β-Methanesulfonyl styrene ($CH_3SO_2CH{=}CH(Ph)$) used as an authentic compound was obtained by dehydrochlorogenation of $CH_3SO_2CH_2CHCl(Ph)$ with triethylamine at room temperature: NMR ($CDCl_3$) δ 7.45 (5 H, s, Ph), 7.80–6.80 (2 H, q, CH=CH), 3.00 (3 H, s, CH_3).

Attempt To Prepare α-Phenylethanesulfonyl Chloride. Kharasch et al.[14] have reported the failure of the preparation of this sulfonyl chloride from salts of its sulfonic acid and PCl_5. We have tried to prepare this sulfonyl chloride by oxidizing its thiourea salt ($CH_3CH(Ph)SCN_2H_4Cl$) by Cl_2 at 0 °C (Johnson and Sprague's method)[26] in the hope that the forming sulfonyl chloride is not so unstable at 0 °C. However, when chlorine gas was conducted into the aqueous solution of the thiourea salt, a white solid which is believed to be sulfonyl chloride precipitated, and then it decomposed rapidly. So, we believe that the sulfonyl chloride is unstable even at 0 °C.

Kinetic Measurements. The rates of disappearances of α-toluenesulfonyl chloride and α-phenyl-β-(methanesulfonyl)ethanesulfonyl chloride were determined by NMR. The sample was prepared directly in an NMR sample tube which can be connected to a vacuum line for degassing of the sample. The thermal decomposition was carried out by placing the degassed sample tube in a temperature-controlled silicon oil bath. ^1H NMR measurements were performed at room temperature at 60 MHz. The rate of decomposition of α-toluenesulfonyl chloride was determined by measuring the ratio of the areas of the peaks due to the CH_2 protons of α-toluenesulfonyl chloride and benzyl chloride. It should be noted that aromatic solvents cannot be used here since the peaks due to the CH_2 protons of α-toluenesulfonyl chloride and benzyl chloride are overlapped in these solvents. The rate of decomposition of α-phenyl-β-(methanesulfonyl)ethanesulfonyl chloride was measured by taking advantage of the fact that that the peaks due to CH_3 protons of reactant and products absorb at different positions.

The decomposition of methanesulfonyl chloride in tetralin was followed by measuring the amount of SO_2 formed by iodometry.[20]

Registry No. I, 6038-47-7; II, 5342-84-7; α-phenyl-β-(methanesulfonyl)ethanesulfonyl chloride, 70551-57-4; α-toluenesulfonyl chloride, 1939-99-7.

Crown Cation Complex Effects. 10. Potassium *tert*-Butoxide Mediated Penultimate Oxidative Hydrolysis of Nitriles

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The failure of phase-transfer catalysis to improve either the yield or rapidity of basic nitrile hydrolysis is due, in part, to the poor solubility of quaternary ammonium hydroxides in nonpolar solutions. An alternative hydrolysis method which involves potassium *tert*-butoxide mediated oxidative cleavage of the nitrile with loss of the cyano carbon is presented. The isolated yields reported here range from 21–93% and are found to be highest for long-chain aliphatic nitriles such as cyanohexadecane.

Introduction

The basic hydrolysis of nitriles directly to the corresponding acids is a simple and high-yield transformation in only the most favorable of cases.[1b] Nitriles often resist basic hydrolysis to amides or acids, sometimes with considerable tenacity. Although the conversion of nitriles to amides (especially in the presence of peroxide[2]) has been known for some time, even this transformation continues to inspire new methodology.[3] We encountered the hydrolysis problem in connection with other work[4] and sought a simple, general method for hydrolysis of common nitriles, especially lipophilic ones.

Results and Discussion

The expedient of phase-transfer catalysis[5] proved of only marginal value in improving the basic hydrolysis of several nitriles which we examined. These experiments were conducted under two-phase conditions using benzene as solvent for the nitrile and aqueous sodium hydroxide as the source of base. Although the notion of using phase-transferred hydroxide seems logical at first, the poor solubility of quaternary ammonium hydroxides in nonpolar media[6] dooms this approach to failure.

