bath shaker at 25 °C operating at 240 rpm. About 0.01-g resin samples were withdrawn periodically, washed with dioxane and ether, and examined by IR spectroscopy (4% KBr pellets) as well as for chlorine content by microanalysis.

Studies on the Decomposition of 5A*. Resin **5A*** was washed completely with dioxane until no radioactivity was detected in the washings. Dry samples of the resin (0.25 g) were subjected to the treatments shown in Table I using 50 mL of dioxane where appropriate. Aliquots of the solution (0.1 mL) were examined periodically for carbon-14 activity. The resins were isolated by filtration, washed, and resuspended in 50 mL of dioxane. A solution of 1 mmol of *n*-propylamine in 10 mL of dioxane was added and the mixtures were shaken at 25 °C for 4 h. The resins were isolated by filtration and analyzed by IR spectroscopy and nitrogen content. Radioactivity in solution was also measured. The amine treatment was repeated at 100 °C for 4 h and the solutions as well as the resins were analyzed in a similar manner.

Reactions of 5A* and *n*-Propylamine in Dioxane–Water. A 0.25-g sample of **5A*** was placed in each flask containing 50 mL of five combinations of dioxane–water (100:0; 75:25; 50:50; 25:75; 0:100). The flasks were shaken at 37 °C for 1 h and 2 mL of 0.2 M *n*-propylamine in dioxane was added. Aliquots of the solution (0.1 mL) were analyzed periodically for carbon-14 activity.

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Registry No.—1, 1592-20-7; 2, 67738-96-9; 3, 56552-12-6; 4, 67738-98-1; **5A**, 67739-00-8; **5A***, 67739-02-0; **5B**, 67739-04-2; **5D**, 67739-06-4; **7**, 67739-08-6; **8**, 67739-10-0; potassium benzoate, 582-25-2; phosgene, 75-44-5; *n*-propylamine, 107-10-8; benzoic acid, 65-85-0; phenylacetic acid, 103-82-2; acetylsalicylic acid, 50-782; [7-^{14}C]benzoic acid, 1589-66-8; benzyl alcohol, 100-51-6.

References and Notes

(1) Author to whom correspondence should be addressed.
(2) (a) J. R. Vaughan, *J. Am. Chem. Soc.*, **74**, 6137 (1952); (b) T. A. Boissonnas, *Helv. Chim. Acta*, **34**, 874 (1951); (c) T. Wieland and H. Bernhard, *Justus Liebigs Ann. Chem.*, **572**, 190 (1951).
(3) Y. G. Perron, W. F. Minor, C. T. Holdrege, W. J. Gottstein, J. C. Godfrey, L. B. Crast, R. B. Babel, and L. C. Cheney, *ibid.*, **82**, 3934 (1960).
(4) D. S. Tarbell, *Acc. Chem. Res.*, **2**, 296 (1969).
(5) D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959), *ibid.*, **26**, 2161 (1961).
(6) M. B. Shambhu and G. A. Digenis, *J. Chem. Soc. Chem. Commun.*, 619 (1974).
(7) G. E. Martin, M. B. Shambhu, and G. A. Digenis, *J. Pharm. Sci.*, **67**, 110 (1978).
(8) J. I. Crowley and H. Rapoport, *Acc. Chem. Res.*, **9**, 135 (1976).
(9) (a) R. L. Letsinger, M. J. Kornet, V. Mahadevan, and D. M. Jerina, *J. Am. Chem. Soc.*, **86**, 5163 (1964); (b) R. L. Letsinger and M. J. Kornet, *ibid.*, **85** 3045 (1963); (c) A. M. Felix and R. B. Merrifield, *ibid.*, **92**, 1385 (1970).
(10) M. A. Kraus and A. Patchornik, *Isr. J. Chem.*, **9**, 269 (1971).
(11) R. B. Merrifield, *Adv. Enzymol.*, **32**, 221 (1969).
(12) J. I. Crowley, T. B. Harvey III, and H. Rapoport, *J. Macromol. Sci. Chem.*, **7**, 1118 (1973).
(13) L. T. Scott, J. Rebek, L. Ovsyanko, and C. L. Sims, *J. Am. Chem. Soc.*, **99**, 625 (1977).
(14) P. Jayalekshym and S. Mazur, *J. Am. Chem. Soc.*, **98**, 6710 (1976).
(15) S. L. Regen, *J. Am. Chem. Soc.*, **96**, 5275 (1974).
(16) J. Altman, E. Kavoly, and N. Maoz, *J. Med. Chem.*, **18**, 627 (1975).
(17) M. B. Shambhu, M. C. Theodorakis, and G. A. Digenis, *J. Polym. Sci.*, **15**, 525 (1977).

