Experimental Section

Melting points were taken on a Yanagimoto micro hotstage and are uncorrected. Infrared spectra on KBr pellets of solids were measured on a JASCO IR-G spectrophotometer. ^1H NMR spectra of $CDCl_3$ solutions with Me_4Si as internal standard (δ = 0 ppm) were recorded on a Hitachi R-40 (90 MHz) spectrometer. The ^{13}C NMR spectra of $CDCl_3$ solutions with Me_4Si as internal standard were taken on a JEOL FX-90Q spectrometer.

General Procedure for High Pressure Reactions. A mixture of testosterone and nitromethane (see Table I) in 0.5 M tetra-*n*-butylammonium fluoride/tetrahydrofuran[9] or in 1,8-diazabicyclo[5.4.0]undec-7-ene/acetonitrile (see Table I) in a 8-mL Teflon tube was pressurized at 900-MPa hydrostatic pressure for 6 days at ca. 30 °C.[10] After release of the pressure, the sample was removed from the high pressure vessel, diluted with ethyl acetate (100 mL), and washed either with water (50 mL × 6 in the case of TBF) or with 1 N HCl, 1 N $NaHCO_3$, and water (in the case of DBU), and then dried over $MgSO_4$. The mixture was concentrated and chromatographed on silica gel with benzene–ethyl acetate (7/3, v/v) as eluent, giving the 1:1 adduct **3** and the 1:2 adduct **4**.

5α-(Nitromethyl)-17β-hydroxyandrostan-3-one (3): mp 209–211 °C; IR (KBr) 1375, 1545 (NO_2), 1715 (CO) cm^{-1}; ^1H NMR (90 MHz) δ 0.77 (s, 3), 1.03 (s, 3), 1.0–4.0 (complex, 22), 2.95 (d, J = 15 Hz, 1), 4.46 (s, 2); ^{13}C NMR (90 MHz) δ 10.9, 17.1, 20.6, 23.2, 26.4, 29.7, 30.3, 31.5, 34.4, 36.5, 36.8, 38.3, 42.0, 45.2, 51.0, 81.3 (d, C-17), 82.5 (t, 5α-CH_2NO_2), 209.5 (s, C=O). Anal. Calcd for $C_{20}H_{31}O_4N$: C, 68.72; H, 8.76; N, 4.01. Found: C, 68.69; H, 9.09; N, 4.09.

3β,5α-Bis(nitromethyl)-17β-hydroxyandrostan-3α-ol (4): 172–174 °C; IR (KBr) 1380, 1545 (NO_2), 3375, 3500 sh (OH) cm^{-1}; ^1H NMR (90 MHz) δ 0.74 (s, 3), 0.94 (s, 3), 1.0–4.0 (complex, 22), 3.80 (s, 1) 4.43 (br s, 4), 5.49 (d, J = 10 Hz, 1); ^{13}C NMR (90 MHz) δ 10.9, 17.6, 20.3, 23.3, 26.7, 27.2, 29.0, 30.6, 31.2, 32.7, 34.7, 36.6, 38.4, 40.5, 41.8, 42.6, 51.2, 71.2 (s, C-3), 81.6 (d, C-17), 83.7 (t, 5α-CH_2NO_2), 86.2 (t, 3β-CH_2NO_2). Anal. Calcd for $C_{21}H_{34}O_6N_2$: C, 61.44; H, 8.35; N, 6.82. Found: C, 61.39; H, 8.35; N, 6.82.

Registry No. 1, 58-22-0; 2, 75-52-5; 3, 92078-58-5; 4, 92078-59-6.

(9) TBF (1 M) in THF is purchased from Aldrich Chemical Co. and is used upon dilution to 0.5 M in THF.

(10) For a description of the high pressure apparatus employed in this study, see: Matsumoto, K.; Sera, A.; Uchida, T. *Synthesis*, in press.

