Synthesis of Ethyl 5, 9-Dimethyl-2, 4, 8-decatrienoates and the Homologs

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(Received November 11, 1966)

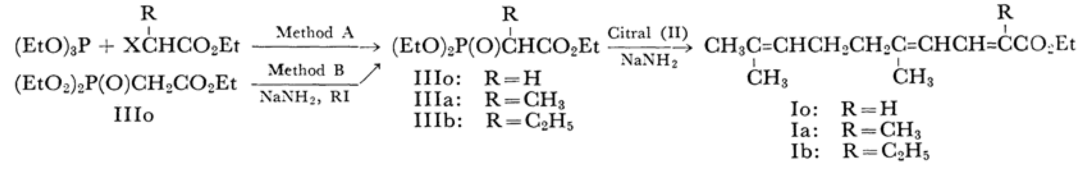
The title compounds (I) were synthesized by means of a modified Wittig reaction in essentially the same way as in previous papers.[1,2] The reaction of citral (II) (either a 96 : 4 mixture of citral a and citral b, or a 2 : 98 mixture of them) with diethyl ethoxycarbonylmethylphosphonate (IIIo) afforded ethyl geranylidene- and ethyl nerylideneacetate (2-*trans*-4-*trans*- and 2-*trans*-4-*cis*-Io) in ratios corresponding to the starting citral a and citral b respectively. The infrared and ultraviolet spectra supported the results.

Ethyl 2, 5, 9-trimethyl- and ethyl 2-ethyl-5, 9-dimethyl-2, 4, 8-decatrienoates (Ia and Ib) were prepared in analogous ways (Methods A and B; see Experimental Section). Gas chromatographic analysis showed, in the last-named product, the presence of 2-*trans*-4-*trans*-, 2-*trans*-4-*cis*-, and 2-*cis*-4-*trans*-isomers. These structures were assigned by means of their infrared and ultraviolet spectra.

The presence of an equimolar amount of sodium iodide in the above reaction resulted in a marked decrease in the reaction rate and reduced the partial isomerization of citrals prior to the condensation, but the stereochemistry of the reaction was not affected at all, or scarcely so.

All the results are summarized in Tables 1 and 2.

The infrared spectra of 2-*trans* compounds showed a band in the 720—770 cm^{-1} region which should be assigned as the "family band" characteristic of a *trans*-α, β-unsaturated carboxylate.[3] The intensities of the bands increased in the order of the substituent at the α-carbon atom; Me>Et>H. This fact suggests that a hyperconjugation effect of the substituent, *i. e.*, a cross conjugation in the system, plays an important role in the intensitification of the band.



$$(EtO)_3P + X\overset{R}{C}HCO_2Et \xrightarrow{\text{Method A}} (EtO)_2P(O)\overset{R}{C}HCO_2Et \xrightarrow[\text{NaNH}_2]{\text{Citral (II)}} CH_3\underset{CH_3}{C}{=}CHCH_2CH_2\underset{CH_3}{C}{=}CHCH{=}\overset{R}{C}CO_2Et$$

$$\underset{\text{IIIo}}{(EtO_2)_2P(O)CH_2CO_2Et} \xrightarrow[\text{NaNH}_2,\ \text{RI}]{\text{Method B}} \nearrow$$

IIIo: $R=H$
IIIa: $R=CH_3$
IIIb: $R=C_2H_5$

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

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[1] K. Sasaki, This Bulletin, **39**, 2703 (1966).
[2] K. Sasaki, *ibid.*, **40**, 2967 (1967).
[3] W. L. Walton and R. B. Hughes, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

TABLE 1. YIELDS AND COMPOSITIONS OF ETHYL 5,9-DIMETHYL-2,4,8-DECATRENOATES AND THE HOMOLOGS

Attempted compound	Citral a)	Method	Bp °C/mmHg	Yield of I, % b)	Composition of the product b)			Analysis			
					2-*trans*-4-*trans*	2-*trans*-4-*cis*	2-*cis*-4-*trans*	C, %		H, %	
								Found	Calcd	Found	Calcd
Io	IIa-rich II	A	103—104/0.5	72	91.2	8.8		75.76	75.63	10.02	9.97
Io	IIb-rich II	A	91—93/0.25	45	2.6	97.4		74.94	75.63	10.10	9.97
Ia	IIa-rich II	A	98—103/0.25	62	89.5	10.5		75.98 c)	76.23	10.18 c)	10.24
Ia	IIb-rich II	A	92—96/0.3 d)	63	3.3	96.7		76.18 c)	76.23	10.44 c)	10.24
Ia	IIa-rich II	B	100—110/0.35 d)	27	92.2	7.8					
Ia	IIb-rich II	B	94—100/0.35 d)	20	1.4	98.6					
Ib	IIa-rich II	A	106—116/0.4 d)	71	72.0	12.4	15.5	76.94 c)	76.76	10.39 c)	10.47
Ib	IIb-rich II	A	99—110/0.4 d)	55	16.0	75.6	8.4	76.36 c)	76.76	10.54 c)	10.47
Ib	IIa-rich II	B	100—117/0.2 d)	43	76.0	9.3	14.7				
Ib	IIb-rich II	B	93—105/0.2 d)	40	4.3	91.4	4.4				
Ib	IIa-rich II	A e)	94—106/0.15 d)	32	78.8	6.6	14.6				
Ib	IIb-rich II	A e)	88—98/0.12 d)	35	3.5	92.2	4.3				