Synthesis of Phenyl Enol Ethers via Decarboxylation of β-Lactones Derived from the Lithium α-Phenoxy-α-lithioacetate Synthon

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The lithium α-phenoxy-α-lithioacetate reagent was prepared from α-phenoxyacetic acid by direct α-lithiation with lithium diisopropylamide (LDA) at −78 °C in THF. Condensation of this versatile enolate carboxylate with aldehyde or ketone electrophiles afforded the corresponding β-hydroxy acids in high yield (~80%). β-Lactonization of these β-hydroxy acids with benzenesulfonyl chloride and subsequent decarboxylation led to the desired phenyl enol ethers. This convenient synthetic sequence was shown to be general for alkyl- and aryl-substituted derivatives of phenyl enol ethers.

The synthesis of enol ethers **1**, especially aryl enol ethers, is still a cumbersome task. Thus, while silyl enol ethers are readily accessible by silylation of enolates with silyl chlorides,[3] reaction with alkyl halides gives mixtures of carbon and oxygen alkylated products which are difficult to separate. Direct arylation of enolates is not feasible.

Among the more successful methods figures the Wittig reaction (eq 1).[4] An alkoxymethylenephosphorane serves as synthon.

$$\mathrm{ROCH{=}PPh_3} + \mathrm{O{=}CR^1R^2} \longrightarrow \underset{\mathbf{1}}{\mathrm{ROCH{=}CR^1R^2}} + \mathrm{Ph_3P{=}O} \quad (1)$$

The shortcomings of this synthetic approach are the carcinogenicity[5] of the halomethyl ethers which serve as the starting materials for the Wittig reagent, the strongly basic conditions, and the lack of stereospecificity.

Previously[6] we demonstrated that β-lactones serve as convenient and efficient synthons for the stereospecific introduction of double bonds by thermal decarboxylation. This synthetic strategy could be adapted into a useful synthesis of

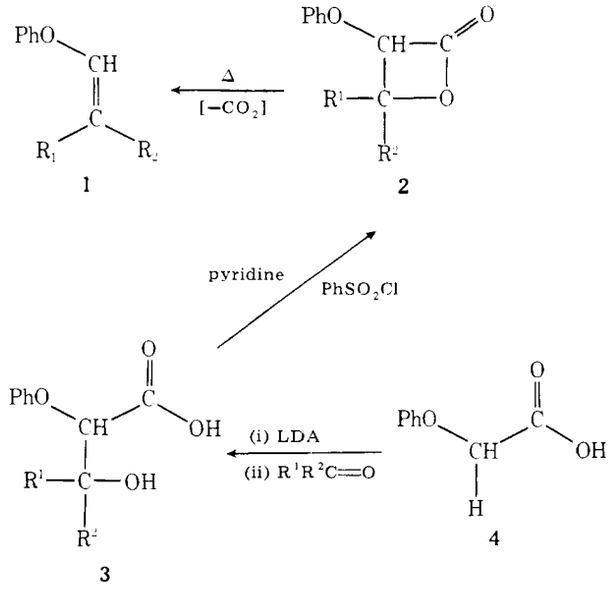

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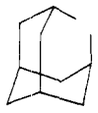
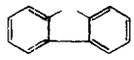
Table I. Yields, Physical Constants, and Spectra Data of β-Hydroxy-α-phenoxycarboxylic Acids 3

