Comparative Study of Photoamidation of a Mixed Olefin $R_FCH=CHR_H$ in Homogeneous and Microscopically Heterogeneous Media

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Photoamidation by formamide of the olefin $C_8F_{17}CH=CHC_{10}H_{21}$ was carried out in two types of reaction media: (1) a homogeneous medium, *tert*-butyl alcohol, and (2) a microscopically heterogeneous medium represented by a nonaqueous microemulsion in which water is replaced by formamide. The olefin and the formamide are both reactants and constituents of the microemulsions. In *tert*-butyl alcohol, amidation occurred preferentially at the α position on the alkyl chain, whereas in the microemulsions, the opposite regioselectivity was observed, with the carbamoyl radical attacking the α position of the fluoroalkyl chain. Differences in regioselectivity in the different media are interpreted in terms of polar and steric effects. In *tert*-butyl alcohol, the reaction appeared to be governed by steric effects, while in the microemulsions, polar effects were more important.

Introduction

Long-chain fluorinated amphiphiles have been the subject of considerable research of both a fundamental and applied nature. We have recently synthesized a new series of molecules with an amide group for a polar head and with two hydrophobic chains, one of which is fluorinated and the other hydrogenated.

$$R_F(CH_2)_nCH(CH_2)_mR_H$$
$$|$$
$$CONH_2$$

$$n = 0, 1; m = 0, 1$$
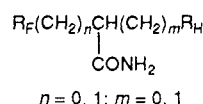
They were prepared by photoamidation of the corresponding olefins $R_FCH=CHR_H$. This reaction, carried out in a dilute medium of *tert*-butyl alcohol, led to a preferential attack of the carbamoyl radical on the carbon bearing the alkyl chain.[1]

In this study, we devised a system that favored synthesis of isomers that are normally obtained as secondary products in low yield. Microemulsions with their structured characteristics appeared particularly attractive in this respect. The regio- and stereoselectivity of certain reactions may be modified in these microscopically structured media.[2,3]

As an example, we describe the results obtained with the photoamidation of the olefin $C_8F_{17}CH=CHC_{10}H_{21}$ (*E* (trans) isomer supplied by ATOCHEM) in microemulsions. The results are compared to those obtained in *tert*-butyl alcohol.

A. Choice of Microemulsion System. A microemulsion is generally defined as a transparent (in the visible range) medium consisting of water, an oil (saturated or unsaturated hydrocarbon), a surfactant, and a cosurfactant (a short-chain amphiphile such as an alcohol or amine).[4]

1. Choice of Formamide in Place of Water. Formamide has the characteristics of a structured solvent like water, and we have demonstrated that nonaqueous microemulsions can be prepared by replacing water with formamide.[5] We have investigated the structure of such

microemulsions and examined the possibilities of using them as media for Diels–Alder reactions,[6] the Wacker process,[7] and metathetic reactions.[8]

Since these microemulsions are also transparent in the visible range, we were able to use them for photoamidation. The microemulsions tested contained formamide, instead of water, and the olefin $C_8F_{17}CH=CHC_{10}H_{21}$ as oil. *The Olefin and the Formamide are thus both constituents of the microemulsions and reactants.* We refer to this as the principle of molecular economy.

2. Choice of Surfactant and Cosurfactant. In order to obtain microemulsions using the olefin $C_8F_{17}CH=CH-C_{10}H_{21}$, a hydrogenated surfactant and a fluorinated surfactant or vice versa are required. This is due to the segregation between hydrogenated and fluorinated chains.[9,10]

We selected as surfactants the ethoxylated nonylphenols of general formula $C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$, for which it is possible to vary the number of ethoxy units n. We chose the fluorinated alcohol $C_4F_9C_2H_4OH$ as cosurfactant.

3. Phase Diagram of the Microemulsions. In the Winsor nomenclature,[11] one-, two-, and three-phase states are distinguished in the phase diagrams of microemulsions: Winsor I (W I), two-phase state for a microemulsion in equilibrium with an organic phase; Winsor II (W II), two-phase state for a microemulsion in equilibrium with an aqueous phase; Winsor III (W III), three-phase state for a microemulsion in equilibrium with both an organic and an aqueous phase; Winsor IV (W IV), one-phase state for microemulsions.

