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Reaction of 6-Methyl-6-*p*-tolyl-4-ethoxy-5,6-dihydro-pyran-2-one[1] with Perchloric Acid

Short Communication

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6-Methyl-6-*p*-tolyl-4-ethoxy-5,6-dihydro-pyran-2-one (**1**) undergoes decarboxylative elimination with perchloric acid in ether to give 4-*p*-tolyl-3-penten-2-one (**3**), the structure of which has been confirmed through an unambiguous synthesis.

(Keywords: Decarboxylative elimination, β-Keto-δ-lactone)

Reaktion von 6-Methyl-6-p-tolyl-4-ethoxy-5,6-dihydro-pyran-2-on mit Perchlorsäure (Kurze Mitteilung)

Die Titelverbindung (**1**) ergibt mit Perchlorsäure unter decarboxylierender Eliminierung 4-*p*-Tolyl-3-penten-2-on (**3**). Die Struktur von **3** wurde mittels eines eindeutigen Syntheseweges festgelegt.

In connection with the synthesis of a natural product[2], we needed 6-methyl-6-*p*-tolyl-3,4,5,6-tetrahydro-pyran-2,4-dione (**2**). A synthesis of the desired β-keto-δ-lactone (**2**) was attempted starting from *p*-methyl acetophenone as shown in the following scheme (**4** → **1** → **2**).

Reformatsky reaction of ethyl 3-ethoxy-4-bromo-2-butenoate in anhydrous *THF* furnished the enol ether of the lactone **2** in 40% yield mp. 107–108°. IR: 1715–1735 cm^{-1} (α, β-unsaturated δ-lactone). NMR: δ 1.3 (3 H, $-OCH_2CH_3$, t, $J = 7$ Hz), 1.6 (3 H, $CH_3-\underset{|}{C}Ar-O$, s), 2.3 (3 H, H_3C-Ar, s), 2.85 (2 H, $-CH_2-$, s), 3.85 (2 H, $-OCH_2CH_3$, q, $J = 7$ Hz), 5.5 (1 H, $=CH-$, s), 7.2 (4 H, *Ar*, m). The enolether in the lactone **1** was hydrolysed with perchloric acid in ether at 25° according

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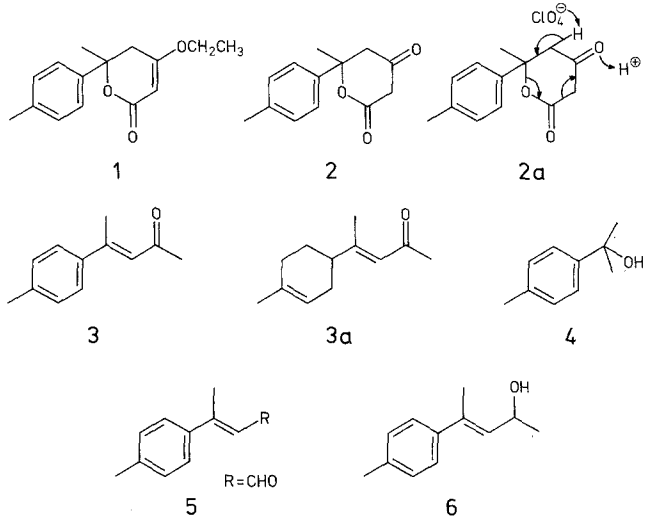
to the procedure of *Levine*[3]. On working up of the reaction mixture, the major product (> 90%) was purified by preparative TLC to afford an oil in 50% yield. IR: 1685 cm^{-1} (conj. carbonyl). NMR of the product showed signals at δ 2.1, 2.2, and 2.4 each integrating for 3 H. The olefinic and aromatic regions have absorptions at 6.4 (1 H) and 7.2 (4 H) respectively. On the basis of above data, we tentatively assigned structure **3** to this product. The formation of the ketone **3** could be rationalized as hydrolysis of the enol ether **1** to afford the β-keto-δ-lactone **2** followed by acid catalysed decarboxylative elimination as shown for **2a** (s. scheme) to give the product **3**. This type of decarboxylative elimination of a β-keto-δ-lactone under these reaction conditions is unprecident[4].



The structure of the unsaturated ketone **3** has been confirmed through an unambiguous synthesis (**4** → **5** → **6** → **3**).

p-Tolyl-2-propanol (**4**) was prepared by the reaction of CH_3MgI on *p*-methylacetophenone in 85% yield. *Vilsmeir* formylation[5] of the tert. alcohol **4** with phosphoryl chloride in anhydrous *DMF* gave the corresponding, α,β-unsaturated aldehyde in 60% yield. I.R.: no absorption due to OH, 2780, 1690 cm^{-1} (conj. —CHO). *Grignard* reaction of CH_3MgI on the above aldehyde resulted in the formation of carbinol **6** in 85% yield. I.R.: no absorption in carbonyl region, 3340-3400 cm^{-1} (OH). NMR: δ 1.1 (3 H, CH_3—CHOH, d, J = 3 Hz), 1.85 (3 H, olefinic CH_3—), 2.2 (3 H, aromatic methyl), 2.45 (1 H,

—CHOH, m), 4.5 (1 H, br, OH), 5.55 (1 H, olefinic H), ~ 7.0 (4 H, aromatic H, m). Oxidation of the unsaturated carbinol with manganese dioxide in dry ether furnished the desired ketone in 75% yield after purification by preparative TLC. It was found to be identical with product **3** (IR, NMR, TLC). *E*-configuration has been assigned to the double bond in ketone **3** in view of the pronounced downfield chemical shift[6] of β-olefinic methyl protons in NMR (δ 2.4). Ketone **3** and a naturally occurring ketone[7] **3a** can be inter-related in that the former may be derived by dehydrogenation from the latter. Actually many compounds having such relations have been isolated from natural sources (e.g. limonene—*p*-cymene, turmerone—*ar*-termerone, piperitone—thymol etc.). It is quite possible that 4-*p*-tolyl-3-penten 2-one (**3**) may be isolated from natural sources in future.

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