ature to reach 15°. Water (200 ml) was added with stirring for an additional 30 min at room temperature. The two layers were separated; the organic layer was washed with water, 5% sodium bicarbonate, and again with water and dried (Na_2SO_4). The solvent was removed under reduced pressure to give 16.5 g (35.8%) of the cyclic sulfate **2**. Recrystallization from ethanol–water or ether–petroleum ether yielded colorless crystals: mp 129–131° (dec), lit.[10] mp 131° (dec); ir [(KBr) 2993, 1469, 1405, 1352, 1214, 1201, 961 883 cm^{-1}] and nmr [δ 1.7 (s)] are consistent with this structure.

Anal. Calcd for $C_6H_{12}O_4S$: C, 40.00; H, 6.67; S, 17.78. Found: C, 40.12; H, 6.56; S, 18.03.

The aqueous layer was neutralized with 20% aqueous sodium hydroxide and evaporated under reduced pressure to yield 25.5 g of a crude mixture of sulfonic acids A (Scheme I). Crystallization of A from 60% aqueous alcohol afforded a mixture of **3** and **4** containing very little inorganic sulfate. Nmr of the mixture (D_2O) reveals peaks at δ 5.75 and 1.16 (**4**) and at δ 4.13 and 1.08 (**3**).

Several recrystallizations from 60% alcohol afforded relatively pure **4**, the assigned structure of which is based on its nmr and ir spectra [(KBr) 3550, 3410, 2980, 1690, 1275, 1240, 1043, 690 cm^{-1}].

Anal. Calcd for $C_6H_{10}Na_2O_7S_2$: C, 23.69; H, 3.32; Na, 15.11; S, 21.07. Found: C, 23.55; H, 4.07; Na, 15.36; S, 21.55.

Sulfonation of Pinacolone with Dioxane–Sulfur Trioxide Complex. To the dioxane–sulfur trioxide complex prepared in the usual manner[11] from sulfur trioxide (23.45 g, 0.293 mol), dioxane (25.8 g, 0.293 mol), and dry 1,2-dichloroethane (125 ml) was added dropwise with stirring 29.3 g (0.293 mol) of pinacolone over a period of 40 min, followed by additional stirring for 60 min at room temperature. Water (200 ml) was added and the organic layer separated. The aqueous layer was neutralized with 15% aqueous sodium hydroxide, and the neutralized solution was evaporated to dryness to yield about 60 g of a crude mixture of sulfonic acids A (Scheme I), containing inorganic sulfate.

Nmr integration of mixture A showed the molar ratio of monosulfonate **3** to disulfonate **4** to be within the range of 1.8–2.5:1. The ratio of **3**:**4** in the mixture is changed with every recrystallization from aqueous alcohol.

Rearrangement of 2. A dispersion of **2** (0.518 g, 2.875 mmol) in 3 ml of 20% sulfuric acid was refluxed for 15 min, followed by addition of 5 ml of water. Extraction with methylene chloride, drying (Na_2SO_4), filtration, and removal of the solvent under reduced pressure gave 0.217 g (75.5%) of pinacolone (**1**) identical with an authentic sample.

Sodium 2-Keto-3,3-dimethylbutanesulfonate (3). Bromination of pinacolone according to the procedure of Boyer and Siraw[12] gave the α-bromination product in 82.3% yield, which was converted to **3** according to the method of Parkes and Tinsley.[13] Recrystallization from 60% aqueous ethanol yielded **3** as colorless plates: mp 216.5–218°; ir (KBr) 3580, 3520, 2970, 2935, 1710, 1645, 1392, 1245, 1215, 1203, 1161, 1056, 745 cm^{-1}; nmr (DMSO-d_6) δ 3.75 (s, 2, CH_2), 1.1 (s, 9, CH_3).

Anal. Calcd for $C_6H_{11}NaO_4S$: C, 35.64; H, 5.48; Na, 11.37; S, 15.84. Found: C, 35.55; H, 5.61; Na, 11.47; S, 15.98.

