sodium-dried ether (20 mL). The amine (0.0047 mol) was added dropwise, and the mixture was stirred for 6 h at 20 °C. The yellowish product was filtered off and washed with ether to give the product (see Table I).

Thermolysis of Tetrahydrodibenz[*c*,*h*]acridinium Tetrafluoroborate 3. The dried salt **3** (2.5 g, 0.0045 mol) and 2,4,6-triphenylpyridine (1.4 g, 0.0045 mol); dried for 2 h, 1.0 mm, 20 °C) were finely ground and dried at 60 °C (2.5 mm, 30 min). The temperature was then raised to 150–160 °C (2.5 mm, 40 min) and the sample finally heated with a direct flame for 5 min. The distillate collected to give styrene (120 mg, 26%), contaminated with 15% ethyl 2-phenylethyl ether.

General Procedure for the Thermolysis of *N*-Alkyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium Trifluoromethanesulfonates (4). Procedure A. The dried derivative **4** (4 g, 0.0064 mol) and 2,4,6-triphenylpyridine (3 g, 0.0098 mol; dried at 40 °C, 0.5–1.0 mm, 2–3 h) were finely ground. The mixture was dried for a further 30 min (60 °C, 500 mm) in the thermolysis apparatus. The trap was then cooled with liquid nitrogen. The temperature was raised until the mixture melted and continuous bubbling was observed (temperature, pressure, and time are recorded in Table V). When the thermolysis appeared to be complete (30 min after bubbling ceased), the temperature was raised to 200 °C (200 mm) for an additional 20 min.

Procedure B. In a typical experiment **4d** (4 g, 0.0069 mol) and 2,4,6-triphenylpyridine (3 g, 0.0098 mol) were dried and ground together finely. The thermolysis flask was heated at 180-200 °C (760 mm) for 8 h, while the trap, containing bromine (1.2 g, 0.0075 mol) dissolved in chloroform (7 mL), was cooled with a salt-ice bath. The chloroform solution was washed with saturated aqueous sodium thiosulphate (3 × 5 mL) and then with H_2O (3 × 5 mL) and dried over anhydrous magnesium sulphate for 2 h. Chloroform was removed in vacuo and the residue distilled at 5 mm to give the product (see Table 5, 6).

Thermolysis of 14-*n*-Dodecyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium Triflate (4j) in the Absence of 2,4,6-Triphenylpyridine. Salt **4j** (3 g, 0.0044 mol) was thermolyzed at 160 °C (20 mm) for 4 h. The temperature was then raised to 180 °C, (20 mm) 2 h to complete distillation. The product (0.73, 99%) was shown by ^{13}C NMR quantiative and qualitative analysis to be a mixture of 1-, *trans*-2-, *cis*-2-, *trans*-3-, *cis*-3-, *trans*-4-, and *cis*-4-dodecenes in the ratio of 36.9:23.8:20.5:12.3:5.4:2.9 (the percentage of the last isomer being difficult to determine). The thermolysis residue was recrystallized from acetic acid to give **5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium trifluoromethanesulfonate (6)**: 99%; yellow prisms; mp 280–285 °C; IR ($CHBr_3$) 1620 cm^{-1}; ^1H NMR (TFA) δ 3.0 (8 H, m), 7.28–7.90 (11 H, m), 8.02–8.38 (2 H, m); ^{13}C NMR (Me_2SO-d_6/$CDCl_3$) δ 25.1 (t, C_5, C_9), 27.0 (t, C_6, C_8), 126.2 (d, C_4, C_{10}), 126.9 (d, C_3, C_{11}), 127.4 (d, C_2, C_{12}), 127.6 (s, C_{6a}, C_{7a}), 128.0 (d, C_o), 128.7 (d, C_p), 128.9 (d, C_m), 131.6 (d, C_1, C_{13}), 132.7 (s, C_i), 134.9 (s, C_{13a}, C_{14b}), 139.1 (s, C_{4a}, C_{9a}), 146.0 (s, C_{13b}, C_{14a}), 154.4 (s, C_7). Anal. Calcd for $C_{28}H_{17}F_3NO_3S$: C, 66.0; H, 4.4; N, 2.8; S, 6.3. Found: C, 65.7; H, 4.3: N, 2.8; S, 6.3.

Acid-Induced Isomerization of 1-Decene. 1-Decene (1 g, 0.006 mol), salt **6** (3.1 g, 0.006 mol), and 2,4,6-triphenylpyridine (1.8 g, 0.006 mol) were refluxed at 160 °C for 5 h. The product was distilled at diminished pressure to give a mixture of 1-, *trans*-2-, *cis*-2-, *trans*-3-, and *cis*-3-decene in the ratio of 59.7:13.3:8.9:18.1 as shown by ^{13}C NMR qualitative[20] and quantitative[20] analyses.

Acknowledgment. We thank Kuwait Institute for Scientific Research, Kuwait, for leave of absence (to A. M.E.-M).

