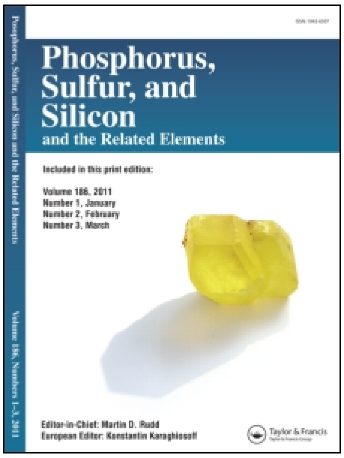


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ORGANOPHOSPHORUS CHEMISTRY, 33[1] ON THE REACTION OF TERVALENT PHOSPHORUS NUCLEOPHILES WITH 2-FURFURYLIDENE-, AND 2-THIENYLIDENE-1,3-INDANDIONES

Maha D. Khidre[a]; Hala M. Abou-yousef[b]; Mohamed Refat H. Mahran[b]
[a] Department of Pesticide Chemistry, National Research Centre, Cairo, Egypt [b] Central Agricultural Pesticides Luboratory, Cairo, Egypt

To cite this Article Khidre, Maha D. , Abou-yousef, Hala M. and Mahran, Mohamed Refat H.(2000) 'ORGANOPHOSPHORUS CHEMISTRY, 33[1] ON THE REACTION OF TERVALENT PHOSPHORUS NUCLEOPHILES WITH 2-FURFURYLIDENE-, AND 2-THIENYLIDENE-1,3-INDANDIONES', Phosphorus, Sulfur, and Silicon and the Related Elements, 160: 1, 181 — 194

To link to this Article: DOI: 10.1080/10426500008043679

URL: http://dx.doi.org/10.1080/10426500008043679

Phosphorus, Sulfur and Silicon, 2000, Vol. 160, pp. 181-194
Reprints available directly from the publisher
Photocopying permitted by license only

ORGANOPHOSPHORUS CHEMISTRY, 33[1] ON THE REACTION OF TERVALENT PHOSPHORUS NUCLEOPHILES WITH 2-FURFURYLIDENE-, AND 2-THIENYLIDENE-1,3-INDANDIONES*

MAHA D. KHIDRE[a], HALA M. ABOU-YOUSEF[b] and
MOHAMED REFAT H. MAHRAN[a†]

[a]*Department of Pesticide Chemistry. National Research Centre, Cairo, Egypt and* [b]*Central Agricultural Pesticides Laboratory, Dokki, Cairo, Egypt*

(Received September 07, 1999; In final form December 09, 1999)

2-Furfurylidene-. (1a) and 2- thienylidene- 1,3- indandione (1b) produce the respective 1:1 adducts (8 a-f) upon reaction with the appropriate dialkyl phosphite (3 a-c). The reaction of 1a,b with trialkyl phosphite (2a-c) yield a mixture of the corresponding phosphonates (7a-d) (major) and (8a-d) (minor). Triphenylphosphine (2d) and hexamethylphosphorustriamide (2e) also reacted with 1a,b. The produced betaines (10a-c) were alkylated with methyl iodide to yield the respective phosphonium iodides (11a-d). Possible reaction mechanisms were discussed. Compatible elemental and spectroscopic results were gained for the new products.

Keywords: 2-Heteroylidene-1,3-indandiones; alkyl phosphites; tertiary phosphines; phosphonates; phosphonium salts

INTRODUCTION

Many organophosphorus compounds broadly used as pesticides, encorporate heterocyclic moieties in thier structures[2,3]. Examples are the insecticides and acaricides; Curacron ®, Dursban ®, Supracide ®, Actellic ®, Hostathion ® and Knox-out ®.

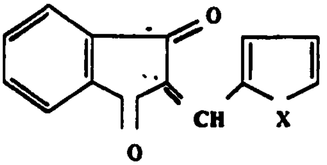
In the search for additional representatives belonging to this class of active materials, we have now prepared new organophosphorus deriva-

---

* Dedicated to Professor M.M. Sidky on the occasion of his 70th birthday.

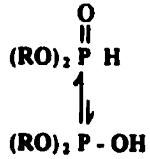
† Author to whom correspondence should be addressed.

tives incorporating a furan and/or a thiophene moiety. Molecular design for the new products was based upon reacting 2-furfurylidene-1,3-indandione (1a) and/or 2- thienylidene- 1,3- indandione (1b) with the appropriate organophosphorus reagents. The α,β-unsaturated carbonyl system in compounds 1 is expected to facilitate the addition of phosphorus nucleophiles[4–7].



