removed. Vacuum distillation gave 15.8 g (75%) of **9** as a clear, colorless liquid: bp 93–96 °C (0.025 mm) (lit.[12] bp 126–128 °C (0.65 mm)); IR (neat) 1740 cm^{-1} (C=O); ^1H NMR ($DCCl_3$) δ 1.28–1.9 (m, 16 H, $(CH_2)_8$), 2.29 (t, 2 H, $CH_2CO_2CH_3$), 3.39 (t, 2 H, CH_2Br), 3.64 (3, 3 H, OCH_3); ^{13}C NMR ($DCCl_3$) ppm 173.9 (C(1)), 51.3 (C(1')), 34.0, 33.8, 32.8, 29.3, 29.1, 28.7, 28.1, 24.9 (C(2)).

Methyl 11-Oxoundecanoate (3a).[13] A mixture of **9** (7.0 g, 25.1 mmol), pyridine *N*-oxide (4.8 g, 50.5 mmol), and $NaHCO_3$ (4.2 g, 50.0 mmol) in dry toluene (32 mL) was heated at reflux under N_2 with vigorous stirring for 6 h. The resulting dark brown mixture was cooled, washed with H_2O (2 × 25 mL), and dried (Na_2SO_4). Removal of the solvent (vacuum) gave a dark brown oil, which was distilled (vacuum) to give 3.7 g (69%) of **3a** as a colorless liquid: bp 95–98 °C (0.05 mm); IR (neat) 1720–1740 cm^{-1} (C=O); ^1H NMR ($DCCl_3$) δ 1.3–1.7 (m, 14 H, $(CH_2)_7$), 3.23–3.5 (m, 4 H, H(2), H(10)), 3.66 (s, 3 H, OCH_3), 9.74 (t, 1 H, CHO).

Methyl 12-(2-Anthryl)-11-dodecenoate (4a). A solution of salt **2** (2.5 g, 4.69 mmol) in anhydrous Me_2SO (65 mL) was added dropwise with stirring under N_2 at room temperature to a 50% mineral oil dispersion of NaH (0.25 g, 5.208 mmol). The resulting blood-red solution was stirred at room temperature for 10 min. A solution of the aldehyde **3a** (1.9 g, 8.879 mmol) in dry Me_2SO (5 mL) was then added in one portion. The mixture was stirred for an additional 48 h at room temperature diluted with H_2O (150 mL), and acidified (litmus) with concentrated HCl. The resulting yellow solid was filtered (vacuum) and air-dried in the dark. The solid was digested twice with 95% ethanol (50 mL) and dried in the dark to give 1.4 g (76.9%) of **4a** as a light yellow powder: mp 121 to >250 °C; ^1H NMR ($DCCl_3$) δ 1.2–1.7 (m, 14 H, $(CH_2)_7$), 2.18–2.62 (m, 1 H, ArCH=C*H*, trans), 7.22–8.35 (m, 10 H, ar H and ArC*H*=CH, trans). A lesser amount (~23%) of the cis isomer was present as indicated by ^1H NMR signals at δ 5.6–5.94 (m, ArCH=C*H*, cis) and 6.6–6.7 (d, ArC*H*=CH, cis). The wide melting point range is apparently due to the cis–trans mxiture.

Methyl 12-(2-Anthryl)dodecanoate (1a). A solution of **4a** (0.4 g, 1.031 mmol) in ethyl acetate (75 mL) was hydrogenated at room temperature and atmospheric pressure in the presence of 10% Pd/C (0.1 g) for 4 h. Addition of diatomaceous earth followed by vacuum filtration and evaporation of the solvent gave an off-white solid. The solid was recrystallized (95% ethanol) twice and then subjected twice to molecular distillation (110 °C (5×10^{-4} mm)) to give 0.3 g (74.6%) of **1a** is a white powder: mp 104.5–105 °C; ^1H NMR ($DCCl_3$) δ 1.29 (m, 18 H, $(CH_2)_9$), 2.28 [t, 2 H, $CH_2CO_2CH_3$], 2.78 (t, 2 H, $ArCH_2$), 3.64 (s, 3 H, OCH_3), 7.21–8.34 (m, 9 H, Ar H); mass spectra, *m/e* (M^+) 390.2559, found 390.2550. Anal. Calcd for $C_{27}H_{34}O_2$: C, 83.08; H, 8.72. Found: C, 83.02; H, 8.99.

