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ORGANOPHOSPHORUS CHEMISTRY 24.¹ WITTIG REACTION OF β -AROYLACRYLIC- AND CINNAMIC ACIDS

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ORGANOPHOSPHORUS CHEMISTRY 24.¹ WITTIG REACTION OF β -AROYLACRYLIC- AND CINNAMIC ACIDS

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The Wittig reaction of β -aroylacrylic-(**2b,c**) and cinnamic (**4b**) acids has been investigated. Depending on the experimental conditions, reaction of **2b,c** with alkylidene phosphoranes (**1a,b**) gives the respective complex ylides **3b-e** and/or the dihydrofurans (**7**), whereas, with benzoylmethylenetriphenylphosphorane (**1c**), ylide **3f** or **3g** is only formed. On the other hand, the reaction of **4b** with **1a,b** proceeded only in ethylacetate, yielding the ylides **9**, accompanied by the decarboxylation of the acid. However, compound **4b** did not react with **1c**, under the above experimental conditions.

Structural assignments are based on analytical and spectroscopic results as well as possible reaction mechanisms are annotated.

Key words: β -Aroylacrylic acids; cinnamic acid; Wittig reagents, C-alkylation, O-alkylation.

INTRODUCTION

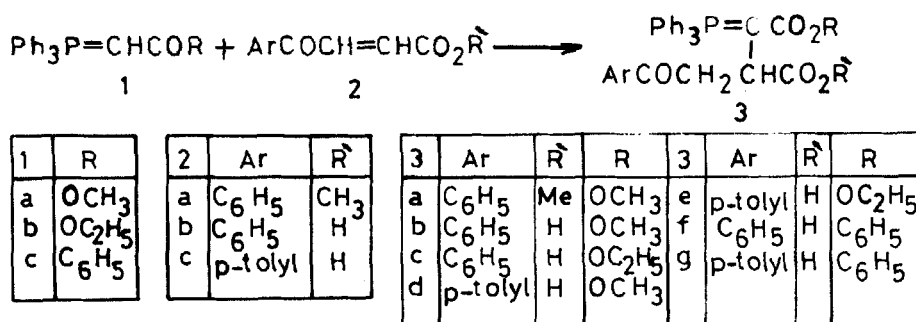
In their early work, Bestmann et al.^{2,3} noted that the reaction of alkylidene phosphorane (**1a**) with α,β -unsaturated carboxylic esters, namely: methyl benzoyl-acrylate (**2a**) led to the formation of an addition product **3a** (92%).

In other instances, cyclopropane hydrocarbons (**5**) have been reported⁴ as a reaction product of ylide **1a** with α -unsaturated carboxylic esters, e.g., methyl cinnamate (**4a**). It seems that no attempt has been made to make a systematic study on their parent acid derivatives. Thus, the work summarized here was undertaken to study, in some detail, the Wittig reaction of β -benzoylacrylic (**2b**), β -tolylacrylic-(**2c**) and cinnamic (**4b**) acids.

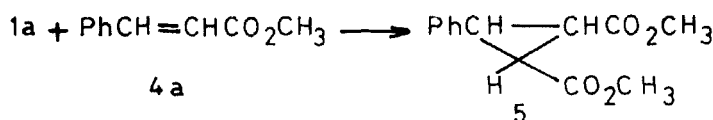
RESULTS AND DISCUSSION

1. Reaction of β -Aroylacrylic Acids (**2b,c**) with Ylides

Carbomethoxy-(**1a**), and carbethoxy-(**1b**) methylene-triphenylphosphoranes were found to react readily in boiling benzene for 6 hr, with benzoyl-(**2b**) and tolyl-(**2c**) acrylic acids according to Scheme I. The new phosphorus ylides (**3b-e**), listed in Table I, generally crystallized from the reaction mixture in high yields and high degree of purity. Carrying out the same reaction in boiling THF, resulted in the isolation of compounds **3b-e** and the cyclic products **7**, Scheme III, in nearly equal amounts. On the other hand, in boiling ethylacetate, the dihydrofuran derivatives **7** were only isolated in good yield. In both instances, using THF or ethylacetate as medium, triphenylphosphine was also isolated and identified.