The Winsor systems have been determined and indicated on the phase diagram (Figure 1). The formamide/olefin ratio (w/w) in *tert*-butyl alcohol of 5.6 employed in a previous study[1] was retained here. The sur-

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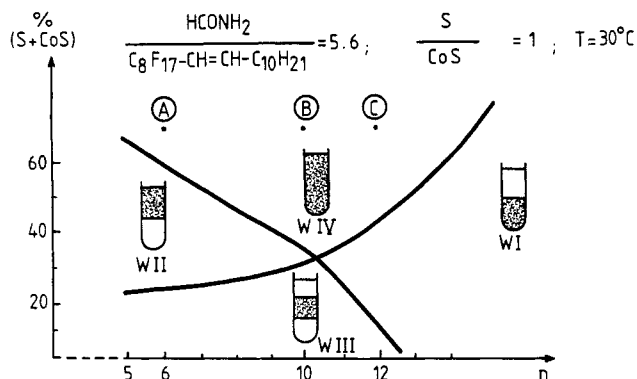(4) (a) Daniellson, L.; Lindman, B. *Colloids Surf.* **1981**, *3*, 381. (b) Langevin, D. *Acc. Chem. Res.* **1988**, *21*, 71, 255.

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Figure 1. Phase diagram of the system $HCONH_2$, $C_8F_{17}CH=CHC_{10}H_{21}$, $C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$, and $C_4F_9C_2H_4OH$. W I = Winsor I system (oil/microemulsion), W II = Winsor II system (microemulsion/formamide), W III = Winsor III system (oil/microemulsion/formamide), and W IV = Winsor IV system (microemulsion); S = surfactant = $C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$, and CoS = cosurfactant = $C_4F_9C_2H_4OH$.

Table I. Photoamidation of $C_8F_{17}CH=CHC_{10}H_{21}$ in Microemulsions A, B, and C (48 h, 30 °C, 300 nm)

microemulsion	n	regioselectivity $(a/b)^a$	yield,[b] %
A	6	0.42	71
B	10	0.40	89
C	12	0.44	94
t-BuOH		7.71	64

[a] The regioisomers a and b were not separated. The regioselectivity was determined by GLC and ^1H NMR of mixtures of isomers in each case (see Experimental Section). [b] Yields are given for the products isolated (both a and b) with respect to the starting olefin, which is the limiting reactant.

factant/cosurfactant ratio (w/w) was fixed at unity as this was found to lead to the largest microemulsion zone. The phase diagram obtained by plotting the total percentages (% surfactant (S) and % cosurfactant (CoS)) against the number of ethoxy units n strongly resembled that found for aqueous systems.[12]

B. Photoamidation of $C_8F_{17}CH=CHC_{10}H_{21}$. Amidation of the olefin was carried out in microemulsions A, B, and C (Figure 1). These microemulsions with a high surfactant and cosurfactant content (65%) maintained a homogeneous reaction medium throughout the course of reaction.
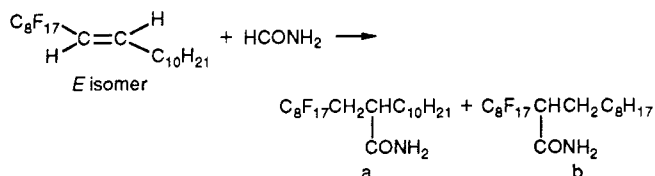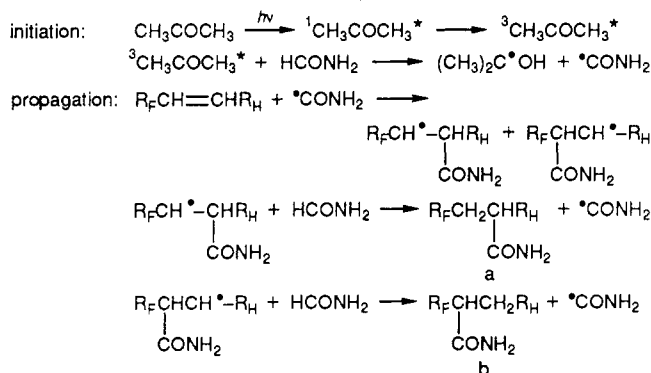

The results obtained along with those obtained in *tert*-butyl alcohol are listed in Table I. The following comments can be made on these results: the regioselectivities observed in the microemulsions are the opposite of those observed in *tert*-butyl alcohol; the yields are considerably higher in the microemulsions than in *tert*-butyl alcohol. It can be seen that increasing the number of ethoxy groups n also increased the yield.