Registry No. **1**, 53217-56-4; **2**, 73377-38-5; **3**, 82135-18-0; **4a**, 76017-85-1; **4b**, 82135-20-4; **4c**, 76017-66-8; **4d**, 82135-22-6; **4e**, 76017-70-4; **4f**, 82135-24-8; **4g**, 82135-26-0; **4h**, 73377-30-7; **4i**, 73377-32-9; **4j**, 73377-34-1; **5a**, 22415-74-3; **5b**, 22415-73-2; **6**, 82135-27-1; $PhCH_2CH_2NH_2$, 64-04-0; $Me_2CHCH_2NH_2$, 78-81-9; $BuNH_2$, 109-73-9; $Me(CH_2)_5NH_2$, 111-26-2; $H_2N(CH_2)_6NH_2$, 124-09-4; $Me(CH_2)_6NH_2$, 111-68-2; $Me(CH_2)_7NH_2$, 111-86-4; $Me(CH_2)_{10}NH_2$, 7307-55-3; $Me(CH_2)_{11}NH_2$, 124-22-1; 2,4,6-triphenylpyridine, 580-35-8; 1,2-dibromo-2-methylpropane, 594-34-3; 1,2-dibromobutane, 533-98-2; *meso*-2,3-dibromobutane, 5780-13-2; *dl*-2,3-dibromobutane, 598-71-0; 1,2-dibromopentane, 3234-49-9; styrene, 100-42-5; 1-hexene, 592-41-6; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8; 1-heptene, 592-76-7; *cis*-2-heptene, 6443-92-1; *trans*-2-heptene, 14686-13-6; *cis*-3-heptene, 7642-10-6; *trans*-3-heptene, 14686-14-7; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9; 1-undecene, 821-95-4; *cis*-2-undecene, 821-96-5; *trans*-2-undecene, 693-61-8; *cis*-3-undecene, 821-97-6; *trans*-3-undecene, 1002-68-2; 1-dodecene, 112-41-4; *cis*-2-dodecene, 7206-26-0; *trans*-2-dodecene, 7206-13-5; *cis*-3-dodecene, 7239-23-8; *trans*-3-dodecene, 7206-14-6.

Supplementary Material Available: Tables II-IV containing ^1H and ^{13}C NMR and IR spectral data for various acridinium trifluoromethanesulfonates (3 pages). Ordering information is given on any current masthead page.

(38) A. R. Katritzky, A. M. El-Mowafy, L. Marzorati, R. C. Patel, and S. S. Thind, *J. Chem. Res., Synop.*, 310 (1980).

Solvolysis of *N*-*n*-Alkylacridiniums in Phenol and Carboxylic Acids. Primary Carbonium Ions as Possible Intermediates

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N-*n*-Octyl (**1a**) and *N*-*n*-dodecylacridinium (**1b**) ions solvolyze in phenol to give mixtures of the *n*-alkyl phenyl ethers and all the isomeric secondary straight-chain *o*- and *p*-alkylphenols. Solvolyses of **1a** in carboxylic acids give a mixture of 1-, 2-, 3-, and 4-octyl carboxylic esters. Structures are deduced by GC/MS. Mechanisms are discussed.

Pyrolyses of the *N*-*n*-alkylacridiniums **1** (Chart I) give olefins in high yield: the isomer distribution led us to conclude that an E1 mechanism involving a primary carbonium ion was probably operative.[1] We have now studied the solvolysis in phenol solution of two representative examples of **1**, i.e., the *n*-octyl (**1a**) and *n*-dodecyl (**1b**) derivatives, and present further evidence in support of our former conclusions.

Initially we carried out a typical bimolecular substitution reaction. The *N*-*n*-octyl derivative **1a** with 1.2 equiv of sodium phenoxide in ethanol gave the S_N2 nucleophilic substitution product **2** (81%) in >99% purity as shown

(1) A. R. Katritzky and A. M. El-Mowafy, *J. Chem. Soc., Chem. Commun.*, 96 (1981); A. R. Katritzky and A. M. El-Mowafy, preceding paper in this issue.

0022-3263/82/1947-3511$01.25/0

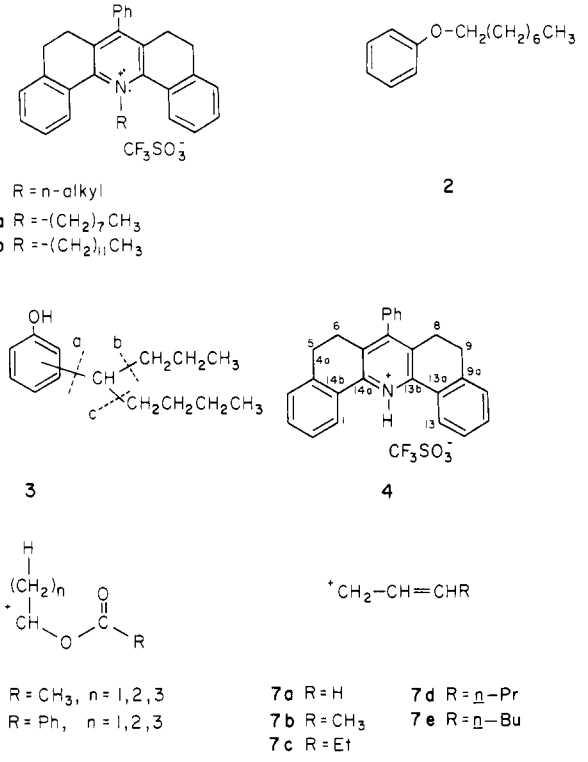
Table I. Structural Data for Components in GLC Peaks of the Octylphenol Solvolysis Mixture from Mass Spectral Peak Intensities (Base = 100)

mass no. of peak	fragment loss[b]	rel intens for GLC peak no. (intens of GLC peak,[a] %)						
		1 (36)	2 (22)	3 (20)	4 (9)	5 (4)	6 (8)	7 (1)
94	C_8H_{16}	100	22	6	5		9	7
107	C_7H_{15}	43	100	87	100	13	100	100
121	C_6H_{13}		6	100	18	100	13	19
135	C_5H_{11}		33		61			
149	C_4H_9	5		11	6			
163	C_3H_7	5		8	5			
177	C_2H_5		13		18			
191	CH_3			5		5		
206		61	17	40	15	12	22	24

component	type	position for GLC peak no.						
		1	2	3	4	5	6	7
major	octyl	1	3	2	3	2	1	1
	ring	ether	ortho	ortho	para	para	ortho	para
minor	octyl	4		4	4			
	ring	ortho		para	para			

[a] Calculated by taking the total yield as 100%. [b] All peaks are shown with the exception of those with m/e's < 50, isotopic peaks, and peaks with an intensity of < 5%.

Chart I



by GLC (OV1, 160 °C). Any octene formed would have been lost during the workup.

