

The Structure and Reactions of Imidoyl Triphenylphosphonium Methylides

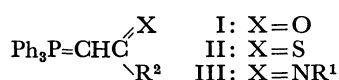
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Twenty-five imidoyl triphenylphosphonium methylides III were prepared from triphenylphosphonium methylide and imidoyl chlorides or imidates in moderate yields. The configuration of these ylides was assigned on the basis of NMR spectroscopic studies. *N*-Tosyl substituted ylides showed no reactivity toward aldehydes, whereas *N*-aryl substituted ylides could be converted easily into α,β -unsaturated ketimines in good yields. The reaction of III with carbon disulfide was also studied.

In recent years a number of phosphonium ylides stabilized by adjacent groups, such as carbonyl, thio-carbonyl, sulfonyl, and cyano, have been isolated, and their physical and chemical properties have been documented.¹⁾

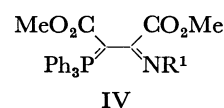


In the course of our studies of *P*- and *S*-ylides and imides,^{2,3)} we have found a useful method for the preparation of imidoyl-stabilized phosphonium ylides, III. Here we will report on the structure and reactions of III.

Results and Discussion

Preparation of Imidoyl Triphenylphosphonium Methylides III. Some imidoyl-substituted ylides III have been reported.⁴⁻⁶⁾ The addition of phenylethynylphospho-

nium salt to aniline gives IIIp.⁴⁾ The thioimide-type ylide IIIk is prepared by the alkylation of thiocarbamoyl triphenylphosphonium methylide with methyl iodide, followed by treatment with a base.⁵⁾ (This route seems to be a good method for the preparation of alkylthio-carbonimidoyl ylides). The addition of phosphinimine with dimethyl acetylenedicarboxylate gives α -imidoyl ylide IV.⁶⁾

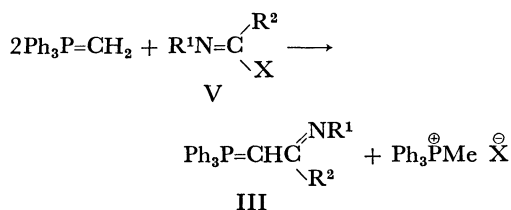


These reported methods seems to have a limited application for the preparation of III with various substituents. We found that imidates, thioimides, and imidoyl chlorides were good reagents for the preparation of imidoyl triphenylphosphonium methylides. The results are shown in Table 1.