In the absence of a phase-transfer catalyst, increasing the concentration of sodium hydroxide in the aqueous phase from 10–50% in increments of 10% did not improve the yield of benzoic acid obtained by hydrolysis of benzonitrile. In fact, with 10%, 20%, 30%, 40%, and 50% aqueous sodium hydroxide solutions and an equal volume of benzene as cosolvent, phenylacetonitrile was converted into phenylacetic acid in 82%, 77%, 54%, 30%, and 4% isolated yields, respectively, after 24 h at reflux (see Experimental Section). The trend can be clearly discerned from Figure 1. The slope of the line is −2.03 and the correlation coefficient is surprisingly good (−0.98). Note that the predicted y intercept is 110% yield, a value which is misleading as well as impossible. The hydrolysis of a nitrile is likely to be very slow under completely neutral conditions. The predicted value (y for $x = 5\%$) of 100% yield at 5% aqueous concentration seems quite reasonable for this simple nitrile.

***tert*-Butoxide-Catalyzed Oxidative Hydrolysis.** Strongly basic conditions such as those available by using phase-transfer catalysis have proved useful for a number

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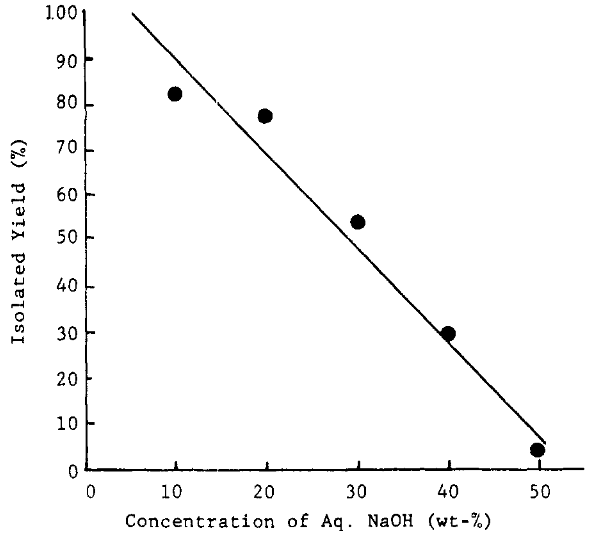


Figure 1. Relationship between phenylacetic acid yield and base concentration in the hydrolysis of phenylacetonitrile.

of oxidations and oxidative cleavages.[7] For example, fluorene readily air oxidizes to fluorenone under phase-transfer conditions[7c] and may even be induced to undergo oxidative cleavage to 2-carboxybiphenyl.[8] The so-called "anhydrous hydroxide" generated from potassium *tert*-butoxide and water[9] induces Haller–Bauer cleavage of amides under conditions which bear a semblance to nonpolar phase-transfer conditions. It occurred to us that the oxidative hydrolysis of nitriles should be possible under conditions similar to those which have been successful in the oxidative cleavage of fluorene. This approach requires loss of the nitrile carbon because deprotonation and oxidation occur at the α carbon.

The "hydrolysis" can be envisioned as a simple oxidation process as illustrated in eq 1. The analogy is suggested

$$RCH_2CN + t\text{-}BuOK \xrightarrow{O_2} RC(O)CN \xrightarrow{H_2O} RCOOH \quad (1)$$

by our work[8] and also by the recent work of Watt[10] and of Parker,[11] who formed cyanohydrins and thence ketones from nitriles.

The mechanism of the oxidation may be carbanionic or radical. In either event, the reaction probably begins by deprotonation at the carbon α to the nitrile. There is no question that this site is the most acidic in such molecules as heptadecanonitrile, but this is also the case for 3-phenylpropionitrile (dihydrocinnamonitrile, 4). The latter fact was demonstrated by treatment of 4 with potassium *tert*-butoxide in THF and then quenching with deuterium oxide. ^{13}C NMR analysis showed clearly that deuterium was bonded only to the α carbon.

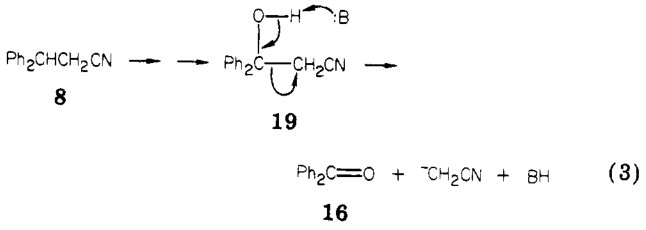
Once the anion is generated, it may react with oxygen to give a hydroperoxide (or hydroperoxide anion) or a radical. It seems likely that in most cases, simple oxidation of the anion occurs and the intermediate acyl cyanide is cleaved by hydroxide generated either in situ or on workup. In the oxidation of 3-phenylpropionitrile, a secondary oxidation of phenylacetic acid or phenylacetic acid cyanide may produce the benzoic acid.

