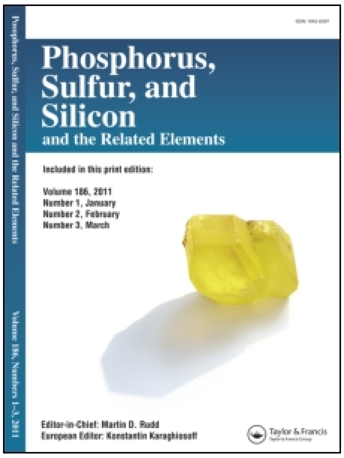


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ORGANOPHOSPHORUS CHEMISTRY 10. THE BEHAVIOUR OF β-AROYLACRYLIC ACIDS TOWARD NUCLEOPHILIC PHOSPHORUS COMPOUNDS

Mohamed R. Mahran[a]; Wafaa M. Abdou[a]; Neven A. F. Ganoub[a]; Mahmoud M. Sidky[a]
[a] Department of Pesticide Chemistry, National Research Centre, Cairo, Egypt

To cite this Article Mahran, Mohamed R. , Abdou, Wafaa M. , Ganoub, Neven A. F. and Sidky, Mahmoud M.(1988) 'ORGANOPHOSPHORUS CHEMISTRY 10. THE BEHAVIOUR OF β-AROYLACRYLIC ACIDS TOWARD NUCLEOPHILIC PHOSPHORUS COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 40: 1, 19 — 26

To link to this Article: DOI: 10.1080/03086648808072888

URL: http://dx.doi.org/10.1080/03086648808072888

Phosphorus and Sulfur, 1988, Vol. 40, pp. 19–26
Reprints available directly from the publisher
Photocopying permitted by license only

ORGANOPHOSPHORUS CHEMISTRY 10.[†] THE BEHAVIOUR OF β-AROYLACRYLIC ACIDS TOWARD NUCLEOPHILIC PHOSPHORUS COMPOUNDS

MOHAMED R. MAHRAN, WAFAA M. ABDOU, NEVEN A. F. GANOUB and MAHMOUD M. SIDKY
Department of Pesticide Chemistry, National Research Centre, Dokki-Cairo, Egypt.

(Received December 6, 1987; in final form May 9, 1988)

The reaction of alkyl phosphites and thiolphosphoric acids with β-aroylacrylic acids **1a**,**b** has been investigated. Dialkyl phosphites (DAP) attacked **1** at the β-carbon atom with respect to the aroyl-carbonyl function, to give phosphonate 1:1 adducts assigned structure **2A**. Thiolphosphoric acids (**7**) attacked **1** at the same centre to give adducts **8**. On the other hand, trialkyl phosphites (TAP) converted **1** into the respective esters **5**, almost exclusively. Structures of the new products were assigned according to consistent analytical and spectroscopic measurements.

Key words: β-Aroylacrylic acids; alkylation; phosphorylation; thiophosphorylation.

INTRODUCTION

Although the reaction of β-aroylacrylic acids of type **1** with nitrogen nucleophiles[1–3] and sulfur nucleophiles[4] has been thoroughly investigated, their behaviour toward phosphorus nucleophiles has not yet been explored. Therefore, we have now studied the reaction of β-benzoylacrylic acid (**1a**) and β-toloylacrylic acid (**1b**) with di-, and trialkyl phosphites. By virtue of the presence of a vinyl (—CH=CH—) group in structure **1**, these compounds can be classified as α-β-unsaturated aryl ketones, α-β-unsaturated carboxylic acids and/or vinylogs[5] of α-keto-carboxylic acids. Reactions involving these three classes of compounds with phosphorus nucleophiles, are well established.[‡] Thus, the present study may shed light and clarify to which of these classes compounds **1** belong upon attack by alkyl phosphites. A comparative study on the behaviour of **1** toward phosphorothioate nucleophiles ($\rangle P(S)\bar{S}$—) is also described.

