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# Regioselective Functionalization Of Unactivated Methylene Groups Induced By Photochemistry In Micellar Solutions

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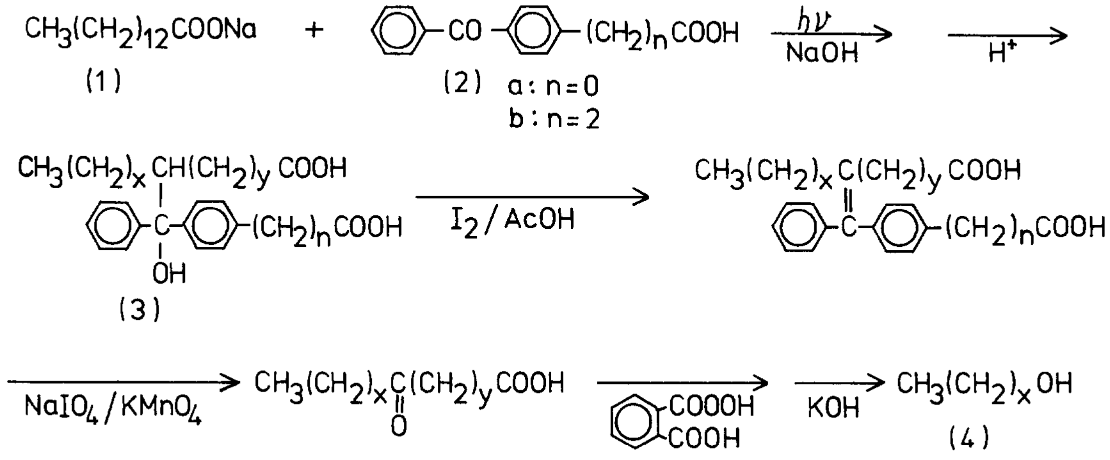
In the course of the investigations on micellar catalysis, a number of results on rate enhancement have been reported[1] while limited attentions have been given to regioselectivity of reaction[2].

We wish here to report our results that benzophenone derivatives solubilized into the micelle induced photochemically the regioselective functionalization of a surfactant forming the micelle[3].

A micellar solution composed of sodium myristirate (1) ($2.9\times10^{-2}$ M), p-benzoylbenzoic acid (2a) ($1.5\times10^{-2}$ M) and sodium hydroxide ($1.5\times10^{-2}$ M) was irradiated using a high-pressure mercury lamp under nitrogen atmosphere for 40 hr. TLC analysis indicated that the reaction mixture after being made acidic contains other product than the starting compounds (Rf=0.22 MeOH). The product was isolated by column-chromatography on silica-gel and assigned a coupling structure (3a). 3a: 15% yield based on 2a; IR (KBr) 3500, 2910, 2840, 1700, 1600 and 1500 $cm^{-1}$; NMR (DMSO-d6) 0.85(t, 3H), 1.30(m, 21H), 2.13(m, 2H), 7.50 (m, 9H) and 11.30 ppm (broad, 2H). Similarly (3b) was prepared from (2b) in 21% yield. (3) was treated following to the scheme in order to determine the position of the new C-C linkage in (3). A distribution of reaction sites was determined by vapor-phase chromatographic analysis of the resulting alcohols (4) and is shown in Table 1. A validity of this method is supported by the result of our control experiment that hexyl and pentyl groups migrated with same probability on Baeyer-Villiger oxidation of 5-keto-undecanoic acid and 6-keto-undecanoic acid. Molecular models indicate that these results should be derived with the preferential conformation of (2) straightforward directed into the micelle core.



Scheme

Table 1. A Distribution of Myristic Acid of Functionalized Carbons[a)]

| | Percent of carbons functionalized[b)] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Benzophenone-alkanoic acid | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 |
| 2a | 0 | 0 | 4.5 | 18 | 25 | 27 | 14 | 11 |
| 2b | 0 | 0 | 19 | 41 | 30 | 10 | 0 | 0 |

a) The reaction was carried out at 58°.

b) The carboxyl group is C-1.

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## References

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