Discussion

The results may be interpreted in terms of the reaction mechanism described in a previous study.[1] This involves

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a free-radical chain reaction initiated with the photoreduction of acetone (excited to the triplet state) by formamide:


The oxamide was the only byproduct obtained with a yield <5% with respect to the starting olefin.

1. Interpretation of the Observed Regioselectivities: $a/b = 7.71$ in *tert*-Butyl Alcohol; $a/b \approx 0.40$ in Microemulsions. In general, radical chain reactions are governed by a complex set of factors. We will mention the principle factors affecting the propagation stage, which effectively controls the regioselectivity.

(i) Stereochemistry of the Olefins. The starting olefin was in the E (trans) form, and we did not observe any change in the stereochemistry of the double bond during the reactions, either in *tert*-butyl alcohol or in the microemulsions.

(ii) Transfer Reactions. The presence of large amounts of formamide argue in favor of a fast transfer reaction and a predominance of the addition reaction, which are thus the limiting stages of propagation of the photoamidation.

(iii) Addition Reactions. Polar Effects. Writing the carbamoyl radical $\cdot CONH_2$ in its resonance structures while maintaining the free electron on the attacking carbon atom,
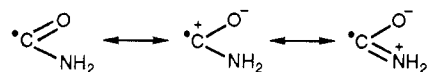
it can be seen that the carbon atom retains a partial positive charge and the carbamoyl radical $\cdot CONH_2$ is thus an electrophile. If polar effects predominate, the addition reaction will tend to take place on the α carbon on the fluorinated chain $R_F\!\!\nleftarrow\!\!\nleftarrow C_\alpha H=C_\beta H\!\!\nleftarrow\!\! R_H$ and isomer b will preponderate.

Steric Effects. On the other hand, the fluorinated chain has a greater steric hindrance than the hydrogenated chain R_H, due to the larger size of the fluoride atoms and a lower conformational mobility. Steric effects thus favor addition to the β carbon of the fluorinated chain, leading to isomer a.

In *tert*-butyl alcohol, the results obtained for photoamidation of $C_8F_{17}CH=CHC_{10}H_{21}$ indicate a predominant role of steric effects, accounting for the preponderance of isomer a.

In microemulsions, the results are less readily interpretable but can be accounted for in terms of the microstructure of the reaction medium. Light-scattering studies indicate the presence of polydispersed aggregates with sizes ranging from 500 to 800 Å. The aggregates were thus predominantly lamellar rather than spherical. An X-ray scattering study is in progress to determine their

structure in more detail. The olefin is thus situated in one channel, while the formamide is in another, and the reaction takes place mainly at the interface. Two possibilities suggest themselves to account for the observed regioselectivities.

The olefin is partially anchored in the interfacial film by the hydrogenated chain, which has the greater affinity for the alkyl chain of the hydrogenated surfactant.[11] The fluorinated chain thus points outwards toward the formamide, which is surrounded by molecules of the fluorinated alchol, thus stabilizing the complex. The α carbon on the fluorinated chain is thus more accessible to attack by the carbamoyl radical. Opposite steric effects to those in *tert*-butyl alcohol will operate and will enhance the polar effects.

The olefin is completely anchored in the film along with molecules of surfactant. In this situation, the α and β carbons of the olefin are equally sterically hindered. Thus polar effects will tend to predominate, with amidation taking place at the α carbon on the fluorinated chain.