1 a, x = O
b, x = S

R_3P:
2 a, R = OCH_3, TMP
b, R = OC_2H_5, TEP
c, R = i-C_3H_7O, TiPP
d, R = C_6H_5, TPP
e, R = $(CH_3)_2N$, HMPT



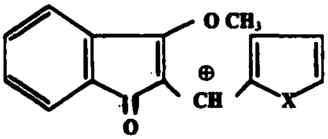
$$(RO)_2\overset{O}{\overset{\|}{P}}H \rightleftharpoons (RO)_2P-OH$$

DAP, 3
3a, R = CH_3 DMP
b, R = C_2H_5 DEP
c, R = i-C_3H_7O DiPP

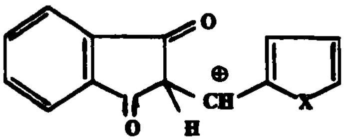
RESULTS AND DISCUSSION

We have found that 2-furfurylidene-1,3- indandione (1a) reacts with trimethyl phosphite (2a, TMP) in the absence of solvent at 100 °C to give a mixture of two products which were resolved by column chromatography. The first (major, 80%) was assigned structure 7a for the following reasons: a) its microanalyses and molecular weight determination (MS) corresponded to $C_{17}H_{17}O_6P$. (b) the IR spectrum of 7a (KBr, cm^{-1}) showed strong absorption bands at 1700 (C= O), 1590, 1610 (C = C, furan and aromatic), 1315 (P = O, free) [8]and 1015 (P O CH_3)[8]. (c) the ^{31}P NMR spectrum of 7a showed a +ve shift at 21.40 ppm which is in agreement with a phosphonate structure[9]. (d) its ^1HNMR spectrum ($CDCl_3$, δ ppm scale) showed protons of the $P(O)(OCH_3)_2$ group as two doublets each with $^3J_{HP}$= 12 Hz at 3.65 and 3.8 ppm; indicating the non-magnetic equivalency of the OCH_3 groups due to the asymmetry of the molecule[10]. Apparently, this asymmatry due to presence of a stereo-centre would render the two methoxyl groups diastereotropic and hence anisochronous, resulting in the observed splitting pattern[10–12]. The spectrum also showed signals at

4.15 (3H, OCH_3, s), 4.90 (1H, HC-P, d, $^2J_{HP}$ = 30 Hz) and at 6.30 – 8.60 (7H, aromatics and furans, m). (e) The mass spectrum of 7a showed the molecular ion peak at m/z 348 (63.7%) which undergoes cleavage at the C-P bond *via* ejection of a $^{\bullet}P(O)(OCH_3)_2$ radical to afford the base peak "A" (X=O) at m/z 239. (f) The ^{13}C NMR spectrum of adduct 7e, taken as an example, consisted of 20 signals. Those due to carbon atoms attached to the oxygen and phosphorus atoms appeared in the sp^3 region[15] in the following sequence: 15.40 (CH_3), 16.22 (CH_3), 32.39 (CH_3), 34.53 (P-CH), 62.70 (CH_2), 62.76 (CH_2) and 68.67 ppm (O-CH_2). The signal due to the C = O group appeared at 193.06 ppm. Signals due to carbon atoms of the thiophene ring appeared at 139.46, 120.20, 124.57 and 126.58. The aromatic and unsaturated carbon atoms (8C) appeared as a cascade of signals at 121.31, 126.96, 127.06, 129.85, 132.08, 132.41. 138.22 and 139.50 ppm.



"A"



"B"

The second product (minor; 5%) was assigned structure 8a for the following reasons: Its microanalyses and molecular weight determination (MS) corresponded to $C_{16}H_{15}O_6P$. Its ^{31}P NMR spectrum (*vs.* 85% H_3PO_4,) gave a signal at + 19.18 ppm (phosphonate)[9]. The ^1HNMR spectrum of 8a ($CDCl_3$; δ ppm) showed protons of the magnetically non-equivalent OCH_3 groups attached to phosphorus as double doublets ($^3J_{HP}$=12 Hz) at 3.5 and 3.7. The HC-P proton (Ha) appeared as a double doublet ($^2J_{HP}$= 26 Hz and J_{HH} = 4.5 Hz) at 4.30 and 4.60. Similarly, the $\mathrm{HC{-}\overset{|}{\underset{|}{C}}{-}P}$ proton (Hb) also gave two doublets ($^3J_{HP}$ = 12 Hz and J_{HH}= 4.5 Hz) at 3.55 and 3.72. The furans and aromatics (7H) gave a multiplet in the 6.1–8 ppm region. The mass spectrum of 8a showed the molecular ion peak at m/z 334 (100%) which undergoes cleavage at the C-P bond *via* ejection of a $^{\bullet}P(O)(OCH_3)_2$ radical to afford cation "B"

