furan–water was stirred at 0 °C. Mercuric chloride (0.027 g, 0.1 mmol) was added, and the disappearance of **4a** was monitored by TLC. After 8 h the mixture was diluted with ether, filtered through celite, washed with saturated aqueous sodium bicarbonate, and concentrated. The product was purified by chromatography on 5 g of silica gel (19:1). GC analysis indicated that the product was a 3.9:1 mixture of *cis*- and *trans*-tetrahydroindanones (**1** and **2**).

A portion of the product (0.030 g, 0.2 mmol) was dissolved in 0.5 mL of tetrahydrofuran and treated with 0.030 mL of a 0.65 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol (0.02 mmol). After 5 min, GC analysis indicated that the ratio of isomers had reached the equilibrium value of 1:2 = 1.1:1.

General Procedures for Oxidative Elimination. Syntheses of Dihydroindanones. A solution of the phenylthio ketone (1.5 mmol) in 15 mL of dichloromethane was treated with 1.5 mmol of *m*-chloroperoxybenzoic acid in 6 mL of dichloromethane at −78 °C. After 10 min the reaction was quenched with 10% aqueous sodium sulfite and warmed to room temperature. The organic layer was dried over magnesium sulfate and concentrated. If elimination was incomplete according to TLC, the residue was dissolved in 5 mL of carbon tetrachloride and heated at 50 °C for 1 h. The reaction mixture was purified by column chromatography on 20 g of silica gel.

6e: mp 75–76 °C (lit.[8] mp 76.5–77 °C); R_f (1:1) 0.29.

7e: R_f (1:1) 0.43; NMR 2.0–3.3 (m, 7 H), 6.0–6.4 (m, 2 H), 6.7–6.9 (m, 1 H).

6f: R_f (9:1) 0.05; NMR 1.27 (d, 3 H, J = 7), 2.2–2.8 (m, 4 H), 3.10 (br s, 3 H), 5.80 (br s, 2 H).

7f: R_f (9:1) 0.25; NMR 1.1–1.95 (m, 2 H), 1.95–3.0 (m, 8 H), 6.1 (br s, 2 H).

6h: mp 90.5–92 °C (petroleum ether); R_f (9:1) 0.12; NMR 1.67 (br s, 3 H), 2.46 (br s, 6 H), 2.85 (br s, 4 H), 5.53 (br s, 1 H); IR ($CHCl_3$) 3000, 2920, 2860, 1698, 1683, 1644, 1438, 1417, 1408, 1270, 1168, 991 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O$: C, 81.05; H, 8.16. Found: C, 80.90; H, 8.18.

7h: R_f (9:1) 0.17; NMR 1.9 (br s, 3 H), 2.1–3.2 (m, 7 H), 5.8–6.1 (m, 1 H), 6.7–6.9 (m, 1 H); IR ($CHCl_3$) 3020, 2980, 2940, 1685, 1651, 1575, 1443, 1234, 1061, 1013, 822 cm^{-1}.

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Registry No. 1, 53921-54-3; **2**, 25050-74-2; **3**, 34780-08-0; **4a**, 75781-75-8; **4b**, 75781-76-9; **4c**, 75781-77-0; **5b**, 75781-78-1; **5c**, 75781-79-2; **6e**, 75781-80-5; **6f**, 75781-81-6; **6h**, 75781-82-7; **7e**, 75781-83-8; **7f**, 75781-84-9; **7h**, 75781-85-0; 1,3-pentadiene, 504-60-9; cyclopentenone, 930-30-3; butadiene, 106-99-0; isoprene, 78-79-5; aluminum chloride, 7446-70-0.

