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Organic Reactivity in Microemulsion Systems

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Abstract: Sulfides are oxidized at a remarkably fast rate (<15 s, 23 °C) when dissolved in an oil-in-water microemulsion containing a 2-fold excess of hypochlorite. Sulfoxide is formed exclusively and quantitatively. As much as 1 mL of sulfide can be oxidized by 15 mL of microemulsion. The process is much faster than phase-transfer catalysis and requires no stirring since the microemulsions are homogeneous. The cosurfactant in the microemulsion (a low molecular weight alcohol) is shown to play a central role in the oxidation by acting as an intermediary between the oil-soluble mustard and the water-soluble hypochlorite. The microemulsion-based method is simple, cheap, mild, selective, and rapid. These properties arise from the fact that microemulsions represent a "community" of molecules that function only by virtue of cooperative action. Each of the six components (water, hydrocarbon, surfactant, cosurfactant, oxidant, and sulfide) has its own particular residence site and its own particular role in the reaction. Self-assembly converts what might have been a useless and intractable mixture into a functioning system that destroys objectionable compounds.

Introduction

From the atomic level, to molecules, to colloids, and ultimately to the cell, one can trace an ever richer design. The sequence involves an increasing organization of matter in which each member is comprised of parts belonging to the preceding level. This organization remains one of the great riddles of the universe. In the words of W. H. Thorpe: "The behavior of large and complex aggregates of elementary particles is not to be understood as a simple extrapolation of the properties of a few particles. Rather, at each level of complexity entirely new properties appear." It is our purpose here to exploit the properties of a multicomponent system to destroy mustard, a loathsome compound being produced worldwide. Operation of the system depends on six entities (water, hydrocarbon, surfactant, cosurfactant, oxidant, and mustard) working in concert within an array of self-organizing molecules. Oxidative destruction of mustard is rapid, cheap, selective, and mild. The strategy appears to have general utility in preparative organic chemistry.[1]

Over the years our research group has examined a variety of organic systems, including micelles, vesicles, films, water pools, laminates, polyaphrons, polymeric systems, and microemulsions. The work is reviewed elsewhere.[2] In the present article, we will focus on only one type of system, the microemulsion. Since microemulsions are not commonplace in "mainstream" organic chemistry, the discussion will begin with a brief description of what they are and why they attracted our attention.

Results and Discussion

A microemulsion is an isotropic and optically clear dispersion of oil-in-water (O/W) or water-in-oil (W/O), where "oil" is a hydrocarbon.[3] The name "microemulsion" derives from the fact that oil droplets in O/W systems or water droplets in W/O systems are small (50–500 Å). Microemulsions are thermodynamically stable, and they remain clear indefinitely. They form spontaneously when the following four components are mixed in specific proportions: water, oil, surfactant, and cosurfactant (generally a low molecular weight alcohol). Figure 1 shows the structure of an O/W microemulsion. The presence of a cosurfactant is critical in reducing the interfacial tension between the droplets and the continuous phase to near zero. In the absence of cosurfactant at the droplet interface, the emulsions become milky and unstable owing to the creation of much larger droplets.

How does one know what proportion of the four components to use? It is possible, of course, to take microemulsion recipes from the abundant literature on the subject.[4] We found it just as simple to develop our own by "titration". Thus, microemulsions were prepared on a 100-g scale by weighing a mixture of alcohol, surfactant, and hydrocarbon into a 250-mL Erlenmeyer flask. This white slurry was swirled into a smooth paste. Water was then added with mild agitation to achieve clarity. A few minutes of sonication was used occasionally to hasten the process. Table I gives the percentage composition by weight of 10 microemulsions examined in our work.

Table I. Percentage Composition by Weight of 10 Microemulsions[a]

ME	water	hydrocarbon[b]	surfactant[c]	cosurfactant[d]
1	82.1	3.2, C_6	4.9, SDS	9.8, B
2	68.9	10.9, C_{12}	10.9, SDS	9.3, P
3	60.0	4.0, C_{16}	18.0, CTAB	18.0, B
4	60.0	4.0, C_{16}	23.6, Brij-96	12.4, B
5	43.2	10.4, C_{16}	14.8, SDS	31.6, H
6	29.6	11.9, nC_6	0	58.5, iPr[e]
7	28.0	5.0, nC_6	37.0, CTAB	30.0, B
8	15.1	67.8, C_7	17.1, AOT	0
9	10.0	41.3, nC_6	0	48.7, iPr[e]
10	5.3	79.9, C_6	4.9, SDS	9.8, B