(X=O) at m/z 225 (75.4%). Moreover, 8a was unequivocally prepared and identified (m.p. and comparative IR and ^{1}HNMR spectra) upon heating 1a with dimethyl phosphite (DMP, 3a) at 100 °C in the absence of solvent. The aforementioned spectral data are in favour of the keto-form 8a. However, existence of 8a in the alternative enol form (9, R = OCH_3); particularly in polar solvents, cannot be excluded. In favour of the latter idea is the finding that 8a reacts with methyl iodide in boiling acetone in presence of anhydrous K_2CO_3 to yield 7a (m.p. and comparative IR & ^{1}HNMR spectra).

The reaction of 1a with triethyl-, (2b) and triisopropyl phosphites also yielded a binary mixture of 7b, 8b and 7c, 8c, in each case which could be resolved by column chromatography and identified by microanalytical and spectroscopic measurements.

In the same sense, 2-thienylidene-1,3- indandione (1b) reacted with trialkyl phosphites (2 a-c) in absence of solvent. In each reaction, a binary mixture of products (cf. 7 d-f and 8 d-f) was obtained. Compounds 8 d-f were obtained and identified (m.p., comparative IR and ^{1}H-NMR spectra) by treating 1b with dimethyl, diethyl and diisopropyl phosphites, respectively in absence of solvent at 100°C.

Structural support for 7d are (a) correct elementary and molecular weight determinations (MS) corresponded to $C_{17}H_{17}O_5PS$. (b) Its IR spectrum (KBr, cm^{-1}) revealed the presence of strong absorption bands at 1700 ($>C = O$). 1610, 1600, 1590 ($C = C$), 1315 ($P = O$, free) and 1020 ($P - O - CH_3$). (c) The ^{31}P NMR spectrum (vs, 85% H_3PO_4,) recorded a +ve shift at 20.18 ppm (phosphonate)[9]. Its ^{1}HNMR spectrum ($CDCl_3$, δ scale ppm) showed protons of the $P(O)(OCH_3)_2$ group as two doublets (each with $^3J_{HP} = 12$ Hz) at 3.60 and 3.75. Signals at 4.20 (3H, OCH_3, s) and at 6.9 – 7.5 (7H, thienyl and benzene ring protons, m) were also observed in the spectrum. The doublet ($^2J_{HP} = 30$ Hz) present at δ 4.95 ppm is attributed to the CH-P proton.

The mass spectrum of 7d showed the molecular ion peak at m/z 364 (24.6%) which ejected a $^{\bullet}P(O)(OCH_3)_2$radical to give the base peak "A" (X=S) at m/z 255.

Evidences for structure 8d are: correct elementary and molecular weight determinations (MS) were compatible with the molecular formula; $C_{16}H_{15}O_5PS$. Its ^{31}P NMR spectrum (CD Cl_3, vs. 85% H_3PO_4) recorded a +ve shift at 19.24 ppm (phosphonate)[9]. The ^{1}H NMR spectrum of 8d

($CDCl_3$, δ ppm) showed protons of the P (O)(OCH_3)$_2$ group as two doublets (each with $^3J_{HP} = 12$ Hz) at 3.60 and 3.70. The HC P proton (Ha) appeared as two doublets (each with $^2J_{HP} = 28$ Hz) at 4.70 and 4.45; the HC-C-P proton (H_b) also gave two doublets each with ($^3J_{HP} = 12$ Hz) at 3.65 and 3.55. Protons of the thiophene ring and benzene ring (7H) gave a multiplet in the 6.75 – 8.00 ppm region. The mass spectrum of 8d showed the molecular ion peak at m/z 350 (100%) which ejects a $^{\bullet}P(O)(OCH_3)_2$ radical to give ion "B" (X = S) at 241 (93%). Upon treatment with CH_3I in boiling acetone in the presence of anhydrous K_2CO_3. compound 8d yielded 7d.