The ^{13}C NMR spectrum of **2** was assigned by analogy with those of *n*-octanol,[2] dihexyl ether,[3] and methyl phenyl ether.[3]

Solvolysis of *N*-*n*-Octylacridinium 1a in Phenol. The *N*-*n*-octyl acridinium derivative **1a** in phenol at 160 °C for 84 h gave 92% of what was initially thought to be a mixture of isomeric octyl phenyl ethers. The IR and ^1H NMR spectra of the mixture were not inconsistent with this conclusion; the ^{13}C NMR spectrum was fairly complex, but peaks for 1-octyl phenyl ether were recognized.

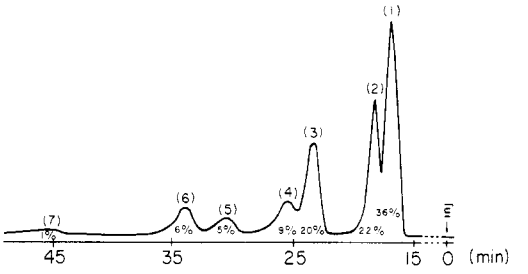


Figure 1. Products from solvolysis of *N*-*n*-octyl derivative **1a** in phenol. Column: 3% OV1 on Chromosorb WHP, temperature 120 °C, helium carrier gas, flow rate 22–23 mL/min.

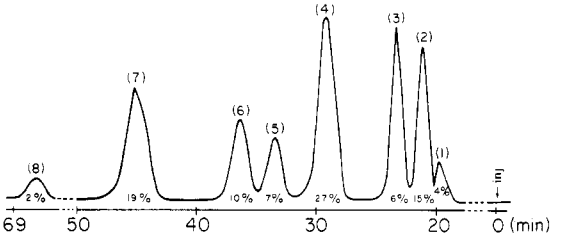


Figure 2. Silylated octyl derivatives: gas chromatographic conditions as above, flow rate 20 mL/min.

GC/MS was more informative: the gas chromatogram (3% OVI/Chromosorb W-HP at 120 °C, helium as the carrier gas (flow rate 20 mL/min) showed seven peaks in the ratio 36:22:20:9:4:8:1 (Figure 1). The mass spectra of each component exhibited molecular ions of m/e 206, consistent with isomeric octyl phenyl ethers. However, C-alkylation could also have taken place in the solvolysis reaction leading to octyl-substituted phenols. Octylphenols are sparingly soluble in water and would not be removed during the basic workup of the reaction mixture.[4] Moreover, the fragment $[C_6H_6O]^+$ ion in the mass spectra of alkyl phenyl ethers is structurally similar to the molecular ion from phenol as demonstrated by ^{13}C labeling studies.[5] Hence, alkyl ethers and the isomeric *C*-alkyl phenols give rise to similar mass spectral fragmentation patterns.

(2) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Am. Chem. Soc.*, **92**, 1338 (1970).
(3) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectroscopy", Wiley-Interscience, New York, 1972, p 447.
(4) This fact is not generally appreciated, despite literature evidence. [G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Am. Chem. Soc.*, **67**, 303 (1945)]; our own sylilation work, vide infra, proves the point.
(5) P. D. Woodgate and C. Djerrasi, *Org. Mass Spectrom.*, **3** (8), 1093 (1970).

Table II. Structural Data for Components in GLC Peaks of the Silylated Octyl Solvolysis Mixture from Mass Spectral Peak Intensities (Base = 100)

mass no. of peak	fragment loss[b]	rel intens for GLC peak no. (intens of GLC peak,[a] %)							
		1 (4)	2 (15)	3 (16)	4 (27)	5 (7)	6 (10)	7 (19)	8 (2)
165	C_8H_{17}	[c]		5	5	[d]		13[e]	
179	C_7H_{15}		100	100	15	88	52	48	100
193	C_6H_{13}				100	5	10	85	
207	C_5H_{11}			72			72		
221	C_4H_9		14			48			
235	C_3H_7		13			36			
249	C_2H_5			22			24		
263	CH_3				5	5	5	5	5
278			10	17	17	14	14	26	31

component	type	position for GLC peak no.							
		1	2	3	4	5	6	7	8
major	octyl ring	1 ether	4 ortho	3 ortho	2 ortho	4 para	3 para	2 para	1 para
minor	octyl ring							1 ortho	

[a] See footnote *a* in Table I. [b] See footnote *b* in Table I. [c] Exhibited the base peaks at *m/e* 94 (100%) and the molecular ion at *m/e* 206 (27%). [d] Base peak at *m/e* 73 (100%). [e] Base peak at *m/e* 73 (100%).

The mixtures were therefore reacted with bis(trimethylsilyl)trifluoroacetamide (BSTFA) to trimethylsilylate any phenolic components. Gas chromatographic/mass spectrometric study of the silyated mixture (Figure 2) revealed eight peaks of which seven corresponded to silylated derivatives of monooctylphenols. The remaining peak was 1-octyl penyl ether.

Structures of the *N*-*n*-Octyl 1a Phenol Solvolysis Products. We believe that the solvolysis mixture consists of *n*-octyl phenyl ether together with the four isomeric *o*-(1-, 2-, 3-, and 4-octyl)phenols and the four isomeric *p*-octylphenols. The seven peaks in Figure 1 are assigned to the nine components in Table I. The eight peaks in Figure 2 are assigned to the ether and the eight silylated octylphenols in Table II.

These assignments are based on the following considerations.

(a) Branched-chain alkyl derivatives undergo preferred cleavage at the branching positions,[6a] e.g. positions a–c in structure **3**. This should give significant fragment ions in the mass spectra of **3** at *m/e*'s corresponding to losses of fragments M – C_8, M – C_3, and M – C_4. Hence, the mass spectrum corresponding to peak no. 1 (Figure 1, Table I) is that of a 3-octyl derivative. Assignment of the other peaks follows similar reasoning.