Sodium 2-Hydroxy-3,3-dimethylbutanesulfonate (5). To a solution of **3** (3.5 g, 17.3 mmol) in 20 ml of distilled water was added sodium borohydride (0.4 g, 10.57 mmol) in 3.5 ml of water dropwise over a period of 20 min, followed by stirring of the reaction mixture for an additional 3.5 hr. Acidification with 2% aqueous sulfuric acid (about 28 ml) was followed by the addition of methanol to make the solution 60% methanolic (v/v). The hydroxysulfonic salt **5** crystallized on cooling. The total amount of two crops was 3.45 g (97.5%): mp 272–276°; ir (KBr) 3385, 2958, 2870, 1630, 1364, 1238, 1168, 1050, 810 cm^{-1}; nmr (D_2O) δ 3.78 (m, 1, CH), 3.03 (m, 2, CH_2), 0.92 (s, 9, CH_3).

Anal. Calcd for $C_6H_{13}NaO_4S$: C, 35.32; H, 6.42; Na, 11.27; S, 15.69. Found: C, 35.73; H, 6.37; Na, 11.49; S, 15.25.

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Registry No.—**1**, 75-97-8; **2**, 52393-63-2; **3**, 52393-64-3; **4**, 52393-65-4; **5**, 52393-66-5; SO_3, 7446-11-9

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Chemistry of "Naked" Anions. III. Reactions of the 18-Crown-6 Complex of Potassium Cyanide with Organic Substrates in Aprotic Organic Solvents[1,2]

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Following Pedersen's discovery that macrocyclic polyethers ("crown" ethers) possess the ability to form crystalline complexes with a variety of inorganic salts and also the ability to solubilize these salts in aprotic organic solvents,[3] attention has been gradually focused toward utilizing the anion of the complex for synthetic purposes.[4] It has recently been reported that poor nucleophiles such as fluoride and acetate ions, solubilized as the potassium salt in CH_3CN or C_6H_6 containing 18-crown-6 (1,4,7,10,13,16-hexaoxacylooctadecane, 1),[3] become sufficiently nucleophilic to react smoothly and quantitatively with a variety of organic substrates.[1,2] These reactive species have been termed "naked" anions.[1] We now wish to report the preparation of the "naked" cyanide reagent and its utilization in a variety of synthetically useful reactions. Substitution, elimination, and addition processes have been explored.

The results are summarized in Table I. The reactions were carried out by simply pouring a substrate–crown solution directly over excess, dry KCN, and stirring the two-phase system vigorously at ambient or reflux temperature until reaction was complete. Little or no reaction was found to take place in the absence of 1 under the same conditions covering the same periods of time (runs 20 and 21, Table I). In all cases, 1 was present in catalytic quantities, indicating that it behaves as a phase-transfer catalyst.[5] In general, the reactions are more rapid in CH_3CN than in C_6H_6.

The reaction of "naked" cyanide with benzyl chloride proceeded quickly and quantitatively to product under mild conditions (run 20, Table I). With primary-substituted alkyl halides, the conversions to nitrile compounds were quantitative, with no elimination products detected (runs 1–12, Table I).[6] Displacement at secondary carbon produced primarily substitution products with only a small percentage of elimination products. These results compare favorably to those obtained with "naked" acetate,[2] but are in direct contrast to those of "naked" fluoride,[1] where large quantities of alkenes were obtained. It appears therefore, that "naked" fluoride may be a stronger base than either "naked" cyanide or "naked" acetate. Cyclohexyl halides gives exclusively elimination product with "naked" cyanide (runs 17 and 18, Table I). No reaction was observed with *o*-dichlorobenzene (run 22, Table I).

Table I[a]
Reactions of "Naked" Cyanide with Organic Substrates in the Presence of 18-Crown-6

