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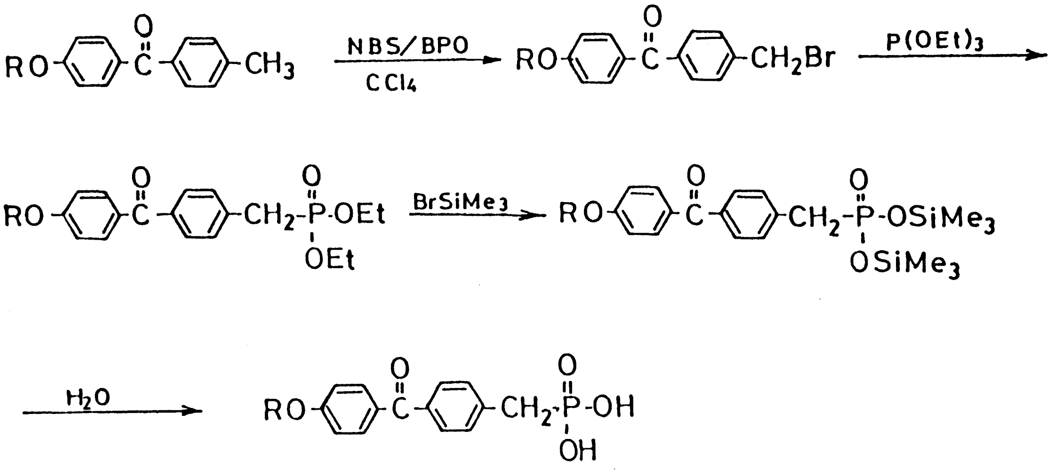
Photochemical Reaction of [4(4'-Alkoxybenzoyl)phenylmethyl]phosphonic Acids. Application to a Photo-degradable Surfactant

Yoshiki OKAMOTO,* Hidetoshi YOSHIDA, and Setsuo TAKAMUKU
The Institute of Scientific and Industrial Research, Osaka
University, Mihogaoka, Ibaraki, Osaka 567

Upon UV-irradiation, the C-P bonds of [4(4'-alkoxybenzoyl)-phenyl]methylphosphonic acids were cleaved in water (pH 12) to give 4-alkoxyphenyl p-tolyl ketones and orthophosphate in high efficiency. It was demonstrated that the acids can be used as photo-degradable surfactants.

We have reported the photochemical C-P bond cleavage of p-nitrobenzylphosphonic acid in basic aqueous solution.[1)] Since the dihydroxyphosphinyl group has a distinct hydrophilic character, this C-P bond cleavage means elimination of a hydrophilic group from amphiphile. This led us to prepare photo-degradable surfactants by further introduction of suitable alkyl groups as hydrophobic moieties to the nitro-aromatic ring. The introduction of an alkyl group in the aromatic ring, however, extinguished the photo-reactivity.[2)] Recently, we have found that the C-P bond of [(benzoylphenyl)methyl]phosphonic acid (**1**) also is cleaved photochemically to give phenyl p-tolyl ketone and orthophosphate. This reactions is similar to that observed for p-nitrobenzylphosphonic acid.[3)] Introduction of alkoxy group to the para position of the benzoyl group of **1** can achieve building up a hydrophobic portion without giving the damage on the capability of photochemical C-P bond cleavage. This paper reports the syntheses and the photo-reactivities of [4(4'-alkoxybenzoyl)phenylmethyl]phosphonic acids (**2**), which can be used as photo-degradable surface active agents. The acids (**2**) were synthesized as follows. 4-Alkoxyphenyl 4-methylphenyl ketones, which were easily prepared by Friedel-Craft reactions of alkyl phenyl ethers with toluoyl chloride, were brominated with N-bromosuccinimide (NBS) in CCl_4 at the presence of benzoyl peroxide (BPO) to give 4-alkoxyphenyl 4-(bromomethyl)phenyl ketones in fairly good yields. The bromides were converted to diethyl [4(4'-alkoxybenzoyl)phenylmethyl]phosphonates by the reaction with triethyl phosphite. Dealkylation of these esters were accomplished by treatment with bromotrimethylsilane in acetonitrile, followed by hydrolysis in water to give **2**.[4)] Pure acids (**2**) were obtained by recrystallization from water or aqueous ethanol.[5)] The yields and UV-spectral data of **2** are shown in Table 1.