RESULTS AND DISCUSSION

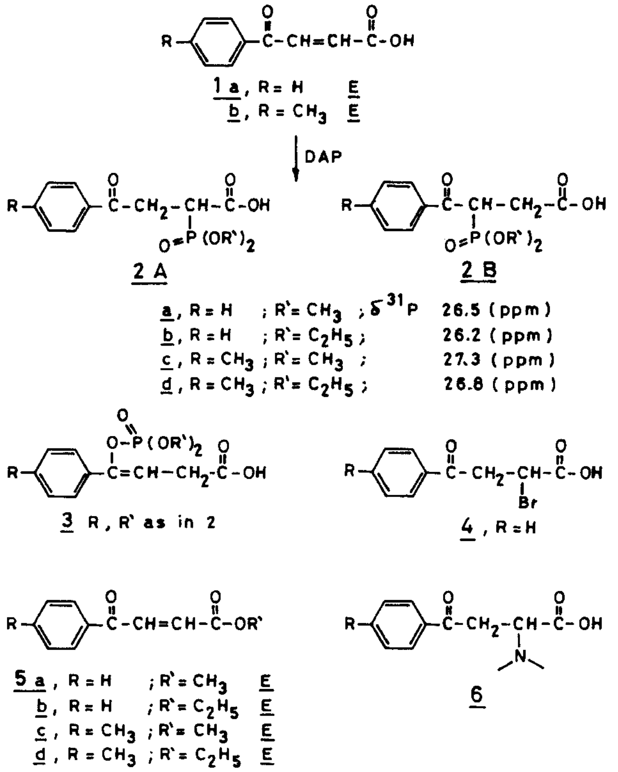
We have found that dimethyl phosphite (DMP) and diethyl phosphite (DEP) react with β-aroylacrylic acids **1a**,**b** in the absence of solvent to give colorless

---

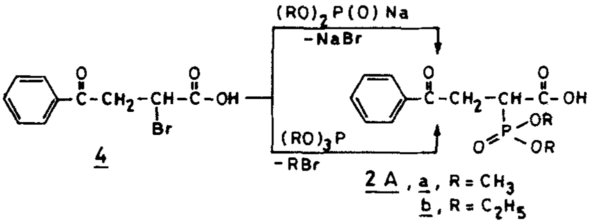
[†] For part **9**, *cf.* M. R. Mahran, W. M. Abdou and N. A. F. Ganoub, *Phosphorus and Sulfur*, **36**, 1988 (in press).

[‡] For the reaction of alkyl phosphites with α-β-unsaturated aryl ketones, α-β-unsaturated carboxylic acids and α-keto-carboxylic acids, *cf.* references Nr. 6, 7 and 8 respectively.

crystalline products assigned a dialkyl phosphonate structure like **2A** (or **2B**) since ^{31}P NMR measurements[9] for these adducts showed positive chemical shifts (*vs.* 85% H_3PO_4) around δ26 ppm. This confirms a structure with a phosphorus-to-carbon linkage[9] and rules out an alternative structure like **3** which incorporates phosphorus-to-oxygen bonding (phosphates).[9] The PMR spectra of adducts **2a–d** (*cf.* Table III) are also compatible with the assigned structure. Thus, the spectrum of **2c**, taken as a representative example, showed signals (δ scale) at 2.35 (3H, Ar-CH_3, s) and 3.82 [6H, $P(O)(OCH_3)_2$, d; $J_{HP} = 12$ Hz]. Moreover, the two doublets present in the PMR spectrum of **1b** at 6.84 (1H, d; $J_{HH} = 16$ Hz) and 8.06 (1H, d, $J_{HH} = 16$ Hz) due to the exocyclic vinyl protons, were absent in the spectrum of **2c**. The methylene protons in **2c** appeared at 3.2 (2H, d of d) while the methine proton occurred at 4.2 (1H, d of t). Other spectral (IR, MS) and analytical data are also compatible with the postulated structure **2A** (or **2B**). However, structure **2A** is more consistent than structure **2B** since approach of the phosphorus nucleophile to **1** is expected to occur at the more electrophilic carbon atom.[2,3] In favour of this conclusion, structures comparable to **2A** parallel the addition products of **1a** with nitrogen nucleophiles[2,3] (*cf.* **6**) and sulfur nucleophiles.[4] Moreover, structure **2A** was rigorously attested by unequivocal routes by reacting 2-bromo-3-benzoylpropionic acid (**4**) either with dialkyl phosphites (sodium salt) or with the appropriate trialkyl phosphite (Michaelis



SCHEME 1



SCHEME 2

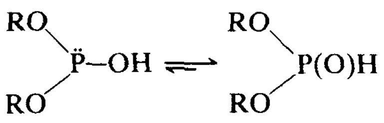
Arbusov reaction)[10] (Scheme 2). As expected,[11] adducts **2** regenerated the starting materials upon heating above their m.ps. under reduced pressure.

