

A Convenient Preparative Method of Jasmone and its Related Compounds

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Abstract

The reaction of (*Z*)-hept-4-enoic acid (1) with vinylmagnesium bromide gave (*Z*)-undeca-1,8-dien-5-one (2). The oxidation of the terminal vinylic group of (2) affords (*Z*)-undec-8-ene-2,5-dione (3). Jasmone (4) was obtained by the usual alkali cyclization of (3). A variety of alkylcyclopentenones were prepared by the same method.

Introduction

Many cyclopentenones are now in general use in the fragrance industry, and constant research is being conducted to make jasmone and its related compounds available to the perfumer at lower prices.¹ We have reported that the reaction of vinylmagnesium bromide with carboxylic acids lead to unsaturated ketones as the main products.² Thus, vinylmagnesium bromide appears to be an excellent reagent for four-carbon chain-lengthening reactions. This paper concerns a new procedure for the preparation of jasmone and its related compounds from carboxylic acids in three steps, namely Grignard reaction with vinylmagnesium bromide, oxidation with oxygen gas and cyclization with alkali.

Experimental

The Reaction of Vinylmagnesium Bromide with (Z)-Hept-4-enoic Acid (1)

A solution of vinylmagnesium bromide in tetrahydrofuran was prepared from 9.0 g (0.37 mol) of magnesium and 36.4 g (0.34 mol) of vinyl bromide in the usual manner. After cuprous chloride (0.99 g, 0.01 mol) had been added to this solution, a mixture of (*Z*)-hept-4-enoic acid (1) (10.4 g, 0.08 mol) and tetrahydrofuran (50 ml) was dropped, over 2 h, into the solution under nitrogen at room temperature. The reaction mixture was agitated for 8 h at room temperature and worked up with aqueous ammonium chloride. The mixture was extracted with isopropyl ether, and the extracts were dried; the solvent was removed, and the residue distilled to give 11.2 g of an oily product, b.p. 108–110°/18 Torr. This fraction was a mixture of (*Z*)-undeca-1,8-dien-5-one (2) (92%) and (*Z*)-3-methylenedeca-1,7-dien-4-ol (8%) by gas chromatographic analysis. Redistillation (b.p. 108–109°/18 Torr) gave 9.2 g of pure compound (2) (isolated yield 70%). I.r. (liquid film, cm⁻¹): 3010, 1720, 1640, 990, 920, 730. N.m.r. δ 0.91, 3H, t, *J* 7.2 Hz, CH₃; 1.90, 6H, m, CH₂CH=CH₂, CH₂CH=CHCH₂; 2.35, 4H, m, CH₂COCH₂; 4.85–6.15, 5H, m, CH=CH₂, CH=CH.

The same technique was used in the reaction of vinylmagnesium bromide with other carboxylic acids, and their main products are listed in Table 1.

¹ Dubs, P., and Stüssi, R., *Helv. Chim. Acta*, 1978, **61**, 990, and other reports.

² Watanabe, S., Suga, K., Fujita, T., and Saito, N., *Aust. J. Chem.*, 1977, **30**, 427.

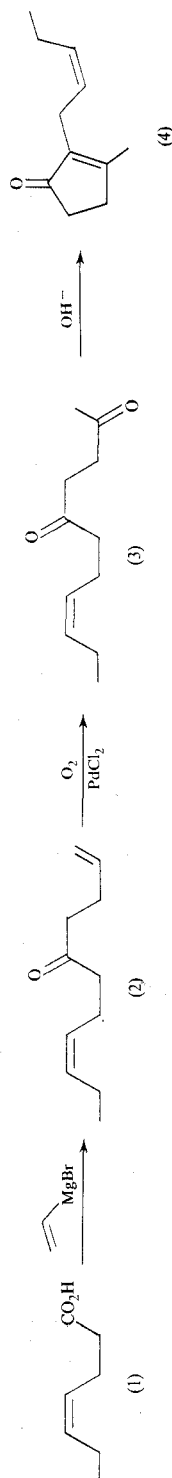
Table 1. Synthesis of 2,3-disubstituted cyclopent-2-enones from carboxylic acids

Yield quoted are isolated yields. Elementary analyses (carbon and hydrogen) agreed with calculated data; results of the analyses are available on application to the Editor-in-Chief, Editorial and Publications Service, CSIRO, 314 Albert Street, East Melbourne, Vic. 3002