It is worthy to note that the 1:1 adducts (8 a-f) formed *via* reacting (1a,b) with the appropriate dialkyl phosphite (3 a-c, DAP) regenerate the starting materials upon heating above their m.ps, under reduced pressure.

The behaviour of 1a,b with tertiary phosphines, namely, triphenylphosphine (TPP, 2d) and hexamethylphosphorustriamide (HMPT, 2e) was also investigated. Thus 1a,b reacted with TPP in boiling THF to give brown crystalline products for which the phosphonium betaine structures 10a and 10c were respectively assigned. In the same sense, 1a,b reacted with hexamethylphosphorustriamide (2e, HMPT) to give the respective betaines 10b and 10d. Correct elemental and spectroscopic structural support were gained for all adducts. Compounds 10 a-d were converted upon reaction with methyl iodide to give the respective phosphonium iodides 11a-d. The ^1H NMR spectrum of compound 11a (in D_2O) showed a signal at 3.30 ppm (OCH_3).

It is evident that the reaction of 1 a,b with the tervalent phosphorus reagents 2 a-c proceeds *via* nucleophilic attack by phosphorus on the terminal C atom of the conjugated system in 1 to afford the intermediate phosphonium species 4. In the case R = C_6H_5or = $N(CH_3)_2$, this resonance stabilized structure (cf. 10) constitutes the final products. In the case R= O-alkyl, the intermediate 4 undergoes a process of intramolecular (or most probably intermolecular) group translocation[13] to afford adducts 7 a-f (major). During the same process, intermediate 4 (R = O-alkyl.) can be solvated by unavoidable moisture as do many phosphobetaine structures[13,14] to give intermediate 6 with pentacovalent phosphorus. The latter decomposes. *via* expulsion of ROH molecule to give compounds 8 a-f (minor). In favour of this idea is the finding that compounds 8 constitute the sole products when the reaction of 1a,b with trialkyl phosphites 2 a-c is performed in the presence of controlled amounts of a protonating agent e.g., H_2O or CH_3COOH, (cf. experimental). However, the reaction of water with the zwitter ion 4 could give rapid protonation of the anion site which would generate hydroxide ion. The latter can attack the R group on the phosphorus (via an SN2 mechanism) to give the final products (8).

CONCLUSION

As a corollary to this work, new organophosphorus compounds encorporating heterocyclic moieties were prepared (cf. 7, 8, 10 and 11). They possess structural functionalities to which many active principles used as pesticides owe their potentialities[2,3]. In principle, attack by the P-reagents on the α, β unsaturated carbonyl system in 1 is carbophilic in nature; creating thus a *carbon-to-phosphrus* linkage in the new molecules. The intermediate phosphonium species (cf. 10) initially formed in these reactions can be trapped by CH_3I to afford phosphonium iodide salts of type 11.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded using UNICAM SP 1100 or PU 7912 infracords. The ^{1}HNMR spectra were recorded on Jeol GLMEX 270 MHz spectrometer (super conducting magnet) in $CDCl_3$ using TMS as an internal standard. ^{31}P-NMR spectra were recorded with Jeol GLMEX 270 MHz spectrometer in $CDCl_3$ (vs 85% H_3PO_4). The mass spectra were obtained with Finnigan MAT-SSQ 7000 Spectrometer at 70 eV. 2-Furfurylidene-1,3-Indandione(16), and 2-thienylidene-1,3-Indandione(17) were prepared by known procedures. The phosphorus reagents 2a-e and 3a-c were available from Aldrich Co. The phosphites were freshly distilled before use.

Reaction of 2-furfurylidene-1,3-indandione 1a and 2-thienylidene-1,3-indandione 1b with Trialkyl phosphites 2a – c

General procedure

A mixture of 1a (or 1b) (0.005 mol) and trialkyl phosphites (trimethyl-, triethyl-, and triisopropyl phosphite, 0.05 mol) was heated at 100 °C for 4 hr in absence of solvent. The reaction mixture was then worked up by column chromatography. The fraction that eluted by 95:5 v/v pet. ether: acetone yielded phosphonates 7 a-f. The fraction eluted by 85:15 v/v pet. ether: acetone gave a substance which was collected, recrystallized to give phosphonate 8 a-f.

Phosphonate 8a was also obtained by reacting 1a (0.005 mol) with trimethyl phosphite (0.05 mol) at 100°C for 2 hr in presence of H_2O (1 ml). After evaporation of the volatile materials in *vacuo*, the residual substance was treated with pet. ether 40/60 (5 ml). The solid material was collected and recrystallized from cyclohexane to give 8a (m.p., mixed m.p.), yield 90%.