When the reaction of DMP or DEP with acids **1** was conducted in dry CH_2Cl_2 in the presence of *p*-TsOH, the alkyl ester **5** (*E*-form)[12] was obtained. The identity of **5a–c**† was supported by correct elemental analyses and molecular weight determinations (MS) as well as by comparison (IR, NMR) with reference samples.[12] The esters **5a–d** were obtained in higher yields (*cf.* Table I) when acids **1** were allowed to react with trimethyl phosphite (TMP) and/or triethyl phosphite (TEP) in boiling CH_2Cl_2. Moreover, esters **5a,c** could be also obtained by heating **1a,b** with other alkylating agent[13] like dimethyl methyl phosphonate (DMMP) in the absence of solvent for 50 h.

TABLE I

Reagents	5a% (time/h)	5b% (time/h)	5c% (time/h)	5d% (time/h)
$(CH_3O)_2POH$/ *p*-TsOH	64.8 (40)	—	74.8 (40)	—
$(C_2H_5O)_2POH$/ *p*-TsOH	—	61.2 (45)	—	69.3 (45)
$(CH_3O)_3P$	83.5 (20)	—	85.3 (20)	—
$(C_2H_5O)_3P$	—	80.2 (24)	—	81.0 (24)
$(CH_3O)_2P(O)CH_3$ (DMMP)	52.4 (50)	—	65.8 (50)	—

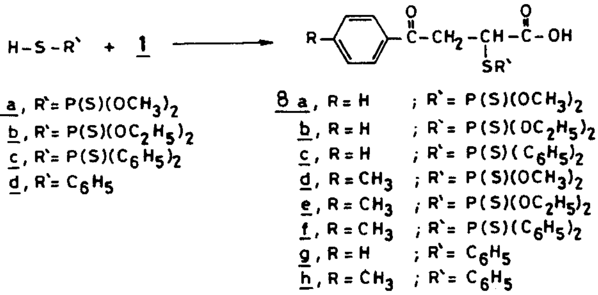
Table I clearly shows that TAP alkylate acids **1** in a least time with a best yield in comparison with DAP/*p*-TsOH or DMMP. This is correlated with the valency state of the phosphorus atom since trivalent phosphorus compounds appear to be more effective than derivatives of pentavalent phosphorus.[14,15] The relatively lower rate of DAP as esterificating agents might be explained in terms of their existence as tautomeric mixture[16] of the trivalent and pentavalent states:



DAP, R = CH_3 or C_2H_5

---

† Ester **5d** was obtained for the first time.