[a] For data on 17 other microemulsions, see: Elrington, A. R. *Rapid Deactivation of Mustard in Microemulsion Technology*, Ph.D. Thesis, Emory University, Atlanta, GA, 1990. [b] C_6 = cyclohexane; nC_6 = *n*-hexane; C_7 = *n*-heptane; C_{12} = *n*-dodecane; C_{16} = *n*-hexadecane. [c] SDS = sodium dodecyl sulfate; CTAB = cetyltrimethylammonium bromide; Brij-96 = $CH_3(CH_2)_7CH{=}CH(CH_2)_8(OCH_2CH_2)_{10}OH$; AOT 1,4-bis(2-ethylhexyl) sodium sulfosuccinate. [d] B = 1-butanol; P = 1-pentanol; iPr = 2-propanol. [e] These are so-called "surfactantless microemulsions" first described by Smith, G. D.; Donelan, C. E.; Barden, R. E. *J. Colloid Interface Sci.* **1977**, *60*, 488.

Let us examine the main feature of Table I. ME-1, containing 3% cyclohexane and 82% water, can reasonably be regarded as an O/W microemulsion in which cyclohexane microdroplets are dispersed in water. An anionic surfactant (SDS, sodium dodecyl sulfate) and an alcoholic cosurfactant (1-butanol) serve as the dispersants. ME-10, with 5% water and 80% cyclohexane, is no doubt a W/O microemulsion. When the amounts of water and oil are similar, there can be uncertainty as to the O/W or W/O identity of the microemulsion.[5] Note that three types of surfactants (anionic, cationic, and nonionic) were used to make the microemulsions, as exemplified by SDS, CTAB (cetyltrimethylammonium bromide), and Brij-96 (a long-chain polyether), respectively. Cosurfactants consisted of 2-propanol (iPr), 1-butanol (B), or 1-pentanol (P). One microemulsion, ME-8, is exceptional

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(5) So-called "bicontinuous" structures can also form in midrange microemulsions. See: Bodet, J.-F.; Bellare, J. R.; Davis, H. T.; Scriven, L. E.; Miller, W. G. *J. Phys. Chem.* **1988**, *92*, 1898.

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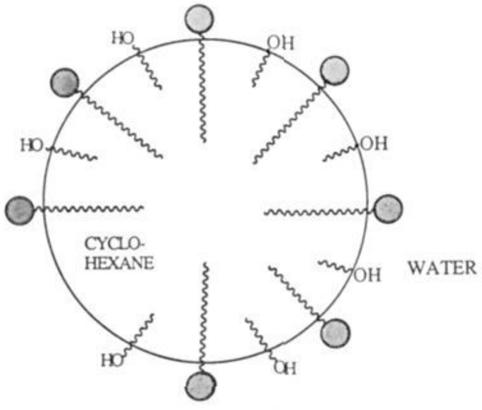

Figure 1. Schematic representation of an oil-in-water microemulsion stabilized by a long-chain surfactant and an alcoholic cosurfactant.

in that it contains no cosurfactant at all. More will be said later of this microemulsion because it was important in certain mechanistic considerations.

Since a wide selection of oils, surfactants, and cosurfactants is available and since their relative concentrations can be varied almost continuously, an inexhaustible assortment of microemulsions is possible. The microemulsions in Table I were formulated rather arbitrarily, the only guiding principle being a desire to achieve representative examples of both the O/W and W/O categories. A full description of the various microemulsion systems would, of course, have entailed the construction of phase diagrams, a laborious task unnecessary for our specific purposes.

Microemulsions were prepared in the hopes of using them as media for organic reactions. This is hardly a new idea; in the past decade several other groups have studied reactions in microemulsions.[6] Our own interest focused on exploiting microemulsions for a problem of considerable practical importance: the detoxification of mustard, a chemical warfare agent known since World War I and deployed even in recent times. Actually, mustard destruction constitutes a challenging problem in organic reactivity that goes far beyond mustard itself. But before elaborating on this point, it might be useful to state briefly certain properties of mustard. Mustard is a potentially fatal vesicant that damages the skin, eyes, and respiratory tract.[7] Blood-forming tissues (marrow, lymph nodes, and spleen) are particularly sensitive to the cytotoxic alkylating properties of mustard. Small repreated doses are cumulative. Unfortunately, mustard can by synthesized by "garbage can chemistry" with cheap and commonly available reagents (eq 1). Although less toxic than nerve agents, mustard

$$\mathrm{HOCH_2CH_2Cl} \xrightarrow[\text{2. HCl}]{\text{1. Na}_2\text{S}} \underset{\text{mustard}}{\mathrm{ClCH_2CH_2SCH_2CH_2Cl}} \qquad (1)$$

is more "persistent" in the environment; compounds lying on a water surface, exposed to sunlight and oxygen, can remain unchanged for months.

