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Synthesis of 1-Azido-5-methyl-4-hexen-2-one and Its Catalytic Dimerization

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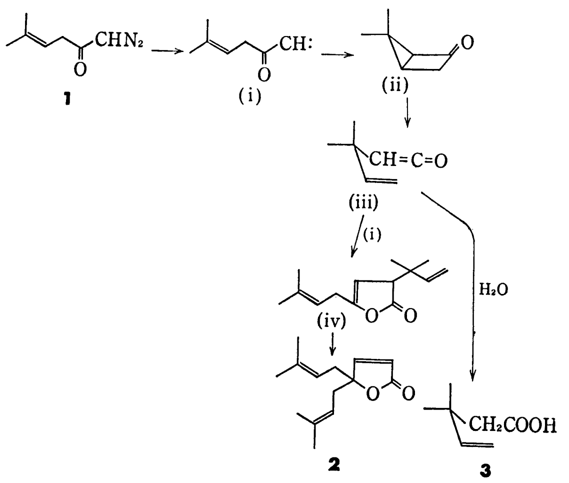
Synopsis. 1-Azido-5-methyl-4-hexen-2-one was synthesized easily from 4-methyl-3-pentenenitrile which was prepared from isoprene. This compound is quite stable. Its catalytic dimerization gave 4,4-bis(3-methyl-2-butenyl)-2-butenolide.

Lokensgard *et al.*[2] studied the decomposition of 1-azido-3-cyclopentenyl-2-propanone and they proposed a mechanism for the decomposition. In this paper, the synthesis and the catalytic dimerization of an acyclic β,γ-unsaturated diazoketone, 1-azido-5-methyl-4-hexen-2-one (**1**), are reported.

The catalytic dimerization of **1** gave a main compound (**2**). The structure of **2** was confirmed to be as follows: The MS showed that **2** was the condensed dimer of **1**. The PMR spectrum showed that the two 3-methyl-2-butenyl groups were equivalent. Since the chemical shifts of the methylene in the above groups were in a higher field than that of **1**, the above groups did not attach to the next carbon of a carbonyl group. Moreover, the coupling constants of the lower olefinic protons (J=6.0 Hz) agreed with that of 2-butenolide.[3] In the IR spectrum, signals at 1750 cm^{-1} for the carbonyl in a five membered lactone and at 1790 cm^{-1} (as the shoulder) were observed, and **2** might be an α,β-unsaturated γ-lactone. From these data, **2** was identified as 4,4-bis(3-methyl-2-butenyl)-2-butenolide (**2**).

The mechanism of the formation of **2** might be as shown in the reaction scheme. Since the acid (**3**) could be obtained when the reaction was quenched with water at the early stage of the reaction, **2** may be produced through the intermediates (ii), (iii), and (iv) as suggested by Lokensgard *et al.*[2]



Experimental

Synthesis of 1-Azido-5-methyl-4-hexen-2-one (1). 1-Chloro-3-methyl-2-butene (60 g), which was prepared from isoprene,[4] was reacted with CuCN(45 g) in benzene (30 ml) in the presence of KI (0.5 g) at 10—20 °C for several hours. From the reaction mixture, 4-methyl-3-pentenenitrile was isolated by the fractional distillation (bp 62—63 °C/15 Torr, 26 g). The nitrile was hydrolyzed by 60 g of 30% aqueous KOH, and 23.7 g of 4-methyl-3-pentenoic acid was obtained. This acid was chlorinated with 30 g of thionyl chloride, and 4-methyl-3-pentenoyl chloride was obtained (bp 60—61 °C/20 Torr, 22.4 g). This chloride was dissolved in ether (30 ml) and the solution was added dropwise into an ether solution (50 ml) of diazomethane, which was prepared from 25 g of nitrosomethylurea, under cooling at 0—5 °C for 3 h. After the addition, the solution was kept at room temperature for 12 h. Careful distillation gave a yellow oil (bp 68—69 °C/3 Torr, 5.3 g). The oil was analyzed by GLC (Apiezon L, 100 °C) (98% purity). This showed the following spectral data: PMR (δ, CCl_4) 1.64 (s, 3H, =$CC\mathbf{H}_3$), 1.76 (s, 3H, =$CC\mathbf{H}_3$), 2.93 (d, 2H, J=7.0 Hz, -$C\mathbf{H}_2$-), 5.12 (s, 1H, -$C\mathbf{H}N_2$), 5.24 (t, 1H, J=7.0 Hz, -C**H**=). IR (cm^{-1}) 2110, 1640.

Catalytic Dimerization of 1. A benzene solution (30 ml) of **1** (5.8 g) was added dropwise to a suspension of 1.0 g of CuO in 100 ml of benzene under reflux with vigorous stirring. After the evolution of nitrogen ceased and the catalyst was removed by filtration, the product was distilled (bp 98—102 °C/3 Torr, 2.8 g). The GLC showed that this distillate contained 84% of a main compound (**2**).

4,4-Bis(3-methyl-2-butenyl)-2-butenolide (2): MS (m/e) 220 (M$^+$), 69 (Base ion, $C_5H_9^+$). PMR (δ, CCl_4) 1.62 (s, 6H, =$CC\mathbf{H}_3$), 1.72 (s, 6H, =$CC\mathbf{H}_3$), 2.41 (d, 4H, J=7.0 Hz, -$C\mathbf{H}_2$-), 5.00 (t, 2H, J=7.0 Hz, -C**H**=), 5.94 (d, 1H, J=6.0 Hz), 7.23 (d, 1H, J=6.0 Hz). IR (cm^{-1}) 1750, 1790. Found: C, 76.22; H, 9.20%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%.

In the other run, when water was added to the reaction mixture as soon as the evolution of nitrogen ceased, a different fraction (bp 65—70 °C/3 Torr) than (**2**) was obtained (15% based on (**1**)). This fraction contained 3,3-dimethyl-4-pentenoic acid (**3**) mainly. (**3**): MS (m/e) 128 (M$^+$). PMR (δ, CCl_4) 1.20 (s, 6H, -$C(C\mathbf{H}_3)_2$), 2.34 (s, 2H, -$C\mathbf{H}_2$-), 5.06 (dd, 1H, J=1.5 Hz, and 10.5 Hz, $\underset{H\diagup\quad\diagdown\mathbf{H}}{\overset{\diagdown\quad\diagup H}{C{=}C}}$), 5.07 (dd, 1H, J=1.5 Hz and 18.0 Hz, $\underset{H\diagup\quad\diagdown H}{\overset{\diagdown\quad\diagup\mathbf{H}}{C{=}C}}$), 6.07 (dd, 1H, J=10.5 Hz and 18.0 Hz, $\underset{\mathbf{H}\diagup\quad\diagdown H}{\overset{\diagdown\quad\diagup H}{C{=}C}}$), 12.27 (s, 1H, -COO**H**). IR (cm^{-1}) 3450, 1710, 995, 915. Found: C, 65.55; H, 10.02%. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.94%.

References

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