Physical, analytical and spectral data of compounds 7(a – f) and 8(a – f) are presented in tables I and II.

Reaction of 2-furfurylidene-1,3-indandione 1a and 2-thienylidene – 1,3-indandione 1b with dialkyl phosphites 3 a-c

General procedure

A mixture of 1a (or 1b) (0.01 mol) and dialkyl phosphites (dimethyl-, diethyl-, and diisopropyl phosphite, 5 ml) was heated in the absence of solvent at 100 °C for 4 – 6 hr. After removing the volatile materials in *vacuo*, the residue was triturated with light petroleum and left to cool. The solid so formed was collected and recrystallized from a suitable solvent to give compounds 8a-f. Physical and analytical data and IR spectra for compounds 8a-f are presented in tables I and II.

Action of heat on phosphonate 8a

Compound 8a (0.05 g) was heated in a cold finger sublimator at 230 °C (bath temperature) under reduced pressure (5 mm/Hg) for 30 minutes. The compound that sublimed was collected (85%), recrystallized from ethyl alcohol to give greenish crystals, proved to be 2-furfurylidene – 1,3-indandione 1a(m.p, mixed m.p 203 °C and comparative IR spectra).

Dimethyl phosphite was detected in the receiver by the development of a violet color on addition of 3,5-dinitrobenzoic acid in the presence of alkali[18].

TABLE I Physical, analytical and IR spectral Data of compounds 7a-f, 8a-f, 10a-d and 11a-d

und	*Yield*[a] *%*	*m.p °C*	*Mol. Form (M. wt.)*	*Anal. (Calcd. /Found)*				M^+ *m/z (%)*	*IR* cm^{-1}		
				C	*H*	*P*	*S*		*C = O*	*P = O*	*P –*
	75	86	$C_{17}H_{17}O_6P$	58.62	4.92	8.89	-	348	1700	1180	10
			348.29	59.02	5.01	8.99		(63.70)			
	70	70	$C_{20}H_{23}O_6P$	61.53	5.93	7.93	-	390	1700	1180	10
			390.37	61.27	6.04	7.96		(55.32)			
	85	90	$C_{23}H_{29}O_6P$	63.88	6.75	7.16	-	432	1700	1240	10
			432.45	64.15	6.84	6.88		(45.05)			
	80	85	$C_{17}H_{17}O_5PS$	56.04	4.70	8.50	8.80	364	1700	1180	10
			364.35	56.42	5.03	8.28	8.50	(24.67)			
	75	73	$C_{20}H_{23}O_5PS$	59.10	5.70	7.62	7.88	406	1700	1220	10
			406.43	58.85	5.32	8.00	7.52	(37.08)			
	85	70	$C_{23}H_{29}O_5PS$	61.59	6.51	6.90	7.14	448	1689	1248	10
			448.51	61.12	6.39	6.67	7.46	(25.08)			
	80	73	$C_{16}H_{15}O_6P$	57.49	4.52	9.26	-	334	1720	1250	10
			334.26	57.18	4.81	9.50		(100)			
	75	80	$C_{18}H_{19}O_6P$	59.67	5.28	8.54	-	362	1700	1200	10

und	*Yield*[a] %	*m.p °C*	*Mol. Form (M. wt.)*	*Anal. (Calcd. /Found)*				*M⁺ m/z (%)*	*IR cm⁻¹*		
				C	*H*	*P*	*S*		*C = O*	*P = O*	*P – (*
			362.31	59.99	5.68	8.98		(66.42)			
	85	85	$C_{20}H_{23}O_6P$	61.53	5.93	7.93	-	390	1720	1200	10
			390.37	61.29	6.30	8.20		(33.35)			
	75	110	$C_{16}H_{15}O_5PS$	54.85	4.31	8.84	9.15	350	1708	1182	10
			350.32	55.12	4.73	9.21	8.99	(100)			
	70	70	$C_{18}H_{19}O_5PS$	57.13	5.06	8.18	8.47	378	1700	1200	10
			378.38	56.90	4.88	7.88	8.24	(40.19)			
	80	90	$C_{20}H_{23}O_5PS$	59.10	5.70	7.62	7.88	406	1700	1200	10
			406.43	60.32	6.01	7.33	8.02	(41.78)			
	65	170	$C_{32}H_{23}O_3P$	79.00	4.76	6.36	-	486	1720	–	C-P
			486.50	78.84	5.15	6.70		(7.01)			14
	70	140	$C_{20}H_{26}N_3O_3P$	62.00	6.76	7.99	-	387	1680	–	14
			387.42	61.82	6.46	8.00		(5.54)			
	60	130	$C_{32}H_{23}O_2PS$	76.47	4.61	6.16	6.37	502	1720	–	14
			502.57	76.82	4.34	6.52	6.74	(15.51)			
	75	170	$C_{20}H_{26}N_3O_2PS$	59.53	6.49	7.67	7.94	403	1685	–	14