Methyl 13-Hydroxytridecanoate (12). A solution of *n*-butyllithium (1.6 M, 44.3 mL, 70.88 mmol) in hexane was added dropwise under N_2 to a stirred solution of 2,4,4-trimethyloxazoline (**10**, Aldrich, 8.0 g, 70.796 mmol) in dry THF (80 mL) at −78 °C. The solution was stirred at −78 °C for an additional 10 min at which time a solution of lithium 11-bromoundecoxide in THF (generated by treatment of 11-bromoundecanol (17.8 g, 70.94 mmol) in 45 mL of dry THF with *n*-butyllithium in hexane (1.6 M, 44.4 mL, 71.04 mmol)) was added dropwise. The mixture was stirred at −78 °C for 10 min and at room temperature for an additional 2 h. The mixture was poured into ice water (250 mL), acidified (litmus) with concentrated HCl, and extracted with ether (100 mL). The aqueous layer was neutralized (with cooling (ice bath)) by using 40% aqueous NaOH, and the mixture was extracted with ether (3 × 100 mL). The organic layer was washed with saturated aqueous NaCl (2 × 1200 mL) and dried ($MgSO_4$). Evaporation of solvent gave **11** as a tan oil, which solidified upon cooling (15.95 g, 79.1%). A solution of the crude oxazoline **11** in CH_3OH (300 mL), H_2O (10 mL), and concentrated H_2SO_4 (12 mL) was heated at reflux in a 500-mL, round-bottomed flask for 18 h. The solution was concentrated to 75 mL, poured into cold H_2O (150 mL), and extracted with ether (2 × 100 mL). The organic layer was washed successively with 5% aqueous $NaHCO_3$ (2 × 100 mL) and saturated aqueous NaCl (2 × 100 mL) and dried ($MgSO_4$). Removal of the solvent left a tan oil, which solidified upon cooling. Recrystallization (petroleum either; bp 37.7–56.9 °C), with cooling to 0 °C, gave 8.2 g (47.5%) of **12** as a white solid: mp 38.5–39.5 °C (lit.[14] mp 40.5–41.5 °C); IR (melt) 2900–3600 (OH), 1740 cm^{-1} (C=O); ^1H NMR ($DCCl_3$) δ 1.28–1.7 (m, 20 H, $(CH_2)10$), 1.8–1.9 (br s, 1 H, OH), 2.42 (t, 2 H, $CH_2CO_2CH_3$), 3.58–3.70 (m, 5 H, OCH_3 and CH_2OH); ^{13}C NMR ($DCCl_3$) ppm 174.1 (C(1)), 62.9 (C(13)), 52.3 (C(α)), 34.1 (C(2)), 32.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.7, 24.9 (C(3)).

Methyl 13-Oxotridecanoate (3b).[15] Chromium trioxide (6.2 g, 62.00 mmol) was added under N_2 to a stirred solution of pyridine (9.7 g, 122.8 mmol) in CH_2Cl_2 (150 mL). After 20 min, a solution of the alcohol **12** (2.5 g, 10.25 mmol) in H_2CCl_2 (20 mL) was added in one portion. After being stirred for an additional 20 min, the solution was decanted, and the tarry residue was washed with ether (2 × 75 mL). The combined organic solutions were washed with 5% aqueous NaOH (4 × 100 mL), 5% aqueous HCl (2 × 100 mL), saturated aqueous $NaHCO_3$ (2 × 100 mL), and saturated aqueous NaCl (150 mL). After drying ($MgSO_4$), the solvent was removed to give 2.38 g (96%) of crude **3b** as a light yellow oil. Aldehyde **3b** was used in subsequent reactions without further purification: IR (neat) 1720–1740 cm^{-1} (C=O); ^1H NMR ($DCCl_3$) δ 1.2–1.7 (m, 18 H, $(CH_2)_9$], 2.2–2.5 (m, 4 H, $CH_2CO_2CH_3$ and CH_2CHO), 3.66 (s, 3 H, OCH_3), 9.74 (t, 1 H, CHO); ^{13}C NMR ($DCCl_3$) ppm 202.6 (C(13)), 174.0 (C(1)), 51.3 (C(α)), 43.8 (C(12)), 34.0 (C(2)), 29.4, 29.35, 29.3, 29.3, 29.1, 24.9 (C(3)), 22.1 (C(11)).