Syntheses of Selected ϵ-(2- or 9-Anthryl)alkanoic Acids and Certain Esters—Carbon-13 Spin-Lattice Relaxation Time Measurements of Methyl 5-(2-Anthryl)pentanoate and Methyl 7-(2-Anthryl)heptanoate

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Fluorescent probes have been widely applied in the study of microenvironments of large biological structures such as proteins and membranes.[1] Such probes with hydrophilic and hydrophobic properties have made it possible to study certain regions of membranes. Waggoner and Stryer[2] synthesized some fluorescent probes to study the hydrophilic regions of membranes. Since the above probes provided only a hydrolyzable fluorescent marker, Stoffel and Michaelis[3] developed a class of anthracene-labeled fatty acids and phospholipids. However, the bulky anthracene residue of the above probes was not transported through the membrane or used by fatty acid kinase or acyltransferase for the biosynthesis of membrane phospholipids of the *E. coli* mutant.[3] In connection with other studies concerned with biological mimics, we had occasion to prepare several ϵ-(2- and 9-anthryl)alkanoic acids and esters which have a general structural formula shown below.

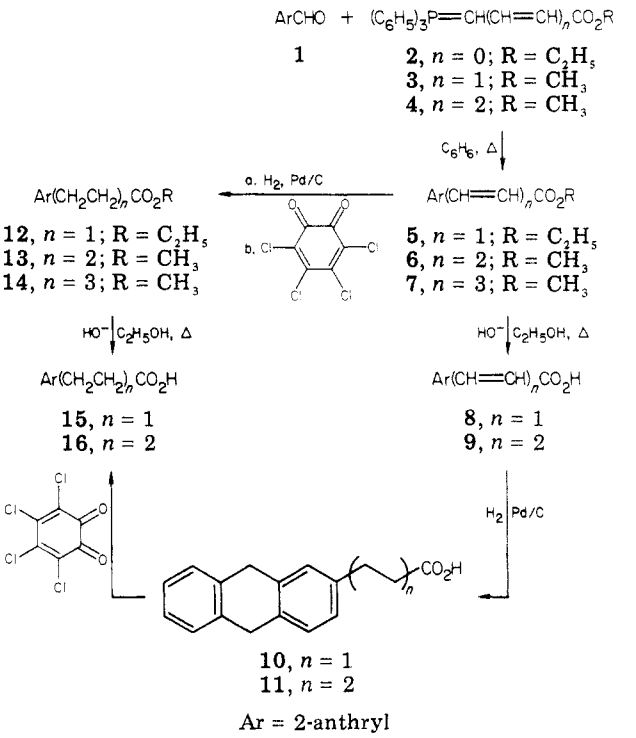
$$Ar(CH_2)_nCO_2R$$

Ar = 2-anthryl, 9-anthryl

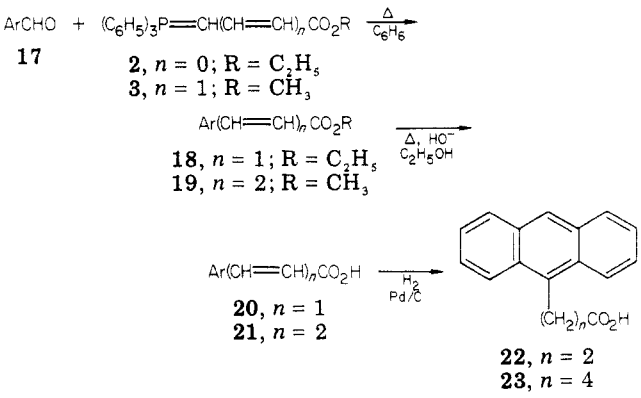
n = 2, 4, 6

R = H, CH_3, C_2H_5

Scheme I



Scheme II



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Only a very few examples of such compounds could be found in the literature. We report herein the syntheses for seven compounds of the general type above as well as spin-lattice relaxation times (T_1 values) for ^{13}C for two of the esters. The relaxation times are well-known to be good indicators of the motional characteristics of the atoms in long-chain mimics.[26] Schemes I and II outline our approach.