TABLE 1. THE PREPARATION OF III

III	V			III		Recryst solvent ^{a)}	Found(Calcd)(%)		
	R ¹	R ²	X	Yield(%)	Mp(°C)		C	H	N
IIIa	Ts	H	OEt	87	193—194	B-P	70.65(70.88)	5.17(5.29)	3.11(3.06)
IIIb	Ts	SMe	SMe	82	272—273	AcOH	66.89(66.78)	5.32(5.20)	2.70(2.78)
IIIc	Ts	SEt	SEt	78	235—238	C-P	67.11(67.29)	5.56(5.45)	2.85(2.71)
IIId	Ts	SPr- <i>i</i>	SPr- <i>i</i>	62	185—186	C-P	67.56(67.77)	5.79(5.69)	2.75(2.63)
IIIe	Ts	OMe	SMe	74	210—211	C-P	68.87(68.98)	5.24(5.38)	2.93(2.87)
IIIf	Ts	OEt	SMe	64	205—206	C-P	69.58(69.44)	5.57(5.63)	2.64(2.79)
IIIg	Ts	OPr- <i>i</i>	SMe	68	180—182	C-P	69.93(69.88)	5.75(5.86)	2.58(2.72)
IIIh	Ts	Ph	Cl	72	176—178	C-P	74.12(74.28)	5.03(5.29)	2.42(2.62)
IIIi	Ts	NMe ₂	SMe	73	227—230	C-P	69.49(69.58)	5.96(5.84)	5.44(5.60)
IIIj	Bs	Me	Cl	51	125—127	C-P	70.97(70.88)	5.37(5.29)	3.16(3.06)
IIIk	Ph	SMe	SMe	67	164 ⁵⁾	C-P	76.02(76.21)	5.51(5.68)	3.28(3.29)
IIIl	Ph	SEt	SEt	63	156—157	C-P	76.38(76.51)	5.89(5.96)	3.03(3.19)
IIIIm	Ph	SPr- <i>i</i>	SPr- <i>i</i>	58	147—150	C-P	76.94(76.79)	6.10(6.22)	3.21(3.09)
IIIIn	Ph	OMe	Cl	63	180—182	E-P	70.08(70.20)	5.83(5.91)	3.39(3.42)
IIIo	Ph	OEt	Cl	53	149—151	E-P	79.30(79.41)	6.04(6.19)	3.25(3.31)
IIIp	Ph	Ph	Cl	71	222—223 ⁴⁾	C-P	84.27(84.37)	5.60(5.75)	3.19(3.07)
IIIq	Ph	<i>p</i> -NO ₂ C ₆ H ₄	Cl	74	230—232	C	76.91(76.79)	5.23(5.03)	5.55(5.60)
IIIr	<i>p</i> -Tol	Ph	Cl	77	184—186	C-P	84.66(84.41)	6.14(6.01)	2.82(2.98)
IIIs	<i>p</i> -Anis	Ph	Cl	74	176—177	C-P	81.74(81.63)	5.72(5.81)	2.78(2.88)
IIIIt	<i>p</i> -NO ₂ C ₆ H ₄	<i>p</i> -NO ₂ CC ₆ H ₄	Cl	68	244—246	C	70.20(70.45)	4.57(4.43)	7.75(7.70)
IIIu	2,4,6-Me ₃ C ₆ H ₂ SO ₂	H	OEt	58	180—181	B-P	71.56(71.73)	5.61(5.81)	2.73(2.88)
IIIv	EtSO ₂	H	OEt	63	167—169	B-P	66.71(66.82)	5.44(5.61)	3.46(3.54)
IIIw	2,4-(NO ₂) ₂ C ₆ H ₃	H	OEt	74	202—203	B	66.75(66.52)	4.53(4.29)	8.82(8.95)

a) B: benzene, C: chloroform, E: ethyl acetate, P: petroleum ether.



The structure of the products were confirmed by the NMR, IR, and elemental analyses.

Although the reaction of V ($\text{R}^1=\text{Ph}$, $\text{R}^2=\text{H}$, $\text{X}=\text{OEt}$; $\text{R}^1=\text{Ph}$, $\text{R}^2=\text{Me}$, $\text{X}=\text{Cl}$; $\text{R}^1=\text{Me}$, $\text{R}^2=\text{Ph}$, $\text{X}=\text{Cl}$) with phosphonium methylide proceeded vigorously, the isolation of the corresponding ylides III ($\text{R}^1=\text{Ph}$, $\text{R}^2=\text{H}$; $\text{R}^1=\text{Ph}$, $\text{R}^2=\text{Me}$; $\text{R}^1=\text{Me}$, $\text{R}^2=\text{Ph}$) failed, yielding only a brown oil. This result suggests that strong electron-withdrawing groups, such as tosyl, *p*-nitrophenyl for the R^1 and/or R^2 of III, stabilize ylides III.

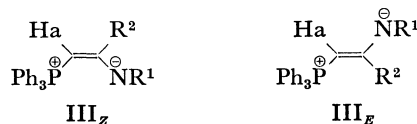
TABLE 2. IR AND pK_a DATA FOR III

III	$\nu_{\text{C}=\text{N}}^{\text{a})} \text{cm}^{-1}$	$pK_a^{\text{b})}$
IIIa	1520	4.42
IIIb	1450	3.60
IIIf	1490	3.86
IIIh		4.35
IIIk	1490	10.7
III n	1470	10.9
IIIp		>12
IIIr	1510	>12
III s	1510	>12
IIIu	1520	4.45

a) Nujol mull. b) In 20% aqueous ethanol.

Structure of III Ylides. Evidence for the resonance interaction of the ylide carbanion with the imino group can be obtained by an examination of the infrared spectra of the imido ylides, III. The C=N stretching frequencies of III occurred at around 1500 cm^{-1} (Table 2). Considering the frequencies of the model compounds⁷⁾ [ketimines (-1650 cm^{-1}), imidates (-1650 cm^{-1}), and thioimides (-1610 cm^{-1})], the shifts of $100-150 \text{ cm}^{-1}$ for III may be attributed to the increased

single-bond character and to the delocalization of the carbanion electrons through the imino groups (*i.e.*, such betain forms as III_E and III_Z).