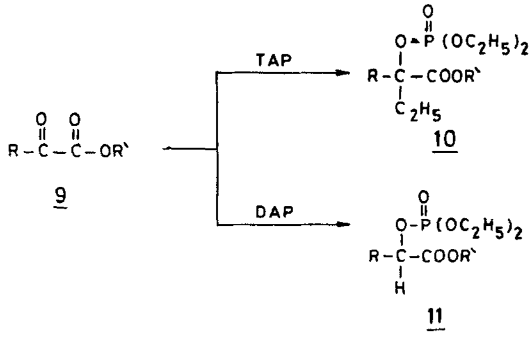


SCHEME 3

When β-benzoylacrylic acid **1a** or **1b** was allowed to react with thiolphosphoric acids, namely, dimethoxy-, diethoxy-, and diphenylphosphinodithioic acid, colorless crystalline products were obtained and assigned structures **8a–f**, respectively. Compounds **8a,b** were equally obtained and identified (mp., mixed m.ps. and comparative IR spectra) by condensing 2-bromo-3-benzoyl-propionic acid (**4**) with the sodium salt of the proper thiolphosphoric acid in benzene (*cf.* Scheme 3). Compounds **8** regenerate the starting materials **1** and **7** upon thermolysis under reduced pressure. Structural reasonings for adducts **8** were gained from compatible analytical and spectroscopic results. For example, elemental analyses and molecular weight determination for **8d** corresponded to $C_{13}H_{17}O_5PS_2$. Its ^{31}P NMR spectrum (in $CDCl_3$, *vs.* 85% H_3PO_4) gave a positive shift at δ 62.13 ppm; a value which falls in the range frequently recorded in the spectra of compounds incorporating the $>$C—S—P(S)$<$ moiety.[9] The PMR spectrum (δ) of **8d** in $CDCl_3$ indicated that the aromatic protons fall in the region 7.26–7.9 (4H, 2d; $J_{HH} = 8\,Hz$). At 3.82 the spectrum showed a doublet with $J_{HP} = 13.5\,Hz$ due to the 6 protons of the methoxy groups attached to the phosphorus atom and at 2.42 a singlet assigned to the tolyl-methyl group. The H—C—P— proton appeared as a doublet of a triplet centered at 4.66; while the methylene protons resonated as a doublet of doublets centered at 3.33 ppm. In addition, the spectrum disclosed the presence of the acidic proton as a singlet at δ 10.8 (1H). The IR(cm^{-1}) of **8d** in KBr revealed bands at 3330 (—OH), 1705 ($>$C=O) and at 1020 cm^{-1} (P—O—CH_3).

CONCLUSION

From the present study, it is clearly shown that β-aroyl-acrylic acids **1a,b** undergo carbophilic attack at the more reactive ketone carbonyl–vinyl system[2,3] by phosphorus nucleophiles (DAP) to produce phosphonate adducts **2**. Phosphorothiolate nucleophiles attack **1** at the same center to give 1:1 adducts of the type **8a–f**. In this respect, the phosphorus nucleophiles and the phosphorothiolate nucleophiles attack **1** in a manner similar to nitrogen nucleophiles[2,3] and sulfur nucleophiles[4] which produce α-amino-γ-ketoacids[2,3] (*cf.* **6**) and α-arylthio-γ-ketoacids[4] (*cf.* **8g**), respectively with substrate **1a**. On the other hand, phosphorus nucleophiles such as TAP alkylate **1** to give the respective esters **5**. This is in marked disparity with the behavior of TAP toward α-ketocarboxylic



SCHEME 4

acid derivatives (**9**).[8] In the latter case, oxophilic attack on **9** by the P(III) nucleophiles occurs to yield phosphate structures of type **10**.[8] A phosphorus-to-oxygen (phosphate) bond is also produced *via* attack by DAP on **9** (*cf.* **11**).[8] Therefore, it is safe to state that β-aroylacrylic acids **1** behave as α-β-unsaturated aryl ketones and not as vinylogs of α-keto-carboxylic acids toward attack by DAP and TAP. Meanwhile, the reaction of TAP with acids **1** to give the respective esters **5** reflects the pronounced activity of trialkyl phosphites as alkylating agents.[14] This process occurs without alteration of the *trans* geometry of the double bond.

EXPERIMENTAL

All melting points are uncorrected. The IR specta were run on a Perkin-Elmer Infracord spectrometer 197 (Grating) in KBr or in $CHCl_3$. The ^1H NMR spectra were recorded on a Bruker Model WH 90 spectrometer. The chemical shifts are recorded in ppm relative to TMS. The ^{31}P spectra were taken on a Varian CFT-20 (*vs.* 85% H_3PO_4). The mass spectra were performed at 70 eV on MS-50 Kratos (A.E.I.) spectrometer. All reactions were carried out under N_2 atmosphere.

Reagents and materials. The dialkyl phosphites (DAP) were freshly distilled. Trialkyl phosphites (TAP) were purified by treatment with sodium ribbon followed by fractional distillation. Dimethyl methyl phosphonate (DMMP),[16] β-aroylacrylic acids **1a,b**[17] and 2-bromo-3-benzoylpropionic acid (**4**)[18] were prepared according to the established procedures.

Preparation of 3-Aroyl-2-phosphonopropionic Acid, P,P-Dialkyl Esters† **2A**. General Procedures:
1. *By the action of DAP on* 1. A mixture of acid (**1**, 0.01 mol) and DAP (DMP or DEP; 0.02 mol) was heated in absence of solvent on a steam bath for 24 h. The excess of DAP was removed under vacuum, then the residue was washed several times with light petroleum and crystallized from the appropriate solvent to give phosphonates **2A** as colorless crystalline products. Percentage yields, physical and analytical data for compounds **2A** are given in Table II and III.

