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

David A. Jaeger,* Craig A. Martin, and Timothy G. Golich

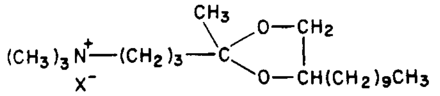
*Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071*

*Received February 27, 1984*

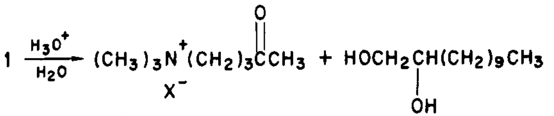
Surfactant-based organized media containing micelles,[1] inverse micelles,[1b,2] and microemulsions[1f,3] have been used infrequently in preparative chemistry. However, the abilities of these media to solubilize, orient, and compartmentalize reactants offer the potential of reactivity control not attainable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



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

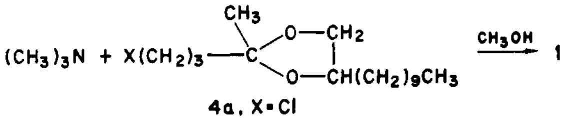


$$1 \xrightarrow[H_2O]{H_3O^+} (CH_3)_3\overset{+}{N}(CH_2)_3\overset{O}{\overset{\|}{C}}CH_3\ X^- + HOCH_2\underset{OH}{\underset{|}{C}H}(CH_2)_9CH_3$$

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

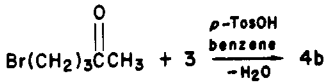
3

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 = $OSO_2CH_3$

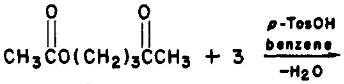
The reaction of 5-bromo-2-pentanone (**5**) with diol **3** yielded bromo ketal **4b** which was converted to **1b** with $Me_3N$ in MeOH at 25 °C. Surfactant **1b** was much less hygroscopic than **1a** and had a critical micelle concentration (cmc) in 0.01 M $NaHCO_3$ of 2.7 × $10^{-3}$ M (without hysteresis).



$$Br(CH_2)_3\overset{O}{\overset{\|}{C}}CH_3 + 3 \xrightarrow[-H_2O]{p\text{-TosOH, benzene}} 4b$$

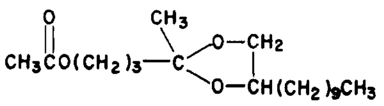
5

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



$$CH_3\overset{O}{\overset{\|}{C}}O(CH_2)_3\overset{O}{\overset{\|}{C}}CH_3 + 3 \xrightarrow[-H_2O]{p\text{-TosOH, benzene}}$$

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.

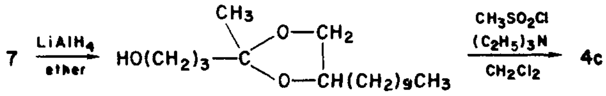
(3) For examples, see: (a) Gonzalez, A.; Holt, S. L. *J. Org. Chem.* **1982**, *47*, 3186. (b) Martin, C. A.; McCrann, P. M.; Angelos, G. H.; Jaeger, D. A. *Tetrahedron Lett.* **1982**, *23*, 4651. (c) Jaeger, D. A.; Ward, M. D.; Martin, C. A. *Tetrahedron*, in press, and references therein.

(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.

0022-3263/84/1949-4545$01.50/0 © 1984 American Chemical Society

transformed into methanesulfonate ketal **4c**. The reaction of **4c** with $Me_3N$ in MeOH at 25 °C gave **1c**. Its cmc in 0.01 M $NaHCO_3$ was ca. $3 \times 10^{-3}$ M (slight hysteresis), and characterization also included fast atom bombardment (FAB) mass spectrometry. Peaks of interest occurred at $m/z$ 328 and 751. The latter corresponds to an adduct of the complete molecule and the surfactant cation [i.e., $(C_{20}H_{42}NO_2^+CH_3SO_3^-)C_{20}H_{42}NO_2^+$] and the former to the surfactant cation as determined by a high resolution measurement. Analogous peaks were observed in the FAB spectrum of hexadecyltrimethylammonium bromide, a typical quanternary ammonium surfactant.