	registry no.	R^1	R^2	yield, %	physical constants	^{1}H NMR type	δ, ppm	no. of H's	multiplicity (J in Hz)	IR $\nu_{C=O}$ cm^{-1}
3a	64682-85-5	CH_3	CH_3	82	mp 62 °C (benzene–hexane)[a,b]	$R^1 + R^2$	1.45	6	s	1740
						>C**H**CO_2H	4.45	1	s	
						O–H	4.40	4	s	
						C_6H_5	6.7–7.4	5	m	
3b	67774-12-3	$+CH_2+_4$		80	mp 80–83 °C (benzene–hexane)[a,b]	$R^1 + R^2$	1.7–2.2	8	m	1730
						>C**H**CO_2H	4.55	1	s	
						O–H	3.8	4	s	
						C_6H_5	6.8–7.5	5	m	
3c	67774-13-4			79	mp 80 °C dec (benzene–hexane)[a,b]	$R^1 + R^2$	1.3–2.5	14	m	1725
						>C**H**CO_2H	5.10	1	s	
						O–H	5.05	4	s	
						C_6H_5	6.7–7.5	5	m	
3d	64682-84-4	Ph	H	50	mp 116–117 °C (hexane–benzene) [lit.[c] mp 93–94 °C]	R^2	5.20	1	d (6)	1720
						>C**H**CO_2H	4.80	1	d (6)	
						O–H	5.8	2	s	
						C_6H_5	6.6–7.6	10	m	
3e	67774-14-5	Ph	Ph	75	mp 168 °C (benzene)[a]	>C**H**CO_2H	5.55	1	s	1715
						OH	d	15	m	
						C_6H_5	6.7–7.8			
3f	67774-15-6			40	168 °C dec (benzene)[a]	>C**H**CO_2H	5.13	1	s	1730
						OH	5.9	2	s	
						aromatic	6.7–7.9	13	m	

[a] Satisfactory elemental analysis; mass spectrum shows M − H_2O peak. [b] Crystallizes with one molecule of water. [c] Reference 8. [d] Not observed.

methyl enol ethers.[7] Furthermore, recently we showed that α-phenoxy enolate carboxylates can be generated in high yield by α-lithiation of phenoxyacetic acid (4) with *n*-BuLi or LDA.[8] These versatile synthons undergo efficient electrophilic substitution with aldehydes and ketones to afford the β-hydroxy acids **3** which are required for the β-lactones **2**. The latter lead to the desired enol ethers **1** on thermal decarboxylation. Presently we report our results on the synthetic sequence outlined in eq 2 for phenyl enol ethers **1**. In fact, the β-hydroxy acids **3** can be dehydrocarbonated (loss of H_2CO_3) directly without the need of isolating the β-lactones **2**. Consequently, this method offers a useful and convenient alternative to the Wittig route (eq 1) to aryl enol ethers **1**.

Results and Discussion

β-Hydroxy Acids 3. The α-phenoxyacetic acid (**4**) was converted to the required β-hydroxy acids **3** (Table I) via its enolate carboxylate **5** by condensation with the appropriate aldehyde or ketone electrophiles as described previously.[8]

$$\underset{\mathbf{5}}{PhOCHCO_2^-}$$

In view of the α effect[9] we expected that α-lithiation with LDA[10] would be difficult. For this reason in the early experiments we used *n*-BuLi directly. Some carbonyl addition always took place and, therefore, an excess of *n*-BuLi could not be tolerated. Subsequently we only employed LDA as base in 50–100% excess, keeping the reaction temperature strictly below −70 °C to avoid decomposition of the enolate carboxylate **5**. Deuteration with D_2O at −78 °C followed by NMR analysis served as monitor for maximizing the extent of α-lithiation. Under optimal conditions the enolate carboxylate **5** could be generated in better than 95% yield as straw yellow colored solution.