It should be noted that acyl cyanides are known[12-14] and readily identifiable species and as such constitute reasonable intermediates in the examples presented here. This does not constitute evidence, however, and we have not succeeded in isolating these hydrolytically unstable species from our reaction mixtures.

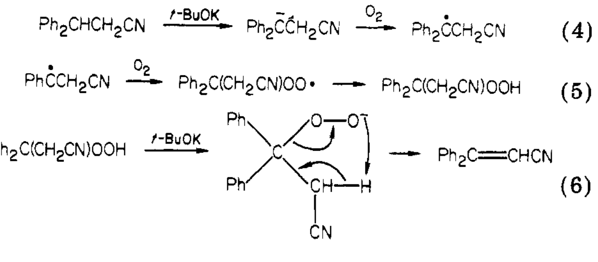
For the simple aliphatic nitriles, deprotonation generally occurs α to the cyano group and oxidation then occurs with eventual loss of the nitile carbon. This is not the case for 3,3-diphenylpropionitrile (**8**) which depronates at the benzhydryl carbon. As shown in eq 2, a mixture of products is formed, with benzophenone (**16**) predominating.

$$\underset{\mathbf{8}}{Ph_2CHCH_2CN} \xrightarrow[O_2,\ THF]{KO\text{-}t\text{-}Bu}$$
$$\underset{\mathbf{16},\ 22\%}{Ph_2C{=}O} + \underset{\mathbf{18},\ 2\%}{Ph_2C{=}CH_2} + \underset{\mathbf{17},\ 2\%}{Ph_2C{=}CHCN} + \underset{7\%}{\mathbf{8}} \quad (2)$$

It seems clear that the benzhydryl carbon in **8** is the most acidic position since the formation of all the products can be rationalized on the basis of deprotonation there. 1,1-Diphenylethene (**18**), for example, is probably formed by a base-catalyzed β-elimination of HCN. The formation of **16** probably results from a retro-aldol type reaction of the β-cyanohydrin (**19**), shown in eq 3. **17** probably results



from a simple dehydration of **19**. Although this might seem an unlikely process, we have shown previously that under basic conditions, benzophenone and acetonitrile condense to form 2,2-diphenylacrylonitrile (**17**) in 84% yield.[4] An alternative explanation of the formation of **17** is shown in eq 4–6. This mechanism seems consistent with



literature proposals and, although more direct than the above, is not as simple and should be regarded as speculative.

Experimental Conditions and Crown Effect. The oxidative hydrolysis reactions were conducted in tetrahydrofuran (THF) at room temperature, using either air or oxygen as oxidant. THF was chosen because it is nonacidic and potassium *tert*-butoxide is so soluble in it (25 g/100 g).[15] In addition, THF appeared to be a good

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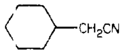
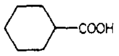
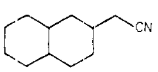
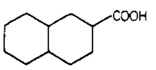
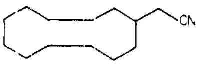
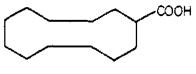
Table I. Potassium *tert*-Butoxide[a] Catalyzed Oxidative Hydrolysis Reaction[b]

no.	reactant structure	no.	product structure	time, h	% yield[c]	product mp, °C obsd	lit. (ref)
1	$CH_3(CH_2)_6CN$	10	$CH_3(CH_2)_5COOH$	48	89	oil	
2		11		48	85	oil	
3	$PhCH_2CN$	12	PhCOOH	48	90[d]	120-122	122
4	$PhCH_2CH_2CN$	12	PhCOOH	48	46	121-122[e]	122
5		13		92	93	56-77	81,[f] 98,[g] (16)
6		14		72	77	95-97	93-95, 98 (17)
7	$CH_3(CH_2)_{15}CN$	15	$CH_3(CH_2)_{14}COOH$	48	86	61-63	63-64 (18)
8	Ph_2CHCH_2CN	16	$Ph_2C{=}O$	48	22[h]	*h*	*h*
		17	$Ph_2C{=}CHCN$		2[i]	*i*	*i*
		18	$Ph_2C{=}CH_2$		2[i]	*i*	*i*
9	$PhCH_2COOH$	12	PhCOOH	48	21[j]	114-116	122