**8**

It is anticipated that "destructible" surfactants **1a–c** will have catalytic abilities analogous to those of other ketal-based systems.[4b] Compound **1c** is an especially attractive catalyst. Since methanesulfonate is a very poor nucleophile, unlike the halide counterions of **1a** and **1b**, **1c** can be used to formulate media for nucleophilic displacement reactions.[3b] The lability of the ketal function under acidic conditions in micellar and microemulsion media was demonstrated with **1c** (see Experimental Section).

## Experimental Section

**General Procedures.** All melting and boiling points are uncorrected. The $^1H$ NMR spectra were obtained at 270 MHz on a JEOL FX-270 spectrometer with $Me_4Si$ and sodium 3-(trimethylsilyl)propionate-*2,2,3,3-d*$_4$ (TSP) as internal standards in nonaqueous solvents and $D_2O$, respectively. The FAB and chemical ionization (CI) mass spectra were obtained at the Midwest Center for Mass Spectrometry at the University of Nebraska–Lincoln. The cmc's were determined from a plot of surface tension (du Noüy ring) vs. the log of surfactant concentration using a Cahn Model RM-2 electrobalance equipped with a Cahn Model 2370 surface tension accessory. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

**[3-(4-Decyl-2-methyl-1,3-dioxolan-2-yl)propyl]trimethylammonium Chloride (1a).** A solution of 18.0 g (59.0 mmol) of **4a**[4b] in 200 mL of 25% (w/v) $Me_3N$–MeOH [50 g (0.85 mol) of $Me_3N$] was held at 45 °C for 2 days in an autoclave. After rotary evaporation, the resultant dark brown solid was dried at 85 °C (0.1 mmHg) and recrystallized twice from MeOH at −15 °C to yield 9.2 g (43%) of **1a** as a very hygroscopic yellow powder: mp 170–177 °C (sealed tube); $^1H$ NMR ($CDCl_3$) $\delta$ 3.95–4.18 (m, 2 H, $OCH_2$), 3.37–3.65 (m + s at 3.48, 12 H total, $(CH_3)_3N$, $NCH_2$, and OCH), 1.55–1.92 (m, 4 H, $NCH_2CH_2CH_2$), 1.15–1.55 (m containing a large singlet at 1.26 and singlet shoulders at 1.31 and 1.34, 21 H total, $(CH_2)_9$ and $OCCH_3$), 0.88 (t, 3 H, $CH_3$); IR (Nujol) 1295 (m), 1245 (m), 1210 (m), 1127 (m), 1110 (m), 1056 (s), 976 (m), 961 (m), 900 (m), 848 (w), 724 $cm^{-1}$ (w).

Attempts to purify **1a** further (recrystallization from other solvents, Norit treatment in EtOAc–$Me_2CO$, column chromatography on $Al_2O_3$, and foam fractionation[7]) were unsuccessful. Since this material was both impure and very hygroscopic, it was converted to the perchlorate analogue **1d**.

**[3-(4-Decyl-2-ethyl-1,3-dioxolan-2-yl)propyl]trimethylammonium Perchlorate (1d).** To a solution of 383 mg (1.05 mmol) of **1a** in 3 mL of 3 M $NH_4OH$ was added 1.5 mL of 1.5 M $NaClO_4 \cdot H_2O$. The resultant yellow precipitate was dried at 70 °C (0.1 mmHg) to give 300 mg (65%) of crude **1d**. This material was recrystallized from 3:1 (v/v) EtOAc–hexane at 25 °C to give 206 mg (46%) of **1d** as a white powder after drying. It exhibited unusual melting behavior: 72 °C, softening; 107 °C, transition to a turbid, blue gel; 180 °C, dec. Anal. Calcd for $C_{20}H_{42}NO_6Cl$: C, 56.12; H, 9.88. Found: C, 56.14; H, 9.89.

**5-Bromo-2-pentanone (5).**[8] A literature procedure[9] was used to prepare (50%) **5** from 2-acetylbutyrolactone (Aldrich). Crude material was used without futher purification.

