A Novel Synthesis of 1, 4-Diketone

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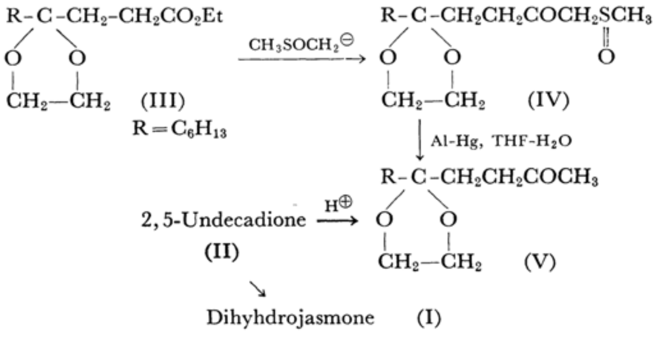
Recently some new ways of preparing dihydrojasmone (I) have been reported in the literature.[1-4] One of the key routes to I is the cyclization of 2, 5-undecadione (II)[2,5,6] or its homologue[7], and so much attention has been paid to the preparation of this diketone (II). In this paper we will describe a synthesis of II via the ω-methylsulfinylmethyl ketone derivative (IV), which is obtainable by the reaction of ethyl γ-ethyleneketaldecanoate (III) with methylsulfinyl carbanion.[8]

The conversion of γ-ketodecanoic acid[9] to the ethyleneketal ester (III), b. p. 117°C/2 mmHg, n_D^{20} 1.4450. Found: C, 65.15; H, 9.99. Calcd. for $C_{14}H_{26}O_4$: C, 65.09; H, 10.14%, IR: 1730 (ester C=O), and 1180, 1140, 1095, and 1045 cm^{-1} (ketal), was carried out by boiling it with ethyl γ-ketodecanoate and ethylene glycol in the presence of *p*-toluenesulfonic acid.[4] The ketal ester (III) was treated with a solution of the methylsulfinyl carbanion (two equivalents) in dimethylsulfoxide-tetrahydrofuran at 0°C under nitrogen.[8] The β-ketosulfoxide (IV) thus produced boiled at 110—120°C/0.08 mmHg (partly isomerized) and gradually solidified, IR: 1705 (C=O) and 1040 cm^{-1} (S=O). The reduction of the crude IV with aluminum amalgam[8] in 90% tetrahydrofuran-10% water gave 5-ethyleneketal-2-undecanone (V), 40% (based on III); b. p. 110°C/2 mmHg, n_D^{20} 1.4648, IR: 1713 (C=O), 1170, 1145, 1100, and 1060 cm^{-1} (ketal). Found: C, 68.29; H, 10.32. Calcd. for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59%. The ketal ketone (V), when heated with dilute acid for 2 hr., was converted into the diketone (II) in a good yield, b. p. 118—120°C/10 mmHg (lit.[5] b. p. 141°C/14 mmHg); IR: 1710 cm^{-1} (C=O). Further evidence for II was obtained by its cyclization to dihydrojasmone (I), whose structure was identified by means of the infrared and mixed-melting-point determination of the 2, 4-dinitrophenylhydrazone of I.[1]

During the course of reaction, the ketonic compounds were purified by using a Girard P reagent. The retention times of the intermediates were as follows (Hitachi F6–D, Chromosorb W (NAW), Silicone SE–30 column, 1 m. long, 0.7 atm. N_2, at 160°C): ethyl γ-ketodecanoate, 14 min.; the ketal ester (III), 38 min.; the ketal ketone (V), 19 min., and the diketone (II), 8 min.



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