[a] Sublimed. [b] All reactions were conducted at ambient temperature in THF solution in the presence of oxygen and 5 mol % 18-crown-6 ether. [c] Yield is of isolated material with purity greater than 95% as judged by ^{1}H NMR analysis. [d] Crude yield; melting point is for material after recrystallization (see Experimental Section). [e] Mixture melting point. [f] Melting point is for the cis,cis,cis isomer. [g] Melting point is for the cis,cis,trans isomer. [h] Isolated as a mixture with 17 and 18; yield determined by VPC analysis. [i] Isolated as a mixture with 16. Yield determined by VPC analysis. [j] Crude yield of material not further purified.

Table II. Factors Affecting the Oxidative Hydrolysis of Cyanohexadecane (7) to Hexadecanoic (Palmitic) Acid in THF Solution

entry	base (equiv)	reaction temp, °C	atmosphere	time, h	added crown, mol %	yield, %
1	*t*-BuOK (4)	25	air	48		90
2	*t*-BuOK (4)	25	air	72		86
3	*t*-BuOK (4)	25	air	48	5	86
4	*t*-BuOK (4)	25	oxygen	48	5	86
5	*t*-BuOK (4)	65	air	1.5		8
6	*t*-BuOK (4)	65	air	1.5	5	40
7	*t*-BuOK (4)	65	oxygen	1.5		73
8	*t*-BuOK (4)	65	oxygen	1.5	5	86
9	KOH (4)	65	oxygen	1.5	5	trace

general solvent for the nitriles examined. Potassium *tert*-butoxide was used in excess (4 mol/mol of nitrile), and the reaction mixture was blanketed by either air or oxygen.

The results of several oxidative hydrolysis experiments are presented in Table I. When there was a single activating function (i.e., nitrile only) present, the oxidative hydrolysis reactions occurred quite readily. When two activating functions were present, as in entry 4, a mixture of products was produced and the carboxylic acid could be isolated in only moderate yield.

The factors affecting the oxidative hydrolysis are summarized in Table II. Heptadecanonitrile was chosen for this study because it is normally quite difficult to hydrolyze under either basic or acidic conditions. In the basic case at least, the low yield is expected because heptadecanonitrile is quite lipophilic and likely to be a poor participant in a heterogeneous reaction (see text and Figure 1). The variations apparent in Table II may therefore be exaggerated for less lipophilic compounds like benzonitrile or phenylacetonitrile.

One crucial requirement is obviously a strong base such as potassium *tert*-butoxide. A poorly solvated hydroxide ion (entry 9) might suffice were it more soluble in the medium, but under the conditions described here, very little oxidative cleavage product is observed when KOH is used as base.

The presence of 18-crown-6 polyether generally seems to have a salutary effect on the oxidation reaction although it is not required for success. Clearly, the reaction rate is enhanced by its presence, just as the reaction rate is enhanced by the concentration increase resulting by substituting pure oxygen for air. These observations are similar to those made during our earlier survey[8] of potassium *tert*-butoxide principally as a nucleophile.

From the information assembled in Table II, it seems clear that the most useful procedure for oxidative hydrolysis is to heat the nitrile with 4 equiv of potassium *tert*-butoxide in THF at reflux under a blanket of oxygen. 18-Crown-6 ether (5 mol %) should be added to ensure that the yield is maximized.

Functional-Group Compatibility. Most traditional nitrile hydrolyses are conducted in the presence either of acid or strong base. Functional groups which are incompatible with strong base will be incompatible with the hydrolysis method reported here. In addition, diaryl ketones and certain amides which are subject to the Haller–Bauer reaction may undergo cleavage. Since both a strong base and oxygen are present, any readily deprotonated carbon acid may likewise be subject to oxidation and subsequent cleavage. Such functional groups should be avoided.