**2-Methyl-2-(3-bromopropyl)-4-decyl-1,3-dioxolane (4b).** A solution of 35.8 g (0.217 mol) of **5**, 53.6 g (0.265 mol) of **3** (Aldrich), and 0.458 g (2.66 mmol) of $p$-$CH_3C_6H_4SO_3H \cdot H_2O$ in 275 mL of $C_6H_6$ was refluxed under a Dean–Stark trap and drying tube ($CaCl_2$) for 44 h. After 0.675 g (9.60 mmol) of $KOCH_3$ was added, the reaction mixture was filtered through a 4.5 cm (i.d.) × $C_{16}H_{30}O_2{}^{79/81}Br$ cm column of neutral $Al_2O_3$ (pH 7.4) using 1:9 (v/v) $Et_2O$–hexane as eluant to give 78.6 g (93%) of **4b** as an oil: $^1H$ NMR ($CDCl_3$) $\delta$ 3.98–4.17 (m, 2 H, $OCH_2$), 3.36–3.54 (m, 3 H, $CH_2Br$, CH), 1.55–2.09 (m, $BrCH_2CH_2CH_2$), 1.15–1.55 (m containing a large singlet at 1.28 and singlet shoulders at 1.33 and 1.37, 21 H total, $(CH_2)_9$ and $OCCH_3$), 0.88 (t, 3 H, $CH_3$); IR (neat) 2925 (s), 2850 (s), 1460 (m), 1375 (m), 1290 (m), 1250 (m), 1200 (m), 1100 (m), 1050 (m), 885 (m), 675 $cm^{-1}$ (m); high-resolution mass spectrum (CI) calcd for $C_{16}H_{30}O_2{}^{79/81}Br$ 333.1429 and 335.1409, found 333.1448 and 335.1390; calcd for $C_{14}H_{27}O_2$ 227.2011, found 227.2033. These compositions correspond to fragment ions resulting from the loss of $CH_3$ and $CH_2CH_2CH_2Br$; a molecular ion was not observed.

**[3-(4-Decyl-2-methyl-1,3-dioxolan-2-yl)propyl]trimethylammonium Bromide (1b).** A solution of 65.6 g (0.186 mol) of **4b** in 225 mL of 25% (w/v) $Me_3N$–MeOH was allowed to stand at 25 °C for 22 h. Then an additional 225 mL of $Me_3N$–MeOH was added, and the solution was refluxed for 6 h under an $Me_2CO$–dry ice condenser. Rotary evaporation left 71.3 g of a yellow solid that was treated 3 times with Norit in EtOAc and then recrystallized from EtOAc to give 47.1 g (63%) of **1b**: mp 150–200 °C dec;[10] $^1H$ NMR ($CDCl_3$) $\delta$ 3.95–4.18 (m, 2 H, $OCH_2$), 3.38–3.69 (m + s at 3.50, 12 H total, $(CH_3)_3N$, $NCH_2$, and OCH), 1.55–2.03 (m, 4 H, $NCH_2CH_2CH_2$), 1.11–2.03 (m containing a large singlet at 1.28 and singlet shoulders at 1.37 and 1.40, 21 H total, $(CH_2)_9$ and $OCCH_3$), 0.88 (t, 3 H, $CH_3$); IR (Nujol) 1295 (w), 1240 (m), 1160 (w), 1130 (m), 1060 (m), 960 (m), 900 (w), 840 $cm^{-1}$ (w). Anal. Calcd for $C_{20}H_{42}O_2NBr$: C, 58.81; H, 10.37. Found: C, 58.89; H, 10.39.

**5-Acetoxy-2-pentanone (6).** A literature procedure[11] was used to prepare (66%) **6** from 5-hydroxy-2-pentanone (Aldrich): bp 96–99 °C (15 mmHg) [lit.[11] 105–107 °C (17–18 mmHg)].