a) IIa-rich II and IIb-rich II represent a 96 : 4 and a 2 : 98 mixture of citral a (IIa) and citral b (IIb), respectively (see Ref. 1).
b) Yields and compositions of the products were determined by the gas chromatography (*cf.* Ref. 1).
c) These values are those of the redistilled products.
d) In these products, there were one or more impurities besides the attempted compounds. Especially, a small amount of a compound that might be reasonably explained as 2-*cis*-4-*cis*-Ib was present in the products containing Ib, but it could not be isolated.
e) The method A was modified by the addition of an equimolar amount of sodium iodide.

TABLE 2. INFRARED AND ULTRAVIOLET ABSORPTION DATA a)

Compound	Infrared absorption (liquid film) cm^{-1}				Ultraviolet absorption	
	$\nu_{C=O}$	$\nu_{C=C}$	δ_{C-H}	Family band	λ_{max} mμ	ε_{max}
2-*Trans*-4-*trans*-Io	1713 vs	1639 vs, 1614 m	980 m	721 w	279	18700
2-*Trans*-4-*cis*-Io	1714 vs	1638 vs, 1614 m	979 m	723 w	279.5	14200
2-*Trans*-4-*trans*-Ia	1706 vs	1637 s, 1607 w		752 s	282	24700
2-*Trans*-4-*cis*-Ia	1705 vs	1631 s, 1605 w		752 s	283	23500
2-*Trans*-4-*trans*-Ib	1705 vs	1636 m, 1601 w		766 m	282	24800
2-*Trans*-4-*cis*-Ib	1705 vs	1635 m, 1599 w		766 m	282.5	22500
2-*Cis*-4-*trans*-Ib	1705 vs	1634 s, 1596 w			281	24900

a) These data are those of the compounds isolated by the gas chromatography except Io, the data of which are those of the mixtures noted in Table 1.

Experimental

Phosphonates. Diethyl ethoxycarbonylmethyl-, diethyl 1-ethoxycarbonylethyl-, and diethyl 1-ethoxycarbonyl-*n*-propylphosphonate (IIIo, IIIa and IIIb) were prepared in a manner similar to that described before.[1,2] IIIo: Bp 132—136°C/9 mmHg ($\nu_{C=O}$ 1742 (vs), $\nu_{P=O}$ 1265 (vs), ν_{P-O} 1164 (s), ν_{C-O} 1048 (vs) cm^{-1}. Found: C, 42.48; H, 7.91%. Calcd for $C_8H_{17}O_5P$: C, 42.86; H, 7.64%). IIIa: Bp 128—132°C/10 mmHg ($\nu_{C=O}$ 1735 (vs), $\nu_{P=O}$ 1256 (vs), ν_{P-O} 1163 (vs), ν_{C-O} 1022 (vs) cm^{-1}. Found: C, 45.11; H, 8.33%. Calcd for $C_9H_{19}O_5P$: C, 45.38; H, 8.04%). IIIb: Bp 136—138°C/10 mmHg ($\nu_{C=O}$ 1740 (vs), $\nu_{P=O}$ 1260 (vs), ν_{P-O} 1162 (s), ν_{C-O} 1024 (vs) cm^{-1}. Found: C, 47.36; H, 8.52%. Calcd for $C_{10}H_{21}O_5P$: C, 47.61; H, 8.39%).

General Procedure. *Method A.*[1] A phosphonate carbanion, prepared from the phosphonate and sodium amide in dry dimethylformamide, was treated with a citral preparation to yield the corresponding isomeric mixture of I.

Method B.[2] The carbanion of IIIo was treated successively with an appropriate alkyl iodide, sodium amide, and a citral preparation to afford the corresponding isomeric mixture of I.

The author is indebted to Professor Masaki Ohta and Assistant Professor Rokuro Sudo of the Tokyo Institute of Technology, and to Dr. Kazuyoshi Fujiwara of Tamura Veterinary Chemicals, Ltd., for their continued support.