Methanesulfonic Acid.[1] A Useful Cyclizing Acidic Reagent

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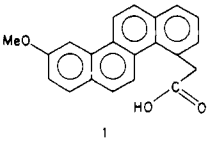
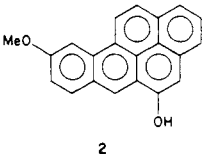
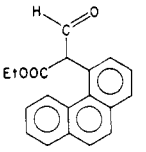
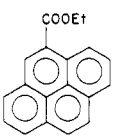
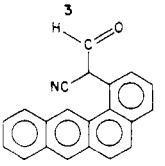
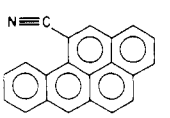
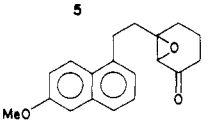
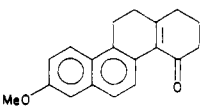
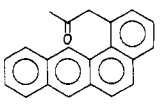
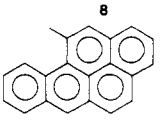
The development of novel synthetic approaches to polycyclic aromatic hydrocarbons (PAH) often requires cyclization reactions of carbonyls (aldehydes, ketones, carboxylic acids, and esters) into aromatic rings. In the past, different conditions have been used to carry out the above-mentioned transformations. Among them, HF, phosphoric acid, and sulfuric acid are the most widely used.

This note intends to introduce methanesulfonic acid (neat and as a CH_2Cl_2 solution) as a milder and versatile reagent for the cyclization of a wide variety of substrates.

Table I

substrate	product[a]	isolated yield,[b] %	method
 1	 2	85	A
 3	 4	84 94	A B
 5	 6	86	B
 7	 8	70	B
 9	 10	74	A[7]

[a] All products were properly characterized. [b] Reported yields correspond to analytical pure material.

Results and Discussion

Methanesulfonic acid (MSA) first came to our attention when we considered Eaton's reagent[2] (MSA/P_2O_5) as a suitable alternative to phosphoric acid for the cyclization of a group of aromatic carboxylic acids. When attempting to test the solubility of our starting materials (benz[*a*]-anthracene and chryseneacetic acids)[3] in MSA we discovered that excellent yields of cyclization product could be obtained by excluding the P_2O_5 from the mixture.

Further investigations have shown that MSA is capable of cyclizing aldehydes and ketones[4] as well as carboxylic acids.[5] Yields are generally excellent and the appearance of often found polymeric material is virtually eliminated.

In some cases, we found that an even milder cyclizing agent was required due to the high sensitivity of the starting material toward polymerization. Solutions of MSA in different organic solvents were tested as an alternative. A 5–10% (v/v) solution of MSA in methylene chloride was found to be a more efficient reagent than neat MSA for the cyclization of very reactive systems such as β-formyl esters[6] and α-epoxy ketones.[5] Some representative examples are given in Table I.

Experimental Section

MSA was obtained as reagent grade from Aldrich and was distilled under reduced pressure (3.0 torr, 70 °C) before using.

(1) MSA is a slightly viscous liquid (d = 1.48) which can be easily purified by distillation at reduced pressure. Most cyclizable substrates are soluble in this reagent. MSA is also soluble in a variety or organic solvents (ethyl, ether, THF, CH_2Cl_2, etc.).

(2) Eaton, P. E.; Carlson, C. R.; Lee, J. T. *J. Org. Chem.* **1973**, *38*, 4071.

(3) Bodine, R. S.; Hylarides, M. D.; Daub, G. H.; VanderJagt, D. L. *J. Org. Chem.* **1978**, *43*, 4025.

(4) Lyle, T. E.; Daub, G. H. *J. Org. Chem.* **1979**, *44*, 4933.

(5) Silverman, I. R.; Daub, Tg. H., unpublished results.

(6) Leon, A. A.; Daub, G. H.; VanderJagt, D. L. *J. Org. Chem.*, in press.

(7) Bodine, R. S.; Daub, G. H. *J. Org. Chem.* **1979**, *44*, 4461.