2. *By the action of DAP on* 4 *in the presence of Na metal.* To a solution of **4** (0.01 mol) in dry toluene (50 ml) was added freshly prepared sodium derivative of DAP (DMP or DEP; 0.1 mol) in toluene (10 ml). After boiling under reflux for 10 h, the mixture was filtered while hot and the inorganic residue (NaBr) washed with boiling toluene. The filterate and the washings were then freed from the volatile materials, *in vacuo*. The residual material was crystallized from the appropriate solvent to give the adducts **2Aa,b**. Identification of the products exactly matched the compounds isolated in procedure 1 with the following yields **2Aa**: 65% and **2Ab**: 57% yield.

---

† The nomenclature is in accord with the IUPAC rules.

TABLE II

		mp.	Mol. form.	Analysis (Calcd./found				M^+	IR			
Cpd.	%[a]	°C	M. Wt.	C	H	P	S	m/e	CM^{-1}			
2a	80	160[b]	$C_{12}H_{15}O_6P$	50.34	5.26	10.82			3420	1740	1690	1025
			286.232	50.54	5.16	10.79		286	OH	C═O	C═O	P—O—C
b	75	82[b]	$C_{14}H_{19}O_6P$	53.50	6.09	9.86			3410	1725	1685	1020
			314.286	53.46	6.02	9.35		314	OH	C═O	C═O	P—O—C
c	85	156[b]	$C_{13}H_{17}O_6P$	52.00	5.70	10.31			3420	1745	1690	1020
			300.259	51.85	5.80	10.27		300	OH	C═O	C═O	P—C—C
d	78	75[b]	$C_{15}H_{21}O_6P$	54.87	6.44	9.44			3400	1710	1670	1030
			328.313	54.69	6.37	9.29		328	OH	C═O	C═O	P—O—C
8a	66	105[c]	$C_{12}H_{15}O_5PS_2$	43.10	4.52	9.26	19.18		3350	1705	1670	1040
			334.364	43.02	4.13	9.17	19.30	334	OH	C═O	C═O	P—O—C
b	72	94[d]	$C_{14}H_{19}O_5PS_2$	46.39	5.28	8.54	17.69		3340	1710	1675	1010
			362.418	46.52	5.16	8.43	17.58	362	OH	C═O	C═O	P—O—C
c	85	158[b]	$C_{22}H_{19}O_3PS_2$	61.95	4.49	7.26	15.03		3345	1715	1670	1000
			426.506	62.89	4.46	7.23	15.13	426	OH	C═O	C═O	P—Ar
d	70	123[e]	$C_{13}H_{17}O_5PS_2$	44.81	4.91	8.89	18.40		3330	1705	1670	1020
			348.391	44.69	4.77	8.79	17.29	348	OH	C═O	C═O	P—O—C
e	76	81[e]	$C_{15}H_{21}O_5PS_2$	47.85	5.62	8.22	17.03		3310	1725	1670	1050
			376.445	47.15	5.57	7.98	17.12	376	OH	C═O	C═O	P—O—C
f	85	113[e]	$C_{23}H_{21}O_3PS_2$	62.70	4.80	7.03	14.55		3340	1710	1675	980
			440.533	62.68	4.75	7.15	14.38	440	OH	C═O	C═O	P—Ar
g	93	134[b]	$C_{16}H_{14}O_3S$	67.11	4.92		11.19		3345	1710	1680	
			286.354	67.09	5.01		11.07	286	OH	C═O	C═O	
h	90	132[b]	$C_{17}H_{16}O_3S$	67.97	5.36		10.67		3330	1705	1690	
			300.381	67.88	5.34		10.58	300	OH	C═O	C═O	

[a] Yields are approximated; [b] Solvent of crystallization is benzene; [c] Solv. of crys. is cyclohexane; [d] Solv. of crys. is light pet. ether, [e] Solv. of crys. is benzene-pet. ether (b.r. 40–60°C).

3. *By the action of TAP on* **4**. To a solution of **4** (0.01 mol) in dry toluene (50 ml) was added TAP (TMP or TEP; 0.02 mol) in toluene (5 ml). The mixture evolved considerable heat and turned red-brown *via* yellow. The mixture was refluxed for 8 h. After removing the volatile materials, in *vacuo*, the residual substance was recrystallized from the appropriate solvent to give the corresponding phosphonate **2Aa,b** in 70 and 63% yield respectively. Compounds **2Aa,b** are confirmed by mp. and mixed mp. and comparative IR spectra.