**2-Methyl-2-(3-acetoxypropyl)-4-decyl-1,3-dioxolane (7).** A solution of 45.2 g (0.314 mol) of **6**, 64.2 g (0.317 mol) of **3**, and 389 mg (2.04 mmol) of $p$-$CH_3C_6H_4SO_3H \cdot H_2O$ in 100 mL of $C_6H_6$ was refluxed for 41 h under a Dean–Stark trap and drying tube ($CaCl_2$). After 0.646 g (9.21 mmol) of $KOCH_3$ was added, filtration of the reaction mixture through a 3.2 cm (i.d.) × 22 cm column of neutral $Al_2O_3$ (pH 7.4) packed in hexane with 750 mL of 1:3 (v/v) $Et_2O$–hexane as eluant gave 89.4 g (87%) of **7** as a yellow oil which was used without further purification: $^1H$ NMR ($CDCl_3$) $\delta$ 3.97–4.13 (m, 4 H, $CH_2OCO$ and $OCH_2CH$), 3.35–3.55 (m, 1 H, OCH), 2.04 (s, 3 H, $CH_3CO$), 1.55–1.80 (m, 4 H, $OCH_2CH_2CH_2$), 1.15–1.55 (m containing a large singlet at 1.26 and singlet shoulders at 1.34 and 1.37, 21 H total, $(CH_2)_9$ and $OCCH_3$), 0.88 (t, 3 H, $CH_3$); IR (neat) 2930 (s), 2860 (m), 1750 (s), 1470 (w), 1460 (w), 1380 (w), 1280 (s), 1050 (m), 795 (w), 660 $cm^{-1}$ (w). An analytical sample was obtained by preparative GLC (205 °C, 6 ft × $^1/_4$ in. 4% SE-30 on 60-80 mesh AW Chromosorb W). Anal. Calcd for $C_{19}H_{36}O_4$: C, 69.47; H, 11.05. Found: C, 69.39, 69.40; H, 11.07, 11.08.

**2-Methyl-2-(3-hydroxypropyl)-4-decyl-1,3-dioxolane (8).** In standard fashion, reduction of 79.1 g (0.241 mol) of **7** with 11.9 g (0.315 mol) of $LiAlH_4$ in $Et_2O$ yielded 57.6 g (83%) of **8** as an oil which was used without further purification: $^1H$ NMR ($CDCl_3$) $\delta$ 3.98–4.15 (m, 2 H, $OCH_2CH$), 3.55–3.68 (m, 2 H, $CH_2OH$),

---

(6) Attempts to form **8** directly from **3** and 5-hydroxy-2-pentanone failed.

(7) Rosen, M. J.; Goldsmith, H. A. "Systematic Analysis of Surface-Active Agents", 2nd ed.; Wiley Interscience: New York, 1972; p 52.

(8) Jäger, H.; Keymer, R. *Arch. Pharm.* (*Weinheim*) **1960**, *293*, 896.

(9) Cannon, G. W.; Ellis, R. C.; Leal, J. R. In "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 597.

(10) The exact mp range depended on the crystalline form of the sample, which was a mixture of diastereomers, as evidenced by the two Me singlets in the $^1H$ NMR spectrum.

(11) Elderfield, R. C.; Gensler, W. J.; Brody, F.; Head, J. D.; Dickermann, S. C.; Weiderhold, L.; Kremer, C. B.; Hageman, H. A.; Kreysa, F. J.; Griffing, J. M.; Kupchan, S. M.; Newman, B.; Maynard, J. T. *J. Am. Chem. Soc.* **1946**, *68*, 1579.

3.40–3.51 (m, 1 H, OCH), 2.95 (br s, 1 H, OH), 1.55–1.81 (m, 4 H, $OCH_2CH_2CH_2$), 1.13–1.55 (m containing a large singlet at 1.27 and singlet shoulders at 1.32 and 1.36, 21 H total, $(CH_2)_9$ and $OCCH_3$), 0.88 (t, 3 H, $CH_3$); IR (neat) 3390 (m), 2910 (s), 2880 (s), 1452 (m), 1370 (m), 1295 (w), 1240 (m), 1195 (m), 1050 (s), 890 (w), 705 cm$^{-1}$ (w); high-resolution mass spectrum (CI) calcd for $C_{17}H_{34}O_3$ 286.2508, found 286.2493.

**2-Methyl-2-[3-(methylsulfonyl)propyl]-4-decyl-1,3-dioxolane (4c).** According to a standard procedure,[12] 20.2 g (70.4 mmol) of **8** was converted into 21.5 g (85%) of **4c**, which decomposed rapidly at 25 °C and slowly at 0 °C. It was used without further purification: $^1H$ NMR ($CDCl_3$) $\delta$ 4.21–4.31 (m, 2 H, $CH_2OSO_2$), 3.96–4.15 (m, 2 H, $OCH_2$), 3.39–3.53 (m, 1 H, OCH), 3.01 (s, 3 H, $CH_3SO_2O$), 1.69–1.95 (m, 4 H, $OCH_2CH_2CH_2$), 1.12–1.53 (m containing a large singlet at 1.26 and singlet shoulders at 1.31 and 1.35, 21 H total, $(CH_2)_9$ and $OCCH_3$), 0.88 (t, 3 H, $CH_3$); IR (neat) 2910 (s), 2850 (m), 1460 (w), 1350 (s), 1170 (s), 1040 (w), 965 (m), 910 (m), 810 (m), 710 cm$^{-1}$ (w).