It was important to add the electrophile at −78 °C and allow warmup to room temperature slowly to avoid decomposition of **5**. Low yields of β-hydroxy acids **3** could usually be ascribed to deterioration of the enolate carboxylate **5** due to insufficient reactivity of the electrophile at −78 °C, thus obliging higher reaction temperatures for the condensation step. For example, fluorenone is relatively unreactive in view of its reduced electrophilicity and steric demand and consequently a relatively low yield (ca. 40%) of **3f** was realized (Table I). The condensation proceeded sluggishly even at ca. −40 °C, resulting in a strongly colored solution which indicated deterioration of the enolate carboxylate **5**. However, in favorable cases, e.g., cyclopentanone and adamantanone (Table I), the straw yellow colored solution of **5** decolorized instantly on addition of the electrophile already at −78 °C.

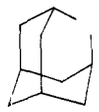
β-Lactones 2. β-Lactonization of the β-hydroxy acids **3** with benzenesulfonyl chloride in pyridine as base and solvent proceeded without difficulty for the β,β-dialkyl-substituted derivatives (Table II). The respective β-lactones **2a–c** were obtained in high yields. The β,β-diaryl derivatives **3e,f** afforded the respective enol ethers **1e,f** directly during the β-lactonization step. Presumably in this polar medium the latter β-lactones decarboxylate in situ at ambient temperatures.

Somewhat discouragingly, the β-hydroxy acid **3d** could not be β-lactonized. Even under more strenuous conditions, e.g., higher temperatures (ca. 60 °C), only unreacted starting material **3d** could be isolated. Thus, one of the limitations of our β-lactonization method[6] is that the β carbon must be disubstituted.

The β-lactones **2** were identified by their characteristic carbonyl band at ca. 1840 cm^{-1} in the infrared, their ^{1}H-NMR spectra (Table II), their characteristic M − 44 (loss of CO_2) peak in their mass spectra, and satisfactory elemental analysis. Purification was achieved by recrystallization and/or silica gel chromatography. In the latter case the chromatography had to be performed below −20 °C to suppress on-column decarboxylation of the labile β-lactones.

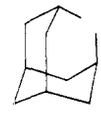
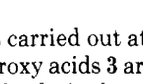
Enol Ethers 1. As expected, the β-lactones **2** readily decarboxylate thermally affording the hard to come by enol ethers **1** (Table III). As already stated in the previous section, the β-lactones **2e,f** did not survive the β-lactonization step, thus yielding directly the enol ethers **1**. In fact, if the β-lac-

Table II. Yields, Physical Constants, and Spectral Data of β-Lactones 2

	registry no.	R^1	R^2	yield, %	physical constants	^{1}H NMR type	^{1}H NMR δ ppm	^{1}H NMR no. of H's	^{1}H NMR multiplicity	IR $\nu_{C=O}$, cm^{-1}
2a	67774-16-7	CH_3	CH_3	80	bp 64 °C (0.05 mm)[a]	$R^1 + R^2$	1.55	3	s	1840
							1.65	3	s	
						>CHO–	5.00	1	s	
						C_6H_5	6.7–7.4	5	m	
2b	67774-17-8	$+CH_2+_4$		90	oil[b]	$R^1 + R^2$	1.3–2.5	8	m	1840
						>CHO–	5.15	1	s	
						C_6H_5	6.6–7.4	5	m	
2c	67774-18-9			89	mp 89 °C (hexane)[a]	$R^1 + R^2$	1.5–2.6	14	m	1840
						>CHO–	4.85	1	s	
						C_6H_5	6.8–7.4	5	m	

[a] Satisfactory elemental analysis; mass spectrum shows M − CO_2 peak. [b] Could not be obtained in analytically pure form even on attempted silica gel chromatography at low temperature; mass spectrum shows M − CO_2 peak.