Methyl 14-(2-Anthryl)-13-tetradecenoate (4b). A solution of the phosphonium salt **2** (2.0 g, 3.753 mmol) in dry Me_2SO (75 mL) was added rapidly under N_2 to a stirred 50% mineral oil dispersion of NaH (0.2 g, 4.167 mmol). The resulting blood-red solution was stirred for 10 min, and a solution of aldehyde **3b** (1.4 g, 5.785 mmol) in dry ether (5 mL) was then added in one portion. The resulting mixture was stirred for 24 h at room temperature, diluted with H_2O (75 mL), and acidified (litmus) with concentrated HCl. Vacuum filtration gave a bright yellow solid, which was digested in 95% ethanol (50 mL) and air-dried in the dark (1.4 g, 89.7%): mp 108 to >250 °C; ^1H NMR ($DCCl_3$) δ 1.04–1.76 (m, 18 H, $(CH_2)_9$), 2.12–2.58 (m, 4 H, $CH{=}CHCH_2$, $CH_2CO_2CH_3$), 3.63 (s, 3 H, OCH_3), 6.32–6.54 (m, 1 H, ArCH=C*H*, trans), 7.24–8.36 (m, 10 H, Ar H, ArC*H*=CH, trans). A small amount of the cis isomer was present as indicated by ^1H NMR signals at δ 5.58–5.9 (m, ArCH=C*H*, cis) and 6.56–6.69 (m, ArC*H*=CH, cis). The wide melting point range is likely due to the cis–trans mixture.

Methyl 14-(2-Anthryl)tetradecanoate (1b). A solution of **4b** (0.5 g, 1.202 mmol) in warm ethyl acetate (150 mL) was hydrogenated at atmospheric pressure in the presence of 10% Pd/C (0.1 g) for 4 h. Diatomaceous earth was added, and the mixture was filtered. Evaporation of the solvent left a pale yellow solid. Recrystallization (95% ethanol) (twice) and molecular distillation (110 °C (5×10^{-4} mm)) (twice) gave 0.4 g (79.6%) of **1b** as a white powder: mp 103–103.5 °C; ^1H NMR ($DCCl_3$) δ 1.2–1.7 (m, 22 H, $CH_2)_{11}$), 2.27 (t, 2 H, $CH_2CO_2CH_3$), 2.78 (t, 2 H, $ArCH_2$), 3.63 (s,

(12) Brown, H. C.; Lane, C. F. *J. Am. Chem. Soc.* **1970**, *92*, 6660.
(13) Stiller, K.; Waiss, A. C.; Haddon, W. F. *Chem. Ind. (London)* **1975**, 652.
(14) Kimura, K.; Takahashi, M.; Tanaka, A. *Chem. Pharm. Bull.* **1960**, *8*, 1059.
(15) Marcinkiewicz, J.; Zeierzykowski, W.; Murawski, R. *Chem. Stosow.* **1972**, *16*, 297; *Chem. Abstr.* **1973**, *78*, 57688v.