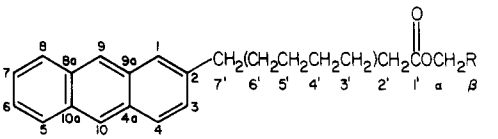
Results and Discussion

2-Anthraldehyde (1) was prepared in several steps from readily available 2-methylanthraquinone (Aldrich)[4-11] in a modest overall yield (37.4%). Phosphoranes **2**, **3**, and **4** were made from the corresponding phosphonium salts by the literature procedures.[12-16] A Wittig reaction[16-18] of **1** with phosphoranes **2**, **3**, and **4** gave the expected unsaturated esters **5**, **6**, and **7**. Saponification of esters **5** and **6** yielded the unsaturated acids **8** and **9** in good yield. Hydrogenation (atmospheric pressure) of **8** and **9** over 10% Pd/C gave 9,10-dihydro derviatives **10** and **11**, respectively. Formation of 9,10-dihydro derivatives during hydrogenation, although not expected, is not unreasonable as the 9 and 10 positions in the anthracene ring are very reactive.[19] The above 9,10-dihydro derivatives were aromatized with *o*-chloranil in benzene. Saturated esters **12**, **13**, and **14** were obtained via hydrogenation and aromatization without isolating the dihydro derivatives of the corresponding unsaturated esters **5**, **6**, and **7**. Saponification of the esters **12** and **13** with 10% alcoholic KOH solution yielded the saturated acids **15** and **16**.

Wittig reaction[18] of 9-anthraldehyde (**17**) with phosphoranes **2**[15] and **3**[13] gave the unsaturated esters **18**[20] and **19**,[18] respectively. Saponification of esters **18** and **19** using 10% alcoholic KOH yielded the corresponding unsaturated acids **20**[21] and **21** which were then hydrogenated over 10% Pd/C to obtain the saturated acids **22** and **23**, respectively.

Structures of compounds **5**–**16** and **18**–**23** were confirmed by spectral data and elemental analyses. IR, UV, and ^1H NMR spectral data, melting points, and elemental analysis for compounds **5**–**16** and **18**–**23** are provided in the experimental section. ^{13}C NMR chemical shifts for esters **12**–**14** and T_1 values for carbons in esters **13** and **14** are listed in Table I. Assignments of ^{13}C chemical shifts were made by using model compounds[22-24] and a good agreement among the data for **12**, **13**, and **14** was observed with respect to the chemical shifts of identical carbon nuclei in the anthracene ring as well as the related carbon nuclei in the alkyl side chain. The T_1 values dropped to a minimum in the middle of the side chain which is also rather normal.[23] Differences in T_1 values of individual carbon nuclei in the side chain of **13** and **14** are perhaps due to a motional gradient (segmental motion[25]) of the alkyl chains. Decreased T_1 values of carbon nuclei that are attached *directly* to an anthracene ring are not surprising since the anthracene ring can probably hinder the independent motion of the ϵ-carbon in the side chain of **15** and **16**. This type of steric interaction is not unusual and a recent study of T_1 measurements on carbon in some 9-(anthroyloxy)alkyl carboxylates[26] supports our observations. In view of the recent observations[28] that 9-anthryl derivatives can cause a large perturbation in the packing of lipid bilayers, no T_1 measurements were performed on **22** or **23**.

Table I. ^{13}C NMR Chemical Shifts[a] (^{13}C T_1 Values)[b] for Anthracene Carboxylic Acid Esters 12, 13, and 14



carbon	12	13	14
C-1	125.9	125.5 (1.5)	125.5 (1.6)
C-2	137.2	138.7 (15.2)	139.2 (14.6)
C-3	128.0	127.8 (1.5)	127.8 (1.5)
C-4	126.7	125.7 (15)	125.6 (1.4)
C-5	127.9	127.2 (1.3)	127.1 (1.1)
C-6[c]	124.9	124.7 (0.9)	124.9 (1.0)
C-7[c]	125.1	124.9 (0.9)	124.6 (1.0)
C-8	128.2	127.9 (1.5)	127.9 (1.5)
C-9	125.4	125.0 (1.1)	125.1 (1.2)
C-10	125.8	125.3 (1.1)	125.1 (1.2)
C-4a	130.4	130.3 (25.1)	130.3 (25.1)
C-8a	131.6	131.6 (22.7)	131.6 (23.0)
C-9a	131.7	131.7 (22.6)	131.7 (22.4)
C-10a	131.3	131.1 (23.3)	131.0 (22.6)
C-1′ (C=O)	172.6	173.6 (37.2)	173.8 (38.5)
C-2′	35.5	35.8 (1.1)	36.0 (1.0)
C-3′	31.3	24.6 (1.4)	24.8 (1.4)
C-4′		33.8 (1.7)	28.8 (1.1)
C-5′		30.2 (1.1)	28.8 (1.1)
C-6′			33.9 (1.9)
C-7′			30.6 (1.0)
C-α	60.3	51.3 (6.1)	51.2 (6.2)
C-β	14.2		

[a] Chemical shifts in parts per million downfield from internal tetramethylsilane in $DCCl_3$. [b] ^{13}C spin-lattice relaxation time in seconds. [c] May be interchanged.