2a; R=Me 2c; R=n-Bu 2f; R=C_8H_{17}
2b; R=Et 2d; R=C_6H_{13}

Typical procedure of photolysis: Five ml of an aqueous solution of **2a** (50 mmol dm^{-3}) was adjusted to pH 12 with sodium hydroxide. Argon was bubbled through the solution before irradiation. The solution was irradiated in a Pyrex tube (ϕ=10 mm) with a high-pressure mercury lamp (350 W) for 30 min under cooling with running water. After irradiation, 5 ml of chloroform was added and the mixture was shaken thoroughly. The organic layer was separated and analyzed. 4-Methoxyphenyl tolyl ketone (**3**) and (4-methoxyphenyl)tolylmethanol (**4**), which were assigned by comparison of GLC retention times and ^{1}H NMR spectra with those of authentic samples, were obtained in 63% and 33% yield, respectively. The ratios of the yields of these products were varied with progress of the photolysis; only **3** was produced at the initial stage, while the yield of **4** increased gradually with prolonged irradiation. The total yield of **3** and **4** was approximately in proportion to the irradiation time. The product **4** may be produced by further photolysis of **3**. The other derivatives **2b-e** also gave the similar results. The quantum yields of C-P bond cleavage of these acids are shown in Table 1. Quantum yield of C-P bond cleavage of **2** became greater with increase in the chain length (R).

Some acids (**2**) having a long alkyl group can be expected to act as surface active agents. Their surface active properties such as surface tension of aqueous solutions of **2** were measured by the use of a Du Nouy surface tensiometer (Shimadzu), and the results are shown in Fig. 1.

Table 1. Yields, UV-spectral data, and quantum yields of C-P bond cleavage of **1** and **2**

Compound	R	Yield /%	λmax$^{a)}$ /nm	ε$^{a)}$ X10^{4}	Quantum$^{b)}$ yield
1	-	58	285.0	1.86	0.40$^{3)}$
2a	CH_3	42	294.8	1.41	0.35
2b	C_2H_5	38	294.8	1.43	0.36
2c	C_4H_9	31	296.8	1.45	0.40
2d	C_6H_{13}	28	295.6	1.44	0.42
2e	C_8H_{17}	34	296.8	2.03	0.45

a) Aqueous solution, pH12.

b) Quantum yields of C-P bond cleavage of **2** were determined on thebasis of the combined yields of **3** and**4**, and chemical actinometry using 2-hexanone: Aqueous solutions, 5X10^{-2} mol dm^{-3}, pH 12, were irradiated in a merry-go-round apparatus employing 313nm monochromatic light.$^{2)}$

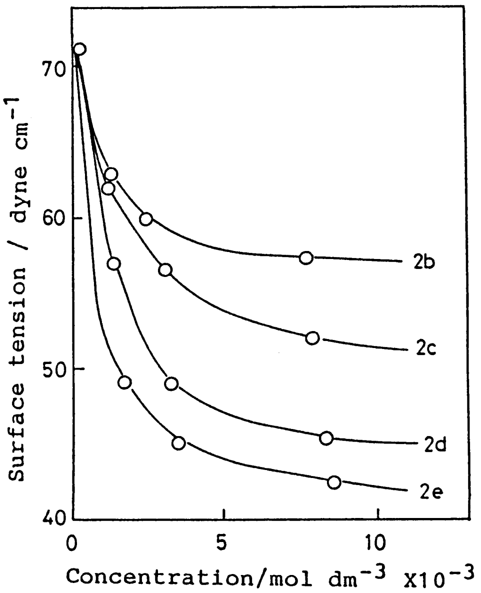
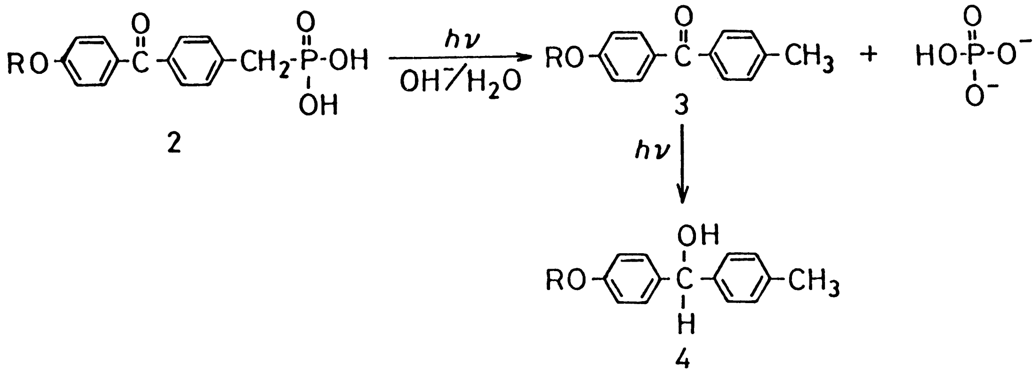