(b) Para-substituted phenols generally have higher boiling points than their ortho analogues (due mainly to the relative symmetry of para-substituted aryl molecules).[7] The GLC column packing was nonpolar (see Experimental Section for details), and similar structures should run on such a column in order of their boiling points[8] (i.e., the lower boiling ones would be expected to have shorter retention times).

(c) Peak-enhancement experiments (in GLC) of the solvolysis products with pure **2** showed that peak no. 1 in Figure 1 coincided with that of **2**.

(d) Straight-chain alkyl derivatives do not fragment significantly within the straight chain,[6b] and the mass spectrum of authentic **2** showed no significant fragment ions at *m/e* 94–206, in agreement with literature data.[9] Because peak no. 1 of Figure 1 also contains another component, the presence of compound **2** could not be positively identified from the GC/MA spectral fragmentation pattern. However, the intense peak at *m/e* 94 is consistent with no. 1 of Figure 1 containing **2**. Peak no. 1 of Figure 2 had a mass spectrum corresponding to that of the authentic ether; this confirms the above assignment.

(e) Comparisons between Tables I and II.

Structural information for the components in each of the GLC peaks deduced by the above arguments is given in Tables I and II; the whole gives a consistent pattern.

Solvolysis of *N*-*n*-Dodecylacridinium 1b in Phenol. Any olefin formed in the solvolysis of **1a** would have been difficult to detect. Solvolysis of the *N*-*n*-dodecyl derivative **1b** was therefore undertaken. Gas chromatographic/mass spectrometric study of the solvolysis mixture showed 12 peaks. The first three peaks (total yield of 0.3%) were isomeric dodecenes as shown by their mass spectra. The other nine peaks were in the ratio of 16:11:32:4:24:3:5:4:0.5; the total yield was 98%. The ^{13}C NMR spectrum ($CDCl_3$) of the mixture clearly showed 1-dodecyl phenyl ether (signals at 68.0 and 159.1 ppm could be assigned to the α-carbon and the ipso carbon, respectively). Had other isomeric dodecyl phenyl ethers (e.g., 2-, 3-, and 4-dodecyl phenyl ethers) been present, signals for the α-methinic carbons should appear at a lower field (ca. 77 ppm) than that of the α-methylene carbon of 1-dodecyl phenyl ether.[10,11] Also, ^{13}C signals for the ipso carbons of isomeric ethers should appear at 156–160 ppm.[12–14] No such signals were found.

Signals at 153.9, 153.7, and 153.2 ppm in the solvolysis mixture spectrum correspond with ^{13}C chemical shifts of 1-carbons in ortho-substituted phenols.[15,16] The signal at

(6) (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, 1967, pp 51–52; (b) *Ibid.*, pp 50–51.

(7) J. G. Grasselli, Ed., "Atlas of Spectral and Physical Constants for Organic Compounds", Chemical Rubber Publishing Co., Cleveland, OH, 1973.

(8) E. Kováts, "Advances in Chromatography", Vol. 1, J. C. Giddings and R. A. Keller, Eds., Marcel Dekker, New York, 1965, p 229. (However, exceptions to this generalization have been noted; see L. Soják, J. Hrivňák, J. Krupčik, and J. Janák, *Anal. Chem.*, **44**, 1701 (1972).

(9) H. D. R. Schueddemage, F. W. MacLafferty, *Arch. Mass Spectral Data*, 1 (2), 350 (1970).

(10) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, pp 139–144.

(11) C. Konno and H. Hikino, *Tetrahedron*, **32**, 325 (1976).

(12) H.-O. Kalinowski and H. Kessler, *Org. Magn. Reson.* **7**, 128 (1975).

(13) V. M. Bzhezovskii, G. A. Kalabin, B. A. Trofimov, V. A. Pestunovich, I. A. Aliev, G. A. Chmutova, M. A. Shakhgel'diev, and A. I. Kuliev, *Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei, 14th*, 129–130 (1975). *Chem. Abstr.*, **88**, 189471 (1978).

(14) P. H. Mazzocchi, H. L. Ammon, and S. E. Colicelli, *Org. Magn. Reson.*, 11 (3), 143 (1978).

(15) D. A. Netzel, *Org. Magn. Reson.*, 11 (2), 58 (1978).

(16) Y. Nakai and F. Yamada, *Org. Magn. Reson.*, 11 (12), 607 (1978).

Table III. Structural Data for Components in GLC Peaks of the Dodecyl Solvolysis Mixture from Mass Spectral Peak Intensities (Base = 100)

mass no. of peak	fragment loss[b]	rel intens for GLC peak no. (intens of GLC peak,[a] %)								
		1 (16)	2 (11)	3 (32)	4 (4)	5 (24)	6 (3)	7 (5)	8 (4)	9 (0.5)
94	$C_{12}H_{25}$		5	100	11	5	13	13	11	27
107	$C_{11}H_{23}$	100	100	54	100	42	100	36	100	100
121	$C_{10}H_{21}$	7	9		7	100	44	100	17	18
135	C_9H_{19}			28	6		88	7		
149	C_8H_{17}		22			8	5			
163	C_7H_{15}	22			25					
177	C_6H_{13}	17			14					
191	C_5H_{11}	15			13					
205	C_4H_9	17			16					
219	C_3H_7		17			6				
233	C_2H_5			12			31			
247	CH_3					5		5		
262		15	13	46	14	26	20	29	40	18

component	type	position for GLC peak no.								
		1	2	3	4	5	6	7	8	9
major	octyl	5	4	1	5	2	3	2	1	1
	ring	ortho	ortho	ether	para	ortho	para	para	ortho	para
minor	octyl	6		3	6	4				
	ring	ortho		ortho	para	para				

[a] See footnote *a* of Table I. [b] See footnote *b* of Table I.