Experimental Section

Melting points (uncorrected) were determined with a Thomas-Hoover capillary apparatus. IR spectral data were collected on a Beckman IR-5A unit. NMR spectral signals were recorded in parts per million (ppm) downfield from Me_4Si on a Varian XL-100(15) NMR spectrometer equipped with a Nicolet TT-100 PFT accessory operating at 100.1 MHz for ^1H NMR and at 25.2 MHz for ^{13}C NMR. All T_1 measurements were made on the above

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NMR spectrometer operating at 25.2 MHz for ^{13}C observation.[27] UV spectral data were recorded on a Cary Model 14 recording spetrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. 2-Anthraldehyde (1) was prepared from 2-methylanthraquinone (Aldrich).[4-11] Phosphoranes 2, 3, and 4 were made by published procedures.[12-16] 9-Anthraldehyde (17, Aldrich) was purchased and used as such. Organic extracts were dried with $MgSO_4$ and a rotoevaporator was used to remove organic solvents during the usual workup. Hydrogenations were performed in a Parr hydrogenation apparatus over a 4-h period in all cases. Workup of the hydrogenation mixture consisted of filtration followed by evaporation of the filtrate to give a semisolid. This crude solid was treated with *o*-chloranil to effect the aromatization of the anthracene ring.

Preparation of Esters 5, 6, 7, 18, and 19. General Method.[17,18] A mixture of the corresponding anthraldehyde and Wittig reagent in benzene was boiled under N_2 for 24 h and the mixture was allowed to cool. Removal of benzene left a semisolid which, upon trituration (petroleum ether or anhydrous C_2H_5OH) and recrystallization, gave the expected unsaturated ester.

Ethyl 3-(2-Anthryl)prop-2-enoate (5).[29] Aldehyde 1 (0.500 g, 2.4 mmol) reacted with phosphorane 2 (0.870 g, 2.4 mmol) to give 0.46 g (68.7%) of 5: mp 203–204 °C (lit.[19] mp 188–89 °C); IR (KBr) ν_{max} 1695, 1626 cm^{-1}; ^1H NMR ($DCCl_3$) δ 1.34 (3 H, t, CH_3), 4.30 (2 H, q, CH_2), 6.50 (1 H, d, vinylic H), 7.40–8.14 (8 H, m, Ar H and vinylic H), 8.38 (2 H, d, Ar H).

Methyl 5-(2-Anthryl)penta-2,4-dienoate (6). Aldehyde 1 (1.0 g, 5 mmol) was condensed with phosphorane 3 (2.4 g, 7 mmol) to produce 0.5 g (36%) of 6: mp 233–234 °C dec (C_6H_6); IR (KBr) ν_{max} 1700, 1625 cm^{-1}; ^1H NMR ($DCCl_3$) δ 3.78 (3 H, s, CH_3), 5.96–6.01 (1 H, d, $H_3CO_2CCH{=}C$), 6.80–8.38 (12 H, m, Ar H and HC=CH); UV (anhydrous C_2H_5OH) λ_{max} 412 nm (ϵ 5856), 385 (5856), 385 (17 117), 367 (19 820), 354 (16 667), 326 (76 677), 314 (64 865), 246 (40 991), 228 (27 928).

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.50; H, 5.70.