Fig. 1. The relationship between surface tension and the concentration of **2** in aqueous solutions at 25 °C, pH 12.



The effects of UV-irradiation on the surface active properties of aqueous solutions of **2d** were shown in Table 2. Irradiation resulted in rise of the surface tension and in decrease of the foaming power of the solution. These results indicate that **2** has promising properties for use of photo-degradable surfactant. Further studies directed towards clarification of detailed characteristic features as well as further applications of these surfactants are currently in progress in our laboratory.

Table 2. Effects of UV-irradiation on the aqueous solution of **2d**[a)]

Irradiation time min	Surface tension[b)] dyn cm^{-1}	Foaming power[c)] Specific volume[d)]
0	49.5	15
10	52.5	-
30	54.0	-
60	57.2	12
120	-	8

a) Concentration; $3X10^{-3}$ mol dm^{-3}, pH 12, 25 °C. b) Irradiated directly with a Xe lamp (150 W). c) Irradiated through a Pyrex filter with a high pressure mercury lamp (350 W). d) Specific volume=foam volume/foam number.6)

References

1) Y. Okamoto, N. Iwamoto, and S. Takamuku, Chem. Lett., 1984, 2091; Y. Okamoto, N. Iwamoto, and S. Takamuku, J. Chem. Soc., Chem. Commun., 1986, 1516.

2) Y. Okamoto, N. Iwamoto, S. Toki, and S. Takamuku, Bull. Chem. Soc. Jpn., 60, 277 (1987).

3) Y. Okamoto, N. Iwamoto, T. Shikata, and S. Takamuku, Nippon Kagaku Kaishi, 1987, 1255.

4) T. Morita, Y. Okamoto, and H. Sakurai, Bull. Chem. Soc. Jpn., 51, 2165 (1978).

5) **1**: mp 188-190 °C; ^1H NMR (D_2O, NaOD, DSS) δ=3.00(2H, d, J_{PH}=20.0 Hz), 7.2-7.6(9H, m).

2a: mp 89-90 °C; δ=2.90(2H, d, J_{PH}=20.0 Hz), 3.83(3H, s), 6.8-7.8(8H, m).

2b: mp 154-155 °C; δ=1.43(3H, t, J_{HH}=7.0 Hz), 3.27(2H, d, J_{PH}=20.0 Hz), 4.00(2H, q, J_{HH}=7.0 Hz), 6.9-7.8(8H, m).

2c: mp 146-147 °C; δ=0.85(3H, t, J_{HH}=7.0 Hz), 1.3-2.1(4H, m), 3.10(2H, d, J_{PH}=21.0 Hz), 3.88(2H, t, J_{HH}=7.0 Hz), 6,5-7.6(8H, m).

2d: mp 117-119 °C; δ=0.92(3H, t, J_{HH}=7.0 Hz), 1.2-2.0(8H, m), 3.00(2H, d, J_{PH}=20.0 Hz), 3.70(2H, t, J_{HH}=7.0 Hz), 6.3-7.6(8H, m).

2e: mp 127-129 °C; δ=0.92(3H, t, J_{HH}=7.0 Hz), 1.1-2.0(12H, m), 3.0(2H, J_{PH}=20.0), 3.40(2H, t, J_{HH}=7.0 Hz), 6.3-7.6(8H, m).

6) C. Kimura, K. Kashiwaya, K. Murai, N. Sato, and t. Nishiyama, Yukagaku, 32, 258 (1983).

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