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Baeyer-Villiger Oxidation of β-Ionone with Surfactant Type Peracid

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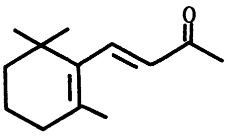
Treatment of β-ionone with 3-heptadesylmonoperphthalic acid in emulsion system facilitates Baeyer-Villiger oxidation

The use of aggregates of surfactant molecules in water to mimic the biological systems is an area of rapidly developing interest.[1,2] We report here the selective Baeyer-Villiger oxidation of β-ionone (**1**), which affords enol acetate, 1-acetoxy-2-(2,6,6-trimethyl-1-cyclohexen-1-yl)-ethene (**2**)[3] as a major product, by the use of surfactant type oxidizing reagent, 3-heptadesyl-monoperphthalic acid (**3**). In general, epoxidation of olefines is normally much faster than Baeyer-Villiger oxiation, therefore, 4-(1,2-epoxy-2,6,6,-trimethylcyclohexan-1-yl)-3-buten-2-one (**4**) and 1-acetoxy-2-(1,2-epoxycyclohexan-1-yl)-ethene (**5**) are known as peracid oxidation products of **1** so far.[4]

Synthesis of **3** was accomplished in several steps starting from heneicosadiene-maleic anhydride cycloadduct **6**.



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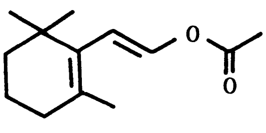

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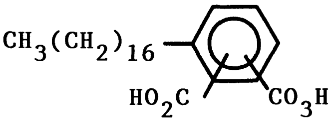

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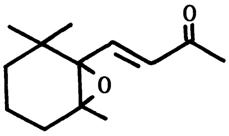

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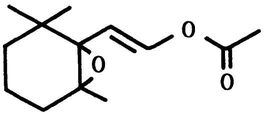

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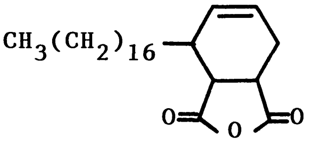

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The typical reaction was initiated by mixing the β-ionone **1** (50 mg), hexane (1 ml), water (10 ml) and 1.1 equiv. of the reagent **3** as monosodium salt. Then the stirring was continued for 24 h. The reaction mixture was treated with 5 ml of 10 % Na$_2$SO$_3$ and exteracted with ether. The organic layer was washed successively with brine, aqueous NaHCO$_3$, and brine. The products ratios and the conversion (%) were determined by GLC (15% DEGS) using lauryl alcohol as an internal standard. The result was compared with monoperphthalic acid (MPPA)[5] and metachloroperbenzoic acid (MCPBA). Variation in the reagents and reaction conditions was done in order to explore possible effects of surfactant on the peracid oxidation as shown in the

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Table 1. Oxidation of β-ionone by peracids

Entry	Reagent	Solvent	Base	Conversion/%	**2**	: **4**	: **5**	Recovery of **1**/%
1	MPPA	Ether	None	86	0	95	5	13
2	MPPA	Hex./H_2O	None	18	2	98	0	70
3	MPPA	Hex./H_2O	SDS	37	85	15	0	30
4	MCPBA	Hex./H_2O	SDS	54	0	100	0	13
5	MPPA	Hex./H_2O	$NaHCO_3$	10	10	90	0	84
6	**3**	Ether	None	38	0	96	0	34
7	**3**	Hex./H_2O	None	33	15	85	0	66
8	**3**	Hex./H_2O	$NaHCO_3$	68	83	11	6	30

Table 1. The results are summarised as follows. Entry 1; When the oxidation was carried out in the homogeneous condition, epoxide **4** was obtained as a major product. Entry 2; When the aqueous hexane-MPPA system was applied, conversion was incomplete and a new product **2**4) was observed. Entry 3; By using the SDS, remarkable conversion of β-ionone **1** to **2** was recognized. Entry 4; On the other hand, in the case of MCPBA, product ratios were not influenced by the additon of sodium dodesylsulfate (SDS). The results of Entries 3 and 4 indicated the presence of carboxylate group, placed nearby the peracid moiety, was crucial for the preparation of **2**. Entry 5; Thus the use of surfactant showed remarkable effect on the selectivity in emulsion system, when compared with that of $NaHCO_3$. Entry 6; Direct oxidation of β-ionone **1** with **3** in homogeneous condition affords **4** in low yield. Entry 7 showed better yield of **2** when compared with Entry 2. Entry 8 clearly indicated favoring Baeyer-Villiger oxidation by the use of **3** as a monosodium salt, giving in 68% conversion and 11 : 83 selectivity.

Selective Baeyer-Villiger oxidation of β-ionone **1**, oriented in the ordered structure of aggregates, can thus be attributed to a differential solvation which is absent in homogeneous solution. Thus, the oxidant **3** "sort out" ketone as a reaction site. Product **2** can serve as an efficient intermediate in the synthesis of various higher terpenoids. Our extention and application of these results will be reported elsewhere.

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