ppm relative to the CH_3 group of **1D** + 1H ($CDCl_3$, 300 ^1H NMR). Subsequently the ee of **1H** was calculated after comparison of the rotation **1D** + **1H** (+18.7°) with a stoichiometrically identical mixture of **1D** wih *racemic* **1H** (+13.1°). The ee of **1H** was established to be 17% in favor of the *same* (+)-isomer (an average of three runs, accuracy 5%). This value was in agreement with the ee of **1H** determined by integration of the enantiomeric methine proton in **1H** using quinine as a shift reagent.[3]

We define the effect of a product ligand acting on the stereochemical course of a reaction as *the principle of enantioselective autoinduction*. The formation of mixed aggregates containing *both* product and starting material fragments influences the stereochemistry of subsequent C–C bond formation.[4,5] A vast majority of asymmetric synthetic reactions proceeding via addition of organometallic reagents to carbonyl compounds, the observation of an autoinductive effect, is pertinent to all these examples.[1,6]

We successfully demonstrated the effect to be operative in a catalytic manner. Recently it was shown that orthotitanates catalyze the widely studied[7] addition of diethylzinc to benzaldehyde.[8,9] We prepared the titanate from **1D** and $TiCl_4$ in ether with triethylamine. One mmol of this compound, a colorless oil, was added to 16 mmol of diethylzinc in toluene (1.1 M solution) at room temperature. Benzaldehyde, 12 mmol, was added, and the homogeneous mixture was left overnight. After hydrolytic workup a 72% yield of **1D** and **1H** was obtained with a ratio of **1D** vs **1H** of 100:512. The ee of **1H** was determined by comparison of the found rotation (+15.5°) with that of a stoichiometrically identical sample of **1D** and racemic **1H** (+4.0°). The optically active alcohol was replicated with an ee of 32% in favor of the same enantiomer completely *without* the assistance of chiral auxiliaries.

Further research is directed toward the realization of more efficient examples as well as to a detailed study of the interplay of enantioselective autoinduction and auxiliary induction with chiral ligands in asymmetric synthesis.

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(3) The double doublet is split into eight lines (1:1 **1D**/**1H**:quinine, $CDCl_3$, 21 °C, 300 MHz ^1H NMR) (+)-isomer at 5.134, 5.120, 5.144, 5.088 and the (−)-isomer 5.124, 5.110, 5.096, 5.082). Rosini, C.; Ucello-Barretta, G.; Pini, D.; Abete, C.; Salvadori, P. *J. Org. Chem.* **1988**, *53*, 4579.

(4) The methyl ether of 1D does not induce an ee of 1H.

(5) Seebach was the first to recognize the potential role of mixed aggregates: Seebach, D.; Amstutz, R.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2622, in a paper with a philosophical character. See, also: Jackman, L. M.; Lange, B. C. *J. Org. Chem.* **1983**, *48*, 4789.

(6) Adverse enantioselective autoinduction takes place in the reaction of a lithium–magnesium reagent with benzaldehyde: addition of a second equivalent of the carbonyl compound is detrimental to the optical yield (Noyori, R.; Suga, S.; Kawai, K.; Okada, S.; Kitamura, M. *Pure Appl. Chem.* **1988**, *60*, 1597). Adverse autoinduction overrules auxiliary induction in the second stage of the quinine-catalyzed bishydroxylation of olefins: the second equivalent is produced with a 7% excess of the "wrong" enantiomer (Sharpless, K. B.; Marko, I.; Svendsen, J. S. *J. Am. Chem. Soc.* **1989**, *111*, 737). Capricious results in asymmetric condensations with enolates and metal alkyls with the first, second, third, and fourth equivalent of the carbonyl compound were obtained earlier: Mukayama, T.; Soai, K.; Sato, T.; Shimizu, H.; Suzuki, K.; *J. Am. Chem. Soc.* **1979**, *101*, 1455. Seebach, D.; Crass, G.; Wilka, E.-M.; Hilvert, D.; Brunner, E. *Helv. Chim. Acta* **1979**, *62*, 2695. Mazaleyerat, J. P.; Cram, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 789. By using the same method with an optically active deuterated hydroxyester, we have studied enantioselective autoinduction in the aldol condensation of the Li enolate of ethyl acetate and benzaldehyde indepth. Small counterproductive effects were observed. However, precipitation of a tetrameric diastereomeric Li–O complex is a crucial factor in the stereochemistry of this process and probably in several of the reactions listed in Table IX in ref 1 Alberts, A. H.; Wynberg, H. to be published). In the perspective of nonlinear effects in asymmetric induction (ref 7), assuming precipitation-inactivation of aggregated complexes with internal mirror planes, we note that in enantioselective autoinduction (as in auxiliary induction processes with partially resolved chiral ligands) the optical purity of the formed product is *not necessarily limited* by the optical purity of the previously added product.

