

A New, Short Synthesis of Z-Jasmone

Marian Mikolajczyk* and Wanda Midura

Centre of Molecular and Macromolecular Studies,
Polish Academy of Sciences,
Department of Organic Sulphur Compounds,
90-362 Lodz, Boczna 5, Poland

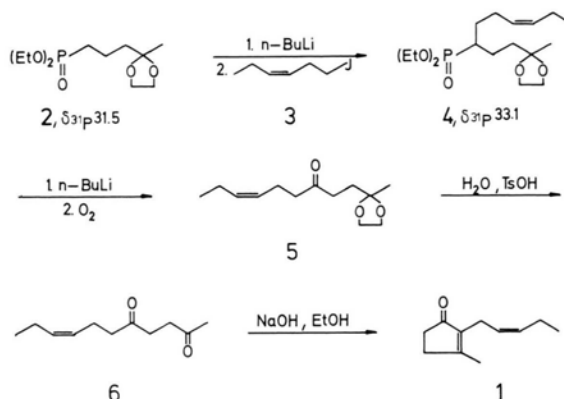
Z. Naturforsch. **41b**, 263–264 (1986);
received October 25, 1985

Z-Jasmone, Synthesis, Ethylene Ketal,
0,0-Diethyl-4-oxo-pentanephosphonate,
Z-3-Hexen-1-yl Iodide

Z-Jasmone (**1**) was prepared from ethylene ketal of 0,0-diethyl-4-oxo-pentanephosphonate (**2**) in four steps in 36% overall yield. A key step in this synthesis is the oxygenation of the α -phosphonate carbanion generated from the monoalkylation product of **2** with Z-3-hexen-1-yl iodide (**3**).

triethyl phosphite and 5-chloro-2-pentanone ethylene ketal [2, 3]. The second one was obtained from the commercially available Z-3-hexen-1-ol (known as a "leaf alcohol" and having more than 98% of isomeric purity) according to the procedure described by Umani-Ronchi [6].

The four-step-synthesis of Z-jasmone (**1**) starting from **2** and **3** is shown below.



The synthesis of 1,4-dicarbonyl compounds has recently attracted great attention in many laboratories [1] since these compounds may be further elaborated into a variety of natural products such as jasmonoids, prostanoids, terpenoids, and methylenomycins having a cyclopentenone ring system. Although many synthetic approaches to 1,4-dicarbonyl compounds are known [1], there is still a need for new routes to a suitably substituted 1,4-dicarbonyl skeleton from simple, easily available, and cheap reagents.

In the course of our studies on the application of organophosphorus and organosulphur reagents for the synthesis of 1,4-dicarbonyl compounds and functionalized cyclopentenones [2, 3] we demonstrated the usefulness of α -phosphoryl sulphides as well as β - and γ -ketophosphonates in the synthesis of dihydro-jasmone and methylenomycin B. Very recently, we have also devised [4] a new route for the synthesis of disubstituted cyclopentenones based on the oxygenation of α -phosphonate carbanions. As an extension of this work we now wish to report a simple and efficient synthesis of Z-jasmone (**1**). This is one of the most important constituents of essential oil derived from jasmine flowers and also of commercial interest [5].

Two key starting materials in our synthesis of **1**, namely ethylene ketal of 0,0-diethyl-4-oxo-pentanephosphonate (**2**) and Z-3-hexen-1-yl iodide (**3**) are easily available and their preparation has already been described. The first substrate was prepared by us [3] in 70% yield *via* the Arbuzov reaction of

The lithium salt of **2**, prepared under standard conditions (THF, -78°C , *n*-BuLi), was alkylated with equimolar amounts of **3** to give the phosphonate **4** in 88% yield [^1H NMR (CDCl_3): δ = 0.91 (t, 3H, J = 7.4 Hz), 1.22 (s, 3H), 1.25 (t, 6H, J = 9.0 Hz), 1.41–2.13 (m, 1H), 3.60–4.24 (m, 8H), 4.84–5.44 (m, 2H); MS (70 eV): m/z = 348 (45%), 233 (7.7%), 303 (11.5%), 87 (100%)]. It is worthy of note that no dialkylation product was observed (^{31}P NMR assay). Then, a solution of the lithium salt of **4** in THF was treated at -78°C with dry oxygen for 10 min and after the usual work-up and preparative TLC (benzene:acetone; 3.5:1) the half-protected 1,4-diketone **5** was obtained in 58% yield [^1H NMR (CDCl_3): δ = 0.92 (t, 3H, J = 7.5 Hz), 1.27 (s, 3H, CH_3), 3.85 (s, 4H), 5.35 (m, 2H); MS (70 eV): m/z = 226 (1.8%), 211 (3.6%), 87 (100%)]. A VPC analysis of this product on a 10% Carbowax column confirmed its stereochemical homogeneity. No attempt was made to optimize the yield of this step. Treatment of **5** dissolved in THF with water in the presence of *p*-toluene-sulphonic acid gave the corresponding 1,4-diketone **6** (yield 90%) [7]. Base-catalyzed cyclization of the latter afforded the desired Z-jasmone (**1**) in 78% yield, which was spectroscopically (^1H NMR, MS) identical to an authentic sample of natural jasmone. In this simple way we were able to synthesize Z-jasmone (**1**) in 36% overall yield.

* Reprint requests to Prof. Dr. M. Mikolajczyk.



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