The structure of the ylide was confirmed on the basis of NMR spectroscopic studies.¹⁰⁾ The results obtained are collected in Tables 3 and 4.

The NMR spectra of ester-stabilized ylides, I and II ($\text{R}^2=\text{O-Alkyl}$), have been shown to be mixtures of *E* and *Z* isomers;⁸⁾ however, the carbonyl-stabilized ylides, I and II ($\text{R}^2=\text{Alkyl}$ or *Aryl*), are only *Z* isomers.⁹⁾

The aldimino-type ylides, IIIa, u, v, and w existed as mixtures of *E* and *Z* isomers in benzene, nitrobenzene, and chloroform, and the *E/Z* ratios increased in accordance with the solvent polarity (benzene–nitrobenzene). The hydrogen-bonding interaction between chloroform and a negative oxygen or sulfur atom^{2,8)} is not as important a factor for IIIa, u, v, and w (Table 3) as for II ($\text{R}^2=\text{H}$). This result reveals that the strong electron-withdrawing effect of the R^1 substituent would stabilize both betain forms, III_E and III_Z.

As is shown in Table 4, two kinds of methyl signals due to ethyl or isopropyl groups of alkoxy-carbonimidoyl or alkylthiocarbonimidoyl ylides III ($\text{R}^2=\text{O-Alkyl}$ or *S-Alkyl*) appeared at δ 0.5–0.8 and 1.2–1.4 respectively. The stereochemistry of these methyl groups was assigned on the assumptions that protons of the R^2 group, neighbouring *cis* to the phosphorus, are shielded by the phenyl groups and that they appear at a higher field than that of the *trans* isomer.⁹⁾ The IIIc, d, e, f, and g ylides were also considered to be mixtures of *E* and *Z* isomers. The *N*-phenyl-substituted ylides, IIIl, m and III n, o were only *Z* and/or *E* isomers respectively (Table 4).

The coupling constants, J_{PCHa} , for the alkoxy-carbonimidoyl, alkylthiocarbonimidoyl, and formimidoyl ylides III ($\text{R}^2=\text{O-Alkyl}$, *S-Alkyl*, and H) show that the constants for the *Z* isomers are larger than those for the

TABLE 3. NMR DATA FOR ALDIMINO YLIDES, III

III	Structure (%)	Solvent			NMR Signals in CDCl_3				
		CDCl_3	PhH	PhNO ₂	Ha(δ)	Hb(δ)	J_{HaHb}	J_{PCHa}	J_{PCHb}
IIIa	<i>E</i>	50	18	35	4.72	a)	14	20	—
	<i>Z</i>	50	82	65	3.96	8.36	7	25	39
IIIu	<i>E</i>	47	16	39	4.51	a)	14	21	—
	<i>Z</i>	53	84	61	3.75	8.32	7	25	39
IIIv	<i>E</i>	51	— ^{b)}	31	4.64	a)	13	20	—
	<i>Z</i>	49	— ^{b)}	69	3.90	8.18	7	25	39
IIIw	<i>E</i>	28	— ^{b)}	10	5.00	a)	13	20	—
	<i>Z</i>	72	— ^{b)}	90	4.32	8.34	6	24	—
II ($\text{R}=\text{H}$) ^{c)}	<i>E</i>	81	10	47	5.94	8.69	15	26	16
	<i>Z</i>	19	90	53	5.17	9.34	8	30	45

a) Signals appeared in the phenyl-proton region. b) The low solubility of IIIv, w inhibited precise studies.

c) Taken from Ref. 2.

TABLE 4. NMR SPECTROSCOPIC STUDIES OF III IN CDCl₃ [δ ppm (J Hz)]