We did not work directly with mustard but, instead, with the less dangerous "half-mustard" that manifests similar chemistry. Even half-mustard, however, should be handled with care in a hood.

$$\underset{\text{half-mustard}}{\mathrm{CH_3CH_2SCH_2CH_2Cl}}$$

Mustard detoxification is more than a pressing technological problem; it also exemplifies an interesting and general problem in organic reactivity. Under laboratory conditions where rates are usually measured at low substrate concentrations (e.g., 10^{-5}–10^{-3} M), mustard is susceptible to rapid hydrolytic deactivation. Thus, Bartlett in 1949 found a half-life of only 3 min at 25 °C in 5% acetone–water.[8] How does this substantial reactivity coincide with the "persistent" nature of mustard that allows it to remain for months on a water surface? The answer lies in the low solubility of mustard in water (0.0043 M at 25 °C). Mustard dissolves so sparingly in water (and interfacial hydrolysis in a mustard–water slurry is so slow) that mustard resting upon a water surface persists for months, not minutes. Adding base to the water actually retards the hydrolysis further (perhaps because the elevated ionic strength reduces the solubility). The problem then resolves to *achieving reasonable deactivation rates when environmentally realistic amounts of material are involved*. We referred above to this being a general problem in organic reactivity because many inherently reactive and potentially dangerous compounds fail to react owing mainly to insolubility.

One possible means for accelerating hydrolysis would be, seemingly, to solubilize the mustard in water with a surfactant. Surfactants in aqueous solutions form micellar aggregates that are capable of binding water-insoluble compounds such as mustards. Micellar catalysis subsequent to such binding is well-documented.[9] Unfortunately, this tactic proved unsuccessful with mustards; micelle-solubilized mustard is virtually inert to hydrolysis. Apparently, the apolar substrate finds its way into the hydrocarbon core of the micelles where formation of the ionic episulfonium ion (an intermediate in mustard solvolysis[10]) is impeded. Although micelles do indeed solubilize mustard, they also kill the reaction.

The above considerations forced us to adopt another strategy, an oxidative one, for deactivating mustards. It was known that the sulfoxide corrresponding to mustard is far less toxic than the parent sulfide.[7] Thus, one could hope to oxidize mustard to its sulfoxide and hence remove the biological threat. Incidentally, since mustard sulfone is an irritant (although not as dangerous as mustard itself), further oxidation to the sulfone would be best avoided in any viable decontamination regimen.

Converting from a hydrolytic to an oxidative method avoids the need for solubilizing mustard in a water-rich medium. One could well imagine an oxidizing agent (e.g., *tert*-butyl hydroperoxide) capable of reaching and destroying a sulfide even if the sulfide were buried in the hydrocarbon-like core of a micelle. But micelles have another serious deficiency that adversely affects their usefulness: micelles are capable of solubilizing only small amounts of substrate. Thus, 0.01–0.10 M surfactant will, typically, enhance water-solubility by only 1 mM or less. Macrocyclic hosts and cyclodextrins are similarly lacking in solubilization capacity.[11] It might be possible, of course, to stir an aqueous solution of a surfactant or host with an insoluble layer of mustard. The hope would be that a mustard molecule reacts within a micelle or host, the product departs, and a new mustard molecule from the insoluble layer is allowed to enter the water à la Le Chatelier. Such a procedure has numerous drawbacks for use in the field, not the least of which is the need for constant stirring. We were, therefore, forced to adopt microemulsion systems which, as will now be demonstrated, permitted the dissolution and destruction of mustard at realistic and useful levels.