**[3-(4-Decyl-2-methyl-1,3-dioxolan-2-yl)propyl]trimethylammonium Methanesulfonate (1c).** A solution of 21.5 g (58.9 mmol) of **4c** in 50 mL of 25% (w/v) $Me_3N$-MeOH was allowed to stand for 4 days at 25 °C. Then an additional 50 mL of $Me_3N$-MeOH was added, and the solution was refluxed for 6 h under an $Me_2CO$–dry ice condenser. Rotary evaporation, followed by drying at 85 °C (0.1 mmHg) left a residue that was recrystallized from 9:1 (v/v) and then from 19:1 (v/v) EtOAc–MeOH to yield 17.9 g (72%) of **1c**: mp 140–144 °C (sealed tube); $^1H$ NMR ($CDCl_3$) $\delta$ 3.96–4.16 (m, 2 H, $OCH_2$), 3.35–3.55 (m + s at 3.34, 12 H total, $(CH_3)_3N$, $NCH_2$, and OCH), 2.72 (s, 3 H, $CH_3SO_3^-$), 1.55–1.91 (m, 4 H, $NCH_2CH_2CH_2$), 1.12–1.55 (m containing a large singlet at 1.26 and singlet shoulders at 1.31 and 1.35, 21 H total, $(CH_2)_9$ and $OCCH_3$), 0.88 (t, 3 H, $CH_3$); IR (Nujol) 1185 (s), 1110 (w), 1040 (s), 950 (w), 895 (w), 825 (w), 760 cm$^{-1}$ (s); high-resolution mass spectrum (FAB) calcd for $C_{20}H_{42}NO_2$[13] 328.3215, found 328.3234. Anal. Calcd for $C_{21}H_{45}NO_5S\cdot0.5H_2O$: C, 58.30; H, 10.72. Found: C, 58.42, 58.39; H, 10.50, 10.49.

**Hydrolysis of Micellar 1c.** A solution of 191 mg (0.450 mmol) of **2c** in 50 mL of 5% aqueous HCl was prepared and immediately extracted with 25 mL of $Et_2O$. The mixture foamed but cleanly separated into two layers within 15 min. The aqueous layer was further extracted with five 15 mL-portions of $Et_2O$ with 15 min between extractions. The combined extracts were dried ($Na_2SO_4$) and rotary evaporated to yield 94 mg (103%) of crude **3**, mp 58–59 °C (lit.[14] mp 60–61 °C). The aqueous solution was rotary evaporated to give 114 mg of a yellow oil which by $^1H$ NMR ($D_2O$) contained **2c** (**2a**).

**Hydrolysis of 1c in a Microemulsion.** A microemulsion composed of 1.02 g (2.41 mmol) of **1c**, 1.03 g of 1-butanol, 0.40 g of hexane, and 7.60 g of 0.01 M $NaHCO_3$ was equilibrated at 40 °C.[15] Then 5 mL of 5% HCl was added, and the mixture was extracted with 5 mL of $Et_2O$. Clean separation of layers occurred within 5 min, and the aqueous layer was then extracted immediately with three 5-mL portions of $Et_2O$ and 1 h later with 5 mL of $Et_2O$. The combined $Et_2O$ extracts were dried ($Na_2SO_4$) and yielded 267 mg (56%) of **3**, mp 58.0–59.5 °C. After the aqueous layer sat overnight at 25 °C, it was extracted with three 5-mL portions of $Et_2O$. The combined extracts were dried ($Na_2SO_4$) and yielded 173 mg (36%) of **3**, mp 57.5–59.0 °C.

For both this and the above hydrolysis, control extractions were performed with the substitution of $H_2O$ for 5% HCl. In each case, persistent emulsions did not form. This behavior is fortuitous and not to be generally expected.[1e,4b,16]

**Acknowledgement** is made to the U.S. Army Research Office, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Marathon Oil Company for support of this research.

**Supplementary Material Available:** Spectral data ($^1H$ NMR and IR) for **1d** and the preparation and characterization of **2a**, **2b**, **2c**, (4-oxopentyl)trimethylammonium tetraphenylborate, and tetramethylammonium methanesulfonate (3 pages). Ordering information is given on any current masthead page.