SCHEME I



SCHEME II

Identity of phosphoranes **3** was confirmed by direct esterification⁵ (see experimental) of the Me-ester **3b** to give a product identical (mp., mixed mp., comparative IR, MS and ¹HNMR spectra) with triphenylphosphine-[(methoxy-carboxyl-2-benzoyl ethyl)-methoxyl carbonylmethylene (**3a**), obtained according to Bestmann's procedure,² upon reacting methyl benzoylacrylate (**2a**) with **1a** (vide supra). In addition, the structure of **3** was established by analytical and spectral (IR, ³¹PNMR, PMR, and MS) analyses (see Tables I and II).

Structural assignment for structure **7** is based upon correct analytical values and compatible IR and PMR spectral data. The IR spectrum of **7a**, taken as an example, shows bands at 1720 (C=O, broad), 1625 (C=C) and 1030 cm⁻¹ (—C=C—O—).⁶ Its PMR spectrum shows absorptions at δ 3.9(3H, s, COOCH₃), 7.55 (5H, m, Ar-H), and 10.2 ppm (1H, broad, —OH). Protons of the dihydrofuran nucleus appeared at 4.02 (1H, dd, proton b, obscured by CH₃), 5.72 (1H, d, proton a, J = 4 Hz) and 6.52 (1H, d, vinyl, proton c, J = 4 Hz).⁶ Moreover, the mass spectrum of **7a** shows the ion peaks at m/z 238 (M⁺, 22%), which loses —CO₂ to give the radical cation at m/z 194 (45%). This latter suffers then loss of —COOCH₃ moiety to give the base peak at m/z 135. The reaction of **2b,c** with benzoylmethylenetriphenylphosphorane (**1c**) was also investigated. No reaction was observed in boiling benzene or THF solution even after 24 hr. On the other hand, when this reaction was carried out in ethylacetate (10 hr), the complex new ylides **3f,g** were obtained as the sole product. Structural assignment is based on strong and broad carbonyl absorption in their IR spectra and on typical (C—CH₂—CH—) peaks in the PMR-spectra (cf. Table II).

It is evident that both the nature of the solvent and/or the phosphorus ylides used, dictate the course of this reaction.

The mechanism proposed to account for the formation of **3** and/or **7** from the reaction of compounds **2b,c** with Wittig reagents **1a-c** is shown in Scheme III. Initial nucleophilic attack by the carbanion centre in the ylide on the reactive ketone

TABLE I
Characteristics of compounds **3b-g** and **7**

Cpd.	Yield in % ^a	mp °C	Mol. Form Mol. Wt.	Anal. Calcd. Found			IR cm ⁻¹		
				C	H	P			
3b	88	198	C ₃₁ H ₂₇ O ₅ P (510.53)	72.93 72.90	5.33 5.32	6.06 6.04	3400 OH	1705 ^b C=O	1675 & 1512 C=P
c	85	182	C ₃₂ H ₂₉ O ₅ P (524.56)	73.27 73.23	5.57 5.55	5.90 5.83	3420 OH	1700 ^b C=O	1656 & 1520 C=P
d	93	202	C ₃₂ H ₂₉ O ₅ P (524.56)	73.27 73.19	5.57 5.55	5.90 5.83	3405 OH	1710 ^b C=O	1665 & 1515 C=P
e	90	178	C ₃₃ H ₃₁ O ₅ P (538.59)	73.59 73.56	5.80 5.77	5.75 5.74	3410 OH	1710 ^b C=O	1670 & 1520 C=P
f	80	212	C ₃₆ H ₂₉ O ₄ P (556.61)	77.68 77.59	5.25 5.26	5.56 5.53	3420 OH	1725 ^b C=O	1662 & 1540 C=P
g	80	218	C ₃₇ H ₃₁ O ₄ P (570.63)	77.88 77.85	5.47 5.44	5.43 5.45	3415 OH	1722 ^b C=O	1660 & 1535 C=P
7a	40	84	C ₁₃ H ₁₂ O ₅ (248.24)	62.90 62.88	4.87 4.86	--	3400 OH	1720 ^b C=O	1030 C=C-O
b	38	65	C ₁₄ H ₁₄ O ₅ (262.26)	64.11 64.09	5.38 5.38	--	3420 OH	1715 ^b C=O	1042 C=C-O
c	42	92	C ₁₄ H ₁₄ O ₅ (262.26)	64.11 64.07	5.38 5.35	--	3410 OH	1722 ^b C=O	1035 C=C-O
d	35	72	C ₁₅ H ₁₆ O ₅ (276.29)	65.20 65.19	5.83 5.80	--	3405 OH	1720 ^b C=O	1055 C=C-O