Substrate	Registry no.	Run	Solvent	Products (yield, %)	Registry no.	Concn, M[b] Crown	Concn, M[b] Substrate	Temp, °C	$t_{1/2}$,[c] hr	t_{end}, hr
1,3-Dibromopropane	109-64-8	1	CH_3CN	Glutaronitrile (97.3)[d]	544-13-8	0.151	1.80	83	7	25
		2	CH_3CN	Glutaronitrile (94.9)[d]		0.147	1.80	Ambient	10.5	48
		3	C_6H_6	Glutaronitrile (100)[e]		0.147	1.80	90	12	40
		4	C_6H_6	Glutaronitrile (100)[e]		0.147	1.80	Ambient	10	49
1-Bromo-3-chloropropane	109-70-6	5	CH_3CN	Glutaronitrile (100)[e]		0.152	1.80	83	1.1	30
1,3-Dichloropropane	142-28-9	6	CH_3CN	Glutaronitrile (96.8)[d]		0.154	1.80	83	0.23	1.5
1,4-Dibromobutane	110-52-1	7	CH_3CN	Adiponitrile (100)[e]	111-69-3	0.141	1.80	83	6.5	14.5
		8	CH_3CN	Adiponitrile (100)[c]		0.141	1.80	Ambient	11	57
1,4-Dichlorobutane	110-56-5	9	CH_3CN	Adiponitrile (94.7)[d]		0.144	1.80	83	0.2	0.7
		10	CH_3CN	Adiponitrile (86)[d]		0.144	1.80	Ambient	8	75
1-Bromohexane	111-25-1	11	CH_3CN	1-Cyanohexane (100)[e]	629-08-3	0.138	1.80	83	10	40
1-Chlorohexane	544-10-5	12	CH_3CN	1-Cyanohexane (90.6)[d]		0.139	1.80	83	0.5	2.2
2-Bromobutane	78-76-2	13	CH_3CN	2-Cyanobutane (69.7)[e]	18936-17-9	0.141	2.00	83	16	32
		14	C_6H_6	2-Cyanobutane (43.4)[e]		0.140	2.01	90	58	66[f]
2-Bromooctane	557-35-7	15	CH_3CN	2-Cyanooctane (56)[d] (62)[e] -octene (17)[e,g]	2570-96-9	0.119	2.00	83	14	78
2-Chlorooctane	628-61-5	16	CH_3CN	2-Cyanooctane (77.5)[e,h] -octene (3.1)[e,g,h]		0.122	2.00	83	59	244[h]
Cyclohexyl bromide	108-85-0	17	CH_3CN	Cyclohexene (46)[e,f]	110-83-8	0.132	1.80	83		53[f]
Cyclohexyl chloride	542-18-7	18	CH_3CN	Cyclohexene (32)[e,f]		0.146	1.80	83		122.5[f]
Benzyl bromide	100-39-0	19	CH_3CN	Benzyl cyanide (100)[e]	140-29-4	0.146	1.80	Ambient	13	25
Benzyl chloride	100-44-7	20	CH_3CN	Benzyl cyanide (94.2)[d]		0.147	1.80	Ambient	0.08	0.4
		21	CH_3CN	Benzyl cyanide (20)[e,f]		0.0	1.80	Ambient		75[f]
o-Dichlorobenzene	95-50-1	22	CH_3CN	No reaction[i]		0.145	1.80	83		109
Methacrylonitrile (Acetone cyanohydrin)[j]	126-98-7	23	CH_3CN	1,2-Dicyanopropane (91.9)[d,l]	623-35-8	0.132	1.51 (1.78)	83	0.3	0.6
		24	CH_3CN	1,2-Dicyanopropane (46)[e,f]		0.132	1.52 (1.72)	Ambient		189[f]
		25	CH_3CN	1,2-Dicyanopropane (77)[d,k]		0.0	1.51 (1.74)	83	6.1	15

[a] For the isolated products, nmr, ir, and mass spectral data confirmed the pure compound's identity. Also, where possible, these spectra and glc data of the products were compared to those of the commercial compounds (runs 1–12). [b] The reactions were run in a total of 25 ml of solution, with a twofold excess of solid KCN per functional group for the substitution reactions, and a catalytic amount (approximately equivalent to 18-crown-6) of salt for the hydrocyanation. [c] $t_{1/2}$ is defined as the time required for 50% of the starting material to react. [d] Isolated yields. For these examples, glc and nmr analysis showed a quantitative conversion to the products. [e] Calculated from glc and nmr data. [f] In these runs, the reactions were stopped before completion. [g] From glc analysis, 1-octene and both *cis*- and *trans*-2-octene were formed. [h] There was difficulty in driving the reaction to completion. At 244 hr, the composition consisted of 7.4% starting material, 89.1% substitution product, and 3.5% olefin by glc analysis. The yields given in Table I are thus based on reacted starting material. [i] The absence of reaction of "naked" cyanide with *o*-dichlorobenzene was in contrast to the results recently reported for the analogous KOH–CH_3OH–crown system in which a 40–50% yield of *o*-chloroanisole was obtained.[4a] [j] 1.18 molar equiv of acetone cyanohydrin was used. It functioned as a proton donor and a cyanide ion regenerator after initiation of the reaction by the "naked" cyanide. [k] Run 25 was monitored frequently during the course of the reaction by glc, and thus a small quantity of product was lost in the transfers. The reaction was quantitative by glc and nmr analyses. [l] Reference 18.