In order to try and discriminate between these two possibilities, we carried out a further set of experiments in microemulsion D in which the surfactant is fluorinated ($C_6F_{13}C_2H_4(OC_2H_4)_{12}OH$) and the cosurfactant is hydrogenated ($C_6H_{13}OH$). Photoamidation was performed under the same conditions as for the other microemulsions ($HCONH_2$/olefin = 5.6; S/CoS = 1; S + CoS = 65%). The amides a and b were obtained in an overall yield of 88% with a ratio a/b = 0.26.

The regioselectivity was thus comparable to that observed in the other microemulsions, which would tend to rule out the possibility of partial anchorage of the olefin in the interfacial film. If this had been the case, the opposite regioselectivity would have been observed. The olefin would tend to be retained in the interfacial film by the fluorinated chain along with fluorinated surfactant, and amidation would have occurred preferentially on the β carbon of the fluorinated chain. This was not, however, the case. It would thus appear that the olefin is totally anchored in the interfacial film, and the regioselectivity is essentially goverened by polar factors.

2. Interpretation of the Yields. Enhanced contact between the reactants will increase yields in both microemulsions and *tert*-butyl alcohol. The yield also increased with increasing number of ethixy units in the surfactant (C > B > A). The increase in n in the surfactant probably enhances contact between the formamide and the olefin by fluidizing the interface.

Conclusion

The aim of this study of photoamidation in microemulsions was to investigate the potential of microemulsion-based media for performing regiospecific reactions using $C_8F_{17}CH=CHC_{10}H_{21}$. The opposite regioselectivity was obtained in the microemulsion systems to that found in *tert*-butyl alcohol. This was interpreted in terms of the structure of the microemulsion which anchored the olefin in the interfacial film. The predominantly steric effects in *tert*-butyl alcohol are thus outweighed by polar effects in the microemulsions. Yields were also higher in the microemulsions than in classical media.

The amides synthesized are being evaluated as fire-extinguishing foams in collaboration with Atochem.[13] These amides are readily hydrolyzed, producing the corresponding carboxylic acids and carboxylates, depending on the nature of the counterion. The surfactant properties of these compounds are also under investigation.[14]

Experimental Section

The olefin $C_8F_{17}CH=CHC_{10}H_{21}$, the alcohol $C_4F_9C_2H_4OH$, and the surfactant $C_6F_{13}(OC_2H_4)_{12}OH$, kindly supplied by Atochem, were at a purity of 99%. The ethoxylated alkylphenols, a gift from SFOS (Elf-Aquitaine), were 99% pure. Acetone, formamide, and *tert*-butyl alcohol (Aldrich) were also 99% pure.

The IR spectra were recorded on a Perkin-Elmer 683 apparatus. The frequencies of the characteristic bands are expressed in cm^{-1}.

The proton and fluorine NMR spectra were recorded on a Bruker AM-300-WB instrument using TMS as internal reference for the ^{1}H and CF_3CO_2H as external reference for the ^{19}F measurements. The chemical shifts are expressed in parts per million with respect to the reference, and the signals are characterized by s (singlet), d (doublet), t (triplet), and m (multiplet).

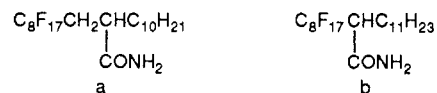Melting points were measured on a Koffler block.

Elemental analyses of the synthesized products were carried out in the CNRS facilities (Lyon, France) and expressed as percentages of required (r) and experimental (f) values.

An Intersmat IGC 120 FL instrument was used for the GLC analyses, with a SE 30 column (10% silicon on Chromosorb PAW 80-100 mesh).

Amidation of $C_8F_{17}CH=CHC_{10}H_{21}$ in *tert*-Butyl Alcohol. After degassing with argon, the following mixture was irradiated at 300 nm in a Rayonet RP 600 instrument for 2 days: 0.012 mol of olefin, 35.3 mL of formamide (0.89 mol), 5 mL of acetone (0.068 mol), and 105 mL of *tert*-butyl alcohol (1.11 mol).

The oxamide produced during the reaction was filtered off and the filtrate evaporated to dryness under vacuum. The residue was recrystallized in water. The product was dried over P_2O_5. The mixture of amides a and b was obtained as a white powder.

