





Figure 1. Microemulsion pseudoternary phase map.

$\text{H}_2\text{O} + \text{KBr}$	aqueous pseudophase
$\text{CTABr} + \text{l-BuOH}$	interphase
hexane + l-BuOH	oil pseudophase

Figure 2. Schematic representation of an idealized microemulsion.

adapted from Bunton and de Buzzaccarini,<sup>6</sup> can be applied, where  $V_i$  is the total interphase volume in a reaction mixture.<sup>7</sup> The fraction of l-butanol in the interphase was estimated by  $^{13}\text{C}$  NMR (67.8 MHz) according to eq 3.<sup>8</sup> The terms  $X_i$  and  $X_o$  are the mole fractions of l-butanol in the interphase (polar) and oil pseudophase (nonpolar), respectively;  $\delta_i$ ,  $\delta_o$ , and  $\delta_{\text{obs}}$  are the chemical shifts (ppm vs.  $\text{Me}_4\text{Si}$ ) of carbon-1 of l-butanol in a polar environment, in a nonpolar environment, and in a microemulsion, respectively.<sup>9</sup> Values of  $V_i$  were then calculated using the molar volumes of micellar CTABr (364 mL/mole)<sup>10</sup> and l-butanol (92 mL/mole, from its density). If the minor amounts of dissociation of  $\text{Br}^-$  from the interphase are neglected,<sup>11</sup> values of  $k_2$  are obtained as listed in Table 1 along with values of  $\delta_{\text{obs}}$ ,  $X_i$ , and  $V_i$ .

$$k_2 = k_\psi V_i / (\text{moles } \text{Br}^- \text{ bound to interphase}) \quad (2) \quad \delta_{\text{obs}} = X_i \delta_i + X_o \delta_o \quad (3)$$

In runs 1-6, the decreases in both  $k_\psi$  and  $k_2$  as the fraction of hexane increases probably reflect a dilution effect. As the volume of the interphase decreases relative to that of the oil pseudophase, the fraction of 1 in the former, the reactive site, decreases also. Relative to  $k_2$  for the reaction in aqueous CTABr micelles (run 7), those for the microemulsions are uniformly lower, again most likely due to a dilution effect. It is interesting to note the similarity of the  $k_2$  values for runs 7 and 9; within the micellar pseudophase the reaction is neither catalyzed nor inhibited relative to that in aqueous ethanol.

**Synthetic Studies.** The approximate upper solubility limits for 1 in the various media are given in Table 2. Although micellar solution 7 gave the largest value of  $k_\psi$ , it solubilized the smallest amount of 1 and is therefore the least suited for practical synthesis. Hexane-rich microemulsions 4-6 can solubilize more 1 (molar basis) than the total amount of  $\text{Br}^-$  present, and all microemulsions, except 3, more 1 than  $\text{KBr}$ .<sup>12</sup>

The reaction media of Table 1 were used in synthetic studies; Table 2 records the product distributions after 12 h at 40.0°C. In solutions 1-6,  $[\text{KBr}]:[\underline{1}] = 10:1$  and total  $[\text{Br}^-]:[\underline{1}] = 36:1$ ; in solutions 7-9,  $[\text{CTABr}(\text{KBr})]:[\underline{1}] = 10:1$ . Water-rich microemulsions 1-3 gave the highest

Table 1. Reaction of Benzyl Chloride with Bromide Ion in Microemulsion and Other Media at 40.0°C.

run	reaction medium	[1], 10 <sup>3</sup> M	10 <sup>3</sup> k <sub>ψ</sub> <sup>a</sup> , min <sup>-1</sup>	δ <sub>obs</sub>	X <sub>i</sub>	V <sub>i</sub> <sup>b</sup> , mL	10 <sup>3</sup> k <sub>2</sub> <sup>c</sup> , M <sup>-1</sup> min <sup>-1</sup>
microemulsions							
	% S    % W    % O						
1	67    28    5	18	2.6 (0.2)	61.876	0.96	7.3	1.9
2	57    24    19	16	1.8 (0.1)	62.007	0.74	5.5	1.2
3	46    18    36	10	1.0 (0.1)	62.085	0.60	4.1	0.62
4	36    15    49	8.1	1.0 (0.1)	62.190	0.43	2.9	0.51
5	24    10    66	5.3	0.62 (0.06)	62.216	0.38	1.8	0.31
6	15    7    78	3.1	0.32 (0.03)	62.320	0.21	1.0	0.14
other media							
7	10% (w/w) CTABr-H <sub>2</sub> O	13	5.9 (0.4)			1.0 <sup>d</sup>	2.9 <sup>e</sup>
8	10% (w/w) CTABr-CHCl <sub>3</sub>	19	2.6 (0.2)			1.0 <sup>d</sup>	0.96 <sup>f</sup>
9	0.40 M KBr in 25% (v/v) H <sub>2</sub> O-C <sub>2</sub> H <sub>5</sub> OH	20	1.2 (0.1)				3.0

<sup>a</sup>Initial rate constant; each run was duplicated; estimated errors are in parentheses. For a typical run, 7-9 points were taken within the first half-life, during which side products 3 and 4 were not detected. Direct analyses of reaction mixture aliquots were made by calibrated HPLC [4.6 mm (i.d.) x 25 cm 10 μ LiChrosorb RP-18; aqueous CH<sub>3</sub>CN gradient elution; 254 nm UV detection]. <sup>b</sup>Calculated interphase volume in 10 g of reaction mixture. <sup>c</sup>For all but run 9, calculated with eq 2. <sup>d</sup>Volume of CTABr. <sup>e</sup>Calculated with α = 0.25 (ref. 11). <sup>f</sup>Calculated with α = 0.