Interestingly, primary chlorides react much faster than the corresponding bromides under the reaction conditions. For example, benzyl chloride reacts about 100 times faster than benzyl bromide (runs 19 and 20, Table I). This observation is contrary to the normally accepted leaving group order.[7] It is also opposite to what has been observed with "naked" acetate and "naked"fluoride.[1,2] With the secondary halides, it appears that bromides react more rapidly than chlorides; however, less alkene[8] and a higher overall yield of substitution product are obtained with the chloride. The causes of these observations are currently being investigated. It is emphasized here, however, that for synthetic purposes chlorides are preferred over bromides under the reaction conditions reported.

Substitutions of halides by cyanide ion have been reported to occur (1) in ethanol–water mixtures under strenuous conditions;[10] (2) in dipolar, aprotic solvents such as DMSO;[11] and (3) by use of tetraalkylammonium or -phosphonium salts to transfer the cyanide ion across a water–organic interface (phase-transfer catalysis).[5,12] Comparatively, the "naked" cyanide system appears to be superior to the ethanol–water method in reaction time, temperature, simplicity of work-up, and yields.[10,13] It also compares favorably to the dipolar, aprotic solvent and phase-transfer catalyst systems in both reaction time and yield for conversion of primary halides to nitriles.[11,12] Advantages of the "naked" cyanide procedure over these latter methods are lower reaction temperature and simplicity of work-up. For secondary substrates, comparable yields to those presented in Table I were obtained in much shorter times in the dipolar, aprotic solvent,[11b] while the phase-transfer catalyst system gave a higher yield of substitution product (no reaction time was reported).[12a] The reaction temperatures, however, were higher in both the DMSO and phase-transfer catalyst systems.[11,12]

The quantitative hydrocyanation reaction (run 23) is included to demonstrate the versatility of the "naked" cyanide reagent. In the absence of crown, reaction was found to proceed at a comparatively slow rate (run 25). The yield obtained in run 23 compares favorably with reported hydrocyanation reactions.[14]

In summary, it has been shown that 1 effectively solubilizes KCN in aprotic solvents, that the resulting "naked" cyanide is both a weak base and a potent nucleophile, and that the reagent produces nitrile compounds smoothly, mildly, and in high yields from a variety of organic substrates.

Experimental Section

The following instruments were used in the analyses: a Varian Model 90-P gas chromatograph for glc analyses, a Varian Model M-66 mass spectrometer for mass spectra, a Varian Model A-60 or T60-A nuclear magnetic resonance spectrometer for nmr spectra, and a Perkin-Elmer Model 237-B spectrophotometer for ir spectra.

The organic reagents and solvents (Aldrich Chemical Co., K & K Laboratories, Fisher Scientific, J. T. Baker Chemical Co., and Eastman Chemical Co.) were commercial compounds used without further purification. The KCN was ground and then dried under vacuum at 100° for 24 hr.

General Procedure. The starting solutions were prepared by weighing the reactive substrate directly into a 25-ml volumetric flask and diluting to the mark with a stock solution (known concentration)[15] of 1 in CH_3CN or C_6H_6. The prepared solutions were placed directly over solid, dry KCN (twofold excess of salt per functional group being displaced) and the reaction mixture was stirred vigorously at ambient or reflux temperature. Small aliquots of solution were removed at intervals and the extent of reaction was followed by glc and/or nmr analysis. Work-up involved separating the solid-liquid phases, removing the bulk of the solvent, diluting the remains with distilled water, extracting the product, and distilling the product after drying and removal of the extraction solvent.