ınd	Yield[a] %	m.p °C	Mol. Form (M. wt.)	Anal. (Calcd. /Found)				M^+ m/z (%)	IR cm^{-1}		
				C	H	P	S		C = O	P = O	P – (
			403.48	59.23	6.61	7.25	7.90	(38.3)			
	85	> 300	$C_{33}H_{26}IO_3P$	63.07	4.17	4.92	-	-	628	1709	14
			628.44	63.32	4.57	5.20			(55.4)		
	80	> 300	$C_{21}H_{29}IN_3O_3P$	47.64	5.52	5.85	-	7.93	529	1700	14
			529.36	47.3	5.93	5.52		7.64	(38.94)		
	87	> 300	$C_{33}H_{26}IO_2PS$	61.49	4.06	4.80	4.97	-	644	1720	14
			644.512	61.82	3.95	5.15	4.65		(33.35)		
	83	> 300	$C_{21}H_{29}IN_3O_2PS$	46.24	5.35	5.67	5.87	7.70	545	1700	14
			545.42	46.55	5.73	5.25	4.93	7.46	(42.50)		

rystallization: $7_{b,c}$, $8_{a,c,F}$ cyclohexane, 7_e pet. ether 40 – 60, 7_F, $8_{b,c}$ pet. ether 60 – 80, $10_{b,d}$ ethylacetate-ether, $11_{a\text{-}d}$ DMF/H_2O.

nated.

TABLE II ^{31}PNMR and ^{1}HNMR Spectral Data of Compounds $\underline{7}_{b\text{-}f}$, $\underline{8}_{b\text{-}f}$ and $\underline{10}_{b,d}$

