Synthesis of Two Stereoisomeric 3, 6, 10-Trimethyl-3, 5, 9-undecatrien-2-ones and Their 3-Ethyl Homologs by a Modified Wittig Reaction

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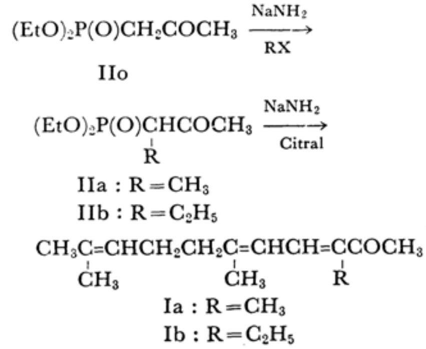
In a preceding paper,1) the present author reported the synthesis of 3, 6, 10-trimethyl-*trans*-3,*trans*-5,9-undecatrien-2-one (3-*trans*-5-*trans*-Ia) and its 5-*cis* isomer (3-*trans*-5-*cis*-Ia) (3-*trans*-5-*trans*- and 3-*trans*-5-*cis*-isomethylpseudoionone) by means of a modified Wittig reaction using diethyl 1-methyl-2-oxopropylphosphonate (IIa). It was also reported, however, that the yield of IIa in the Michaelis-Arbuzov reaction2) was very poor. Another method of preparing diethyl 1-alkyl-2-oxopropylphosphonate was, therefore, sought.

In the present work, the carbanion of diethyl 2-oxopropylphosphonate (IIo) was treated with methyl or ethyl iodide in tetrahydrofuran (THF) or dimethylformamide (DMF), and the resultant 1-methyl- or 1-ethyl-2-oxopropylphosphonate (IIa or IIb) was condensed with citrals to yield 3-methyl- or 3-ethyl-6, 10-dimethyl-3, 5, 9-undecatrien-2-one (Ia or Ib).3)



$$(EtO)_2P(O)CH_2COCH_3 \xrightarrow[RX]{NaNH_2}$$

IIo

$$(EtO)_2P(O)\underset{R}{C}HCOCH_3 \xrightarrow[Citral]{NaNH_2}$$

IIa : $R=CH_3$
IIb : $R=C_2H_5$

$$CH_3\underset{CH_3}{C}=CHCH_2CH_2\underset{CH_3}{C}=CHCH=\underset{R}{C}COCH_3$$

Ia : $R=CH_3$
Ib : $R=C_2H_5$

The results are summarized in Table 1. The infrared spectra of the products containing Ia were superimposable on those of authentic samples.1) Two stereoisomers of Ib were isolated by preparative gas chromatography; their structures were confirmed by the infrared and ultraviolet spectra, and by the elemental analyses of the semicarbazones.

The difference in the ratios of the isomeric products may be ascribed to the partial isomerization of the starting citrals, which was promoted more in DMF than in THF.

The reaction rate of IIb with the citrals in DMF was very slow, and the yield was poor. A peak whose retention-time was close to that of 3-*trans*-5-*cis*-Ib was also present on the gas chromatograms; it might be the 3-*cis*-5-*trans*-Ib. In THF, the reaction did not occur.

Experimental

3, 6, 10-Trimethyl-*trans*-3, *trans*-5, 9-undecatrien-2-one and Its 5-*cis* Isomer (3-*trans*-5-*trans*- and 3-*trans*-5-*cis*-Ia). To the carbanion of IIo, prepared from 7.77 g (0.04 mol) of IIo and 1.56 g (0.04 mol) of sodium amide in 50 m*l* of dry THF, was added 5.60 g (0.042 mol) of methyl iodide; the solution was then allowed to stand overnight at room temperature. The resultant IIa was treated successively with 1.56 g (0.04 mol) of sodium amide and 6.09 g

Table 1. Yields and isomeric compositions of 3-alkyl-6, 10-dimethyl-3, 5, 9-undecatrien-2-ones

Reagent		Medium	Yield* %	Isomeric composition of the product*	
Citral (a : b)	Phosphonate and halide			3-*trans*-5-*trans*	3-*trans*-5-*cis*
96 : 4	IIo and MeI	THF	47.9	95.8	4.2
2 : 98	IIo and MeI	THF	32.9	2.9	97.1
96 : 4	IIo and MeI	DMF	47.8	92.3	7.7
96 : 4	IIo and EtI	DMF	18.2	74.1	25.9
2 : 98	IIo and EtI	DMF	16.7	33.0	67.0

* Yields and compositions of the products were calculated from the peak-areas of the respective gas chromatograms in the same manner as described in the previous paper.1) Apparatus, Hitachi F-6 Gas Chromatograph equipped with hydrogen flame ionization detector. Helium. 180°C. SE-30 + Polyneopentylglycol succinate (for Ia), Apiezon grease M (for Ib).

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1) K. Sasaki, This Bulletin, **39**, 2703 (1966).

2) G. M. Kosolapoff, "Organophosphorus Compounds," 1st Ed., John Wiley & Sons Inc., New York, N. Y. (1950), Chap. 7.

3) *Cf.* W. S. Wadsworth Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

(0.04 mol) of citral a-rich citral (citral a : b=96 : 4)[1] to yield 4.9 g of a product with a boiling point of 97—100°C/0.4 mmHg. By the same procedure using citral b-rich citral (citral a : b=2 : 98),[1] 3.6 g of a product with a boiling point of 94—98°C/0.45 mmHg was obtained. The same scale reaction with the citral a-rich citral in DMF gave 5.6 g of a product with a boiling point of 95—103°C/0.45 mmHg.

3-Ethyl-5, 9-dimethyl-*trans*-3, *trans*-5, 9-undecatrien-2-one and Its 5-*cis* Isomer (3-*trans*-5-*trans*- and 3-*trans*-5-*cis*-Ib). A similar reaction of IIo with 6.50 g (0.042 mol) of ethyl iodide, followed by treatment with the two citral samples in DMF, afforded 2.9 g of a product with a boiling point of 92—112°C/0.25 mmHg and 3.0 g of a product with a boiling point of 90—116°C/0.35 mmHg respectively. Both the products contained a small amount of a compound whose relative retention-time was 0.92—0.93 (3-*trans*-5-*cis*-Ib=1. *Cf.* 3-*trans*-5-*trans*-Ib=1.25—1.28). 3-*Trans*-5-*trans*- and 3-*trans*-5-*cis*-Ib were collected in a pure state by preparative gas chromatography.[*1] 3-*Trans*-5-*trans*-Ib: $\nu_{C=O}$ 1660 (vs), $\nu_{C=C}$ 1632 (vs) and 1591 (m) cm^{-1} (liquid film); λ_{max}^{EtOH} 295 mμ (28000); semicarbazone, mp 164.5—166°C (Found: C, 69.08; H, 9.73; N, 15.30%. Calcd for $C_{16}H_{27}N_3O$: C, 69.27; H, 9.81; N, 15.15%). 3-*Trans*-5-*cis*-Ib: $\nu_{C=O}$ 1662 (vs), $\nu_{C=C}$ 1629 (vs) and 1590 (m) cm^{-1} (liquid film); λ_{max}^{EtOH} 295 mμ (25000); semicarbazone, mp 152—154°C (Found: C, 68.90; H, 9.67; N, 15.35%. Calcd for $C_{16}H_{27}N_3O$: C, 69.27; H, 9.81; N, 15.15%).

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[*1] Preparative gas chromatography: Apparatus, Ohkura Gas Chromatograph Model 1100. Helium. 160°C. Apiezon grease L (8 mm × 3 m).