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(9) The zinc alkoxide, prepared in situ by addition of 0.1 equiv of (+)-**1D** to 10 mmol of diethylzinc, catalyzed this reaction less effectively (3 days, 20 °C, 54% yield) and with an enantioselectivity in favor of the (+)-isomer slightly above experimental error, confirming the results of Oguni, N.; Omi, T. *Tetrahedron Lett.* **1984**, *25*, 2823.

Reaction in the Bicontinuous Phase of a Nonaqueous Microemulsion: Amidation of the Olefin $C_8F_{17}CH{=}CH_2$ by γ Radiolysis

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A microemulsion is generally defined as a transparent medium made up of water, oil (saturated or unsaturated hydrocarbon), a surfactant, and a cosurfactant (a short chain amphiphile such as an alcohol or an amine).[1] Depending on the proportions of the constituents, three main types of structure can be distinguished:[1,2] reverse micelles (**W/O**), direct micelles (**O/W**), or bicontinuous structures (Figure 1). In general, reactions carried out in microemulsions take place either in the direct micellar zone or more commonly in the reverse micellar zone.[3] There are few reports of reactions taking place in the bicontinuous phase.[4]

We have demonstrated for the first time the use of microemulsions based on formamide instead of water to produce media for carrying out chemical reactions.[5] Formamide was employed in view of the low solubility of many organic compounds in water. Moreover, formamide can be used as a reactant, with the preparation of microemulsions in which the two main components (oil and formamide) are reactants.

We describe here the amidation of the olefin $C_8F_{17}CH{=}CH_2$ by γ radiolysis in a formamide (**F**) microemulsion containing 1,1,2-trihydroperfluoro-1-decene ($C_8F_{17}CH{=}CH_2$) as oil (**O**), potassium 2,2,3,3-tetrahydroperfluoroundecanoate ($C_8F_{17}C_2H_4CO_2K$) as surfactant (**S**), and 1,1,2,2-tetrahydroperfluorohexanol ($C_4F_9C_2H_4OH$) as cosurfactant (**CoS**). The phase diagram of this system reported in a previous publication[6] was explored after γ radiolysis. Study of self-diffusion by ^1H NMR[7] enabled the structures of the various microemulsions to be determined. The results are shown in Figure 2 and Table I.

Self-Diffusion Measurements. The self-diffusion coefficients (cf. Table I) defined three microemulsion zones similar to those of the corresponding aqueous systems: (a) Microemulsions 1 and 2 have an **O/F** structure similar to that of direct micelles (**O/W**); the olefin in droplets has a much lower self-diffusion coefficient than that of the pure liquid, while formamide, making up the continuous phase, diffuses readily. (b) In contrast, microemulsions 4 and 5 have a **F/O** structure similar to reverse micelles (**W/O**); the formamide in droplets has a low self-diffusion coefficient unlike that of the olefin. (c) In microemulsion 3, the coefficients of self-diffusion of formamide and oil are similar, indicating the presence of a bicontinuous phase, not organized in micelles. This type of structure, well-known in aqueous media,[6] is described here for the first time in nonaqueous microemulsions.

These results show that by judicious choice of surfactant and cosurfactant, it is possible to find systems in formamide micro-

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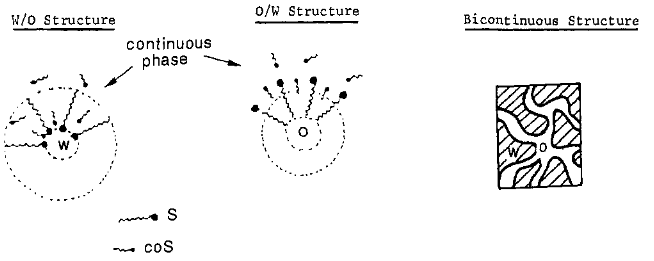

Figure 1. Structures of the microemulsions (**O** = oil, **W** = water, **S** = surfactant, **CoS** = cosurfactant).

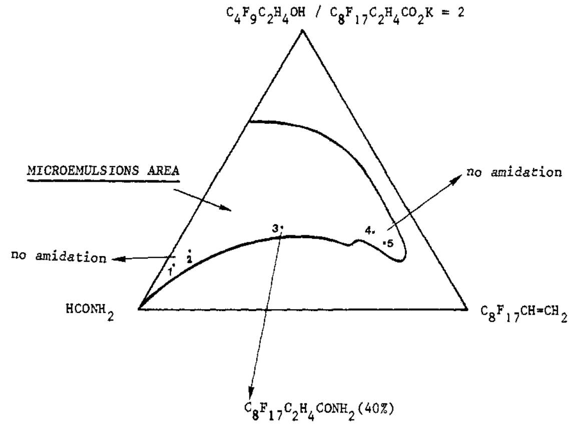

Figure 2. γ radiolysis at 25 °C of microemulsion system ($HCONH_2$, C_8F_{17}-$CH{=}CH_2$, $C_4F_9C_2H_4OH/C_8F_{17}C_2H_4CO_2K$ = 2).