Methyl 7-(2-Anthryl)hepta-2,4,6-trienoate (7). [6-(Methoxycarbonyl)hexa-2,4-dien-1-yl]triphenylphosphonium bromide[16] (4.53 g, 10 mmol) was dissolved in water (300 mL), made alkaline with aqueous NaOH (10%) solution, and then extracted with benzene (5 × 100 mL). The dried benzene extract was concentrated (ca. 50 mL), and this was treated with aldehyde 1 (1.0 g, 5 mmol) to yield 0.3 g (19.7%) of 7: mp 234.5–236 °C dec (C_6H_6); IR (KBr) ν_{max} 1710, 1625 cm^{-1}; ^1H NMR ($DCCl_3$) δ 3.8 (3 H, s, CH_3), 5.99–6.14 (1 H, d, CH), 7.00–7.12 (1 H, d, CH), 7.44–8.40 [13 H, m, Ar H and $(CH{=}HC)_2$]; UV (anhydrous C_2H_5OH) λ_{max} 415 nm (ϵ 30 496), 410 (35 816), 390 (35 106), 354 (63 830), 340 (32 624), 225 (14 184), 220 (12 766).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.04; H, 5.84.

Ethyl 3-(9-Anthryl)prop-2-enoate (18).[20] Reaction of aldehyde 17 (1.03 g, 5 mmol) with phosphorane 2 (1.74 g, 5 mmol) gave 1.10 g (80%) of 18: mp 79–80 °C (petroleum ether, lit.[20] mp 79–80 °C); IR (KBr) ν_{max} 1694, 1626 cm^{-1}; ^1H NMR ($DCCl_3$) δ 1.38 (3 H, t, CH_3), 4.3 (2 H, q, CH_2), 6.34 (1 H, d, C=CH), 7.3–8.7 (10 H, m, Ar H).

Methyl 5-(9-Anthryl)penta-2,4-dienoate (19).[18] Aldehyde 17 (1.03 g, 5 mmol) condensed with phosphorane 3 (1.79 g, 5 mmol) to produce 1.20 g (83%) of 19: mp 147–148 °C (lit.[18] mp 150 °C); IR (KBr) ν_{max} 1694, 1626 cm^{-1}; ^1H NMR ($DCCl_3$) δ 3.8 (3 H, s, CH_3), 6.02 (1 H, dd, C=CH), 6.70 (1 H, dd, C=CH), 7.34–8.20 (10 H, m, C=CH and Ar H), 8.34 (1 H, s, Ar H).

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.33; H, 5.55. Found: C, 83.47; H, 5.95.

3-(2-Anthryl)prop-2-enoic Acid (8).[28] Hydrolysis of ester 5 (0.550 g, 2 mmol) with 10% alcoholic KOH solution (50 mL) over a 2-h period afforded 0.420 g (85%) of acid 8: mp >310 °C (lit.[28] mp >310 °C); IR (KBr) ν_{max} 1681, 1613 cm^{-1}.

5-(2-Anthryl)penta-2,4-dienoic Acid (9). Hydrolysis of ester 6 (30 mL) over a 2-h period afforded 0.280 g (82%) of acid 9: mp 294–296 °C; IR (KBr) ν_{max} 1667, 1600 cm^{-1}. This highly insoluble material was used in the next step without further purification to give the new acid 11.

3-(9-Anthryl)prop-2-enoic Acid (20).[21] Hydrolysis of ester 18 (0.550 g, 2.5 mmol) with 10% alcoholic KOH solution (20 mL) over a 2-h period gave 0.450 g (90%) of acid 20: mp 244–245 °C (C_2H_5OH, lit.[21] mp 247 °C); IR (KBr) ν_{max} 1695, 1600 cm^{-1}.

5-(9-Anthryl)penta-2,4-dienoic Acid (21). Hydrolysis of ester 19 (0.720 g, 2.5 mmol) with alcoholic KOH solution (50 mL) yielded after 3 h 0.600 g (88%) of acid 21: mp 271–272 °C (C_2H_5OH); IR (KBr) ν_{max} 1667, 1600 cm^{-1}; ^1H NMR ($DCCl_3$–TFA) δ 6.00 (1 H, d, C=CH), 6.72 (1 H, dd, C=CH), 7.20–7.40 (4 H, m, C=CH and Ar H), 7.64–7.70 (1 H, m, Ar H), 7.84–7.88 (1 H, m, Ar H), 7.9–8.14 (2 H, m, Ar H), 8.20–8.35 (2 H, m, Ar H), 8.4 (1 H, s, Ar H).

Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.21; H, 5.10. Found: C, 82.82; H, 5.37.

3-(9,10-Dihydro-2-anthryl)propanoic Acid (10). Hydrogenation (atmospheric pressure) of acid 8 (0.248 g, 1 mmol) in anhydrous C_2H_5OH (20 mL) over 10% Pd/C (30 mg) afforded 0.210 g (84%) of acid 10: mp 141–142 °C (ether–petroleum ether); IR (KBr) ν_{max} 1695, 1587 cm^{-1}; ^1H NMR $DCCl_3$) δ 2.6–2.7 (2 H, m, CH_2), 2.73–3.20 (3 H, m, H_2CCO_2H), 3.8 (4 H, s, CH_2), 7.1–7.4 (7 H, m, Ar H).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.95; H, 6.35. Found: C, 80.79; H, 6.52.

5-(9,10-Dihydro-2-anthryl)penta-2,4-dienoic Acid (11). Hydrogenation (atmospheric pressure) of acid 9 (0.274 g, 1 mmol) over 10% Pd/C (30 mg) in anhydrous C_2H_5OH (30 mL) afforded 0.230 g (83%) of acid 11: mp 120–121 °C (ether–petroleum ether; IR (KBr) ν_{max} 1695, 1587 cm^{-1}; ^1H NMR ($DCCl_3$) δ 1.60–1.90 (4 H, m, CH_2), 2.30–3.00 (4 H, m, CH_2), 2.30–3.00 (4 H, m, CH_2), 3.88 (4 H, s, CH_2), 6.9–7.5 (7 H, m, Ar H).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.43; H, 7.14. Found: C, 81.49; H, 7.15.

Ethyl 3-(2-Anthryl)propanoate (12). Ester 5 (0.3 g, 1.1 mmol) was hydrogenated (atmospheric pressure) over 10% Pd/C (40 mg) in anhydrous C_2H_5OH and the product obtained was boiled with *o*-chloranil (Aldrich, 0.270 g, 1.1 mmol) in benzene (ca. 10 mL) for 3 h under N_2. Workup of the reaction mixture afforded 0.225 g (75%) of ester 12: mp 121–123 °C (C_2H_5OH); IR (KBr) ν_{max} 1725 cm^{-1}; ^1H NMR ($DCCl_3$) δ 1.1–1.3 (3 H, t, CH_3), 4.02–4.22 (2 H, q, O–CH_2), 3.06–3.22 (2 H, t, $C(O)CH_2$), 2.68–2.82 (2 H, t, CH_2CH_2), 7.22–8.30 (9 H, m, Ar H); ^{13}C NMR (see Table I); UV (anhydrous C_2H_5OH) λ_{max} 376 nm (ϵ 5568), 367 (2561) 357 (6570), 347 (3675), 340 (4844), 329 (2895), 324 (3007), 316 (2394), 307 (3452), 255 (248 148), 247 (103 704).

Anal. Calcd for $C_{19}H_{18}O$: C, 81.99; H, 6.52. Found: C, 81.80; H, 6.77.

Methyl 5-(2-Anthryl)pentanoate (13). Ester 6 (0.4 g, 1.4 mmol) was hydrogenated (atmospheric pressure) over 10% Pd/C (60 mg) in anhydrous C_2H_5OH (75 mL), and the product obtained was then boiled with *o*-chloranil (Aldrich, 0.35 g, 1.4 mmol) in benzene (50 mL) for 3 h under N_2. Workup of the reaction mixture afforded 0.182 g (45%) of ester 13: mp 105–106 °C (C_2H_5OH); IR (KBr) ν_{max} 1725 cm^{-1}; ^1H NMR ($DCCl_3$) δ 1.68–1.78 (4 H, m, CH_2CH_2), 2.3–2.46 (2 H, m, Ar CH_2), 2.72–2.88 (2 H, m, $H_3OCO_2CCH_2$), 3.64 (3 H, s, CH_3), 7.32–8.34 (9 H, m, Ar H); ^{13}C NMR (see Table I); UV (anhydrous C_2H_5OH) λ_{max} 377 nm (ϵ 5343), 368 (2306), 357 (6153), 348 (3431), 339 (4499), 325 (2778), 313 (1462), 255 (251 852), 247 (107 407).