^{1}PNMR	^{1}HNMR^a
	1.2 (t, 3H, C-O-C-$\underline{CH}_3$), 1.4[d of t, 6 H,P-(O-C-(C$\underline{H}_3$)$_2$], 4.1 [d of quint, 4 H, P-(O-$\underline{CH}_2$-C)$_2$], 4.75(quartet, 2H, C-O-$\underline{CH}_2$-C), 1 H, $^2J_{HP}$ = 30 Hz, P-$\underline{CH}$-), 6.3–7 (m, 7H, aromatics and furans).
9.08	1.2 [d, 6H, C-O-C-($\underline{CH}_3$)$_2$], 1.4 (m, 12 H, P-[O-C- ($\underline{CH}_3$)$_2$]$_2$, 4.7 (d of sept., 2H, P-(O-$\underline{CH}$-C)$_2$], 4.85(d, 1H $^2J_{HP}$ = 30 Hz, P- 5.2 (sept., 1H C-O-$\underline{CH}$-C), 6.2- 7.5 (m, 7H, aromatics and furans).
	1.2 (t, 3H, C-O-C-$\underline{CH}_3$), 1.35 [d of t, 6H, P-(O-C-$\underline{CH}_3$)$_2$], 4.2[d of quint, 4H, P-(O-$\underline{CH}_2$-C)$_2$], 4.7(q, 2H, C-O-$\underline{CH}_2$- C), 5.00 $^2J_{HP}$ = 26 Hz, P-$\underline{CH}$-), 6.9- 7.55 (m, 7H, aromatics and thiophenes).
	1.25[d, 6H, C-O-C-($\underline{CH}_3$)$_2$], 1.35[m, 12H,P-(O-C-(C$\underline{H}_3$)$_2$)$_2$], 4.65 [d of sept., 2 H, P-(O-CH-C)$_2$], 4.85 (d, 1H $^2J_{HP}$ = 30 Hz, P-C$\underline{H}$-), 5.2 (sept., 1H, C-O-C$\underline{H}$-C), 6.85 – 7.60 (m, 7H, aromatics and furans).
2.27	1.20 [d of t, 6H, P-(O-C-$\underline{CH}_3$)$_2$], 4.00 (d of quint., 4H, P-(O-$\underline{CH}_2$-C)$_2$], 3.6 (2d, $^3J_{HP}$ = 12 Hz, Hb, P-C-$\underline{CH}$), 4.50 (2d, H$\underline{a}$, ^{2}J 26 Hz P-CH), 6.10- 8.00 (m, 7H, aromatics and furans).
	1.2 [m, 12 H, P-(O-C-($\underline{CH}_3$)$_2$)$_2$], 3.65 (2d, Hb, $^3J_{HP}$= 12 Hz P-C-$\underline{CH}$-), 4.3 (2d, H$\underline{a}$, $^2J_{HP}$ = 27 Hz, P-$\underline{CH}$-), 4.6 [d of Sept., 2 P-(O-C$\underline{H}$-C-)$_2$], 6.25- 8.00 (m, 7H, aromatics and furans).
	1.3 [d of t, 6H, P-(O-C-($\underline{CH}_3$)$_2$], 3.75 (d of quint., 4 H P-(O$\underline{CH}_2$-C-)$_2$], 4.0 (2d, H$\underline{b}$, $^3J_{HP}$= 12 Hz, P-C-$\underline{CH}$-), 4.75 (2d, H$\underline{a}$, $^2J_{HP}$ = 26 Hz, P-$\underline{CH}$-), 6.85- 8.00 (m, 7H, aromatics and thiophenes).
7.38	1.2 [m, 12 H, P-(O-C-($\underline{CH}_3$)$_2$)$_2$], 4.25 (2d, H$\underline{b}$, $^3J_{HP}$ = 12 Hz, P-C-$\underline{CH}$), 4.7 (2d, H$\underline{a}$, $^2J_{HP}$ = 26 Hz, P-$\underline{CH}$), 4.65 (d of sept., 2 P-(O-C$\underline{H}$-C)$_2$], 6.80- 8.05 (7H, aromatics and thiophenes).
.84	2.75 (m, 18H, P-[N-($\underline{CH}_3$)$_2$]$_3$, 5.45 (d, 1H, $^2J_{HP}$= 26 Hz P-$\underline{CH}$), 6.25–8.00 (m, 7H, aromatics and furans).
.18	2.80 (m, 18H, P-[N-($\underline{CH}_3$)$_2$]$_3$, 5.33 (d, 1H, $^2J_{HP}$= 26 Hz P-$\underline{CH}$, 6.80- 8.20 (m, 7H, aromatics and furans).

DCl$_3$

The reaction of Phosphonates 8a, 8d with methyl iodide

A mixture of 8a (0.2 g), methyl iodide (5 g) and anhydrous K_2CO_3 (5 g) in dry acetone (100 ml) was refluxed for 12 hr. The inorganic material was filtered and washed with a small amount of dry acetone. After evaporation of the filtrate and washings to dryness, the residue was recrystallized from pet. ether (b.r 40 – 60 °C) to give yellow crystals m.p 86°C proved to be 7a (m.p, mixed m.p and comparative IR spectra).

Similary, compound 7d was obtained (yield 80%) and identified (m.p, mixed m.p and comparative IR spectra) upon refluxing a mixture of 8d (0.2 g), methyliodide (5 g) in acetone (100 ml) for 12 hr., in presence of' anhydrous K_2CO_3 (5 g).

Reaction of 1 a,b with Triphenylphosphine 2d

General procedure

A mixture of 1a (2.24 g, 0.01 mol) and TPP 2d (0.01 mol) in dry tetrahydrofuran (50 ml) was refluxed for 12 hr. The solid product was collected and recrystallized from benzene to give 10a

Similarly, *10b* was isolated upon reacting 1b with 2d(cf. Tables I and II).