Table IV. Structural Data for Components in GLC Peaks of the Silylated Dodecyl Solvolysis Mixture from Mass Spectral Peak Intensities (Base = 100)

mass no. of peak	fragment loss[b]	rel intens for GLC peak no. (intens of GLC peak,[a] %)								
		1 (13)	2 (7)	3 (28)	4 (24)	5 (6)	6 (7)	7 (8)	8 (6)	9 (1)
165	$C_{12}H_{25}$	5	6	*c*					21	6
179	$C_{11}H_{23}$	100	100	58	37	100	60	9	100	100
193	$C_{10}H_{21}$				100	32	12	100	15	8
207	C_9H_{19}			54		6	100			
221	C_8H_{17}		24			84				
235	C_7H_{15}	19			8					
249	C_6H_{13}	7			7					
263	C_5H_{11}	6			5					
277	C_4H_9	14			5					
291	C_3H_7		14			33				
305	C_2H_5			11			24			
319	CH_3				5	5	5	5		
334		11	12	10	20	21	16	9	54	28

component	type	position for GLC peak no.								
		1	2	3	4	5	6	7	8	9
major	octyl	5	4	3	2	4	3	2	1	1
	ring	ortho	ortho	ortho	ortho	para	para	para	ortho	para
minor	octyl	6		1	5 + 6	2				
	ring	ortho		ether[d]	para + para	ortho				

[a] See footnote *a* of Table I. [b] See footnote *b* of Table I. [c] Exhibited the base peak at *m/e* 94 (100%). [d] Exhibited the molecular ion peak at *m/e* 262 (26%).

66.1 ppm (as well as that at 68.0 ppm) in the proton-decoupled ^{13}C NMR spectrum occurred as a triplet in the off-resonance decoupled spectra spectrum, indicating a methylenic carbon and not methinic carbon.

The GC/MS data form the solvolysis mixture before and after silylation are shown in Tables III and IV, respectively. The structure of the components in the various peaks were assigned by the same criteria as used for the octyl derivative. The pattern found is in complete agreement with that for the octyl derivatives.

Solvolyses in Carboxylic Acids. We have also investigated solvolysis in poorly nucleophilic carboxylic acid solvents. The acridinium **1a** in acetic acid at 150 °C for 48 h gave a mixture of octyl acetates. The ^{13}C NMR spectrum of the mixture showed clearly the 1-octyl acetate as the major component. The GC/MS study revealed the presence of four components in the ratio of 87.1:6.2:3.9:2.8. In none of the corresponding mass spectra was the expected molecular ion at *m/e* 172 obwerved, in accordance with literature mass spectral data[17] of *n*- and *sec*-octyl acetates. The major fragmentation pathway gives a cation of type **5**, and this is reflected in the mass spectra by peaks at *m/e* 73, 87, 101, and 115 for structures **5** where $n = 0$–3, respectively. In the mass spectrum of the major GC fraction (no. 4 of Table V) we find an intense peak at *m/e* 73, with no signal at *m/e* 87, 101, and 115, proving that peak no. 4 corresponds to 1-octyl acetate. Similarly, peak no. 1 shows an *m/e* peak at 115 and no signal at *m/e* 73, 87, and 101, proving it to be 4-octyl acetate. Peaks no. 2 and 3 are similarly identified as 3- and 2-octyl acetate, respectively. The mass spectrum of GC fragment no. 4 is identical with the literature[17] mass spectrum of 1-octyl acetate.

(17) S. R. Heller and G. W. Milane Eds., "EPA Mass Spectral Data Base", National Bureau of Standards, Washington, DC, 1978.

Table V. Structural Data for Components in GLC Peaks[a] of the Octyl Acetate Solvolysis Mixture from Mass Spectral Peak Intensities (Base = 100)

m/e of peak[b]	corresponding fragment	fragment lost	rel intens for GLC peak no. (reaction time, s; intens of GLC peak, %; octyl position)			
			1 (376; 2.8; 4)	2 (410; 3.9; 3)	3 (464; 6.2; 2)	4 (836; 87.1; 1)
41	**7a**	CH_3CO_2H (C_5H_{11})	15.1	14.5	16.1	22.8
43	CH_3CO	$C_5H_{17}O$	100	100	100	100
45	C_3H_8	$C_7H_{11}O_2$	1.7	2	2.9	1
53	C_4H_5	$C_6H_{15}O_2$		1.1	1.1	1.2
55	**7b**	CH_3CO_2H (C_4H_9)	12.4	12.6	15.8	24.5
57	C_4H_9	$C_6H_{11}O_2^+$	4.6	5.7	6.6	10.0
59	CH_3CO_2	C_8H_{17}		2.1	2.1	
61	$CH_3(OH)C{=}OH^+$	C_8H_{15}		1.5	2.8	18.6
69	**7c**	CH_3CO_2H (C_3H_7)	6.0	4.8	6.2	17.4
71	C_5H_{11}	$C_5H_9O_2$	2.6	2.1	3.6	4.6
73	**5** ($n = 0$)	(C_7H_{15})		1.1		5.0
83	**7d**	CH_3CO_2H (C_2H_5)	3.1	5.5	4.9	12.7
87	**5** ($n = 1$)	(C_6H_{13})	1.1		20.1	
97	**7e**	CH_3CO_2H, CH_3			1.5	1.3
101	**5** ($n = 2$)	C_5H_{11}		9.0		
112	C_8 alkene	CH_3COOH	3.4	3.8	4.9	3.7
115	**5** ($n = 3$)	C_4H_9	5.9			
129	$C_7H_{13}O_2$	C_3H_7	4.1			PTO
143	$C_8H_{15}O_2$	C_2H_5		1.6		

[a] GLC conditions: 5 ft × 0.25 in., 10% DEGS-PS column, 90 °C, flow rate 30 mL/min, helium carier gas. [b] Excluding peaks with $m/e < 41$, peaks with an intensity of <1%, and isotopic peaks.