Summary. We present here a useful method for the

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oxidative hydrolysis of even very lipophilic nitriles. The reaction is strong base catalyzed and base-sensitive functional groups must be avoided in this method as in the classical strong base hydrolysis of nitriles. An important difference between this approach and classical basic hydrolysis is that reaction is initiated not by nucleophilic addition to the nitrile but by deprotonation at a C–H adjacent to the nitrile. "Hydrolysis" in this case actually involves an oxidative cleavage which transforms the carbon α to the nitrile into the carboxyl group.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary device and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 and are calibrated against the 1601-cm^{-1} line of polystyrene. NMR spectra were recorded on a Varian Associates A-60A as ca. 15 wt % solutions in $CDCl_3$, unless otherwise noted. Chemical shifts are reported in parts per million (δ) downfield from internal Me_4Si and coupling constants (J) are reported in Hz. Mass spectra were determined on an AEI-MS 902 instrument at an ionizing voltage of 70 eV. Gas chromatographic analyses were conducted with a Varian Associates Model 2720 or 920 analytical gas chromatograph equipped with a thermal-conductivity detector and a 5 ft × 0.25 in. 10% SE-30 on NAW Chromosorb P column, except where noted. Helium was used as a carrier gas and the flow rate was ca. 60 mL/min.

THF was distilled from $LiAlH_4$ through a 30-cm Vigreux column just prior to use. The potassium *tert*-butoxide was sublimed and stored thereafter under dry nitrogen in a desiccator. All other solvents were purified according to literature procedures and stored under dry nitrogen and in contact with 4-Å molecular sieves.

Two-Phase Hydrolysis of Phenylacetonitrile Using Different Concentrations of Base. A 50-mL round-bottomed flask, equipped with a reflux condenser, N_2 inlet, and stirring bar was charged with phenylacetonitrile (1.17 g, 0.01 mol), C_6H_6 (5 mL), NaOH (1.60 g, 0.04 mol), and enough water to dilute the NaOH to 10%, 20%, 30%, 40%, or 50%, respectively. After 24 h at reflux, the reaction mixture was worked up and the product isolated. The phenylacetic acid was recrystallized from petroleum ether. The yields of acid, having a melting range no broader than 75–77 °C, are as follows: 10% NaOH, 82%; 20% NaOH, 77%; 30% NaOH, 54%; 40% NaOH, 30%; 50% NaOH, 4%. Addition of tetrabutylammonium hydrogen sulfate (Synecon, Sweden) had only a marginal effect on the reaction. Residual starting material generally accounted for the nonacidic material, although in the two most concentrated reactions, a material believed to be the dimer of phenylacetonitrile was isolated. Likewise, some hexadecanamide (mp 104–105 °C) was obtained.

General Procedure for the Penultimate Oxidative Hydrolysis of Nitriles to Carboxylic Acids by Potassium *tert*-Butoxide in Tetrahydrofuran. A 100-mL, three-necked, round-bottomed flask equipped with a magentic stirring bar, addition funnel, N_2 inlet, and reflux condenser, if required, was charged with KO-*t*-Bu, 18-crown-6 (if used), and THF (25 mL). The solution was equilibrated at the desired temperature and the nitrile in THF (10 mL) was added dropwise over a period of 5 min. In reactions conducted at reflux, the oxidant (oxygen or air) was introduced just above the hot solution and vented through the condenser. After the indicated length of time, the reaction was quenched with H_2O (5 mL) and diluted with Et_2O (25 mL) and then H_2O (25 mL), and finally the aqueous phase was separated. The organic phase was washed with H_2O (50 mL), and the combined aqueous phase was acidified with concentrated HCl. When the free acid was water soluble, the aqueous phase was saturated with NaCl prior to acidification. The acid was extracted with Et_2O (3 × 50 mL), dried over $MgSO_4$, and evaporated in vacuo. Purification, when requried, was accomplished by column chromatography on silica gel 60 (70–230 mesh, E. Merck) or by recrystallization. Unreacted nitrile, when recovered, was isolated from the dried organic phase upon evaporation in vacuo.

Oxidative Hydrolysis of Cyanooctane (1). Cyanooctane (1, 0.62 g, 5 mmol) was oxidized with KO-*t*-Bu (2.24 g, 20 mmol), O_2, and 18-crown-6 (0.132 g, 0.5 mmol, 2.5 mol %) for 48 h at 25 °C as described in the general procedure. After workup, 10 (0.57 g, 89%) was obtained as a light yellow oil whose spectral properties were identical with those of a commercial (Aldrich) sample.

Oxidative Hydrolysis of Cyclohexylacetonitrile (2). Cyclohexylacetonitrile[8] (2, 1.23 g, 10 mmol) was oxidized with KO-*t*-Bu (4.48 g, 40 mmol), O_2, and 18-crown-6 (0.264 g, 1 mmol, 2.5 mol %) for 48 h at 25 °C as described in the general procedure. After workup, 11 (1.09 g, 85%) was obtained as a light yellow oil whose spectral properties were identical with those in the literature.[19] NMR (CCl_4) is 1.05–2.65 (m, 12 H), 11.8 (m, 1 H); IR (neat) 2930 (m), 2855 (w), 1709 (s), 1454 (m), 1416 (m), 1255 (w), 1213 (w), 1135 (w), 895 (w) cm^{-1}.

