NOTES

Synthesis of Pseudoionone and its Homologues Using the Wittig Reaction

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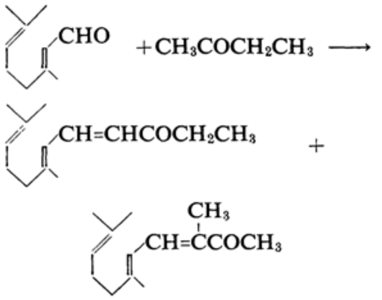
(Received May 1, 1962)

Pseudoionone and its homologues are prepared by the condensation of citral with ketone in the presence of alkali; in the case of unsymmetrical alkyl ketones, however, a mixture of isomers is produced. For example, ethyl methyl ketone gives a mixture of *n*-methylpseudoionone and isomethylpseudoionone, and the separation of these isomers is very difficult. In order to obtain pure *n*-methylpseudoionone and isomethylpseudoionone separately, the Wittig olefin synthesis[1], in which the olefinic double bond is to be located in a given position, was adopted. For this paper pseudoionone and three of its homologues were synthesized by means of the Wittig reaction, i. e., the reaction of citral with triphenylphosphineacylmethylene. The products were identified as their 2, 4-dinitrophenylhydrazones.



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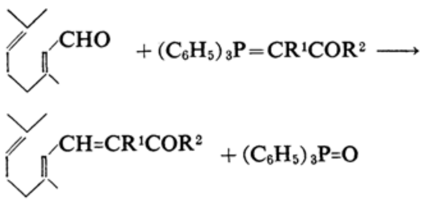
[1] U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

TABLE I. $(C_6H_5)_3P{=}CR^1COR^2$

R^1	R^2	M. p. °C	Yield		Anal. Calcd. %	Anal. Found %	M. p. °C
H	CH_3	205~206 (from $MeOH+H_2O$)	71%				205~206[2]
H	C_6H_5	190~192 (from C_6H_6+petr. ether)	58%	$C_{26}H_{21}OP$	C: 82.10 H: 5.57	81.74 5.81	178~180[2]
H	C_2H_5	221~222 (from $MeOH+H_2O$)	82%	$C_{22}H_{21}OP$	C: 79.50 H: 6.37	79.71 6.38	
CH_3	CH_3	193~195 (from $MeOH+H_2O$)	55%	$C_{22}H_{21}OP$	C: 79.50 H: 6.37	79.67 6.56	

TABLE II. 2, 4-DINITROPHENYLHYDRAZONE OF PSEUDOIONONE AND ITS HOMOLOGUES

R^1	R^2	M. p. °C		Anal. Calcd. %	Anal. Found %	M. p. °C
H	CH_3	144~145	$C_{19}H_{24}N_4O_4$	C: 61.27 H: 6.48 N: 15.05	60.94 6.74 15.18	143
H	C_6H_5	126~127	$C_{24}H_{26}N_4O_4$	C: 66.34 H: 6.03 N: 12.90	65.69 6.16 12.92	
H	C_2H_5	149~150	$C_{20}H_{26}N_4O_4$	C: 62.16 H: 6.78 N: 14.50	61.83 6.91 14.56	151~151.5[5]
CH_3	CH_3	113~115	$C_{20}H_{26}N_4O_4$	C: 62.16 H: 6.78 N: 14.50	62.37 6.43 14.51	113~113.5[6]



Triphenylphosphineacylmethylenes were prepared by Ramirez's method[2] through the phosphonium salts obtained from triphenylphosphine with appropriated α-halogenoketones. Different structures have been suggested for the triphenylphosphineacylmethylenes by Michaelis[3], Wittig[4] and Ramirez[2]. The elementary analysis of carbon and hydrogen for the triphenylphosphineacylmethylenes obtained favored the formulae $(C_6H_5)_3P{=}CR^1\cdot COR^2$) which Ramirez suggested.

Pseudoionone and its homologues were obtained by the reaction of citral with triphenylphosphineacylmethylenes in *n*-butyl ether at 100°C for 4~5 hr. and thereafter treated with 2, 4-dinitrophenylhydrazonium sulfate to give their hydrazones (see Table II). Moreover, the pseudoionone obtained above gave α-ionone by the usual method, heating with 85% phosphoric acid: this α-ionone was identified as its 2, 4-dinitrophenylhydrazone (m. p., 144~145°C, Found: N, 15.28; Calcd. for $C_{19}H_{24}\cdot N_4O_4$: N, 15.05%).

Experimental

Triphenylphosphineacylmethylenes. — Triphenylphosphineacylmethylenes were prepared according to the methods described in Ramirez's paper. A solution of triphenylphosphine and α-haloketone was allowed to stand at room temperature for 1 day; then triphenylphosphineacylmethylene was obtained as a crystal by shaking the obtained phosphonium salt with 10% aqueous sodium carbonate.

Pseudoionone and its Homologues.—A solution of citral (0.01 mol.) and triphenylphosphineacylmethylene (0.01 mol.) in *n*-butyl ether (10 cc.) was heated at 100°C for 4~5 hr. The solvent was removed in vacuo, ether was added to the residue, and then the crystallized triphenylphosphine oxide was filtered off. The oily residue obtained on the removal of the solvent from the ether solution was

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[2] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

[3] A. Michaelis and E. Kohler, *Ber.*, 32, 1566 (1899).

[4] G. Wittig and U. Schöllkopf, ibid., **87**, 1318 (1954).

[5] Y. Naves, *Bull. soc. chim. France*, **1951**, 640.

[6] H. Barbier, et al., ibid., **1951**, 254.

taken up in ethanol and then treated with an aqueous ethanolic solution of 2, 4-dinitrophenylhydrazonium sulfate. The crude 2, 4-dinitrophenylhydrazones were recrystallized from ethanol.

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