Table III. Yields Physical Constants, and Spectral Data of Enol Ethers 1

	registry no.	R^1	R^2	yield, %	physical constants	^{1}H NMR type	^{1}H NMR δ, ppm	^{1}H NMR no. of H's	^{1}H NMR multiplicity (J in Hz)	IR, $\nu_{C=O}$, cm^{-1}
1a	5820-20-2	CH_3	CH_3	91	bp 47 °C (1 mm) [lit.[a] bp 122–23 °C (75 mm)]	$R^1 + R^2$	1.65	6	broad s	1690
						=CH—	6.05	1	m	
						C_6H_5	6.6–7.4	5	m	
1b	67774-19-0	$+CH_2+_4$		90	bp 75 °C (0.3 mm)[b]	$R^1 + R^2$	1.4–1.9	4	m	1690
							2.0–2.6	4	m	
						=CH—	6.10	1	quint (1)	
						C_6H_5	6.5–7.1	5	m	
1c	67774-20-3			92	mp 39–39 °C (hexane)[b]	$R^1 + R^2$	1.6–2.7	12	m	1690
							2.2–2.5	1	m	
							2.9–3.2	1	m	
						=CH—	6.00	1	s	
						C_6H_5	6.6–7.3	5	m	
1e	67774-21-4	Ph	Ph	30	mp 58 °C (lit.[c] mp 54–55 °C)	=CH—	6.75	1	s	1645
						C_6H_5	6.8–7.4	15	m	
1f	67774-22-5			40	mp 46–48 °C (methanol/water)[b]	all protons	6.8–7.8		m	1660

[a] Reference 12. [b] Satisfactory elemental analysis; mass spectrum shows M peak. [c] Reference 4.

tonization process is carried out at elevated (ca. 60 °C) temperatures, the β-hydroxy acids **3** are dehydrocarbonated (loss of H_2CO_3) in situ to the desired enol ethers **1** in fair yields (ca. 30–40%). However, the recommended procedure is first to isolate the β-lactone **2** and decarboxylate it after purification, rather than employing the one-pot conversion of **3** into **1**. The overall yields are higher and the product cleaner.

The recently published procedure[11] of direct dehydrocarbonation of β-hydroxy acids with diethyl azodicarboxylate and triphenylphosphine was also performed on **3**. However, the results were less satisfactory than our sequence.

The enol ethers **1** were characterized by their olefinic C–H at 3100 cm^{-1} and the enol double bond at 1645–1690-cm^{-1} bands in the infrared, their ^{1}H-NMR spectra, the parent peak in the mass spectrum, and satisfactory elemental analyses. It is of interest to note that the aryl-substituted enol ethers exhibit a bathochromic shift of the double bond frequency in the infrared compared to the alkyl-substituted ones. Acid-catalyzed hydrolysis afforded the expected aldehydes as confirmed by TLC and spectral data.

Our synthetic sequence **4** → **3** → **2** → **1** offers a convenient preparative method for enol ethers **1**, especially phenyl enol ethers, from readily available starting materials and reagents. Thus, the β-lactone unit is a useful and effective vice for regiospecific fixation of functionalized double bonds. In the case of diastereomeric β-hydroxy acids **3**, separation into the isomerically pure β-hydroxyacids, followed by β-lactonization and decarboxylation, offers the opportunity to fix stereospecifically functionalized double bonds.[6] Consequently, our synthetic sequence represents a useful alternative to the Wittig reaction.