Oxidative Hydrolysis of Phenylacetonitrile (3). Phenylacetonitrile (3, 0.59 g, 5 mmol) was oxidized with KO-*t*-Bu (2.24 g, 20 mmol), O_2, and 18-crown-6 (0.264 g, 1 mmol, 5.0 mol %) for 48 h at 25 °C as described in the general procedure. After workup, benzoic acid (0.58 g, 95%) was obtained as a tan-colored solid. Recrystallization gave pure 12 (0.33 g, 54%) as a white solid: mp 120–122 °C; mmp 120–122 °C (lit.[2] mp 122 °C).

Oxidative Hydrolysis of Dihydrocinnamonitrile (4). Dihydrocinnamonitrile[8] (3, 0.62 g, 5 mmol) was oxidized with KO-*t*-Bu (2.24 g, 20 mmol), O_2, and 18-crown-6 (0.132 g, 0.5 mmol, 2.5 mol %) for 48 h at 25 °C as described in the general procedure. After workup, the crude acid was purified by column chromatography (silica, 1:9 (v/v), ether–hexane) to give benzoic acid (0.28 g, 46%). The infrared spectrum of 12 compared well with that of an authentic sample and was homogeneous by TLC: mp 115–117 °C; mmp 121–122 °C (lit.[20] mp 122 °C).

Oxidative Hydrolysis of 3-(Cyanomethyl)bicyclo[4.4.0]decane (5). 3-(Cyanomethyl)bicyclo[4.4.0]decane[21] (5, 0.53 g, 3 mmol) was oxidized with KO-*t*-Bu (1.34 g, 12 mmol), O_2 and 18-crown-6 (0.158 g, 0.6 mmol, 5.0 mol %) for 72 h at 25 °C as described in the general procedure. After workup, 3-(carboxymethyl)bicyclo[4.4.0]decane (0.51 g, 93%) was obtained as a light tan oil (presumably as a isomer mixture) which slowly crystallized; mp 56–77 °C [lit.[16] mp 81 °C (cis,cis,cis isomer), 98 °C (cis,cis,trans isomer)]. The purity of 13 was verified by IR, NMR, and TLC (silica, 1:4 (v/v), ether–hexane): R_f ca. 0.5; NMR (CCl_4) δ 1.02–2.5 (m, 17 H), 11.58 (m, 1 H); IR (neat) 2925 (m), 2845 (m), 1695 (s), 1445 (m), 1420 (m), 1272 (w), 1248 (w), 1212 (w) cm^{-1}.

Oxidative Hydrolysis of Cyclododecylacetonitrile (6). Cyclododecylacetonitrile[21] (6, 0.52 g, 2.5 mmol) was oxidized with KO-*t*-Bu (1.12 g, 10 mmol), O_2, and 18-crown-6 (0.132 g, 0.5 mmol, 5.0 mol-%) for 72 h at 25 °C as described in the general procedure. After workup, cyclododecylcarboxylic acid 14 (0.47 g, 77%) was obtained as an off-white solid: mp 95–97 °C (lit.[17] mp 93–95 °C, 98 °C); NMR δ 1.2–1.9 (m, 22 H), 2.4–2.7 (m, 1 H), 10.86 (m, 1 H).

Preparation of Cyanohexadecane (7). The nitrile was prepared by heating chlorohexadecane with sodium cyanide under the phase-transfer catalytic conditions described by Starks[22] to yield 71%, mp 32–33 °C, after crystallization from aqueous ethanol.

Oxidative Hydrolysis of 7. Cyanohexadecane (7, 0.63 g, 2.5 mmol) was oxidized with KO-*t*-Bu (1.12 g, 10 mmol), O_2, and 18-crown-6 (0.132 g, 0.5 mmol, 5 mol %) for 48 h at 25 °C as described in the general procedure. After workup, hexadecanoic (palmitic) acid was isolated (0.55 g, 86%) as an off-white solid, mp 61–63 °C (lit.[18] 63–64 °C).