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 81.78, H, 7.10.

Methyl 7-(2-Anthryl)heptanoate (14). Ester 7 (0.440 g, 1.4 mmol) was hydrogenated (atmospheric pressure) over 10% Pd/C (60 mg) in anhydrous C_2H_5OH and the product obtained was boiled with *o*-chloranil (Aldrich, 0.350 g, 1.4 mmol) in benzene (15 mL) for 3 h under N_2. Workup of the reaction mixture afforded 0.240 g (54%) of ester 14: mp 93–95 °C (C_2H_5OH); IR (KBr) ν_{max} 1725 cm^{-1} (C=O); ^1H NMR ($DCCl_3$) δ 3.64 (3 H, s, CH_3), 2.7–2.86 (2 H, t, CH_2), 2.12–2.37 (2 H, t, CH_2), 1.38–1.7 (8 H, m, $(CH_2)_4$, 7.32–8.34 (9 H, m, Ar H); ^{13}C NMR (see Table I); UV (anhydrous C_2H_5OH) λ_{max} 377 nm (ϵ 5031), 368 (2201), 357 (5786), 348 (3459), 339 (4402), 325 (2956), 313 (2201), 255 (265 000), 247 (128 750).

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.57; H, 7.62.

3-(2-Anthryl)propanoic Acid (15). Ester 5 (0.552 g, 2 mmol) in anhydrous C_2H_5OH (50 mL) was hydrogenated over 10% Pd/C (60 mg), and the product obtained was boiled with *o*-chloranil (0.545 g, 1.2 mmol) in C_6H_6 for 3 h under N_2. Hydrolysis of the crude product from the above reaction with 10% alcoholic KOH

(50 mL) afforded 0.400 g (80%) of **15**: mp 249–250 °C (C_2H_5OH); IR (KBr) ν_{max} 1709, 1600 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.68 (2 H, t, CH_2), 3.04 (2 H, t, H_2CCO_2H), 7.34–7.56 (3 H, m, Ar H), 7.86 (1 H, s, Ar H), 7.96–8.12 (3 H, m, Ar H), 8.50 (2 H, d, Ar H); UV (anhydrous C_2H_5OH) λ_{max} 376 nm (ϵ 3800), 357 (4400), 340 (3200), 325 (1900), 255 (200 000), 247 (90 000).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.60; H, 5.60. Found: C, 81.33; H, 5.84.

5-(2-Anthryl)pentanoic Acid (16). Ester **6** (0.548 g, 2 mmol) was hydrogenated over 10% Pd/C in anhydrous C_2H_5OH (50 mL), and the product obtained was boiled with *o*-chloranil (0.590 g, 1.2 mmol) for 3 h under N_2. Hydrolysis of the product from the above reaction with 10 alcoholic KOH solution (20 mL) afforded 0.410 g (71%) of acid **16**: mp 191–192 °C (C_2H_5OH); IR (KBr) ν_{max} 1695, 1575 cm^{-1}; ^1H NMR ($DCCl_3$) δ 1.6 (4 H, m, CH_2) 2.2–2.3 (2 H, m, CH_2), 2.82 (2 H, m, CH_2), 7.3–7.5 (3 H, m, Ar H), 7.72 (1 H, m, Ar H), 7.88 (3 H, m, Ar H), 8.00–8.32 (2 H, m, Ar H); UV (anhydrous C_2H_5OH) λ_{max} 377 nm (ϵ 5400), 358 (6100), 341 (4400), 327 (2500), 291 (700), 254 (237 000), 249 (88 900).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.01; H, 6.44. Found: C, 82.13; H, 6.56.