One may ask whether our self-imposed requirement for "realistic and useful levels" is appropriate for a research program (and journal) devoted to basic chemistry. We have never felt, in this regard, that encounters with the real world in any way devalues

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Table II. Oxidation of Half-Mustard by *tert*-Butyl Hydroperoxide[a] and Hypochlorite[b] in Microemulsion Systems at 23 °C

	reaction time[c]	
microemulsion[c]	*tert*-butyl hydroperoxide	hypochlorite[d]
1	5 min	<15 s
2	25 min	5 min
3	60 min	<15 s
4	80 min	<15 s
5	60 min	
6		<15 s
7		<15 s
8		>6 h
9		<15 s
10		>6 h

[a] Half-mustard (0.25 g, 2.0 mmol); 15.0 mL of microemulsion; *tert*-butyl hydroperoxide (0.28 g, 2.2 mmol); $\mathrm{VO(acac)_2}$ (0.038 g, 0.14 mmol); acetic acid (0.2 mL). [b] Half-mustard (0.18 g, 1.45 mmol); NaOCl (4.0 mL of 5.3% bleach, 2.9 mmol); 15.0 mL of microemulsion. [c] Time for complete destruction of half-mustard (6 half-lives). [d] Product is exclusively sulfoxide (no detectable sulfone).

the science. David F. Horrobin wrote: "Many now suffer from the illusion that basic discoveries always precede practical research. Historical evidence suggests that the traffic is just as frequently in the other direction".[12]

The microemulsions in Table I (15-mL samples) readily dissolve 1.45 mmol of both half-mustard and dibutyl sulfide. This corresponds to 0.18 and 0.25 mL of substrate, respectively. During the oxidations a few of the microemulsions became cloudy, but this did not seem to impede the rate of the reaction. Up to 1 mL or more of mustard simulant is miscible with microemulsions having >10% oil. Owing to their large volume, oil droplets in the O/W microemulsions (and the continuous oil phase in W/O microemulsions) are capable of dissolving "realistic and useful levels" of water-insoluble organic reactant.

Selection of a suitable oxidizing agent was the last major decision with regard to experimental conditions. Originally, the $\mathrm{VO(acac)_2}$/*tert*-butyl hydroperoxide pair[13] was called upon to effect oxidation. A typical system was composed of a microemulsion from Table I (15 mL), half-mustard (0.25 g, 2 mmol), 70% *tert*-butyl hydroperoxide (0.28 g, 2.1 mmol), $\mathrm{VO(acac)_2}$ (0.038 g, 0.14 mmol), and acetic acid (0.2 mL). Reaction times at room temperature (>6 half-lives) for ME-1, ME-2, and ME-5 (to cite a few examples) were 5 min, 25 min, and 60 min, respectively (Table II). A total reaction time of 5 min meets the Mackay stipulation of "decontamination within a cigarette break".[14]

Oxidations were monitored by ^{1}H NMR. Thus, the destruction of half-mustard could be followed from the decay of the reactant signals at 2.6 (quartet) and 2.8 ppm (triplet) after diluting the sample in acetone-d_6–$\mathrm{CDCl_3}$. The concomitant appearance of sulfoxide was evident from signals at 2.9 (multiplet) and 3.1 ppm (triplet). If sulfone was also produced, then a signal centered at 3.38 ppm was observed. TLC on silica plates (hexane–ethyl acetate–ethanol, 4:2:1) confirmed the NMR analysis. Sulfoxide was isolated by column chromatography (46–88% yield) with ME-1, ME-2, and ME-4.

Oxidation with the $\mathrm{VO(acac)_2}$/*tert*-butyl hydroperoxide pair entailed a long list of components: water, hydrocarbon, surfactant, cosurfactant, half-mustard, $\mathrm{VO(acac)_2}$, acetic acid, and peroxide. Only self-organization spared us from chaos. This brings up the important matter of where the various species are located within the system. The constituents of the O/W microemulsions (water, oil, surfactant, and cosurfactant) are organized as shown in Figure 1 according to decades of work by others.[7] We hasten to add that Figure 1 should not imply that surfactant and cosurfactant reside exclusively at the oil/water interface; interfacial material exists in equilibrium with small and unknown quantities within the continuous and discontinuous phases. Half-mustard is unquestionably located in the oil because its concentration in 15 mL of microemulsion far exceeded the solubility in pure water of equal volume. Partitioning of *tert*-butyl hydroperoxide between water and heptane, determined by iodometric titration, favors the water ($K_{w/h} = 3.3$). Things are not so simple, however, because when 1-pentanol was added to the heptane, partitioning occurred preferentially into the heptane–alcohol phase over the water–alcohol layer. Partitioning of $\mathrm{VO(acac)_2}$, determined spectrophotometrically, favored water over heptane even in the presence of 1-pentanol.