a) Yields are approximated.

b) Carbonyl group is broad.

carbonyl-vinyl system (carbonyl group is sterically hindered)^{7,8} gives a resonance hybide like (**6**). Even though, **6** may be reasonably (R is an electron-withdrawing group)^{2,3} stabilized through proton migration, giving rise to a new ylides **3**,⁹ it is partly, stabilized by O-alkylation with expulsion of triphenylphosphine to give the dihydrofuran derivatives (**7**). Such observation was previously reported on several occasions.^{10,11}

II. Reaction of Cinnamic Acid with Phosphorus Ylides

The reaction of cinnamic acid (**4b**) with carbmethoxy-methylene-(**1a**) or carbethoxymethylene-triphenylphosphorane (**1b**) was sluggish in boiling benzene or tetrahydrofuran for 24 hr. However, triphenylphosphine-[(2-phenyl)-ethyl]-meth-

TABLE II
¹H and ³¹P-NMR spectral data^a for the adducts 3 and 7

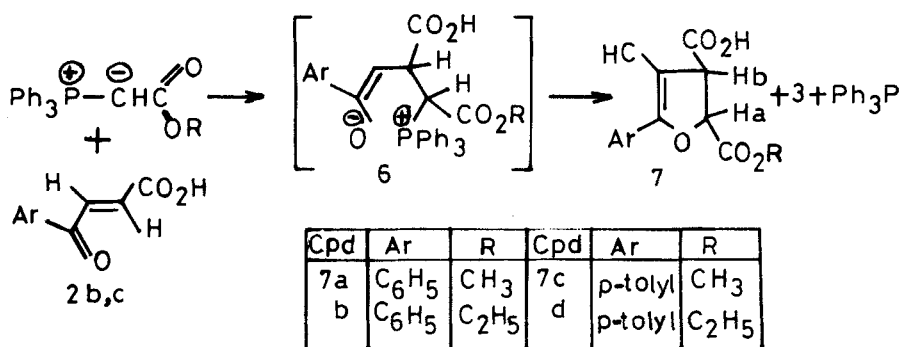
Cpd.	31p	¹ H (δ, ppm) ^b						
		OC.CH ₃	-CH ₃ tolyl	-CH ₂ C	OCH ₂ OCH ₂	C.CH	Ar-H	OH
3b	22.5			3.3 (d of d)c J=4.5; 8.5 2H	3.77 (s) 3H	4.2 (d of t)c J = 15; 8.5 1H	7.66 (m) 20H	10.3 (s) 1H
C	24.63	0.83(t) J=6 3H		3.4 (d of d)c J = 4.0; 8.5 2H	3.82 (q) J = 6 2H	4.18 (d of t)c J = 15; 8.5 1H	7.74 (m) 20H	9.98 (s) 1H
d	22.77		2.42 (s) 3H	3.28 (d of d)c J = 4.0; 6 2H	3.67 (s) 3H	4.4 (d of t)c J = 16; 6 1H	7.82 (m) 19H	10.8 (s) 1H
e	24.68	0.77(t) J = 6 3H	2.36 (s) 3H	3.42 (d of d)c J = 4.5; 6.5 2H	4.1 - 4.3(m) OCH ₂ & CH 3H		7.49 (m) 19H	11.0 (s) 1H
f	21.40			3.62 (d of d)c J = 6; 10.4 2H		4.48 (d of t)c J = 16; 6.2 1H	7.94 (m) 25H	9.6 (s) 1H
g	23.55		2.40 (s) 3H	3.45 (d of d)c J = 6; 10.5 2H		4.35 (d of t)c J = 15.5; 6.5 1H	7.87 (m) 24H	10.6 (s) 1H
7a	—			4.02 (d of d) J = 4 1 Hb	3.9 (s) 3H	5.72 (d) J = 4.5 1 Ha	6.5 7.55 J = 4 (m) 1Hc 5H	10.2 (s) 1H
b	—	0.87(t) J = 6 3H		4.33 (d of d) J = 4 1 Hb	4.19 (q) 2H	5.67 (d) J = 4.5 1 Ha	6.6 7.62 J=4 (m) 1H 5H	10.5 (s) 1H
7c	—		2.35 (s) 3H	4.6 (d of d) J = 4 1 Hb	3.86 (s) 3H	5.76 (d) J = 4 1 Ha	6.2 (d) 7.47 J = 4 (m) 1 Hc 4H	11.0 (s) 1H
d	—	0.74(t) J=6 3H	2.32 (s) 3H	4.57 (d of d) J = 4 1 Hb	4.13 (q) J = 6 2H	5.48 (d) J = 4 1 Ha	6.4[d] 7.60 J = 4 (m) 1 Hc 4H	11.3 (s) 1H