Action of Heat on the Adduct **2a**. The phosphonate adduct **2a** (0.8 g) was heated in a cold finger sublimator at 220°C (bath temperature) for about 30 minutes under reduced pressure (10 mm/Hg). The substance which sublimed was recrystallized from benzene to give (0.38 g. 78%) of β-benzoylacrylic acid (**1a**; identified by mp., mixed mp. and comparative IR spectra with an authentic sample).[17] DMP was detected in the receiver by the development of a violet color on addition of 3,5-dinitrobenzoic acid in the presence of an alkali.[19]

Action of DAP on β-Aroylacrylic Acids **1** *in the presence of p-TsOH*. A mixture of **1a** (1.76 g; 0.01 mol), DMP (2.2 ml, 0.02 mol), and *p*-TsOH (30 mg) was refluxed in methylene chloride (30 ml) for 40–45 h. After removing the volatile materials *in vacuo*, the residual substance was washed with H_2O and the oily material was extracted with ether. After evaporation of ether, the residual oil was distilled under reduced pressure to give the corresponding ester **5a** (1.2 g, 64%) bp. 169/17 mmHg[12] (comparative TLC and IR spectra). M. W.: Calcd. 190.2; Found (MS): 190.

Under similar conditions, the reaction of **1a** with DEP in presence of *p*-TsOH afforded *E*-ethyl β-benzoylacrylate (**5b**; 1.2 g, 61%). Compound **5b** was obtained as a yellow oil (bp. 184/24 mmHg).[12] M.W.: Calcd. 204.228; Found (MS): 204.

In the same manner, the following esters were prepared by the action of DMP and DEP respectively on compound **1b** and in presence of *p*-TsOH: a) *E*- Methyl β-*p*-toloylacrylate (**5c**, 1.52 g, 74%) as a yellow liquid bp. 240–245°/115 mmHg.[12] b) *E*-Ethyl β-*p*-toloyl acrylate (**5d**, 1.5 g, 69%) was obtained for the first time as a yellow oil (bp. 250–255°/85 mmHg) which solidified after

TABLE III

^1H NMR Spectral Data[a]

Cpd[b]	$POCH_2CH_3$	$—CH_3$ tolyl	$—CH_3—CH$	$P—O—CH_2$	$P—O—CH_3$	$CH_2—CH$	Arom.	—OH
2a			3.4 dd $J_{HH} = 8.5$ 2H		3.8 d $J_{HP} = 13.5$ 6H	4.2 dt $J_{HH} = 8.5$ 1H	7.2–8.0 m 5H	9.9 s 1H
b	0.73 dt $J_{HP} = 11.5$ 6H		3.2 dd $J_{HH} = 8.5$ 2H	3.7 qt[c] $J_{HP} = 11.5$ 4H		4.18 dt $J_{HH} = 8.5$ 1H	7.1–8.0 m 5H	9.98 s 1H
c		2.35 s 3H	3.2 dd $J_{HH} = 8.5$ 2H		3.82 d $J_{HP} = 12$ 6H	4.2 dt $J_{HH} = 8.5$ 1H	7.2–7.9 2d 4H	10.1 s 1H
d	1.3 dt $J_{HP} = 11.5$ 6H	2.42 s 3H	3.66 dd $J_{HH} = 8$ 2H	4.3 qt $J_{HP} = 11.5$ 4H		4.2 dt $J_{HH} = 8$ 1H	6.9–8.0 2d 4H	10.8 s 1H
8a			3.57 dd $J_{HH} = 8$ 2H		3.75 d $J_{HP} = 13.5$ 6H	4.17 dt $J_{HH} = 8$ 1H	7.28–8.1 m 5H	11.2 s 1H
b	1.53 dt $J_{HP} = 11$ 6H		3.46 dd $J_{HH} = 9$ 2H	4.24 qt $J_{HP} = 11$ 4H		4.46 dt $J_{HH} = 9$ 1H	7.1–7.95 m 5H	10.9 s 1H
c			3.62 dd $J_{HH} = 8.5$ 2H			4.26 dt $J_{HH} = 8.5$ 1H	7.35–8.1 m 15H	11.3 s 1H
d		2.42 s 3H	3.33 dd $J_{HH} = 8.0$ 2H		3.82 d $J_{HP} = 13.5$ 6H	4.66 dt $J_{HH} = 8$ 1H	7.26–7.9 2d 4H	10.8 s 1H
e	1.33 dt $J_{HP} = 11$ 6H	2.40 s 3H	3.64 dd $J_{HH} = 9$ 2H	4.2 qt $J_{HP} = 11$ 4H		4.48 dt $J_{HH} = 9$ 1H	7.2–7.9 2d 4H	11.1 s 1H
f		2.40 s 3H	3.6 dd $J_{HH} = 9$ 2H			4.4 dt $J_{HH} = 9$ 1H	7.24–8.2 m 14 H	9.62 s 1H
g			3.42 d $J_{HH} = 8.5$ 2H			4.24 t $J_{HH} = 8.5$ 1H	7.22–7.9 m 10H	11.0 s 1H
h		2.41 s 3H	3.44 d $J_{HH} = 8.5$ 2H			4.23 t $J_{HH} = 8.5$ 1H	7.1–8.0 m 9H	9.86 s 1H