3 H, OCH_3)), 7.2-8.34 (m, 9 H, Ar H); mass spectra, m/e (M^+) 418.2872, found 418.2862.

Methyl 16-Hydroxyhexadecanoate (14). A solution of dihydroambrettolide (**13**, Columbia, 5.0 g, 19.685 mmol) and *p*-toluenesulfonic acid (PTSA, 1.0 g) in methanol (250 mL) was heated at reflux under N_2 for 18 H. The solution was concentrated to 75 mL, poured into cold H_2O (100 mL), and extracted with ether (3 × 75 mL). The organic layer was washed with 10% aqueous $NaHCO_3$ (2 × 75 mL) and dried ($MgSO_4$). Removal of the solvent left a waxy white solid. Recrystallization (petroleum ether) gave 4.8 g (85.3%) of **14** as a flaky white solid: mp 56-57 °C; IR (melt) 2900-3600 (OH), 1740 cm^{-1} (C=O); ^{13}C NMR ($DCCl_3$) ppm 174.1 (C(1)), 62.8 (C(16)), 52.3 (C(α)), 34.1 (C(2)), 32.8, 29.6, 29.4, 29.2, 29.1, 25.8, 24.9 (C(3)).

Methyl 16-Oxohexadecanoate (3c). Chromium trioxide (6.3 g, 63.0 mmol) wsa added under N_2 to a stirred solution of pyridine (9.9 g, 125.3 mmol) in HC_2Cl_2 (150 mL). After 20 min, a solution of alcohol **14** (3.0 g, 10.489 mmol) in HC_2Cl_2 (20 mL) was added in one portion. After an additional 20 min, the solution was decanted, and the tarry residue was washed with ether (2 × 75 mL). The combined organic solutions were washed successively with 5% aqueous NaOH (4 × 100 mL), 5% aqueous HCl (2 × 100 mL), saturated aqueous $NaHCO_3$ (2 × 100 mL), and saturated aqueous NaCl (150 mL). After drying ($MgSO_4$), the solvent was evaporated to give 2.5 g (83.9%) of crude **3c** as a white solid. This solid was used in subsequent reactions without further purification: mp 67-69 °C; IR (melt) 1720-1740 cm^{-1} (C=O); ^{13}C NMR ($DCCl_3$) ppm 202.4 (C(16)), 173.9 (C(1)), 51.2 (C(α)), 43.7 (C(15)), 34.0 (C(2)), 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 24.8 (C(3)), 22.0 (C(14)).

Methyl 17-(2-Anthryl)-16-heptadecenoate (4c). A solution of the phosphonium salt **2** (2.0 g, 3.753 mmol) in dry Me_2SO (75 mL) was added rapidly under N_2 to a stirred mineral oil dispersion of NaH (50%, 0.2 g, 4.167 mmol). After 10 min, a solution of the crude aldehyde **3c** (1.9 g, 6.69 mmol) in dry ether (50 mL) was added to the blood-red solution. After being stirred for 30 h at room temperature, the mixture was diluted with H_2O (100 mL) and acidified (litmus) with concentrated HCl. The mixture was filtered (vacuum) to give a yellow powder. The filtrate was extracted with $HCCl_3$ (3 × 50 mL). The organic layers were combined and dried (Na_2SO_4). Removal of the solvent left a yellow semisolid. The combined solids were digested in 95% ethanol (40 mL) and air-dried in the dark to give 1.4 g (81.4%) of **4c** as a yellow powder: mp 110 to >250 °C; ^1H NMR ($DCCl_3$) δ 1.1-1.75 (m, 24 H, $(CH_2)12$), 2.17-2.6 (m, 4 H, CH=CHCH_2, C$H_2CO_2CH_3$), 3.65 (s, 3 H, OCH_3), 6.55-6.8 (m, 1 H, ArCH=C*H*, trans), 7.45-8.6 (m, 10 H, Ar H, ArC*H*=CH, trans). A lesser amount of the cis iosomer was present as indicated by the ^1H NMR signals at δ 5.85-6.2 (m, ArCH=C*H*, cis) and 6.8-6.9 (m, ArC*H*=CH, cis). The wide melting point range is probably due to the cis-trans mixture.

Methyl 17-(2-Anthryl)heptadecanoate (1c). A warm solution of **4c** (0.5 g, 1.092 mmol) in ethyl acetate (175 mL) was hydrogenated at atmospheric pressure in the presence of 10% Pd/C (0.1 g) for 4 h. Addition of diatomaceous earth, vacuum filtration, and evaporation of the solvent gave an off-white powder. The solid was recrystallized twice (95% ethanol) and subjected twice to molecular distillation (140 °C (5 × 10^{-4} mm)) to give 0.4 g (80%) of **1c** as a white powder: mp 104.5-105.5 °C; ^1H NMR ($DCCl_3$) δ 1.2-1.85 (m, 28 H, $(CH_2)_{14}$), 2.29 (t, 2 H, C$H_2CO_2CH_3$), 2.79 (t, 2 H, ArCH_2), 3.65 (s, 3 H, OCH_3), 7.2-8.34 (m, 9 H, Ar H); mass spectra m/e (M^+) 460.3341, found, 460.3349.