a) See experimental for details for NMR experiments

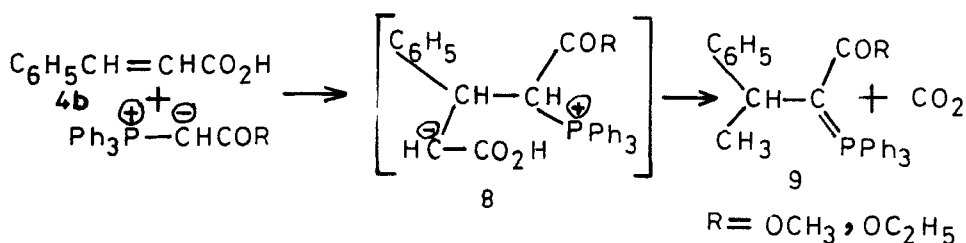
b) Coupling constant is recorded in Hertz.

c) The first data for J is due to the coupling with phosphorus while the second due to the coupling with hydrogen.

oxycarbonylmethylene (9a) or triphenylphosphine-[(2-phenyl) ethyl]-ethoxy-carbonylmethylene (9b) was obtained when the reactants were refluxed in ethyl-acetate for 18 hr. under similar experimental conditions. No reaction has been observed when 4b was allowed to react with 1c. Compounds 9 were identified by elementary analyses, IR, and NMR spectra (see experimental). All showed the lack of —OH absorption and the presence of absorption bands at ~1645 and 1535



SCHEME III



SCHEME IV

cm^{-1} ascribed to $\text{C}=\text{P}$ moiety in their infrared spectra. This concept was further substantiated by a signal at $\delta \sim 20$ ppm in their ^{31}P -NMR spectra.¹² The ^1H -NMR spectra of compounds **9** showed, among other signals a doublet (3H) at $\sim \delta$ 1.3 ppm and a quartet (1H) at $\sim \delta$ 4.15 ppm, each with a coupling constant of 7 Hz. These signals assigned ($\text{CH}-\text{CH}_3$) species. To rationalize this result, it could be suggested that **9** arises by the decarboxylation of the betaine species **8**, a yet-unrearranged intermediate-in the first step. Decarboxylation process can be looked upon as being catalysed by the alkylidene phosphoranes acting as Lewis bases,¹³ albeit, the basicity of these compounds are less than other phosphorus reagents like trialkyl phosphites or phosphonates,¹⁴ there are instances where they are incompatible with sensitive substrates.^{15,16}