[a] See experimental for details of NMR experiments.
[b] The solvent is $CDCl_3$; [c] qt. = quintet.

treatment with *n*-pentane to give pale yellow crystals, mp. 52–54°. Anal. Calcd. for $C_{13}H_{14}O_3$ (218.255); C, 71.54; H, 4.49. Found: C, 71.31; H, 4.38; M.W. = 218 (MS). IR(cm^{-1}): Bands at 1725 & 1680 (—C=O, ester) and (—C=O, toloyl) and at 1605 (—CH=CH—). ^1H NMR: Signals at 1.25 (t, $—COOCH_2CH_3$), 2.4 (s. Ar—CH_3), 4.05 (q, $—COOCH_2CH_3$), 6.88 & 8.0 (2d, —*CH*=*CH*—, $J_{HH} = 16$) and at 7.33 & 7.88 (2d, arom., $J_{HH} = 8$).

Action of Trialkyl Phosphites (TAP) on β-Aroylacrylic Acids

General Procedure. To a stirred solution of **1a** (1.76 g; 0.01 mol) in 20 ml of CH_2Cl_2 at 0–5° was added a solution of trimethyl phosphite (TMP, 2.2 ml; 0.02 mol) in CH_2Cl_2 (5 ml). The reaction mixture was allowed to warm to r.t. (3 h), then refluxed for 20–24 h. The removal of the solvent at 20° first at 20 mm and then at 0.05 mm, yielded a yellow oil which was subjected to distillation to give a yellow oil, proved to be the corresponding methyl ester **5a**[12] bp. 169/17 mm (1.5, 83%) (comparative TLC, IR and NMR spectra).

Under similar conditions, *E* ethyl β-benzoylacrylate (**5b**, 1.6 g, 80.3%) bp. 185/25 mm was obtained by the reaction of **1a** with TEP for 24 h.

Similarly, the reaction of compound **1b** with TAP (TMP and/or TEP) afforded the respective ester **5c** (or **5d**). Table I should be consulted for yields of the esters **5a–d**.

Action of Dimethyl Methyl Phosphonate (DMMP) on β-Aroylacrylic Acid. The reaction of DMMP (2.24 ml, 0.02 mol) with **1** (1.76 g, 0.01 mol) in CH_2Cl_2 was conducted for 50 h. Working up of the reaction mixture in the usual manner afforded the methyl ester of the respective acid **1a** and/or **1b**. Identification of the products was accomplished by TLC as well as by comparative IR and NMR spectra. For yields *cf.* Table I.

Preparation of 3-*Aroyl-2-mercaptopropionic Acids* **8a–h**

General Procedures: 1) *By the action of thiophenol and thiolphosphoric acids* (7) *on* **1**. To a solution of **1** (0.01 mol) in benzene (50 ml) was added the thiol (0.011 mol) and the reaction mixture was heated at reflux temperature for 30 h. At the end of the experiment, the volatile materials were removed under reduced pressure, the residue was washed with light petroleum and recrystallized from the suitable solvent to give colorless crystals **8a–h**. Percentage yields, physical and analytical data for compounds **8** are given in Tables II and III.

