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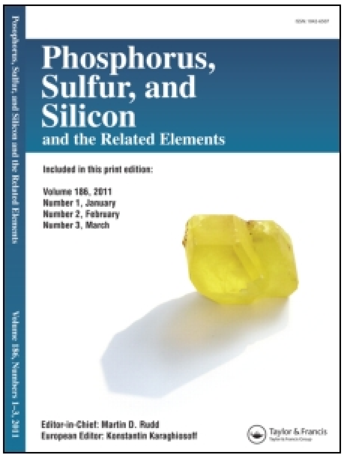

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SYNTHESIS OF DIETHYL 1-ARYLVINYL PHOSPHATES FROM PHENACYL BENZOATES WITH TRIETHYL PHOSPHITE

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SYNTHESIS OF DIETHYL 1-ARYLVINYL PHOSPHATES FROM PHENACYL BENZOATES WITH TRIETHYL PHOSPHITE

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The reaction of phenacyl benzoates ($X-C_6H_4-COCH_2OCO-C_6H_4-Y$: X; H, *p*-Me, *p*-MeO, *p*-Cl, Y; H, *p*-Me, *p*-MeO, *m*-MeO, *p*-Cl, *m*-Cl) with triethyl phosphite at 140°C exclusively leads to diethyl 1-arylvinyl phosphates and ethyl benzoates in very high yields. The mechanism of this reaction is discussed.

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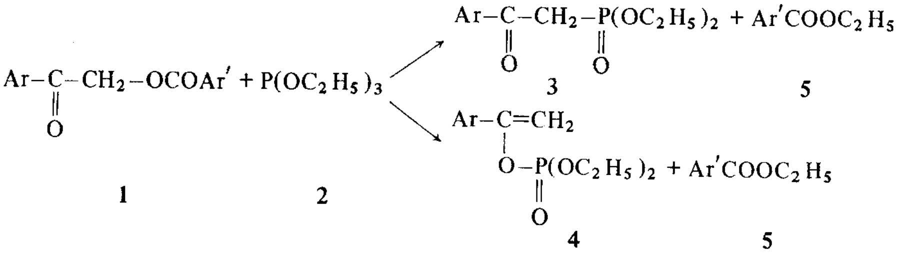
Various studies have been published on the scope and mechanism of the Perkow reaction with α-halo ketones.[1-8] And it is well known that the reactions of these halides with triethyl phosphite (**2**) lead to ketophosphonates (**3**) and/or enol phosphates (**4**), and that the nature of the halogen atom in these halides and the reaction temperature have substantial effects on the course of the reaction.

However, no work has been reported on the study of the reaction using phenacyl benzoates (**1**). In this paper, we wish to report on the reaction of a series of phenacyl benzoates with **2**.

The reaction of phenacyl benzoate (**1a**) with **2** without solvent at 140°C gives diethyl 1-phenylvinyl phosphate (**4a**) and ethyl benzoate (**5**) in 97 and 96% yield, respectively. The product **4a** was identified by nmr, mass and ir spectra, and also from the acetophenone and triethyl phosphate formed (both compounds were identified by mass spectrum and GLC) by treating **4a** with absolute ethanol in the presence of catalytic amounts of *p*-toluenesulfonic acid.[1] The product **5** was identified by comparison of its gas chromatogram with that of an authentic sample.

Similarly, the reactions of the other phenacyl benzoates (**1b–1i**) with **2**, and the identifications of the reaction products were carried out by the method described above. These results are shown in Table I.

It is interesting that this reaction gives exclusively **4** in contrast with that of the corresponding α-bromoacetophenones which give mixtures of vinyl- and ketophosphonates; the α-chloroacetophenones give exclusively vinyl phosphates.[8, 9] The increasing occurrence of the Michaelis-Arbuzov reaction is in the order Cl < Br < I for the halogen. The fact can be explained by the increase in the polarization of the carbon-halogen bond, which facilitates the elimination of the halide ion and thus favors the initial nucleophilic attack of the phosphorus on the α-carbon atom rather than on the carbonyl.[4] Since the facility of the elimination of leaving groups in the S_N2 reaction is generally in the order I > Br Cl > $OCOCH_3$,[10] the elimination of halogen atom should be easier than that of benzoyloxy groups. From these facts, it is considered that this reaction leads exclusively to vinyl phosphates from phenacyl