Ultimately, the $\mathrm{VO(acac)_2}$ approach was abandoned, despite its success, because (a) we desired reaction times even faster than 5 min, our best value, and (b) we found a simpler and cheaper oxidant, hypochlorite, that required no catalyst. Expense is often ignored in modern synthetic methodology, but in our case cost was an important consideration.

Upon discovering that hypochlorite oxidized sulfides even faster than did $\mathrm{VO(acac)_2}$/*tert*-butyl hydroperoxide, we immediately switched over to the simpler and more efficient system. Oxidations were performed in the following manner. Aqueous hypochlorite (5% as found in grocery store bleach) was added to half-mustard (0.18 mL) dissolved in 15 mL of microemulsion. Oxidant was used in a 2-fold molar excess over sulfide. As seen in Table II, with many of the microemulsion systems the oxidation was complete in less than 15 s at room temperature. This represents an extremely fast and generally useful protocol.

The key features of the sulfide oxidation are now summarized.

1. The product is exclusively sulfoxide. Within the limits of NMR detection, no sulfone is formed. Selectivity of the microemulsion systems is beneficial from the point of view of converting mustard into the relatively nontoxic sulfoxide.

2. Reaction capacity is excellent, with 15 mL of microemulsion being capable of oxidizing 0.18 mL of sulfide in a homogeneous mixture. This represents a decided advantage over reactions promoted by micelles, cyclodextrin, and synthetic hosts that typically employ substrate levels of 1 mM or less. An even larger scale oxidation was carried out by mixing the following components: butyl sulfide (1.5 mL, 8.7 mmol), 15 mL of ME-2 or ME-6, and 24 mL of 5.3% aqueous hypochlorite. Although the composition of the original microemulsion was altered drastically by the large volume of water needed to provide sufficient oxidant, the mixtures remained homogeneous and the reactions occurred instantaneously. However, considerable amounts of sulfone (32–45%) were formed. Conceivably, sulfone formation could be suppressed here by using a more concentrated hypochlorite solution (and hence less water as in the smaller scale reactions), but the possibility has not yet been tested.

3. All components of the multicomponent system are cheap and readily available. This is an important point, because the system is not catalytic (i.e., the hypochlorite oxidant is consumed stoichiometrically) and because economics is a key consideration in the field if not in the academic laboratory.

4. The microemulsion system circumvents conditions (heating, stirring, irradiation by light, use of anhydrous solvents, etc.) that are debilitative if not fatal for many applications outside the laboratory. For example, one would not want to irradiate a mustard-contaminated surface nor spray it with a heterogeneous mixture that required constant mixing.

5. Surface tensions of ME-1 and ME-5 are low (24 and 22 dyn/cm) compared to that of water (72 dyn/cm) and mustard (42 dyn/cm).[7] This means that the microemulsions will tend to flow into cracks and crevices where toxic substances may be hiding. Water itself will not readily access such areas.

6. If the five above items appear "applied" in nature, then this is certainly not true of the most valuable feature of our system: speed. Both basic and applied chemistry are intimately concerned with new methods for accelerating reactions. To judge the speed of our 15-s maximum reaction times, consider the many months during which mustard can lie dormant in direct contact with water, air, and sunlight. Although this may be an unfair comparison, it does show that mustard is an inherently stable molecule under

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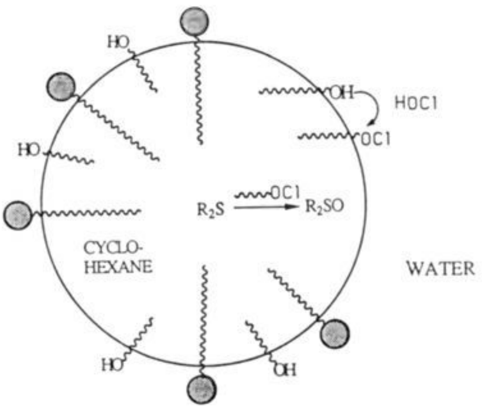

Figure 2. Proposed mechanism for oxidation of mustard by hypochlorite in an oil-in-water microemulsion. The speed of the reaction (see text) can be attributed to a large hydrocarbon/water contact area that permits "communication" between the water-soluble HOCl and the oil-soluble mustard with an interfacial cosurfactant serving as an intermediary.

environmental conditions (and for this reason is termed a "persistent" chemical warfare agent). Perhaps a better comparison would be between our microemulsion reaction and the hypochlorite oxidation of sulfides via phase-transfer catalysis. The best reported reaction time under the latter mode is 20 min.[15] Not only is this much slower than the times in Table II, but phase-transfer catalysis, unlike the microemulsion technology, requires stirring for success.