Acid	Vinyl ketone (yield)	1,4-Diketone (yield)	Cyclopent-2-enone (yield)
Butyric	oct-7-en-4-one (69%)	octane-2,5-dione (70%)	2-ethyl-3-methyl (70%)
Crotonic	octa-2,7-dien-4-one (10%)	nonane-2,5-dione (72%)	3-methyl-2-propyl (75%)
Pentanoic	non-1-en-5-one (68%)	7-methyloctane-2,5-dione (67%)	2-isopropyl-3-methyl (69%)
3-Methylbutanoic	2-methyloct-7-en-4-one (66%)	decane-2,5-dione (80%)	2-butyl-3-methyl (74%)
Hexanoic	dec-1-en-5-one (71%)	dec-7-ene-2,5-dione (60%)	2-(but-1-en-1-yl)-3-methyl (70%)
Hex-3-enoic	deca-1,7-dien-5-one (34%)	—	—
Hex-2-enoic	deca-1,6-dien-5-one (17%)	6-ethyloctane-2,5-dione (64%)	—
2-Ethylbutyric	3-ethyloct-7-en-4-one (33%)	(Z)-undec-8-ene-2,5-dione (64%)	3-methyl-2-[(Z)-pent-2-en-1-yl] ^a (80%)
(Z)-Hept-4-enoic	(Z)-undeca-1,8-dien-5-one (70%)	undecane-2,5-dione (74%)	3-methyl-2-pentyl ^b (80%)
Heptanoic	undec-1-en-5-one (64%)	(Z)-dodec-9-ene-2,5-dione (66%)	2-[(Z)-hex-3-en-1-yl]-3-methyl (78%)
(Z)-Oct-5-enoic	(Z)-dodeca-1,9-dien-5-one (70%)	dodecane-2,5-dione (76%)	2-hexyl-3-methyl (70%)
Octanoic	dodec-1-en-5-one (78%)	7,9,9-trimethyldodecane-2,5-dione (80%)	3-methyl-2-(1,3,3-trimethylbutyl) (76%)
3,5,5-Trimethylhexanoic	7,9,9-trimethyldec-1-en-5-one (79%)	tridecane-2,5-dione (80%)	2-heptyl-3-methyl (73%)
Nonanoic	tridec-1-en-5-one (80%)	—	—

^a A. Jasmone.

^b Dihydrojasmane.



Scheme 1

Palladium(II)-Catalysed Oxidation of (Z)-Undeca-1,8-dien-5-one (2)

A mixture of palladium(II) chloride (0.4 g, 2.3 mmol), cupric chloride (0.4 g, 2.9 mmol), dimethylformamide (60 ml) and water (3 ml) was stirred at 60–70° for 1 h in a current of oxygen. To this solution, (Z)-undeca-1,8-dien-5-one (2) (2.3 g, 14 mmol) was added dropwise over 1 h; the reaction mixture was stirred for 1 h at 60–70° under a stream of oxygen gas, and treated in the usual way to give a fraction (1.7 g, 67% yield) boiling at 55–57°/5 Torr. This fraction was pure (Z)-undec-8-ene-2,5-dione (3) by gas chromatographic analysis. I.r. (cm^{-1}): 3010, 1720, 1710, 730. N.m.r. δ 0.90, 3H, t, J 7.0 Hz, CH_3 ; 1.77–2.06, 4H, m, $\text{CH}_2\text{CH}=\text{CHCH}_2$; 2.08, 3H, s, COCH_3 ; 2.33, 2H, t, J 5.8 Hz, $\text{CH}_2\text{CH}_2\text{CO}$; 2.53, 4H, s, $\text{COCH}_2\text{CH}_2\text{CO}$; 5.15–5.45, 2H, m, $\text{CH}=\text{CH}$.

The same technique was used for the oxidation of other olefinic ketones, and the results are listed in Table 1.

Jasmone (4) from (Z)-Undec-8-ene-2,5-dione (3)

A mixture of (Z)-undec-8-ene-2,5-dione (3) (1.0 g, 5.5 mmol), 0.5 N sodium hydroxide solution (15 ml) and ethanol (5 ml) was agitated for 6 h under reflux. It was extracted with ether several times, and the combined extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed, and the residue distilled to give 0.78 g (yield 80%) of jasmone (4), b.p. 70–72°/3 Torr. Jasmone (4) was characterized by comparison (i.r., g.l.c. and n.m.r.) with an authentic sample.

Cyclizations of other 1,4-diketones were carried out in the same manner, and the results are listed in Table 1.

Results and Discussion

It is known that the reaction of vinylmagnesium bromide with carboxylic acids gives mixtures of alkenones and alkenols as the main products.² By using this chain-lengthening reaction, the authors prepared jasmone (4) and its related compounds as shown in Scheme 1.

Thus, (Z)-undeca-1,8-dien-5-one (2) was obtained by the reaction of vinylmagnesium bromide with (Z)-hept-4-enoic acid (1) in 70% isolated yield. Various vinyl ketones from corresponding carboxylic acids were prepared in moderate yields, and the results are shown in Table 1. The use of a little cuprous chloride in the reaction is essential in order to obtain the vinyl ketones as the main products.

The oxidations, at terminal double bonds, of olefins to methyl ketones by palladium(II) chloride were recently reported.^{3,4} We have found that such oxidations of terminal vinyl ketones afford the corresponding 1,4-diketones, and an internal double bond is not oxidized. For example, the oxidation of (Z)-undeca-1,8-dien-5-one (2) by palladium(II) chloride gave good yields (67%) of the corresponding methyl ketone, (Z)-undec-8-ene-2,5-dione (3). Similar oxidations of ketones having terminal double bonds give 1,4-diketones in good yields (Table 1). Jasmone (4) can be prepared by an alkali cyclization of (Z)-undec-8-ene-2,5-dione (3). Other cyclopentenones were prepared similarly (Table 1).

Cyclopentenones, which have linear side chains of five or six carbons or with a (Z)-substituted double bond, exhibit a sweet smell like that of jasmone. 2-Isopropyl-3-methylcyclopent-2-enone, which was prepared from isovaleric acid, has a fragrance of mint.

Manuscript received 23 February 1982

³ Tsuji, J., Shimizu, I., and Yamamoto, K., *Tetrahedron Lett.*, 1976, 287.

⁴ McQuillin, F. J., and Perker, D. G., *J. Chem. Soc., Perkin Trans. 1*, 1974, 809.