## 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.<sup>1-4)</sup> One of the key routes to I is the cyclization of 2, 5undecadione (II)<sup>2,5,6)</sup> or its homologue<sup>7)</sup>, 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  $\omega$ -methylsulfinylmethyl ketone derivative (IV), which is obtainable by the reaction of ethyl  $\gamma$ -ethyleneketaldecanoate (III) with methylsulfinyl carbanion.<sup>8)</sup>

The conversion of  $\gamma$ -ketodecanoic acid<sup>9)</sup> 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<sub>14</sub>H<sub>26</sub>O<sub>4</sub>: C, 65.09; H, 10.14%, IR: 1730 (ester C=O), and 1180, 1140, 1095, and 1045 cm<sup>-1</sup> (ketal), was carried out by boiling it with ethyl  $\gamma$ -ketodecanoate and ethylene glycol in the presence of *p*-toluenesulfonic acid.<sup>4)</sup> The ketal ester (III) was treated with a solution of the methylsulfoxide-tetrahydrofuran at 0°C under nitrogen.<sup>8)</sup> The  $\beta$ -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<sup>8</sup>) in 90% tetrahydrofuran-10% water gave 5-ethyleneketal-2-undecanone (V), 40% (based on III); b. p. 110°C/2mmHg, n<sup>20</sup><sub>D</sub> 1.4648, IR: 1713 (C=O), 1170, 1145, 1100, and  $1060 \text{ cm}^{-1}$  (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.<sup>5</sup>) b. p. 141°C/14 mmHg); IR: 1710 cm<sup>-1</sup> (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.<sup>1</sup>

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<sub>2</sub>, at 160°C): ethyl  $\gamma$ -ketodecanoate, 14 min.; the ketal ester (III), 38 min.; the ketal ketone (V), 19 min., and the diketone (II), 8 min.

$$\begin{array}{c|cccc} R-C-CH_2-CH_2CO_2Et & R-C-CH_2CH_2COCH_2SCH_3\\ \hline O & O & & & & & \\ CH_2-CH_2 & (III) & & & \\ R=C_6H_{13} & & & & & \\ 2,5-Undecadione & \stackrel{H^{\oplus}}{\longrightarrow} & O & & \\ (II) & & & & \\ Dihyhdrojasmone & (I) \end{array}$$

- 1) K. Sisido, S. Torii and M. Kawanisi, J. Org. Chem., 29, 904 (1964).
- G. Stork and J. Borch, J. Am. Chem. Soc., 86, 935 (1964).
  J. L. E. Erickson and F. E. Collins, J. Org. Chem., 30, 1050 (1965).
- 4) E. Gordon, F. Martens and H. Gault, Compt. rend., 261, 4129 (1965).
- 5) H. Hunsdiecker, Ber., 75, 455 (1942).

- 6) J. H. Amin, R. K. Razden and S. C. Bhattacharyya, Perfumery Essent. Oil Record, 49, 502 (1958).
- 7) L. Crombie, J. B. Edgar, S. H. Harper, M. W. Lowe and D. Thompson, J. Chem. Soc., 1950, 3552.
- 8) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 84, 866 (1962); ibid., 86, 1639 (1964); ibid., 87, 1345 (1965).
- 9) A. Takeda, K. Takahasi, S. Torii and T. Moriwake, J. Org. Chem., 31, 616 (1966).