Table VI. Structural Data for Components in GLC[a] Peaks of the Octyl Benzoate Solvolysis Mixture from Mass Spectral[b] Peak Intensities (Base = 100)

m/e of peak	corresponding fragment	fragment loss	rel intens for GLC peak no. (intens of GLC peak, %)			
			1 (2.8)	2 (3.9)	3 (6.2)	4 (87.1)
41	**7a**	$C_{11}H_{18}O_2$	15	13.9	17.8	24.2
43	C_3H_7	$C_{12}H_{15}O_2$	7.1	7.3	15.7	20.3
51	C_4H_5	$C_{11}H_{17}O_2$	6.3	6.6	8.1	12.3
53	C_4H_7	$C_{11}H_{15}O_2$	1.6	1.6	1.8	1.8
55	**7b**	$C_{11}H_{15}O_2$	11.0	10.8	15.9	20.3
57	C_4H_9	$C_{11}H_{13}O_2$	5.5	5.6	9.2	8.4
67	C_5H_7	$C_{10}H_{15}O_2$			1.0	1.9
69	**7c**	$C_{10}H_{13}O_2$	5.6	5.4	8.1	14.9
70			11.7	12.3	19.2	25.4
71	C_5H_{11}	$C_{10}H_{11}O_2$	2.0	2.3		3.4
77	C_6H_5	$C_9H_{17}O_2$	25.1	24.1	28.3	44.7
79				1.0	1.6	5.4
83	**7d**	$C_9H_{11}O_2$	6.5	6.0	9.5	13.1
97	**7e**	$C_8H_9O_2$			1.0	1.3
105	C_6H_5CO	$C_8H_{17}O$	100	100	100	99.9
112	C_8 alkene	$C_6H_5CO_2H$	14.3	13.7	19.3	11.2
123	$C_7H_7O_2$	C_8H_{15}	14.6	1.9	27.4	100.0
129	$C_8H_{17}O$	C_6H_5CO	1.7	1.6	2.2	
149	**6** ($n = 1$)	C_6H_{13}			1.5	
163	**6** ($n = 2$)	C_5H_{11}		0.5		
177	**6** ($n = 3$)	C_4H_9	0.4			
234	M^+					0.4

[a] GLC conditions: 5 ft × 0.25 in. 10% DEGS-PS column, 150 °C, flow rate 30 mL/min, helium carier gas. [b] Excluding peaks with $m/e < 41$, peaks with an intensity of <1% (unless of particular significance), and isotopic peaks.

Solvolysis of **1a** in molten benzoic acid at 150 °C for 48 h gave a similar mixture comprising four components in the ratio of 87.5:5.6:3.9:3. Only in the mass spectrum of the major component was the molecular ion at m/e 234 observed. In each of the three mass spectra of the remaining components a peak at m/e 149, 163, or 177 was observed, demonstrating the presence of structures **6** and thus of 2-, 3-, and 4-octyl benzoates (see Table VI).

Discussion

The rearrangement of alkyl aryl ethers to substituted phenols is well-known[18] but requires drastic conditions, e.g., $AlCl_3$ or BF_3 at 100 °C. Alkyl phenyl ether rearrangement is intramolecular with $AlBr_3$ as the catalyst and chlorobenzene as the solvent,[19] while it is intermolecular with $AlCl_3$[20] or BF_3.[21] 2-, 3-, and 4-octyl phenyl ethers rearrange, while 1-octyl phenyl ether did not rearrange even with BF_3 at 150 °C for 3 h.[21]

In our solvolysis reactions, such rearrangement at 160 °C could be catalyzed by the salt **4** of the leaving group and triflic acid; cf. the use of pyridine hydrochloride in the

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cleavage of ethers.[22] The fact that we obtain the 1-octyl and 1-dodecyl phenyl ethers as products, but none of the isomeric secondary alkyl phenyl ethers, is indirect confirmation of the relative stability of the former compounds.

We heated synthetic 2-octyl phenyl ether with the acridinium triflate 4 and obtained a mixture of *o*- and *p*-monooctylphenols, containing also 38% of dioctylphenols. The formation of the dioctylphenols was supressed when we heated 2-octyl phenyl ether with 4 in phenol as the solvent. The mixture of monooctylphenols obtained consisted of *o*-(4-octyl)-, *o*-(3-octyl)-, *o*-(2-octyl)-, *p*-(4-octyl)-, *p*-(3-octyl)-, and *p*-(2-octyl)phenols in the ratio of 15.2:19.9:37.7:5.2:9.2:12.8. This confirmed the action of 4 as the catalyst in the octyl phenyl ether rearrangements. It is unlikely that 1-octene could be formed and undergo an isomerization reaction to give 2-octene, etc., as the volatile olefins would have distilled out of the reaction mixture at 160 °C.

In the solvolysis products (Tables I and III) the 1-octyl and 1-dodecyl phenyl ethers could have arisen from either S_N1 or S_N2 pathways. However, the C-alkylated products probably arose via secondary octyl and dodecyl ethers and not via the corresponding primary ethers since phenyl 1-octyl ether does not rearrange.[21] These secondary alkyl phenyl ethers can only have arisen from a carbonium ion intermediate. The higher proportions of ortho-substituted phenols as shown in the ^{13}C NMR give some indication that the rearrangement was mainly intramolecular.[23] We have interpretated the formation of the C-alkylated phenols as arising via *sec*-alkyl phenyl ethers, but should the *C*-alkyl phenols be primary products, this does not invalidate the argument in favor of carbonium ion intermediates.

These results provide indirect evidence for the involvement of unimolecular processes in the solvolysis reactions and probably also for the previously discussed[1] eliminations in the pentacyclic system 1. Further evidence has been provided from the solvolyses in acetic acid and benzoic acid which led to an almost identical ratio of the 1-, 2-, 3-, and 4-octyl esters. The latter results seem to indicate the formation of a primary carbonium which undergoes partial rearrangement to secondary carbonium ions before being trapped by the solvent molecules in such solvolysis reactions. The present work indicates the need for further studies to determine the significance of primary carbonium ion intermediates.