CONCLUSION

Significantly, the two reactions of Wittig reagent reported here are indicative of the broad reaction spectrum of which ylides are capable in addition to the usual olefin-forming reactions. Moreover, it has been shown from this behavior and the previous results,²⁻⁴ that alkylidene phosphoranes react with unsaturated carboxylic acids **2b,c** and **4b** in a manner rather different from the already known²⁻⁴ with their respective carboxylic esters (vide supra). Thus, Wittig reaction with acids is very sensitive to the operating conditions and to the substitutions of the substrates. Furthermore, albeit this anomalous behavior of the acids **2**, formation of five

membered dihydrofuran ring, is a new reaction for phosphoranes with olefines, it is not surprising as the inter- and intra-molecular Wittig reactions have become an indispensable means of cyclization, particularly for macrocyclic system.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded in KBr, with Perkin-Elmer Infracord Model 137 and Beckman Infracord Model 4220. The PMR spectra were taken in CDCl_3 with a Varian Spectrometer at 90 MHz, using TMS as an internal reference. ^{31}P -NMR spectra were recorded, relative to external H_3PO_4 (85%), with a Varian FT-80 Spectrometer. The mass spectra were run at 70 eV on Kratos MS equipment and/or Varian MAT 311 A Spectrometer.

Reaction of β -aroylacrylic acids (2b,c) with ylides (1a,b).

a) In boiling benzene: To 0.02 mol of the acid (**2b**)¹⁷ (or **2c**)¹⁷ in 50 ml of benzene, was added in one portion 0.021 mol of the ylide (**1a**)¹⁸ and/or (**1b**)¹⁸ in 20 ml of solvent. When the reaction was complete (~6 hr, TLC), the solution was concentrated and cooled. The brown crystals were filtered and recrystallized from ethanol to give the new ylides (**3b-e**). The physical and spectroscopic data are summarized in Tables I and II.

b) In boiling THF: Acid **2b** (or **2c**) (0.02 mol) was refluxed in 50 ml of THF containing 0.022 mol of the proper ylide (**1a,b**). When the reaction was complete (~6 hr, TLC), and after cooling, the precipitated material was collected, recrystallized from ethanol to give brown crystals, proved to be ylides (**3b-e**) in approximately 40% yield.

The mother liquors were evaporated, in vacuo, and the residual material was redissolved in methanol (50 ml) and evaporated to dryness in the presence of silica gel (5g). The mixture was then added to a column, previously charged with silica gel in petroleum ether. The column was developed with petroleum ether containing increasing amounts of chloroform. The fraction with 100% petroleum ether eluted colorless needles, mp. 80°C (~45% yield) of triphenylphosphine (mp, mixed mps, and comparative IR spectra). The fraction (up to 4:1 v/v) yielded yellow products, recrystallized from acetone to give yellow crystals identified as the dihydrofuran derivatives **7**, percentage yields, physical and analytical data are given in Tables I and II.

c) In boiling ethylacetate: A mixture of **2b,c** (0.02 mol) and Wittig reagent **1a,b** (0.022 mol) was refluxed in ethylacetate (50 ml) for ~6 hr. The reaction mixture was evaporated under reduced pressure, and the residue was applied to silica gel column, using pet. ether/chloroform (4:1 v/v) as eluent. Adducts **7** were separated in ~70% yield as yellow crystals. Triphenylphosphine was also separated (mp and mixed mps).