$$\underset{\mathbf{1}}{Ar-\underset{\underset{O}{\|}}{C}-CH_2-OCOAr'} + \underset{\mathbf{2}}{P(OC_2H_5)_3} \begin{cases} \xrightarrow{} \underset{\mathbf{3}}{Ar-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2} + \underset{\mathbf{5}}{Ar'COOC_2H_5} \\ \xrightarrow{} \underset{\mathbf{4}}{Ar-\underset{\underset{O-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2}{|}}{C}=CH_2} + \underset{\mathbf{5}}{Ar'COOC_2H_5} \end{cases}$$

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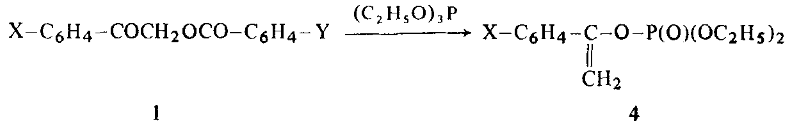
TABLE I

Synthesis of Diethyl 1-Arylvinyl Phosphates (4) from Phenacyl Benzoates (1) with Triethyl Phosphite (2)



$$\underset{\mathbf{1}}{X{-}C_6H_4{-}COCH_2OCO{-}C_6H_4{-}Y} \xrightarrow{(C_2H_5O)_3P} \underset{\mathbf{4}}{X{-}C_6H_4{-}\underset{\underset{CH_2}{\|}}{C}{-}O{-}P(O)(OC_2H_5)_2}}$$

	Materials, 1		Reactn. time, hr	Products, 4		Yield, %	Bp, °C/mm Hg	Anal.		
	X	Y			X			NMR ($CDCl_3$), δ	Ir, cm^{-1} (KBr)	MS *m/e* (M^+)
a	H	H	5.0	a	H	97	113–115/0.4	1.10–1.60 (t, 6, CH_3, *J* = 7 Hz) 3.90–4.50 (q, 4, CH_2, *J* = 7 Hz) 5.10–5.40 (m, 2, C = CH_2) 7.20–7.80 (m, 5, aryl)	1640 (>C=CH_2) 1260 (P=O) 1020 (P–O–C_2H_5)	256
b	H	*p*-Me	7.0	a	H	86	99–106/0.25	The same results as described above.		
c	H	*p*-MeO	7.5	a	H	88	100–105/0.1			
d	H	*m*-MeO	4.5	a	H	90	103–108/0.2			
e	H	*p*-Cl	2.5	a	H	88	98–104/0.1			
f	H	*m*-Cl	2.0	a	H	88	103–110/0.2			
g	*p*-Me	H	19.0	**b**	*p*-Me	87	110–118/0.2	1.10–1.60 (t, 6, CH_3, *J* = 7 Hz) 2.35 (s, 3, CH_3) 3.80–4.40 (q, 4, CH_2, *J* = 7 Hz) 5.00–5.20 (m, 2, C = CH_2) 6.90–7.60 (m, 4, aryl)	1645 (>C=CH_2) 1270 (P=O) 1025 (P–O–C_2H_5)	270
h	*p*-MeO	H	24.0	c	*p*-MeO	79	118–124/0.08	1.10–1.60 (t, 6, CH_3, *J* = 7 Hz) 3.75 (s, 3, OCH_3) 3.85–4.45 (q, 4, CH_2, *J* = 7 Hz) 4.95–5.15 (m, 2, C = CH_2) 6.60–7.60 (m, 4, aryl)	1635 (>C=CH_2) 1260 (P=O) 1020 (P–O–C_2H_5)	286
i	*p*-Cl	H	1.5	**d**	*p*-Cl	91	107–116/0.15	1.10–1.60 (t, 6, CH_3, *J* = 7 Hz) 3.80–4.50 (q, 4, CH_2, *J* = 7 Hz) 5.05–5.30 (m, 2, C = CH_2) 7.00–7.60 (m, 4, aryl)	1640 (>C=CH_2) 1265 (P=O) 1025 (P–O–C_2H_5)	290

[a] All reactions were carried out using 0.02 mol of **1** and 0.03 mol of **2** at 140°C.

benzoates via the enol phosphonium salt, which is formed by the initial selective attack of phosphorus on the carbonyl oxygen atom of the phenacyl groups followed by the elimination of benzoate ion.