Experimental Section

IR spectra were measured for $CHBr_3$ mulls with a Perkin-Elmer 257 instrument. ^1H NMR and ^{13}C NMR spectra were recorded with Perkin-Elmer R12 (60 MHz) and JEOL FX100 spectrometers, respectively (Me_4Si as an internal standard). Gas–liquid chromatograms utilized a Perkin-Elmer Model F11 flame-ionization chromatograph with an OV1 column and nitrogen as the carrier gas.

Gas chromatographic mass spectra were recorded by using a Kratos MS-25 mass spectrometer interfaced to a Perkin-Elmer Sigma 3 gas chromatograph or, alternatively, on an AEI MS-30 mass spectrometer (utilizing a Kratos DS-55 data system) interfaced to a Pye 104 gas chromatograph. The column packings employed were 3% OV1 on 100–120-mesh Chromosorb W-HP, 10% DEGS-PS on 80–100-mesh Supelcoport, 3% SP-2100 on 100–120-mesh Supelcoport, or 3% SP-2250 on 100–120-mesh Supelcoport (2 m, × 0.25 in. glass columns; helium as the carrier gas at flow rates and temperatures as specified).

Nucleophilic Displacement Reaction of the *N*-*n*-Octyl Derivative 1a with Sodium Phenoxide. Dry phenol (380 mg, 0.004 mol) was added to an ethanolic sodium ethoxide (93 mg, 0.004 mol, of sodium in 25 mL of magnesium-dried ethanol), and the solution was stirred at 20 °C for 15 min. To this was added the *N*-*n*-octyl derivative **1a**[1] (2.5 g, 0.004 mol), and the mixture was refluxed for 4 h. The addition of H_2O (1 mL) and stirring at 20 °C for 6 h gave a precipitate which was filtered, and the solvent was removed in vacuo. Ether (50 mL) was added to the residue, and the etherial layer was decanted and washed with H_2O (2 × 10 mL), with NaOH solution (10%, 10 mL), and with H_2O (2 × 10 mL). The ether was evaporated in vacuo to the residue, dissolved in EtOH (15 mL), was added perchloric acid (70%, 0.9 mL), and the mixture was refluxed for 1 h. The solution was concentrated on a water bath, and the residue was triturated with ether (40 mL) and filtered. The dried ($MgSO_4$) filterate was chromatographed on a silica gel column (60–120 mesh) with ethyl acetate/petroleum ether (bp 40–60 °C) (60:40) as the eluent. The solvent was removed in vacuo to give 1-octyl phenyl ether (660 mg, 81%). The product was further purified by distillation; bp 115–120 °C (1.0 mm) [lit.[24] bp 140–142 °C (10 mm)]. The product was shown by gas chromatography (OV1, 160 °C, t_R = 642 s, nitrogen as the carrier gas, flow rate 18 mL/min; 3% OV1 on Chromosorb W-HP, 120 °C, t_R = 1560 s, helium as the carrier gas, flow rate 20 mL/min) to be >99% pure; ^{13}C NMR ($CDCl_3$) δ 14.1 (q, C_8), 22.7 (t, C_7), 26.1 (t, C_3), 29.4 (t, C_2, C_4, C_5), 31.9 (t, C_6), 67.6 (t, C_1), 114.4 (d, C_o), 120.3 (d, C_p), 129.3 (d, C_m), 159.1 (s, C_i).

Solvolysis of *N*-*n*-Octyl Derivative 1a in Phenol. Compound **1a** (2.4 g, 0.0039 mol) was heated in dried phenol (10 g) at 160 °C for 84 h. Ether trituration (100 mL) of the reaction mixture afforded the acridinium triflate 4 (1.98, 97%) which crystallized from acetic acid as yellow prisms, mp 280–285 °C.[1]

The ether layer was extracted with sodium hydroxide solution (20%, 6 × 15 mL), washed with H_2O (3 × 20 mL), dried ($MgSO_4$, 2 h), and filtered off. The ether was removed in vacuo and the residue distilled under reduced pressure. The fractions boiling at 189–200 °C (0.5 mm) were collected (750 mg, 94%; see Figure 1 for GC/MS study).

The mixture was silylated as follows: BSTFA (0.2 mL) was added to 50 mg of the mixture in dry dichloromethane (2 mL), and the solution was stirred at 20 °C for 1 h (see Figure 2 for GC/MS study).

Similarly *N*-*n*-dodecyl derivative **1b** was heated at 150 °C for 80 h, and the reaction mixture was worked up to give the products (98%; GC conditions as in Figure 1).

The mixture was silylated as described above for the octyl derivatives (GC conditions as in Figure 2).

Solvolysis of *N*-*n*-Octyl Derivative 1a in Acetic Acid. Salt **1a** (3 g, 0.004 83 mol) was heated with acetic acid (6 mL) in a sealed tube at 150 °C for 48 h. Ether (100 mL) was added and the precipitate filtered off. Solvents in the filtrate were removed in vacuo, and the residue was distilled at diminished pressure. The fractions boiling at 50–55 °C (0.5 mm) were collected to give the product (700 mg, 84%). The ^{13}C NMR spectrum ($CDCl_3$) of the mixture showed the following resonances for the major component, 1-octyl acetate: δ 14.0 (C_8), 20.8 ($OCOCH_3$), 22.7 (C_7), 26.0 (C_3), 28.7 (C_2), 29.3 (C_4, C_5), 31.8 (C_6), 64.6 (C_1), 170.9 ($OCOCH_3$). See Table V for the GC/MS study.

Solvolysis of *N*-*n*-Octyl Derivative 1a in Benzoic Acid. Salt **1a** (3 g, 0.004 83 mol) was heated under reflux with benzoic acid (5 g, excess) at 150 °C for 48 h. The mixture was then dissolved in ether (100 mL) and extracted with sodium hydroxide solution (10%, 3 × 15 mL) and then with H_2O (2 × 10 mL). The ether layer was dried ($MgSO_4$) and the solvent removed in vacuo. The residue was distilled under diminished pressure. The fraction boiling at 90–105 °C (0.7 mm) was collected to give the product (860 mg, 90%). The ^{13}C NMR spectrum ($CDCl_3$) of the mixture displayed the following resonances of the major component, 1-octyl benzoate: δ 14.1 (C_8), 22.7 (C_7), 26.1 (C_3), 28.8 (C_2), 29.3 (C_4, C_5), 31.8 (C_6), 65.0 (C_1), 128.2 (C_o), 129.5 (C_m), 130.6 (C_i), 132.7 (C_p), 166.4 OCOPh). See Table V for the GC/MS study.