Characteristics of carboxamides a and b:

$$C_8F_{17}CH_2\underset{\underset{a}{\overset{|}{CONH_2}}}{CHC_{10}H_{21}} \qquad C_8F_{17}\underset{\underset{b}{\overset{|}{CONH_2}}}{CHC_{11}H_{23}}$$

MW = 631; mp 92 °C; IR 3420 (NH free), 3200 (NH coupled), 1670 (C=O), 1200 (CF); ^{1}H NMR (CD_3COCD_3) 0.99 (3 H, t, CH$_3$), 1.40 (18 H, m, CH$_2$), 2.40 (1 H, m, CH), 2.96 (2 H, m, CH$_2\alpha$CF$_2$), 6.50-7.19 (2 H, m, NH); ^{19}F NMR (CD_3COCD_3) -5.31 (3 F, t, CF$_3$), -37.32 (2 F, m, CF$_2\alpha$CH$_2$), -46.11 (6 F, m, CF$_2$), -46.94 (2 F, m, CF$_2\gamma$CF$_3$), -47.82 (2 F, m, CF$_2\beta$CF$_3$), -50.43 (2 F, m, CF$_2\alpha$CF$_3$). Anal. Found: C, 39.89; H, 4.07; N, 2.55; F, 49.72. $C_{21}H_{26}NF_{17}O$ requires: C, 39.07; H, 4.03; N, 2.17; F, 50.08.

Determination of the Regioselectivity. GLC of the mixture of the two amides gave two closely separated peaks (a minor one at 220 °C and a major one at 245 °C). The ratio of the areas of the two = 7.71.

^{1}H NMR of the mixture of the two isomers a and b showed the almost exclusive presence of a (α CH$_2$ to the CF$_2$). The major peak (245 °C) was thus attributed to isomer a and the minor peak to isomer b.

Amidation of $C_8F_{17}CH=CHC_{10}H_{21}$ in Microemulsions. A microemulsion prepared from the following constituents was placed in a Pyrex flask: 0.26 g of olefin, 1.48 g of formamide, 1.63 g of surfactant, 1.63 g of cosurfactant, and 0.18 mL of acetone. As for *tert*-butyl alcohol, the mixture was degassed with argon before irradiation. The oxamide was filtered off as above. The filtrate was evaporated under vacuum and the residue taken up in 20 mL of $CFCl_2CF_2Cl$ supplied by Atochem (98%). The precipitate was recrystallized and then dried over P_2O_5.

Characteristics of carboxamides a and b: MW = 631; mp 95 °C; ^{1}H NMR (CD_3COCD_3) 1.00 (3 H, t, CH$_3$), 1.40 (20 H, m, CH$_2$), 2.45 (1 H, m, CH), 6.55-7.30 (2 H, m, NH). Anal. Found: C, 39.78; H, 4.05; N, 2.47; F, 49.92. $C_{21}H_{26}NF_{17}O$ requires: C, 39.07; H, 4.03; N, 2.17; F, 50.08.

Determination of the Regioselectivity. On GLC, the two peaks described above were detected after direct injection of the microemulsions. To check that the retention times were un-

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(14) Gautier, M.; Rico, I.; Lattes, A.; Bertocchio, R. BF No. 8702009, Application 02/17/87.

changed, we injected the mixture of isomers produced by the reaction in *tert*-butyl alcohol. The regioselectivity was given by the ratio of the areas of the two peaks (*a/b*).
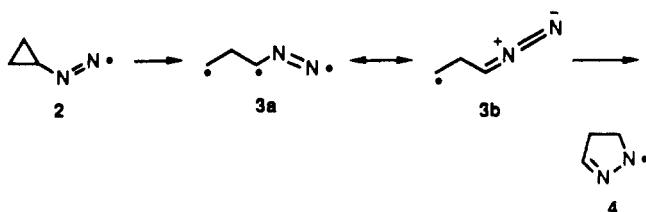
Photochemistry of ((Trifluoromethyl)azo)cyclopropane: A Reinvestigation

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The solution-phase photolysis of ((trifluoromethyl)azo)cyclopropane (TFMACP) leads to a very different product distribution than the one reported previously. While CF$_3$H was claimed to be the major product, we instead find much *cis*-TFMACP, 1-(trifluoromethyl)-2-pyrazoline (5), and (trifluoromethyl)cyclopropane. The four primary photoreactions responsible for these products are exactly analogous to those taking place in azocyclopropane.