III	Conf(%)	Ha(J_{PCHa})	Others ^{b)}
IIIc	$\{E(46)$ $\{Z(54)$	4.83(18) 3.85(24)	0.75(t, $J=7$, CH ₂ CH ₃), 2.44 (s, CH ₃ C ₆ H ₄), 2.86 (q, CH ₂ CH ₃) 1.39(t, $J=7$, CH ₂ CH ₃), 2.38 (s, CH ₃ C ₆ H ₄), 2.98 (q, CH ₂ CH ₃)
IIId	$\{E(69)$ $\{Z(31)$	4.76(20) 3.83(24)	0.81(d, $J=7$, CHMe ₂), 2.36(s, CH ₃ C ₆ H ₄) 1.36(d, $J=7$, CHMe ₂), 2.28(s, CH ₃ C ₆ H ₄)
IIIe	$\{E(96)$ $\{Z(4)$	3.97(20) a)	2.39(s, CH ₃ C ₆ H ₄), 3.35(s, OMe) 2.29(s, CH ₃ C ₆ H ₄), 3.88(s, OMe)
IIIf	$\{E(93)$ $\{Z(7)$	3.89(20) a)	0.52(t, $J=7$, CH ₂ CH ₃), 2.36(s, CH ₃ C ₆ H ₄), 3.85(q, CH ₂ CH ₃) 1.23(t, $J=7$, CH ₂ CH ₃), 2.29(s, CH ₃ C ₆ H ₄)
IIIg	$\{E(93)$ $\{Z(7)$	3.90(19) a)	0.63(d, $J=6$, CHMe ₂), 2.38(s, CH ₃ C ₆ H ₄), 4.99(hept, CHMe ₂) 1.01(d, $J=6$, CHMe ₂), 2.26(s, CH ₃ C ₆ H ₄)
IIIh	Z	4.02(28)	2.34(s, CH ₃ C ₆ H ₄)
IIIi		a)	2.40(s, CH ₃ C ₆ H ₄), 3.41(s, NMe ₂)
IIIj	Z	3.85(26)	2.39(d, $J=1$, Me)
IIIk	Z	3.05(24)	2.35(s, SMe).
IIIl	Z	3.13(24)	1.26(t, $J=8$, CH ₂ CH ₃), 2.90(q, CH ₂ CH ₃)
IIIIm	Z	a)	1.26(d, $J=7$, CHMe ₂)
IIIn	E	2.46(20)	3.53(s, OMe)
IIIo	E	a)	0.69(t, $J=7$, CH ₂ CH ₃), 4.05(q, CH ₂ CH ₃)
IIIp	Z	a)	
IIIq	Z	3.21(23)	
IIIr	Z	3.27(27)	2.19(s, CH ₃ C ₆ H ₄)
IIIs	Z	a)	3.60(s, OMe)
IIIt	Z	3.92(24)	

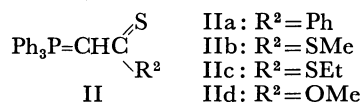
a) Not observed. b) Phenyl-ring protons appeared at 6.5–8.0.

TABLE 5. THE REACTION OF III WITH CARBON DISULFIDE IN CHLOROFORM

III	Temp	Time(day)	Product(%)
IIIc	r.t	7	—
IIIh	r.t	7	—
IIIk	r.t.	1	IIb(82) PhNCS
IIIl	40 °C	1	IIc(85) PhNCS
IIIp	40 °C	1	IIa(66) PhNCS
IIIr	r.t.	1	IIa(71) <i>p</i> -TolNCS
IIIn	r.t.	1	VIII(76)

E isomers (24–25 and 18–20 Hz respectively). This result suggests that the structures of the ketimino-type ylides, IIIh, i, j, p, q, r, s, and t may be considered to be *Z* isomers on the basis of their coupling constants J_{PCHa} (23–28 Hz).

The Reaction of III with Carbon Disulfide. The electrophilic attack of carbon disulfide on phosphonium methylides¹⁾ occurred at the ylide carbanions. The ylides III(R¹=Aryl) can react easily with carbon disulfide, as is shown in Table 5. The reaction of the alkylthiocarbonimidoyl ylides, IIIk and l with carbon disulfide gave the thiocarbonyl ylides, IIb and c (R²=SMe and SEt), and phenyl isothiocyanate in good yields. The products were identified by comparing their NMR and mps with those of authentic samples.²⁾