Reaction of 1 a,b with Hexamethyl phosphorustriamide 2e

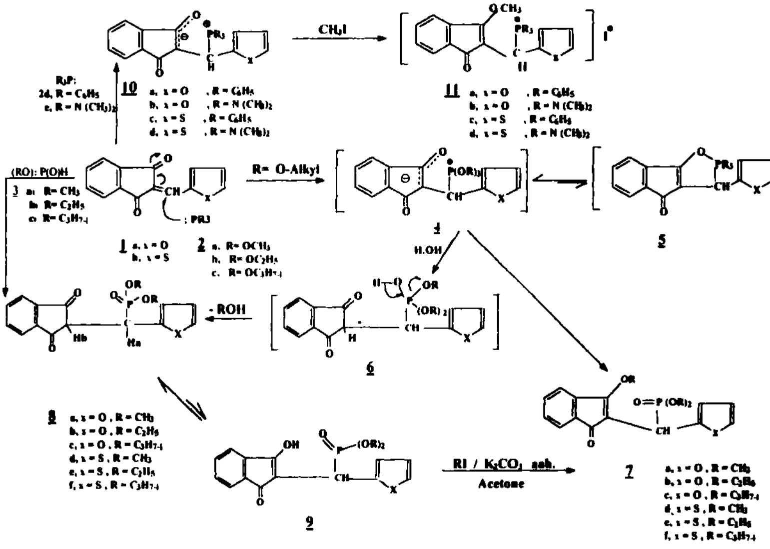
General procedure

A mixture of 1a (2.24 g, 0.01 mol) and HMPT 2e (0.01 mol) in dry tetrahydrofuran (50 ml) was kept at room temperature for 2 hr. and the solid formed was collected then recrystallized from ethylacetate to give *10b.*

Similary, *10d* was isolated upon reacting 1b with 2e (yield 85%). Physical, analytical and spectral data of compounds 10 (b,d) are presented in tables I and II.

The reaction of the phosphonium betaines 10a, 10d with methyl iodide

A mixture of *10a* or *10d* (0.2 gm), methyl iodide (3 gm) in dry tetrahydrofuran (50 ml) was left at room temperature for 6 hr. After evaporation of the solvent, the residue was recrystallized from DMF/H_2O to give white



SCHEME 1

crystals, m.p > 300°C. Physical, analytical data and IR spectra for compounds *11a*, *11d* are presented in tables I and II.

References

1. For part 32 of this series, cf. T.S. Hafez; M.M. Henry and M.R Mahran, Phosphorus, Sulfur and Silicon, 1999, in press.
2. K.H. Büchel (ed.) "Chemistry of Pesticides", Wiley Inter-science, New York, N.Y. (1983).
3. H. Aizawa "Metabolic Maps of Pesticides" Vol. 2 pp. 138–178, Academic Press, Inc., USA (1989).
4. A. Mustafa, M.M. Sidky and F.M. Soliman, Tetrahedron, *23*, 99 (1967).
5. M.M. Sidky, F.M. Soliman and R. Shabana, Egyptian J. Chem., *15*, 79 (1972); *ibid.*, *21*, 37 (1978).
6. M.M. Sidky, A.A. El-Kateb, M.R. Mahran, I.T. Hennawy and H.A. Abdel-Malek, Phosphorus, Sulfur and Silicon, *29*, 11 (1986).
7. M.R. Mahran, W.M. Abdo, N.M. Abd El-Rahman and M.M. Sidky, Phosphorus, Sulfur and Silicon, *45*, 47 (1989).
8. M. Hesse, H. Meier and B. Zeek "Spektroskopische Methoden in der organischen Chemie". G. Thieme Verlag, (Stuttgart), 82 (1979).
9. M.M. Crutchfield, O.H. Dungan, J.H. Letcher, V. Mark and J.R. van Wazer, in "Topics in phosphorus Chemistry", Vol. *5*, Interscience Publishers, New York pp. 227–447 (1967).
10. F. Ramirez, O.P. Madan and S.R. Heller, J. Am. Chem. Soc., *87*, 731 (1965).

11. A.O. Fitton, J.P. Frost, P.G. Houghton and H. Suchitzky, J. Chem. Soc. Perkin I, 1691 (1979).
12. M.D. Khidre, H.M. Abou-Yousef and M.R. Mahran. Phosphorus, Sulfur and Silicon, *140*, 147 (1998).
13. M.R. Mahran, T.S. Hafez and M.M. Henary. Phosphorus, Sulfur and Silicon, *139*, 13 (1998).
14. F. Ramirez, S.B. Bhatia and C.P. Smith, J. Org. Chem., *31*, 4105 (1966).
15. F. W-Wehrli and T. Wirthlin "Interpretation of Carbon-13 NMR Spectra", Heyden & Sons Ltd., (London, U.K.) (1978).
16. W. Wislicenus und Kötzle, Ber., *30*, 2143, (1897).
17. NG. PH. BUU-Hoï, NG. HOÀN. and DENISE LAVIT., J. Chem. Soc., 2130–4 Part III (1950).
18. B.C. Saunders and B.P. Stark, Tetrahedron, *4*, 187 (1958).