Experimental Section

All melting points and boiling points are uncorrected. Solvents and starting materials were purified according to standard literature procedures and the latter either purchased from standard sources or prepared according to literature procedures. The infrared spectra were measured on a Perkin-Elmer infracord Model 237B and the ^{1}H-NMR spectra on an Hitachi-Perkin-Elmer R-24 spectrometer. Elemental analyses were performed by Atlantic Analytical Laboratories, Atlanta, Ga. or Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

General Method for the Preparation of β-Hydroxy-α-phenoxycarboxylic Acids 3. A 50-mL, two-necked, round-bottomed flask, provided with a magnetic spinbar, a rubber septum, and nitrogen inlet and outlet tubes, was flame dried under a nitrogen atmosphere. The flask was charged with anhydrous tetrahydrofuran (THF) and the required amount of diisopropylamine to make a 1.0 M solution. At −78 °C and while stirring magnetically the stoichiometric amount (equal to the quantity of the amine) of *n*-BuLi in hexane was syringed slowly into the reaction flask. After warming up to room temperature and stirring for 10 min, the mixture was cooled again to −78 °C. Half of the stoichiometric amount (one-fourth of the

amount of amine) of the phenoxyacetic acid **4** was added as a 1.0 M solution in anhydrous THF. After stirring at −78 °C for 15 min an excess of the ketone or aldehyde electrophile (twice the amount of the acid) was added as a 3.0 M solution in anhydrous THF. The solution was stirred at −78 °C for 15 min to 12 h, poured on 2–3 volumes of crushed ice, and transferred into a separatory funnel. After extraction with 2 × 15 mL of ethyl ether to remove neutral products, the aqueous layer was acidified with 10% HCl to pH ~3 and extracted with 4 × 20 mL of ethyl ether. The combined ether extracts were dried over $MgSO_4$ and the solvent rotoevaporated at 30 °C, first at 25 mm and finally at 1 mm. The residue was recrystallized from the appropriate solvent. The yields, physical constants, and spectral data are summarized in Table I.

General Method for the Preparation of α-Phenoxy-β-lactones 2. The β-hydroxy-α-phenoxycarboxylic acid **3** (1 mol) was dissolved in 10–20 mL of anhydrous pyridine, placed into a 50-mL stoppered Erlenmeyer flask, cooled to 0 °C and 2 mol of benzensulfonyl chloride was added. When the β-hydroxy acid **3** contains 1 mol of water of crystallization, 3 mol of benzenesulfonyl chloride must be used. After storing overnight in the refrigerator, the mixture was poured onto 3–4 volumes of crushed ice and extracted with 4 × 15 mL of ethyl ether. The combined ether extracts were washed with 2 × 20 mL of saturated bicarbonate and 1 × 20 mL of water and dried over $MgSO_4$. The solvent was rotoevaporated at 30 °C, first at 25 mm and finally at 1 mm, and the residue was recrystallized from the appropriate solvent. When the β-lactone **2** failed to crystallize, it was purified by silica gel chromatography at ca. −20 °C. The yields, physical constants, and spectral data are given in Table II.

General Method for the Preparation of Enol Ethers 1. Thermal Decarboxylation of the β-Lactones 2. The β-lactone (1.0 mmol) was placed into a 10-mL, one-necked, round-bottomed flask, provided with a gas outlet tube, and heated to 150 °C in an oil bath until cessation of CO_2 evolution. After cooling to room temperature, the enol ether product was distilled at reduced pressure or recrystallized from the appropriate solvent. The reaction yields, physical constants, and spectral data are given in Table III.

Direct Dehydrocarbonation of β-Hydroxy Acids 3. A 100-mL one-necked, round-bottomed flask, provided with a spin-bar and condenser with a gas outlet tube which was protected with a $CaCl_2$ drying tube, was charged with 2.0 mmol of the β-hydroxy-α-phenoxycarboxylic acid **3** in ca. 15 mL of anhydrous pyridine. To this solution was added 4.0 mmol of benzenesulfonyl chloride (6.0 mmol in the case of **3** containing 1.0 mmol of water of crystallization) and the mixture was stirred at 50–55 °C overnight. The dark mixture was poured onto 4–5 volumes of crushed ice and extracted with 2 × 15 mL of ethyl ether. The combined ether extracts were washed with 1 × 10 mL of 10% HCl, then with 1 × 10 mL of saturated $NaHCO_3$, and finally with 2 × 10 mL of water. After drying over $MgSO_4$, the solvent was rotoevaporated at 30 °C (30 mm). The residue was purified by distillation at reduced pressure or recrystallized from the appropriate solvent.