Oxidative Hydrolysis of 3,3-Diphenylpropionitrile (8). A 100-mL, three-necked, round-bottomed flask was equipped with a magnetic stirring bar and an O_2 inlet. After being purged with O_2 for 5 min, the flask was charged with KO-*t*-Bu (2.24 g, 20 mmol), 18-crown-6 (0.26 g, 1 mmol), and dry THF (50 mL). A solution of 8 (2.07 g, 10 mmol) in THF (10 mL) was added in one portion and the mixture was allowed to stir at ambient temperature under an O_2 purge for 48 h. The mixture was then filtered and evaporated in vacuo, and the residue was dissolved in Et_2O (50 mL). The ether layer was washed with 5% aqueous HCl, H_2O, and brine and then dried (Na_2SO_4). The ether was

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[19] "Sadtler Standard Spectra"; Vol. 1, 1971; p 223.

[20] See ref 18, p 132.

[21] Prepared by hydrogenation of 3-(cyanomethyl)idene[4.4.0]decane as described in ref 8.

[22] Starks, C. M. *J. Am. Chem. Soc.* 1971, *93*, 195.

evaporated (in vacuo) and the residue was chromatographed over alumina (30 g, eluant, Et$_2$O–hexanes, 3:7). Two fractions were obtained: F-1, 100 mL, 0.27 g; F-2, 100 mL, 0.22 g. Gas chromatographic analysis (5 ft × 0.25 in., 1.5% OV-101 on 100/120 mesh Chromosorb G, column temperature 150 °C) revealed that F-1 was a 1:5 mixture of **18** and **16** and F-2 was a 5:1 mixture of **16** and **17**. The components were identified by IR, ^{1}H NMR, and mass spectral analysis and confirmed by comparison with authentic mixtures. On the basis of fraction weights and VPC analysis, the yields were as follows: **16**, 22%; **17**, 2.5%; **18**, 2.25%, and 7% of **8** was recovered.

Oxidative Hydrolysis of Phenylacetic Acid (9). Phenylacetic acid (**9**, 0.68 g, 5 mmol) was oxidized with KO-*t*-Bu (2.80 g, 25 mmol), O_2, and 18-crown-6 (0.33 g, 1.25 mmol, 5.0 mol %) for 48 h at 25 °C as described in the general procedure. After the workup, the crude material was purified by column chromatography (silica, 5:95 (v/v) ether–hexane) to give **12** (0.13 g, 21%) which was identified by NMR and TLC, mp 114–116 °C.

Deuteration of Dihydrocinnamonitrile (4). A 50-mL, round-bottomed flask equipped with a magnetic stirring bar was charged with KO-*t*-Bu (0.45 g, 4 mmol), 18-crown-6 (0.05 g, 0.2 mmol, 5.0 mol %), and THF (15 mL). Dihydrocinnamonitrile (**4**, 0.131 g, 1 mmol) in THF (5 mL) was added dropwise and the solution stirred for 2 h, quenched with D$_2$O (2 mL), diluted with ether (20 mL), and washed with water (20 mL). The organic phase was dried (MgSO$_4$) and evaporated in vacuo to a pale yellow oil. ^{13}C NMR analysis indicated deuteration at the carbon α to the nitrile function: ^{13}C NMR (CDCl$_3$) 17.88 (m, 4, CHC(D)CN), 31.37 (s, 26, C$_6$H$_5$CH$_2$), 127.14 (s, 62, CH), 126.51 (s, 9, ipso carbon), 128.17 (s, 87), 128.7 (s, 100, ortho and meta carbons), 138.01 (s, 6, para carbon).

General Procedures for Entries in Table II. Potassium *tert*-butoxide (1.12 g, 10 mmol) and cyanohexadecane (**7**) in THF solution (25 mL) were stirred at the temperature and for the time period indicated. After addition of water, acidification, and extraction, hexadecanoic (palmitic) acid (**15**) was obtained in the specified yield as a white solid (lit.[18] mp 63–64 °C).

Entry 1. The reaction was conducted under an air atmosphere at 25 °C for 48 h. After workup, **15** was isolated (0.58 g, 90%) as an off-white solid, mp 61–63 °C.

Entry 2. The reaction was conducted under an air atmosphere at 25 °C for 72 h. After workup, **15** was isolated (0.55 g, 86%) as an off-white solid, mp 61–63 °C, mmp 61–63 °C.