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‡ Deceased June 4, 1984.

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Substrates could be cyclized in analytical pure or crude form. In both cases purification of the products was required.

General Method A. A solution of the substrate in MSA (0.3 mmol/mL) was allowed to stir at room temperature for 20–24 h. The resulting deep red solution was poured into ice water to afford a precipitate that was filtered, washed with water, and dried to afford a crude product that could be purified by conventional methods.

General Method B. To a solution of the substrate in methylene chloride (0.03 mmol/mL) was added MSA (5–10 mL/100 mL CH_2Cl_2) dropwise. The resultant red solution was allowed to stir at room temperature under an N_2 atmosphere for 24 h after which it was poured into ice water. A two-phase mixture was obtained which was diluted with CH_2Cl_2 and washed with 5% aqueous $NaHCO_3$ and water. After drying over anhydrous $MgSO_4$, filtering, and evaporating the solvent under reduced pressure, good yields of product were obtained.

Acknowledgment. Financial support from the Chemistry Department at the University of New Mexico is appreciated.

Registry No. 1, 92096-68-9; 2, 92096-69-0; 3, 92096-70-3; 4, 68841-73-6; 5, 92096-71-4; 6, 92096-72-5; 7, 92096-73-6; 8, 92096-74-7; 9, 71718-29-1; 10, 16757-80-5; CH_3SO_3H, 75-75-2.

"Destructible" Surfactants Based on a Ketal Group

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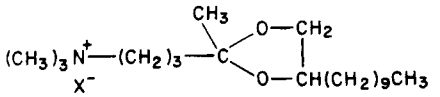
Surfactant-based organized media containing micelles,[1] inverse micelles,[1b,2] and microemulsions[1f,3] have been used infrequently in preparative chemistry. However, the abilities of these media to solubilize, orient, and compartmentalize reactants offer the potential of reactivity control not attainable in conventional solvents.

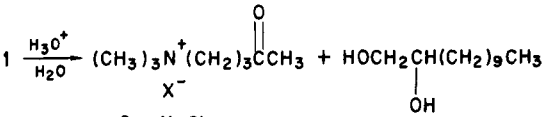
A difficulty inherent in the isolation of products from surfactant-based media involves emulsion formation during extraction procedures. In some instances with ionic surfactants this problem can be avoided by precipitation of the surfactant ion by the addition of an appropriate counterion (i.e., Ca^{2+} for dodecyl sulfate and ClO_4^- for hexadecyltrimethylammonium). A normal workup then follows removal of the precipitate by filtration or centrifugation/decantation. In order to circumvent the emulsion problem entirely and with generality, we and others have introduced[4] the concept of "destructible" (cleavable) surfactants that can be converted by hydrolysis or other reactions to nonsurfactant products under mild conditions. Straightforward extraction procedures are then employed. Thus, "destructible" systems should facilitate the application of surfactants in preparative chemistry.

Previously, we reported the first "destructible" surfactants for organic synthesis[4a,b] and in the present study have prepared additional examples **1a**, **1b**, and **1c**. These



1a, X = Cl
b, X = Br
c, X = OSO_2CH_3
d, X = ClO_4

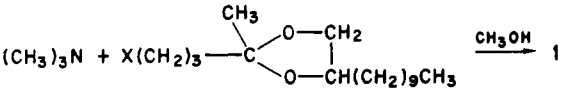
materials have been utilized already in the formulation of microemulsions.[5] They are based on the ketal group and therefore can be used to catalyze reactions under neutral and basic conditions, followed by their conversion to nonsurfactant keto ammonium compounds **2** and 1,2-dodecanediol (**3**) under acidic conditions prior to workup.