Twenty years ago, Chakravorty, Pearson, and Szwarc (CPS)[1] reported that the vapor-phase photolysis of ((trifluoromethyl)azo)cyclopropane (TFMACP) afforded the products shown in Scheme I. The numbers represent the mole ratio of product to nitrogen and were stated to be accurate to ±0.05. In solution, photolysis of TFMACP gave a different product distribution (cf. Scheme II). This study is important because TFMACP was only the second reported azoalkane with a cyclopropyl group attached directly to the azo linkage. Moreover, formation of 1 was rationalized on the basis of the diazenyl radical rearrangement (2 → 4), which in turn requires stepwise


2   **3a**   **3b**

4

azoalkane homolysis.[2] Since photochemical deazatation of ((trifluoromethyl)azo)alkanes has been proposed as a method for introducing CF$_3$ groups,[3] the yield of (trifluoromethyl)cyclopropane is of interest.

These results of CPS raised a number of questions. The drastic experimental conditions used in the photolysis of TFMACP implies that the quantum yield is remarkably low since dilute solutions (<10^{-4} M) were irradiated with a powerful lamp (GE AH-6) for extended periods (30–50 h). Moreover, virtually all acyclic azoalkanes are converted photochemically to their cis isomers,[4] but CPS made no mention of this reaction. The yield of products containing CF$_3$ moieties exceeded the total amount of N$_2$ in both gas and solution, leading the authors to suspect formation of a nitrogen-containing product. However, such a product,

Scheme I. Vapor-Phase Photolysis Products of TFMACP According to CPS[1]
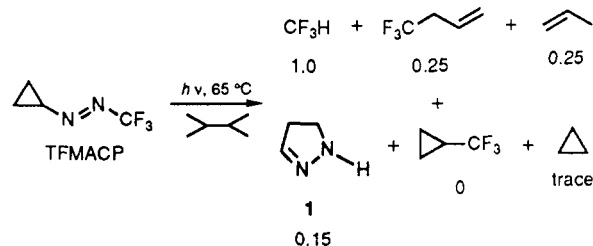
Scheme II. Solution-Phase Photolysis Products of TFMACP According to CPS[1]
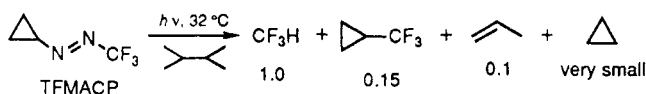
1, was found only in the gas phase. We wondered about the source of the NH hydrogen atom in 1 since the hydrazonyl radical 4 is highly stabilized and would not be a good hydrogen abstracting agent.[5] Even more unusual is the rearrangement of 2 to 4, which would have to compete with the deazatation of 2, whose activation free energy is only 7.1 kcal/mol.[6] Since the vinylcyclopropane rearrangement of azocyclopropane (ACP) exhibits $\Delta G^{\ddagger} = 40.0$ kcal/mol,[7] some large driving force would have to lower $\Delta G^{\ddagger}$ for the radical rearrangement 2 → 4 by 32.9 kcal/mol (40.0 – 7.1) relative to its nonradical counterpart if we are to observe 2 → 4. Such a driving force might exist if 2 → 4 were more exothermic than the rearrangement of ACP; however, we estimate that the opposite situation holds. Thus single cyclopropyl–N bond cleavage of ACP requires $E_a \sim 54$ kcal/mol,[8] while the same process in *N*-cyclopropyl-2-pyrazoline would have $E_a \sim 80$ kcal/mol[5] because the pyrazoline is much more stable than its azo isomer. It follows that the roughly 25 kcal/mol exothermicity of azo vinylcyclopropane rearrangement would be reduced by 26 kcal/mol for 2 → 4, making the latter close to thermoneutral.

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