Acknowledgment. We gratefully acknowledge partial support by the National Science Foundation for funds to purchase the XL-300 NMR spectrometer (NSF Grant CHE81-06157).

Registry No. **1a**, 88229-60-1; **1b**, 88229-61-2; **1c**, 88229-62-3; **2**, 88229-63-4; **3a**, 1931-65-3; **3b**, 1608-77-1; **3c**, 45247-78-7; **4a**, 88229-64-5; **4b**, 88229-65-6; **4c**, 88229-66-7; **6**, 22863-82-7; **7**, 31124-71-7; **9**, 6287-90-7; **10**, 4195-89-5; **11**, 88229-67-8; **12**, 7147-29-7; **13**, 109-29-5; **14**, 36575-67-4; **15a**, 75802-32-3; **15b**, 75802-33-4; **15c**, 75802-34-5; triphenylphosphine, 603-35-0; lithium 11-bromoundecoxide, 88229-68-9; 11-bromoundecanol, 1611-56-9.

Reduction by a Model of NAD(P)H. 45. Mechanism for the Dediazoniation of Arenediazonium Salts Initiated by One-Electron Transfer from an NAD(P)H Model

Shinro Yasui,* Kaoru Nakamura,† and Atsuyoshi Ohno†

Tezukayama Junior College, 3-1, Gakuen-Minami, Nara 631, Japan, and Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Received July 15, 1983

Arenediazonium fluoroborates, ArN_2BF_4 (**1a**, Ar = *p*-$CH_3C_6H_4$; **1b**, Ar = *p*-BrC_6H_4; **1c**, Ar = *p*-$NO_2C_6H_4$) react with an NAD(P)H model, *N*-benzyl-1,4-dihydronicotinamide (BNAH), in methanol, giving the corresponding reduction products ArH (**2**). The stoichiometry for the starting materials and reduction products clearly indicates that this reduction involves a radical-chain path initiated by BNAH. The mechanism is supported by the effect of spin-trapping agents on the yields of the products. From the results from experiments with methanol-d_4, we have found that under a nitrogen atmosphere, the radical chain is more favorable in the order **1a** < **1b** < **1c**, which is the same as the order in the thermal dediazoniation of **1** in acidic methanol. The results presented here provide direct evidence for a one-electron transfer mechanism for reduction with an NAD(P)H model.

Within the last three decades, many reports on the mechanism for reduction with an NAD(P)H model have been presented.[1-13] An exciting contradiction concerns the process of net "hydride-ion" transfer from a model to a substrate in the course of the reduction.[6-13] Results based on kinetics[10,11] and product analyses[13] have demonstrated that the reduction proceeds via one-electorn transfer followed by a proton (or a hydrogen atom) transfer. Nevertheless, evidence supporting a one-step hydride-transfer mechanism is not negligible. For example, it has been

† Institute for Chemical Research, Kyoto University.

(1) Sigman, D. S.; Hajdu, J.; Creighton, D. J. "Bioorganic Chemistry"; van Tamelen, E. E., Ed.; Academic Press: New York, 1978; Vol. IV, pp 385-407; Kill, R. J.; Widdowson, D. A. pp 239-275.
(2) Ohno, A.; Yasui, S.; Gase, R. A.; Oka, S.; Pandit, U. K. *Bioorg. Chem.* **1980**, *9*, 199.
(3) Ohno, A.; Yasui, S.; Yamamoto, H.; Oka, S.; Ohnishi, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 294.
(4) Ohno, A.; Nakai, J.; Nakamura, K.; Goto, T.; Oka, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3486.

0022-3263/84/1949-0878$01.50/0