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Registry No.—Acetone, 67-64-1; cyclopentanone, 120-92-3; tricyclo[3.3.1.1^{3,7}]decanone, 700-58-3; benzaldehyde, 100-52-7; diphenylmethanone, 119-61-9; 9*H*-fluoren-9-one, 486-25-9; **4**, 122-59-8; LDA, 411-54-0; lithium α-phenoxy-α-lithioacetate, 67774-23-6.

References and Notes

(1) NIH Career Development Awardee, 1975–1980.
(2) F. Effenberger, *Angew. Chem.*, **81**, 374 (1969).
(3) J. K. Rasmussen, *Synthesis*, 91 (1977).
(4) G. Wittig, W. Böll, and K. H. Krück, *Chem. Ber.*, **95**, 2514 (1962).
(5) *Chem. Eng. News*, 50 (1972).
(6) W. Adam, J. Baeza, and J.-C. Liu, *J. Am. Chem. Soc.*, **94**, 2000 (1972).
(7) G. Caron and J. Lessard, *Can. J. Chem.*, **51**, 981 (1973).
(8) W. Adam and H.-H. Fick, *J. Org. Chem.*, **43**, 772 (1978).
(9) F. Bernardi, I. G. Czismadia, A. Mangini, H. B. Schlagel, M. H. Whangbo, and S. Wolfe, *J. Am. Chem. Soc.*, **97**, 2209 (1975).
(10) (a) P. L. Greger, *J. Org. Chem.*, **37**, 1907 (1972); (b) P. E. Pfeffer and L. S. Silbert, *ibid.*, **35**, 262 (1970); (c) P. L. Creger, *J. Am. Chem. Soc.*, **89**, 2500 (1967).
(11) (a) J. Mulzer and G. Brüntrup, *Angew. Chem., Int. Ed. Engl.*, **16**, 255 (1976); (b) J. Mulzer, J. Segner, and G. Brüntrup, *Tetrahedron Lett.*, 4651 (1977).
(12) M. Julia and M. Baillarge, *Bull. Chem. Soc. Fr.*, 734 (1966).

Modified Crown Ether Catalysts. 1. Synthesis of Alkanoyl-, Aroyl-, and α-Hydroxyalkylbenzo Crown Ethers[1]

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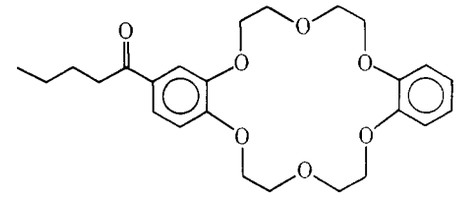
Crown ethers bearing lipophilic substituents were prepared for testing as improved catalysts. Fifteen alkanoylbenzo crown ethers were prepared in yields of 50–92%. The most satisfactory method of acylation proved to be treatment of the benzo crown with a slight excess of carboxylic acid and 1 equiv of phosphorus pentoxide in anhydrous methanesulfonic acid. Several of the resulting ketones were reduced in high yield to the corresponding alcohols with sodium borohydride in ethanol.

The recent report by Hautala and Hastings[2] on the preparation of 2,3-(4′-valeroylbenzo)-11,12-benzo-18-crown-6 (**1**) has prompted us to report the results of work which has been progressing in our laboratories.

Crown ethers are well known for their ability to form strong complexes with alkali metal and organic cations (log K_s for the 18-crown-6·K^+ complex in methanol is 6.0).[3] They have been used to dissolve potassium permanganate in benzene ("purple benzene"),[4] to stabilize diazonium salts,[5] and to bring



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