2) *By the action of thiolphosphoric acids* (**7a,b**) *on* 4 *in the presence of Na metal.* To a solution of **4** (0.01 mol) in dry toluene (50 ml) was added the freshly prepared sodium derivative of the thiolphosphoric acids (**7a,b**) in toluene (10 ml). After boiling under reflux for 18 h, the mixture was filtered while hot and the inorganic residue (NaBr) washed with boiling toluene. The filtrate and washings were then freed from the volatile materials, *in vacuo*. The residual material was crystallized from the appropriate solvent to give the adducts **8a,b**. Identification of the products exactly matched the compounds isolated in procedure **1** with the following yields **8a**: 45% and **8b**: 40% yield.

Action of Heat on the Adduct **8c**. Compound **8c** (0.5 g) was heated in a cold finger sublimator at 210° (bath temperature) for about 30 minutes under reduced pressure (0.5 mmHg). The substance that sublimed was boiled in light petroleum. The undissolved material was recrystallized from benzene, and proved to be β-benzoylacrylic acid (mp., and mixed mp. and comparative IR spectra).[17]

REFERENCES

1. M. M. Fraser and R. A. Raphael, *J. Chem. Soc.*, 2245 (1950).
2. J. Bougault, *Ann. Chim. Phys.*, **15,** 491 (1908).
3. N. H. Cromwell, P. L. Greger and K. E. Cook, *J. Am. Chem. Soc.*, **78,** 4412 (1956).
4. J. Bougault and P. Chabrier, *Compt. rend*, **224,** 395 (1947).
5. R. C. Fuson, *Chem. Revs.*, **16,** 1 (1935).
6. F. Ramirez, O. P. Madan and R. Heller, *J. Am. Chem. Soc.*, **87,** 731 (1965); A. Mustafa, M. M. Sidky and F. M. A. Soliman, *Tetrahedron,* **23,** 99 (1967); A. Mustafa, M. M. Sidky, S. M. A. D. Zayed and W. M. Abdou, *Tetrahedron,* **24,** 4725 (1968).
7. G. Kamai and V. A. Kukhtin, *Doklady Akad. Nauk., S.S.S.R.*, **109,** 91 (1956); *C.A.*, **51,** 1827 (1957).
8. G. Kamai and V. A. Kukhtin, *Trudy Kazan Khim. Tekhnol. Inst., im. S. M. Kirova,* **23,** 133 (1957); *C.A.*, **52,** 9948 (1958); G. H. Birum and J. L. Dever, U.S., 2,980,722 (1961); *C.A.*, **56,** 329 (1962).
9. M. M. Crutchfield, O. H. Dungan, J. H. Letcher, V. Mark and J. R. van Wazer, ^{31}P Nuclear Magnetic Resonance, Interscience, New York, 1967, p. 227; F. Ramirez, *Pure and Appl. Chem.*, **9,** 337 (1964) and references therein cited.
10. R. G. Harvey and E. R. DeSombre, "Topics in Phosphorus Chemistry", Vol. **I**, M. Grayson and E. J. Griffith, Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y., p. 60–79 (1964).
11. A. Mustafa, M. M. Sidky and F. M. Soliman, *Tetrahedron,* **22,** 393 (1966).
12. G. P. Rice, *J. Am. Chem. Soc.*, **45,** 233 (1923); R. E. Lutz, *J. Am. Chem. Soc.*, **52,** 3430 (1930); A. G. Oddy, *J. Am. Chem. Soc.*, **45,** 2157 (1923).
13. P. Sutter and C. D. Weis, *Phosphorus and Sulfur,* **4,** 335 (1978).
14. Y. Kashman, *J. Org. Chem.*, **37,** 912 (1972); M. M. Sidky, M. R. Mahran, M. F. Zayed, W. M. Abdou and T. S. Hafez, *Org. Prep., and Procedures Int.*, **14,** 225 (1982).
15. I. W. Daach, *J. Am. Chem. Soc.*, **80,** 5301 (1958).
16. S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).
17. D. Papa, E. Schwenk, F. Villani and E. Kligsberg, *J. Am. Chem. Soc.*, **70,** 3356 (1948).
18. J. Bougault, *Compt. rend.*, **146,** 141 (1908).
19. B. C. Saunders and B. P. Stark, *Tetrahedron,* **4,** 197 (1958).