EXPERIMENTAL

Instruments. NMR spectra were recorded on a Hitachi Model R-24 (60Mc) spectrometer using Me_4Si as an internal standard. Ir spectra were determined on a Shimazu Model IR-27C infrared spectrometer. Mass spectra were recorded on a Hitachi Model RM-50GC (70 eV) gas chromatography-mass spectrometer. GLC measurements were done on a Shimazu Model GC-4BPT instrument equipped with a 0.5 x 200 cm Silicone SE-30 (5%) on Chromosorb G (60-80 mesh) column. Melting points were determined on a Yanaco MP apparatus and were uncorrected.

Materials. Phenacyl benzoates (**1**) were prepared from the corresponding phenacyl bromides and the sodium benzoates by means of the usual method.[11, 12]

Phenacyl benzoate (**1a**): mp 118.0-118.5°C [lit.[13] mp 117.0-117.5°C]; nmr ($CDCl_3$) δ 5.50 (s, 2, CH_2), 7.20-8.30 (m, 10, aryl); mass spectrum *m/e* 240 (M^+). Phenacyl 4-methylbenzoate (**1b**): mp 103.5-104.0°C; nmr ($CDCl_3$) δ 2.40 (s, 3, CH_3), 5.50 (s, 2, CH_2), 7.10-8.10 (m, 9, aryl); mass spectrum *m/e* 254 (M^+). Phenacyl 4-methoxybenzoate (**1c**): mp 138.5-139.0°C; nmr ($CDCl_3$) δ 3.80 (s, 3, OCH_3), 5.45 (s, 2, CH_2), 6.75-8.15 (m, 9, aryl); mass spectrum *m/e* 270 (M^+). Phenacyl 3-methoxybenzoate (**1d**): mp 84.0-84.5°C; nmr ($CDCl_3$) δ 3.85 (s, 3, OCH_3), 5.50 (s, 2, CH_2), 7.00-8.00 (m, 9, aryl); mass spectrum *m/e* 270 (M^+). Phenacyl 4-chlorobenzoate (**1e**): mp 90.0-90.4°C; nmr ($CDCl_3$) δ 5.50 (s, 2, CH_2), 7.20-8.10 (m, 9, aryl); mass spectrum *m/e* 274 (M^+). Phenacyl 3-chlorobenzoate (**1f**): mp 118.8-119.6°C; nmr ($CDCl_3$) δ 5.50 (s, 2, CH_2), 7.15-8.15 (m, 9, aryl); mass spectrum *m/e* 274 (M^+). 4-Methylphenacyl benzoate (**1g**): mp 98.5-99.0°C; nmr ($CDCl_3$) δ 2.40 (s, 3, CH_3), 5.50 (s, 2, CH_2), 7.15-8.30 (m, 9, aryl); mass spectrum *m/e* 254 (M^+). 4-Methoxyphenacyl benzoate (**1h**): mp 110.5-110.7°C; nmr ($CDCl_3$) δ 3.80 (s, 3, OCH_3), 5.45 (s, 2, CH_2), 6.75-8.15 (m, 9, aryl); mass spectrum *m/e* 270 (M^+). 4-Chlorophenacyl benzoate (**1i**): mp 118.7-119.2°C; nmr ($CDCl_3$) δ 5.40

(s, 2, CH_2), 7.20-8.30 (m, 9, aryl); mass spectrum *m/e* 274 (M^+). Triethyl phosphite (**2**) was prepared from the reaction of PCl_3 with ethanol in the presence of a base, and distilled from metallic sodium.[14] bp 54.0-55.0°C/18 mmHg [lit.[14] bp 57-58°C/16 mmHg].

General Procedure. A mixture of 0.02 mole of **1** and 0.03 mole of freshly distilled **2** in a round flask was heated at 140°C for a given time. After excess **2** had been removed from the resultant mixture under water aspirator pressure, the residual liquid was distilled *in vacuo* to give **4** and **5**.

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