Esterification of the Me-ester 3b: Methylation of **3b** was carried out according to the procedure of Scarpati et al.⁵ with minor modifications. To a solution of **3b** (0.5g) in dry acetone (100 ml), was added anhydrous K_2CO_3 (6g) and freshly distilled methyl iodide 20 ml. After boiling under reflux for 8 hr, the mixture was filtered while hot and the inorganic residue washed with boiling acetone. The filtrate and washings were then freed from the volatile materials, in vacuo. The residual material was recrystallized from benzene (or ethanol) to give a substance, mp 187°C, proved to be triphenylphosphine-[(methoxycarboxyl-2-benzoyl)ethyl] ethyl] methoxy carbonylmethylene (**3a**) (mp, mixed mps, and comparative IR, PMR and MS spectra).²

Reaction of β -aroylacrylic acids with ylide (1c).

a) In boiling benzene or THF: Benzoylmethylenetriphenylphosphorane (**1c**)¹⁹ (0.021 mol) was added to a solution of **2b** (or **2c**) (0.02 mol) in 50 ml benzene (THF) and the stirred mixture was refluxed for 24 hr. After cooling, the precipitated material was filtered off, recrystallized from benzene to give a colorless material proved to be **1c** (mp, mixed mp); yield 92%. The filtrate was freed from the volatile materials, in vacuo, and the residual substance was recrystallized from cyclohexane to give a colorless substance proved to be **2b** (or **2c**) (90%).¹⁷

b) In boiling ethylacetate: A mixture of 0.02 mol of the acid (**2b**, or **2c**) and 0.021 mol of ylide (**1c**) in 50 ml of ethylacetate was heated under reflux for 10 hr. After cooling to the room temperature, the reaction mixture was evaporated on a rotavapor under reduced pressure, and the residue was recrystallized from ethanol to give **3f** (or **3g**) as brown crystals in 80% yield. Physical and spectroscopic data are listed in Tables I and II.

II. Reaction of cinnamic acid (4b) with ylides (1a,b). A solution of cinnamic acid (4b)²⁰ (1.48 g, 0.010 mol) and 1a (3.6 g, 0.011 mol) in ethylacetate (50 ml) was refluxed for 18 hr., the solvent then evaporated, and the residue crystallized from ethylacetate to give 9a as brown crystals mp 182–189 (3.3 g, 74%). Anal. Calcd. for C₂₉H₂₇O₂P (438.515) C, 79.43; H, 6.26; P, 7.06. Found: C, 79.41; H, 6.15; P, 7.17%. IR bands at 1725 (C=O, ester), 1645 and 1530 (P=C) PMR, (DMSO, δ ppm): 1.35 (3H, C.CH₃, d, J = 7 Hz), 3.8 (3H, OCH₃, s), 4.15 (1H, CH.C, q, J = 7 Hz) and 7.0–7.7 ppm (5H, Ar-H, m). ³¹P-NMR (DMSO): δ 20.45 ppm. MS: m/z 438 (M⁺, 33%).

In a similar way carbethoxymethylene triphenylphosphorane (1b) with cinnamic acid (4b) gave 9b (68%), mp 245–247° (from toluene). Anal. Calcd. for C₃₀H₂₉O₂P (452.54) C, 79.62; H, 6.45; P, 6.84. Found: C, 79.56; H, 6.44; P, 6.86%. IR bands at 1730 (C=O, ester), 1655 and 1535 (C=P). PMR (DMSO, δ): 1.02 (3H, OC.CH₃, t, J = 7 Hz), 1.35 (3H, C.CH₃, d, J = 7 Hz), 4.06 (2H, OCH₂, q, J = 7 Hz), 4.18 (1H, CH, q, J = 7 Hz), and 7.1–7.75 (5H, Ar-H, m). ³¹P-NMR (DMSO): δ = 21.58 ppm. MS: m/z 452 (M⁺, 28%).

Compounds 9a and 9b are not soluble in 5% aqueous sodium hydroxide solution and exhibits no color reaction with alcoholic ferric chloride.

Compound 4b was recovered almost quantitatively and identified (mp and mixed mp. 134°C, comparative IR, NMR spectra)²⁰ upon its reaction with 1c under the above conditions.

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