3-(9-Anthryl)propanoic Acid (22).[20] Hydrogenation of acid **20** (0.496 g, 2 mmol) over 10% Pd/C (50 mg) in anhydrous C_2H_5OH (20 mL) afforded 0.450 g (90%) of acid **22**: mp 188–190 °C (C_2H_5OH–H_2O, lit.[20] mp 191–192 °C); IR (KBr) 1695, 1600 cm^{-1}; ^1H NMR ($DCCl_3$) δ 2.78–2.96 (2 H, br t, CH_2), 3.8–4.0 (2 H, br t, CH_2), 7.40–7.55 (5 H, m, Ar H); 7.9–8.1 (2 H, m, Ar H), 8.2–8.4 (2 H, m, Ar H); UV (anhydrous C_2H_5OH) λ_{max} 386 nm (ϵ 5000), 361 (5180), 347 (380), 332 (1450), 256 (95 700).

5-(9-Anthryl)pentanoic Acid (23). Hydrogenation of acid **21** (0.556 g, 2 mmol) in anhydrous C_2H_5OH (30 mL) over 10% Pd/C (70 mg) afforded 0.440 g (79%) of acid **23**: mp 112–113 °C (ether–petroleum ether); IR (KBr) ν_{max} 1695, 1613 cm^{-1}; ^1H NMR ($DCCl_3$) δ 1.70–1.98 (4 H, d, CH_2), 2.42 (2 H, m, CH_2), 3.58 (2 H, m, CH_2), 7.16 (1 H, s, Ar H), 7.26–7.60 (4 H, m, Ar H), 7.94–8.20 (2 H, m, Ar H), 8.10–8.32 (1 H, m, Ar H), 11.14 (1 H, s, CO_2H); UV (anhydrous C_2H_5OH) λ_{max} 387 nm (ϵ 8830), 382 (4640), 367 (8990), 348 (5420), 331 (2490), 318 (1020), 257 (169 000), 250 (80 900), 236 (21 600), 223 (6700).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.01; H, 6.44. Found: C, 81.87; H, 6.65.

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Desiccant Efficiency in Solvent and Reagent Drying. 5. Amines[1-4]

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The use of amines in synthesis can be divided into three principal areas: (i) as basic agents for the promotion of dehydroeliminations, (ii) as nucleophiles in simple displacements, and (iii) as precursors of various metalated derivatives. Because of strong N–H hydrogen bonding, in all these uses, water present in the amine system may exert damaging, i.e., yield lowering, effects by interfering with absolute basicity and nucleophilicity[6] and/or reacting either as free water or hydroxide ion with unstable intermediates or sensitive products.[7] However, despite the existence of an arsenal of desiccants, the presence of water in these systems continues to be a problem for the synthetic chemist. This is because the recommended agents for removal of water and polar impurities[9] from other solvent and reagent types[1-4] may not be suitable for amines. Therefore the radiotracer method for water assay previously developed by us[10] has now been applied to obtain quantitative data on the drying of some representative amines.

The Pyridine Group. For pyridine, and indeed generally for the amine class, the traditionally recommended siccatives are the alkali and alkali earth hydroxides and oxides.[11] Thus, literature prescriptions commonly advocate distillation from KOH,[12a,b] standing over BaO,[12c] or distillation from CaH_2,[13] the employment of the latter procedure reportedly yielding samples containing 18–20 ppm of residual water. The use of Al_2O_3 has also been occasionally reported.[14] Our results for pyridine obtained by application of the radiotracer technique are summarized in Table I. The results are largely self-explanatory, and as can be seen, a horizontal line drawn under the entry for KOH sharply demarcates *serious desiccants* from those which are less efficaceous. Surprisingly perhaps, alumina is seen to be rather unimpressive; however, this ineffectiveness in the drying of polar reagents has been noted previously.[1,3] It is also worth noting that the use of sodium is to be avoided; it is not particularly efficient and contributes to material loss by a wasteful side reaction which produces bipyridyls.

Alkylated derivatives of pyridine are more basic and often less nucleophilic than pyridine itself, and these attributes are considered advantageous in synthesis. We therefore thought it of interest to compare the difficulty

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(5) Abstracted in part from the Final Year Project of Andrew S. C. Tan, 1978–1979.

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(7) In a pertinent example from our own laboratories, the literature preparation of methyl diphenylphosphinite calls for reaction between chlorodiphenylphosphine and methanol in the presence of pyridine and gives a reported yield of 52%.[8] In our hands, the use of rigorously dried pyridine and methanol increased the yield to 75%.

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