Table 2. Solubility Limits of 1 in Microemulsion and Other Media and Product Distributions after 12 h at 40.0°C.

solubility limit of <u>1</u> , M	soln	initial [1], 10 <sup>3</sup> M <sup>a</sup>	yields, % <sup>b</sup>			
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
0.84	1	37	8 (27)	83 (66)	7 (6)	2 (1)
0.52	2	30	18 (33)	77 (63)	4 (3)	1 (1)
0.16	3	21	21 (41)	75 (57)	3 (2)	1 (0)
0.64	4	16	50	50	0	0
1.9	5	11	64	36	0	0
2.0	6	5.8	83 (79)	17 (21)	0 (0)	0 (0)
0.10	7	28	23	66		11
>4.4	8	38	50	50		
0.47	9	40	55	44		1

<sup>a</sup>Initial concentration in the synthetic runs. <sup>b</sup>Relative yields by HPLC; controls with an internal standard (anisole) indicated that they adequately represent absolute yields.

yields of 2 but also the greatest amounts of side products, benzyl butyl ether (3) and benzyl alcohol (4). In general, the conversion of 1 and the formation of 3 and 4 decreased with increasing hexane content. These decreases are a consequence of decreasing rates since the molar ratio of total Br<sup>-</sup> to 1 is constant in solutions 1-6. Table 2 also contains yields in parentheses for analogous runs made with total [Br<sup>-</sup>]:[1] = 7.2:1; they decreased somewhat or remained essentially unchanged relative to those obtained with the five-fold higher ratio. Almost complete reaction of 1 results when water-rich solutions 1-3 and 7 stand overnight; side products 3 and 4 then constitute 10-25% of the product mixtures.

Overall, the conversions of 1 to 2 in the water-rich microemulsions equal or exceed those

reported for phase transfer<sup>3a</sup> and triphase<sup>3b</sup> catalyzed reactions. Organic products can be isolated by the addition of aqueous  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  to precipitate  $\text{CTAClO}_4$ , followed by hexane extraction of the filtrate.<sup>13</sup>

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#### References and Notes

1. (a) Prince, L. M., Ed. "Microemulsions: Theory and Practice"; Academic Press: New York, 1977. (b) Danielsson, I.; Lindman, B. Colloids Surf. **1981**, 3, 391.
2. Microemulsions have been used previously as reaction media; for examples, see Mackay, R. A. Adv. Colloid Interface Sci. **1981**, 15, 131, and references therein. However, to our knowledge, only one study has had synthetic objectives (Gonzales, A.; Holt, S. L. J. Org. Chem. **1981**, 46, 2594); it used detergentless microemulsions.
3. (a) Jonczyk, A.; Ludwikow, M.; Makosza, M. Angew. Chem., Int. Ed. Engl. **1978**, 17, 62. (b) Regen, S. L. J. Org. Chem. **1977**, 42, 875.
4. Dispersion tests and conductivity and other data indicate that 1 and 2 are o/w and 6 is w/o the results for 3-5 are inconclusive.
5. This assumption is supported by the fact that for runs without KBr corresponding otherwise to 1, 3, and 6, the same  $k_{\psi}$  values were obtained within experimental error.
6. Bunton, C. A.; de Buzzaccarini, F. J. Phys. Chem. **1981**, 85, 3142.
7. Lower-limit  $k_2$ 's result because the calculation of  $V_i$  neglects contributions due to water of hydration for CTABr and possible penetration of hexane.
8. Tricot, Y.; Kiwi, J.; Niederberger, W.; Grätzel, M. J. Phys. Chem. **1981**, 85, 862.
9. The  $\delta_{\text{obs}}$  and  $\delta_i$  (61.850) values were obtained with microemulsions and a 70:30 (w/w) S-W solution, respectively, containing <1%  $\text{Me}_4\text{Si}$  and  $\text{D}_2\text{O}$  substituted for  $\text{H}_2\text{O}$ , and the  $\delta_0$  value (62.443) with a hexane solution containing 5% 1-butanol and <1%  $\text{Me}_4\text{Si}$  (coaxial  $\text{D}_2\text{O}$  lock.)
10. Güveli, D. E.; Kayes, J. B.; Davis, S. S. J. Colloid Interface Sci. **1981**, 82, 307.
11. With the assumption that the dissociation equilibrium in these media is the same as that for aqueous micellar CTABr (Fabre, H.; Kamenka, N.; Khan, A.; Lindblom, G.; Lindman, B.; Tiddy, G. J. T. J. Phys. Chem. **1980**, 84, 3428), a dissociation constant was calculated ( $K = 8.3 \times 10^{-2}$  M) and used to determine  $\alpha$ , the fraction of  $\text{Br}^-$  dissociated from the interphase (CTABr) in the presence of KBr. In runs 1-6,  $\alpha$  decreases from 0.05 to 0.01, respectively.
12. Of course, high conversions in the present reaction can be obtained only with total  $[\text{Br}^-]$ : [1] > 1.
13. The low recoveries obtained (ca. 50%) resulted from losses due to co-distillation (demonstrated for 1 and assumed for 2) with hexane and 1-butanol during rotary-evaporation of extracts and thus do not fairly represent the ability to isolate organic products from microemulsions. In any event, the use of destructible surfactants (Jaeger, D. A.; Frey, M. R. J. Org. Chem. **1982**, 47, 311; Jaeger, D. A.; Ward, M. D. ibid. **1982**, 47, 2221) will simplify product isolation from microemulsions.

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