---

[12] Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

[13] This composition corresponds to that of the surfactant cation (see text).

[14] Swern, D.; Billen, G. N.; Scanlan, J. T. *J. Am. Chem. Soc.* **1946**, *68*, 1504.

[15] For a complete pseudoternary phase diagram, see ref. 5.

[16] Martin, C. A.; McCrann, P. M.; Ward, M. D.; Angelos, G. H.; Jaeger, D. A. *J. Org. Chem.*, **1984**, in press.

---

# Reaction of 1,1,1-Trichloro-3-nitro-2-propene with Furans: A Reexamination

Terry M. Balthazor,[1] Bruce Gaede,*[1] Donald E. Korte,[1] and Huey-Sheng Shieh[2]

*Monsanto Co., St. Louis, Missouri 63167*

*Received May 8, 1984*

We have recently examined the chemistry of 1,1,1-trichloro-3-nitro-2-propene (**1**).[3-5] Burkett and Wright[3] report that furan (**2a**), 2,5-dimethylfuran (**2b**), and 2-chlorobutadiene with **1** give only starting materials under a variety of conditions. Other workers[6] have reported on the facile reaction of nitroethylene with furans, and a report has appeared[7] on the reaction of 2,3,4,5-tetramethylfuran with **1**. In contrast to the results of Burkett and Wright we find that equimolar amounts of **1** and furans **2a–c** condense at room temperature in the absence of solvents to give Diels–Alder adducts cleanly and in good yield (Scheme I).

Furan (**2a**) and **1** are observed (by $^1H$ NMR) to react slowly, reaching an equilibrium at 90% conversion after 14 days at room temperature. Two products are observed to form in a ratio of 1.2:1, and the ratio does not change throughout the course of the reaction. The adducts **3a** and **4a** may be separated by preparative liquid chromatography in 45% and 41% isolated yields, respectively. Their structures are assigned by consideration of the coupling of the protons adjacent to the nitro and trichloromethyl groups with the adjacent bridgehead protons. Thus the $CHNO_2$ signal of **3a** at 4.65 is a doublet with $J = 4.4$ Hz and the $CHCCl_3$ signal at 4.48 is a double doublet with $J = 4.4$ and 4.4 Hz. Since endo protons in bicyclo[2.2.1]heptanes couple with their adjacent bridgehead protons with $J = 0$–2 Hz and exo protons couple with $J = 4$–7 Hz,[6] the $CHCCl_3$ proton must be exo, and the $CHNO_2$ proton must be endo, consistent with structure **3a**. The nitroolefin **1** is trans, and the coupling of 4.4 Hz is consistent with the expected 3–6 Hz trans coupling in substituted bicyclo[2.2.1]heptanes.[6]

Condensation of 2,5-dimethylfuran (**2b**) and **1** reaches equilibrium at 81% conversion after 11 days. A single product is observed in the $^1H$ NMR throughout the course of the reaction; however, no structural assignment can be made from analysis of the spectrum. The product crystallizes after chromatography, and an X-ray crystal structure analysis (Figure 1) results in assignment of structure **3b**.

The reaction of 2-methylfuran (**2c**) and **1** is much faster, reaching 83% conversion after 4 h. A 4:1 ratio of **3c** and **4c** is formed, and this ratio does not vary throughout the course of the reaction. The structures are assigned by $^1H$

---

[1] Research Department, Monsanto Agricultural Products Co.

[2] Corporate Research Laboratories, Monsanto Co.

[3] Burkett, H.; Wright, W. *J. Org. Chem.* **1960**, *25*, 27.

[4] Dudinskaya, A. A.; Novikov, S. S.; Shvekhgeimer, G. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1965**, 2024.

[5] Viktorova, N. M.; Knyazeve, S. P.; Zefirov, N. S. *Zh. Org. Khim.* **1972**, *8*, 944.

[6] Eggltе, T. A.; de Koning, H.; Huisman, H. O. *Heterocycles* **1976**, *4*, 19.

[7] Yur'ev, Y. Y.; Zefirov, N. S.; Ivanova, R. A. *Zh. Obshch. Khim.* **1962**, *33*, 3512.

0022-3263/84/1949-4547$01.50/0 © 1984 American Chemical Society