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2-Octyl Phenyl Ether. 2-Bromooctane (3.0 g, 0.015 54 mol) was added to ethanolic sodium ethoxide (360 mg, 0.01554 mol, of sodium in 100 mL of magnesium-dried ethanol), and the solution was refluxed for 6 h. Ethanol was removed in vacuo, and ether (50 mL) was added. The ether layer was filtered and washed with H_2O (10 mL), sodium hydroxide solution (5%, 2 × 10 mL), and then H_2O (2 × 10 mL). The ether layer was dried ($MgSO_4$, 2 h), the ether removed in vacuo, and the residue distilled to give 2-octyl phenyl ether: 1.73 g (54%); bp 90–94 °C (0.2 mm) [lit.[24] yield 35–38%; bp 136 °C (10 mm)]; ^{13}C NMR ($CDCl_3$) δ 14.1 (q, C_8), 19.8 (q, C_1), 22.7 (t, C_7), 25.6 (t, C_4), 29.4 (t, C_5), 31.9 (t, C_6), 36.6 (t, C_3), 73.7 (d, C_2), 115.9 (d, C_o), 120.4 (d, C_p), 129.4 (d, C_m), 158.3 (s, C_i).

Rearrangement of 2-Octyl Phenyl Ether. The title compound (1.0 g, 0.004 85 mol) was heated with acridinium trifluoromethanesulfonate 4 (2.4 g, 0.004 85 mol) in phenol (5 g, excess) at 160 °C for 48 h. The mixture was triturated with ether (100 mL) and filtered. The ether layer was washed with NaOH solution (10%, 3 × 20 mL) and H_2O (2 × 15 mL) and dried ($MgSO_4$, 2 h). The ether was removed and the residue distilled at diminished pressure to give a mixture (860 mg, 86%) of *o*-(4-octyl)-, *o*-(3-octyl)-, *o*-(2-octyl)-, *p*-(4-octyl)-, *p*-(3-octyl)-, and *p*-2-octyl)phenols in the ratio of 15.2:19.9:37.7:5.2:9.2:12.8 as shown by GC/MS (gas chromatographic conditions: 10% DEGS-PS column, 190 °C isothermal, flow rate 30 mL/min; retention times 910, 952, 1144, 1378, 1433, and 1336 s, respectively). The corresponding mass spectra were identical with those from the solvolysis of *N*-*n*-octyl derivative **1a** in phenol.

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Registry No. 1a, 73377-30-7; **1b**, 73377-34-1; **4**, 81898-31-9; phenol, 108-95-2; acetic acid, 64-19-7; benzoic acid, 65-85-0; 2-bromooctane, 557-35-7; 2-octyl phenyl ether, 20012-43-5.

Reaction of Hemiacetal Esters, Acetals, and Acylals with Alcohols or Acetic Acid

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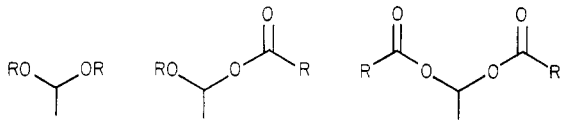
Hemiacetal esters undergo rapid exchange with alcohols at room temperature to give mixtures of hemiacetal ester and acetal. The equilibration requires acid catalysis, and equilibrium lies far in favor of the acetal (>95%). Acetals undergo exchange with carboxylic acids to give the same equilibrium mixtures as that achieved by using the corresponding hemiacetal ester and alcohol. The use of a large excess of carboxylic acid can convert acetals to hemiacetal esters. Under more vigorous conditions, both acetals and hemiacetal esters react with acetic acid to form acetates. The reaction of hemiacetal esters or acetals with anhydrous hydrogen chloride yields α-chloro ethers. The thermolysis of hemiacetal esters is also examined. Acylals do not undergo substitution as observed for acetals and hemiacetal esters. The reaction of acylals with alcohols results in ester formation with no exchange. Under acid conditions, hemiacetal esters are more reactive than either acetals or acylals.

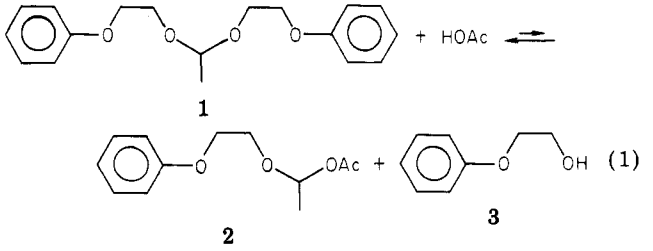
The preparation and reactions of acetals (I) have received considerable attention, in part due to the utility of acetals as aldehyde protecting groups.[1] However, aside from the reactions of the cyclic hemiacetal ester derivatives of carbohydrates,[2,3] the chemistry of compounds structurally related to acetals, hemiacetal esters (II),[4,5] and acylals (III)[6] has received less attention. We have examined the relationship between structure and reactivity for acetals, hemiacetal esters, and acylals. Results indicate substantial differences in reactivity caused by the replacement of an alkoxy group by an ester group. This investigation focuses on the acid-catalyzed reactions of acetals, hemiacetal esters, and acylals with alcohols or acetic acid. The mechanism of the thermolysis of hemiacetal esters has also been examined.



I II III

Results and Discussion

Reactions of Acetals. The reaction of acetal 1 with acetic acid at room temperature is slow. With equivalent amounts of acetic acid and acetal, only a very small amount of hemiacetal ester 2 is observed (eq 1). The equilibrium



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