Entry 3. The reaction was conducted under an air atmosphere at 25 °C for 48 h in the presence of 5 mol % 18-crown-6. After workup, **15** was isolated (0.55 g, 86%) as a white solid, mp 61–63 °C.

Entry 4. The reaction was conducted under an oxygen atmosphere at 25 °C for 48 h in the presence of 5 mol % 18-crown-6. After workup, **15** was isolated (0.55 g, 86%) as an off-white solid, mp 61–63 °C.

Entry 5. The reaction was conducted under an air atmosphere at THF reflux for 1.5 h. After workup, **15** was isolated (0.05 g, 8%) as an off-white solid, mp 61–63 °C. Unreacted **7** (0.50 g, 79%) was recovered as a white solid, mp 32–34 °C.

Entry 6. The reaction was conducted under an air atmosphere at THF reflux for 1.5 h in the presence of 5 mol % 18-crown-6. After workup, **15** was isolated (0.26 g, 40%) as an off-white solid, mp 61–63 °C. Unreacted **7** (0.25 g, 39%) was recovered as a white solid, mp 31–32 °C.

Entry 7. The reaction was conducted under an oxygen atmosphere at THF reflux for 1.5 h. After workup, **15** was isolated (0.46 g, 73%) as a white solid, mp 61–63 °C. Unreacted **7** (0.16 g, 26%) was recovered as a white solid, mp 31–32 °C.

Entry 8. The reaction was conducted under an oxygen atmosphere at THF reflux for 1.5 h in the presence of 5 mol % 18-crown-6. After workup, **15** was isolated (0.55 g, 86%) as an off-white solid, mp 61–63 °C.

Entry 9. KOH (0.66 g, 10 mmol, 85% pellets) and 18-crown-6 (0.132 g, 5 mmol), 5 mol %) were heated at reflux with **7** (0.63 g, 2.5 mmol) in THF (25 mL) under a dry O_2 atmosphere for 1.5 h. During this experiment, no ammonia could be detected. After workup, only a trace of **15** could be isolated. Unreacted **7** (0.53 g, 85%) was recovered as a white solid, mp 30–32 °C.

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Registry No. **1**, 124-12-9; **2**, 4435-14-7; **3**, 140-29-4; **4**, 645-59-0; **5**, 74244-55-6; **6**, 21963-16-6; **7**, 5399-02-0; **8**, 2286-54-6; **9**, 103-82-2; **10**, 111-14-8; **11**, 98-89-5; **12**, 65-85-0; **13**, 13032-41-2; **14**, 884-36-6; **15**, 57-10-3; **16**, 119-61-9; **17**, 3531-24-6; **18**, 530-48-3; potassium *tert*-butoxide, 865-47-4.

Sulfur Heterocycles. 3. Heterogeneous, Phase-Transfer, and Acid-Catalyzed Potassium Permanganate Oxidation of Sulfides to Sulfones and a Survey of their Carbon-13 Nuclear Magnetic Resonance Spectra

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Although numerous oxidation methods are available for the transformation of sulfides into sulfones, low-molecular-weight, heterocyclic sulfides are often not amenable to these oxidation techniques. The method presented here is a general and economical oxidation using potassium permanganate and various catalysts. Nineteen low-molecular-weight and heterocyclic sulfides were successfully oxidized by variations of this technique, and the results are presented here. In addition, the carbon-13 NMR spectra of these compounds and about two dozen others are reported. General chemical shift trends are reported for selected compounds, and details can be found in the supplementary material.

During our recent studies of the thermal demasking of certain oxathiolane *S*,*S*-dioxides,[2,3] we required a general oxidation method for cyclic sulfides which was effective, rapid, and inexpensive. In addition, we required that the method be reasonably successful for the oxidation of acid-sensitive sulfides, some of which are hemithioacetals.

Although the oxidation of sulfides to sulfones has been accomplished by a variety of methods,[4] for most purposes, hydrogen peroxide (H$_2$O$_2$) or peracid (e.g., *m*-chloroper-

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[1] Taken in part from the Ph.D. Dissertation of H.M.G., The Pennsylvania State University, 1979.

[2] Gokel, G. W.; Gerdes, H. M.; Miles, D. E.; Hufnal, J. M.; Zerby, G. A. *Tetrahedron Lett.* **1979**, 3375.

[3] Gerdes, H. M.; Gokel, G. W. *Tetrahedron Lett.* **1979**, 3379.

[4] For a recent summary of oxidation methodology, see: Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978; p 16.

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