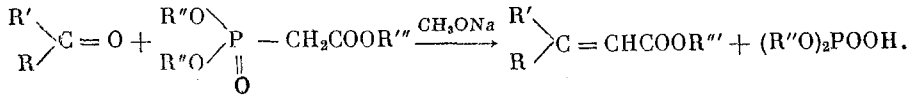
SYNTHESIS OF ISOPRENOID ACIDS FROM ISOPRENOID KETONES BY THE ACTION OF THE DIETHYL ESTER OF CARBETHOXYMETHYLPHOSPHONIC ACID

B. G. Kovalev, L. A. Yanovskaya and V. F. Kucherov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 10, pp. 1876-1877, October, 1962
Original article submitted May 8, 1962

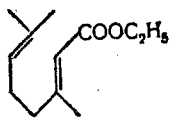
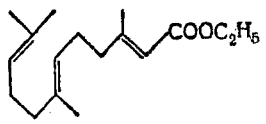
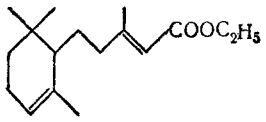
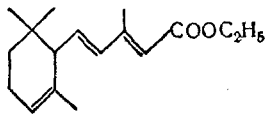
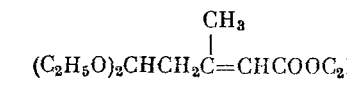
It was shown by us in [1] and by other authors [2] that carbethoxymethylenetriphenylphosphoran does not react with aliphatic ketones under ordinary Fittig reaction conditions. Recently, in a review of his own patents [3] Pommer noted that in the presence of alkali the diethyl ester of carbethoxymethylphosphonic acid reacts with carbonyl compounds as follows



He used this reaction for the ketone C_{18}. Later, it was shown that this reagent also reacts with acetone [4].

We were interested in the possibility of using the diethyl ester of carbethoxymethylphosphonic acid for synthesizing various α, β-unsaturated acids based on isoprenoid ketones. It was found that methylheptenone, geranylacetone,

Properties of the Isoprenoid Esters Obtained

Formula	Yield, B.p., °C (p, mm Hg)	n_D (t, °C)	λ_{max} (ε) (in alcohol)	Lit. ref.
	43,2 55(0,23)	1,4653	218,5 (11,000)	[5]
	53,2 107—108(0,27)	1,4789 (21)	219 (7950)	[6]
	43,8 86—89(0,16)	1,4852 (19,5)	219 (6250)	[6,7]
	27,4 114—117(0,1)	1,5261 (20,5)	272,5 (16800)	[7]
	31,8* 114—117(6)	1,4459 (20)	222 (7500)	

* Product described for the first time. Found: C 62.86, 62.90; H 9.92, 9.75%. $C_{12}H_{22}O_4$. Calculated: C 62.58; H 9.63%.

α-ionone, α-dihydroionone and the diethyl acetal of acetoacetic aldehyde reacts comparatively readily with the diethyl ester of carbethoxymethylphosphonic acid, forming the corresponding esters of isoprenoid acids with a satisfactory yield (see Table).

Under the reaction conditions pseudoionone becames tarry, while β-ionone remains unchanged. An investigation by means of gas-liquid chromatography of the ethyl ester of geranic acid obtained in this way (chromatography conditions: length of column 2 m with 2% polyethylene glycol on refractory brick, carrier gas He, input 80 ml/min, 130°) showed that it is a mixture of the cis- and trans- isomers, their ratio being approximately 1 : 1. Therefore, in this case the reaction is not stereospecific.

EXPERIMENTAL

All the experiments were carried out by standard procedure. To a solution of 0.025-0.03 mole of the diethyl ester of carbethoxymethylphosphonic acid in 40-45 ml of dimethylformamide was added dropwise a solution of 0.025-0.03 mole of sodium ethylate in 14-15 ml of absolute alcohol. The mixture was stirred for 1 hr at room temperature; it was then heated at 70-80° for 5-7 hr. cooled, poured into 400 ml of water, extracted with ether, dried with magnesium sulfate, and distilled. The constants and ultraviolet spectra of the compounds obtained agree with literature data.

SUMMARY

A method for the synthesis of isoprenoid acids is proposed, based on the reaction of isoprenoid ketones with the diethyl ester of carbethoxymethylphosphonic acid.

LITERATURE CITED

1. V. F. Kucherov, L. A. Yanovskaya, B. G. Kovalev, Dokl. AN SSSR 133, 370 (1960).
2. S. Trippett, D. M. Walker, J. Chem. Soc., 1266 (1961).
3. H. Pommer, Angew. Chemie 72, 811 (1960).
4. W. Wadsworth, W. Emmons, J. Amer. Chem. Soc. 83, 1733 (1961).
5. I. N. Nazarov, Zh. A. Krasnaya, V. P. Vinogradov, Zh. Obshch. khimii 28, 460 (1958).
6. A. Caliezi, H. Schinz, Helv. chim. acta 35, 1637 (1952).
7. A. Caliezi, H. Schinz, Helv. chim. acta 33, 1129 (1950).