Why is the microemulsion-based oxidation so fast? Examination of Tables I and II shows that the nature of the surfactant is not critical. Anionic, cationic, and nonionic surfactants (SDS, CTAB, and Brij-96, respectively) are all effective. Reactions in O/W microemulsions were "instantaneous" regardless of surfactant charge. Moreover, a <15-s reaction time was observed with "surfactantless" microemulsions, ME-6 and ME-9. On the other hand, the cosurfactant appeared to play a necessary role apart from stabilizing the microemulsion. ME-8, an unusual microemulsion in that it lacks a cosurfactant, displayed only slow oxidation rates (>6 h). ME-8 contains a unique surfactant, Aerosol-OT, but this cannot be the source of its slow rate because the oxidation was over in less than 15 s with a microemulsion consisting of 56% water, 24% *n*-heptane, 8% Aerosol-OT, and 12% 1-butanol as the cosurfactant. This, plus the fact that pure ethanol was found to be an excellent oxidation medium, suggests that the alcoholic cosurfactant participates in the actual chemistry of the oxidative process.

The most reasonable explanation for our results is that an alkyl hypochlorite[16] forms at the oil/water interface where the cosurfactant is known to reside[3] (Figure 2). Subsequent oxidation of the half-mustard then proceeds either in or on the oil droplets. The speed of the sulfide oxidation can be attributed to a huge hydrocarbon/water contact area (10^9 cm^2/L)[17] that permits "communication" between the water-soluble HOCl and the oil-soluble sulfide with the interfacial cosurfactant serving as the intermediary.[18]

In summary, the O/W microemulsion performs several functions. (a) It solubilizes the water-insoluble substrate into a homogeneous medium containing largely water. (b) The oil droplets offer a huge surface area to the aqueous phase whereby guest substrates can come into contact with water-soluble reagents. (c) Cosurfactant at the interface acts as a chemical messenger in the sense that it covalently accepts the oxidant (Cl^+) and delivers it to the substrate in or on the microdroplet. The summation of the three effects leads to a remarkably fast and potentially useful reactivity. Other hydrophobic materials that contaminate the environment (DDT, PCB, polycyclic aromatics, etc.) might also be amenable to destruction by microemulsion methods.[19]

We conclude by picking up on the theme that began this article. Microemulsions represent a "community" of molecules that function only by virtue of cooperative action. Each of the six components (water, oil, surfactant, cosurfactant, oxidant, and substrate) has its own particular residence site and its own particular role in the reaction. Self-assembly converts what might have been a useless and intractable mixture into a system that can undo what mankind should not have wrought in the first place.

Experimental Section

Only those experimental details not woven into the previous section are presented here. 2-Chloroethyl ethyl sulfide (half-mustard), alcohols, SDS, and CTAB were purchased from Aldrich and used as received. Brij-96 was obtained from Sigma and Aerosol-OT from Fisher; the latter was purified as described previously.[20] VO(acac)$_2$ from Alfa was recrystallized twice from anhydrous acetone. Surface tension measurements were carried out on a Fisher Tensiomat, while NMR monitoring of the reactions was accomplished with the aid of a GE 300-MHz spectrometer. TLC detection of product used silica plates and hexane–ethyl acetate–ethanol (4:2:1) as the eluting solvent (R_f = 0.7 for half-mustard).

Acknowledgment. This work was supported by the Army Research Office. We are also grateful to LASPAU (Latin American Scholarship Program of American Universities) for a fellowship.

Registry No. $CH_3CH_2SCH_2CH_2Cl$, 693-07-2.

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[18] In Brij-96-based microemulsions, both the surfactant and cosurfactant are capable of forming hypochlorites.

[19] For important work on the destruction of DDT in organized media, see: Stadler, E.; Zanette, D.; Rezende, M. C.; Nome, F. *J. Phys. Chem.* **1984**, *88*, 1892.

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