Table I. Self-Diffusion Coefficients of $HCONH_2$ (D1) and $C_8F_{17}CH{=}CH_2$ (D2) in the Microemulsions at 25 °C[a]

	microemulsions (% wt)					
no.	F	O	S	CoS	$D1$	$D2$
1	87	7	2	4	3.62	0.54
2	78	10	4	8	3.37	0.60
3	44	44	4	8	0.85	1.21
4	12	61	9	18	0.60	2.89
5	10	66	8	16	0.60	2.98
	pure $HCONH_2$				5.21	
	pure $C_8F_{17}CH{=}CH_2$					5.32

[a] F = $HCONH_2$, O = $C_8F_{17}CH{=}CH_2$, S = $C_8F_{17}C_2H_4CO_2K$, CoS = $C_4F_9C_2H_4OH$. Unit for $D = 10^{-10}$ $m^2 \cdot s^{-1} \pm 0.08 \times 10^{-10}$ $m^2 \cdot s^{-1}$.

emulsions analogous to aqueous systems.

Amidation of $C_8F_{17}CH{=}CH_2$ by γ Radiolysis. The following results were obtained (cf. Figure 2). (i) In microemulsions 1, 2, 4, and 5, the olefin does not react, and only the oxamide $CONH_2$-$CONH_2$ is obtained in low yield ($\approx$5% with respect to the starting formamide).[8] (ii) The amidation reaction only takes place in microemulsion 3. The terminal amide $C_8F_{17}CH_2CH_2CONH_2$ is isolated in a 40% yield with respect to the starting olefin which is the limiting reactant.[8] The oxamide $CONH_2$-$CONH_2$ is also obtained in low yield ($\approx$5% with respect to the starting formamide).

These results can be interpreted in terms of the general mechanism of an amidation reaction.[9]

Initiation

$$HCONH_2 \xrightarrow{\gamma} {}^{\bullet}H + {}^{\bullet}CONH_2$$

Propagation

$$C_8F_{17}CH{=}CH_2 + {}^{\bullet}CONH_2 \rightarrow C_8F_{17}CH^{\bullet}CH_2CONH_2$$

$$C_8F_{17}CH^{\bullet}CH_2CONH_2 + HCONH_2 \rightarrow C_8F_{17}CH_2CH_2CONH_2 + {}^{\bullet}CONH_2$$

Termination

$$2{}^{\bullet}CONH_2 \rightarrow CONH_2\text{-}CONH_2$$

In the reverse microemulsions 4 and 5, formamide is confined to the droplets, as demonstrated by the self-diffusion measurements, the carbamoyl radicals diffuse little being restrained in a micellar cage, and only the oxamide is formed.

On the other hand, in the direct microemulsions 1 and 2, the olefin is confined in the micelles. The self-diffusion measurements show that the olefin in fact diffuses little into the medium, and so does not interact greatly with the carbamoyl radicals.

However, in microemulsion 3 with a bicontinuous structure, the constituents (also reactants) diffuse together (Table I), and suitable contact between formamide and the olefin can take place hence enabling reaction.

These results show the potential of the relatively orderless bicontinuous phase as a medium for chemical reactions. These structures, which favor simultaneous diffusion of reactants, enable reactions to be carried out that would be impossible in a strictly micellar medium. These results also confirm the similarity between formamide and aqueous microemulsions, with a first demonstration of a bicontinuous structure in a nonaqueous medium.

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(8) The fluorinated derivatives (99% pure) were a generous gift of Atochem. Formamide (Aldrich 99% pure) was kept on a molecular sieve and contained less than 1% water (Karl-Fisher). The following reaction conditions were employed: 50 mL of degassed microemulsion were irradiated for 70 h at 9.1.10^5 $cm^{-3} \cdot rad \cdot h^{-1}$ in a Gammacell 220 apparatus containing a ^{60}Co source emitting γ radiation at 1.33 and 1.17 MeV. The reaction was followed by GLC (SE30 column with 10% silicone on Chromasorb PAW 80/100 mesh). The amide $C_8F_{17}C_2H_4CONH_2$ and the oxamide were the only products. The oxamide, insoluble in the microemulsion, was filtered off at the end of the irradiation. The amide $C_8F_{17}C_2H_4CONH_2$ was recovered as a solid after precipitation in the microemulsion diluted in a 5-fold volume of water. The products were identified by ^1H (and ^{19}F) NMR and elemental analysis.

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INEPT in a Chemical Way. Polarization Transfer from Parahydrogen to ^{31}P by Oxidative Addition and Dipolar Relaxation

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Parahydrogen induced polarization (PHIP) leading to enhanced ^1H NMR absorptions and emissions arises in hydrogenation and hydrogen addition reactions when H_2 enriched in the para state is added pairwise to substrate.[1,2] If this addition occurs fast relative to proton relaxation, then the transferred protons reflect initially the nuclear spin populations of the starting dihydrogen and yield polarized transitions for the product resonances. In this paper we report that the inverted ^1H nuclear spin populations

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