2a, X = Cl
b, X = Br
c, X = OSO_2CH_3

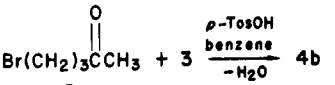
3

Surfactants **1a**, **1b**, and **1c** were prepared as follows. The reaction of previously reported[4b] chloro ketal **4a** with Me_3N in MeOH in an autoclave at 45 °C yielded **1a**. This material was very hygroscopic, so it was converted to perchlorate **1d** for characterization.



4a, X = Cl
b, X = Br
c, X = OSO_2CH_3

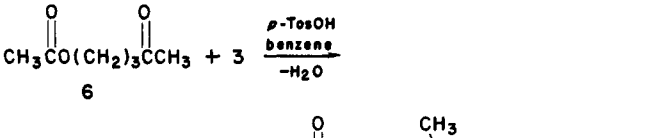
The reaction of 5-bromo-2-pentanone (**5**) with diol **3** yielded bromo ketal **4b** which was converted to **1b** with Me_3N in MeOH at 25 °C. Surfactant **1b** was much less



5

hygroscopic than **1a** and had a critical micelle concentration (cmc) in 0.01 M $NaHCO_3$ of 2.7×10^{-3} M (without hysteresis).

The reaction of keto acetate **6** and diol **3** gave ketal **7**.



6

7

Its reduction with $LiAlH_4$ yielded **8**,[6] which was then

(1) For examples, see: (a) Link, C. M.; Jansen, D. K.; Sukenik, C. N. *J. Am. Chem. Soc.* **1980**, *102*, 7798. (b) Armstrong, D. W.; Seguin, R.; McNeal, C. J.; Macfarlane, R. D.; Fendler, J. H. *Ibid.* **1978**, *100*, 4605. (c) Sutter, J. K.; Sukenik, C. N. *J. Org. Chem.* **1982**, *47*, 4174. (d) Jaeger, D. A.; Robertson, R. E. *Ibid.* **1977**, *42*, 3298. (e) Menger, F. M.; Rhee, J. U.; Rhee, H. K. *Ibid.* **1975**, *40*, 3803. (f) Breslow, R.; Maitra, U.; Rideout, D. *Tetrahedron Lett.* **1983**, *24*, 1901. (g) Nikles, J. A.; Sukenik, C. N. *Ibid.* **1982**, *23*, 4211. (h) Onyiriuka, S. O.; Suckling, C. J.; Wilson, A. A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1103. (i) Reger, D. L.; Habib, M. M. *J. Mol. Chem.* **1980**, *7*, 365 and references therein.

(2) For examples, see: (a) Armstrong, D. W.; Nome, F.; Fendler, J. H.; Nagyvary, J. *J. Mol. Evol.* **1977**, *9*, 213. (b) Jaeger, D. A.; Ippoliti, J. T. *J. Org. Chem.* **1981**, *46*, 4964.

(3) For examples, see: (a) Gonzalez, A.; Holt, S. L. *J. Org. Chem.* **1982**, *47*, 3186. (b) Martin, C. A.; McCrann, P. M.; Angelos, G. H.; Jaeger, D. A. *Tetrahedron Lett.* **1982**, *23*, 4651. (c) Jaeger, D. A.; Ward, M. D.; Martin, C. A. *Tetrahedron*, in press, and references therein.

(4) (a) Jaeger, D. A.; Ward, M. D. *J. Org. Chem.* **1982**, *47*, 2221. (b) Jaeger, D. A.; Frey, M. R. *Ibid.* **1982**, *47*, 311. (c) Keana, J. F. W.; Guzikowski, A. P.; Morat, C.; Volwerk, J. J. *Ibid.* **1983**, *48*, 2661. (d) Cuomo, J.; Merrifield, J. H.; Keana, J. F. W. *Ibid.* **1980**, *45*, 4216. (e) Epstein, W. W.; Jones, D. S.; Bruenger, E.; Rilling, H. C. *Anal. Biochem.* **1982**, *119*, 304.

(5) Martin, C. A.; Golich, T. G.; Jaeger, D. A. *J. Colloid Interface Sci.* **1984**, *99*, 561.

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