1,4,7,10,13,16-Hexaoxacylooctadecane (18-Crown-6,[3a] 1) The crown was synthesized and purified by a previously described procedure.[16]

Preparation of Nitrile Compounds. Preparation of 1,3-Dicyanopropane (Glutaronitrile, 2). A. Into a 50-ml round bottom flask equipped with a magnetic stirring bar and a condenser-drying tube system were placed 11.7 g (0.18 mol) of dry KCN (Fisher Scientific) and 25 ml of an acetonitrile solution containing 5.08 g (0.045 mol) of 1,3-dichloropropane (Aldrich Chemical Co.) and 1.01 g (0.0038 mol) of **1**. The two-phase system was heated to reflux with vigorous stirring and the extent of reaction was followed by glc techniques. After 1.5 hr, the reaction mixture was cooled, filtered, and evaporated to *ca.* one-third volume. Distilled water was then added, and the mixture was extracted with CH_2Cl_2.[17] The CH_2Cl_2 solution was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The residue was distilled under vacuum to give 4.10 g (96.8%) of **2:** bp 78–82° (0.15 mm); ir (neat, NaCl plates) 2950, 2875, 2240, 1450, 1420 cm^{-1}; ^1H nmr (neat, external TMS, $CHCl_3$) 2.65 (t, 4 H), 2.15 ppm ("spiked" q, 2 H); mass spectrum *m/e* 94, 93, 54, 41, 28; these spectra and glc analysis of the synthesized product corresponded to those of commercial 2 (K & K Laboratories).

Preparation of 1,2-Dicyanopropane (3). B. Into a 50-ml round-bottom flask equipped as in A were placed 0.32 g (0.005 mol) of dry KCN, 25 ml of an acetonitrile solution containing 3.03 g (0.045 mol) of methacrylonitrile (Eastman Chemical Co.) and 1.04 g (0.0039 mol) of **1**, and 4.42 g (0.052 mol) of acetone cyanohydrin (J. T. Baker Chemical Co.). The system was brought rapidly to reflux with vigorous stirring and the extent of reaction was monitored by glc and nmr techniques. After 0.6 hr, the system was cooled and the solution was worked up as in A.[17] Distillation of the isolated crude product[18] gave 3.89 g (91.9%) of the colorless, transparent liquid **3:** bp 68–71° (0.15 mm); ir (neat, NaCl plates) 2975, 2940, 2250, 1520, 1425, 1380 cm^{-1}; ^1H nmr (neat, external TMS, $CHCl_3$) 3.05 (m, 1 H), 2.65 (d, with spikes, 2 H), 1.35 ppm (d, 3 H); mass spectrum *m/e* 94, 93, 54, 41, 28.

Registry No.—Cyanide, 57-12-5; 18-crown-6, 17455-13-9; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9.

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(17) Extraction of the nitrile compounds can be accomplished by hand (three to five extractions) or by a CH_2Cl_2 continuous extractor (20–24 hr). As nitriles are soluble in H_2O (especially dinitriles) to various extents, the continuous-extraction method is recommended in cases where small quantities are involved and complete extraction from the water layer is desired. For larger runs, the hand-extraction technique is preferred. Both methods were used with comparable results in preparing this report.

(18) On evaporation of the extraction solvent, the crystalline adduct (complex) of **7** and **1** precipitates spontaneously. However, on heating the distillation flask the complex readily melts, and the liquid **7** is then easily distilled. The characteristics of this and a number of other crystalline complexes of nitrile compounds and **1** have been reported: F. L. Cook, H. P. Harris, and C. L. Liotta, *J. Org. Chem.*, submitted for publication.

Carbanion Mechanism in the Alkylation of Certain Tosylhydrazones. 9,9-Disubstituted Fluorenes from Fluorenone Tosylhydrazone

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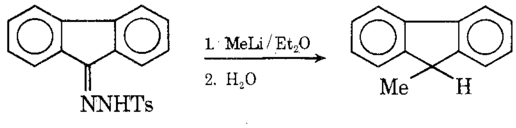
In the first publication of the reaction of tosylhydrazones with alkyllithium reagents it was reported that fluorenone tosylhydrazone (I) undergoes substitution, since elimination is precluded.[1] Herz and his coworkers have more recently shown that substitution of this type occurs with tosylhydrazones capable of undergoing elimination, provided that a very large excess of alkyllithium reagent is used.[2,3]



I

It was suggested that the reaction proceeds by way of an S$_N$2′ mechanism with the key intermediate being a carbanion.[2,4]

We have now trapped the carbanion generated from I with D_2O, CH_3CH_2Br, and CO_2 demonstrating its existence as well as providing a new route to 9,9-disubstituted fluorenes. The probable reaction route is illustrated in the following sequence.