The ketimino ylides, IIIp and r also showed a high reactivity toward carbon disulfide. The NMR spectroscopic study of this reaction seems to be interesting. To

a solution of IIIr in chloroform-*d* we added a large excess amount of carbon disulfide in one portion, yielding a red solution within a minute. The NMR spectrum of this reaction mixture showed two new, nearly equivalent methyl signals of *p*-tolyl groups at δ 2.11 and 2.33, whose original signals appeared at 2.19. On standing at 40 °C for 2 days or heating at 70 °C for 12 h the higher-field signal disappeared almost entirely. The reaction products were triphenylphosphonium thiobenzoylmethylide, IIa, and *p*-tolyl isothiocyanate. To find the initial reaction products, controlled experiment was undertaken. IIIr (1 mmol) was dissolved in 3 ml of carbon disulfide. Three minutes later, to the resulting red mixture we added methyl iodide (0.66 mmol) in one portion and stirred the mixture well. Then all the liquid was removed *in vacuo*, and the benzene-soluble part was separated. Concentration and crystallization from chloroform-hexane yielded triphenylphosphonium[(methylthio)thiocarbonyl] (*N*-*p*-tolyl-benzimidoyl)methylide VIb (R¹=*p*-Tol, R²=Ph) in a 19% yield. The structure of VIb was confirmed on the basis of NMR, MS, and a methylation reaction, yielding VIIb (R¹=*p*-Tol, R²=Ph). A similar treatment of IIIp with carbon disulfide yielded VIa (R¹=R²=Ph) in a 23% yield.

On the other hand, the reaction of IIIn with carbon disulfide proceeded slowly to give not IId,²⁾ but VIII, as an isolable product in a 76% yield (based on the methyl groups). The structure of VIII was confirmed on the basis of NMR (SMe and OMe groups), MS, and methylation with methyl iodide to yield IX.

The marked difference in the reactivity of these ylides III with carbon disulfide may be attributed to the pK_a values of the conjugate acids of the ylide carbanions.

TABLE 6. THE REACTION OF III WITH ALDEHYDES(X)

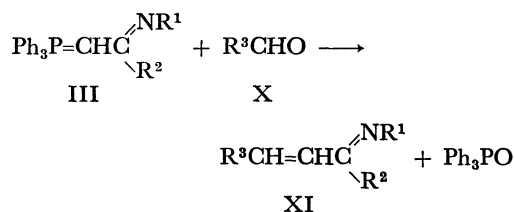
III	X R ³ CHO	XI			Yield(%)	Mp(°C)	M ⁺	NMR(δ in CDCl ₃) ^{a)}	Found(Calcd) (%)		
		R ¹	R ²	R ³					C	H	N
IIIk	PhCHO	Ph	SMc	Ph	91	90—91	235	2.51(s, SMe)	75.63 (75.85)	6.28 (6.42)	5.42 (5.53)
	MeCHO	Ph	SMc	Me	85	oil	191	1.70(dd, $J=6$ and 1, $\underline{\text{MeCH=}}$), 2.32(s, SMe)	69.21 (69.07)	6.73 (6.85)	7.48 (7.32)
IIII	PhCHO	Ph	SEt	Ph	90	50—51	267	1.37(t, $J=7$, CH ₃), 3.08(q, CH ₂)	76.49 (76.36)	6.23 (6.41)	5.16 (5.28)
IIIn	PhCHO	Ph	OMe	Ph	92	68—69	237	3.89(s, OMe)	80.74 (80.98)	6.28 (6.37)	6.02 (5.90)
	MeCHO	Ph	OMe	Me	82	oil	175	1.73 and 1.91 (d, $J=6$, 3:1, $\underline{\text{MeCH=}}$), 3.80 and 3.83 (s, 3:1, OMe)	75.16 (75.40)	7.55 (7.48)	7.68 (7.99)
IIIp	PhCHO	Ph	Ph	Ph	94	108—109	283		89.17 (89.01)	6.18 (6.05)	4.98 (4.94)
IIIr	$p\text{-ClC}_6\text{H}_4\text{-CHO}$	$p\text{-Tol}$	Ph	$p\text{-ClC}_6\text{H}_4$	96	118—120	331	2.21 and 2.38 (s, 2:5, CH ₃)	79.51 (79.63)	5.64 (5.47)	4.37 (4.22)
	PhCHO	$p\text{-Tol}$	Ph	Ph	91	94—95	297	2.20 and 2.38 (s, 1:3, CH ₃)	88.67 (88.85)	6.23 (6.44)	4.39 (4.71)
	MeCHO	$p\text{-Tol}$	Ph	Me	87	oil	235	1.74 and 1.83 (d, $J=6$, 3:1, $\underline{\text{MeCH=}}$), 2.15 and 2.31 (s, 1:3, $\underline{\text{CH}_3\text{C}_6\text{H}_4}$)	86.84 (86.77)	7.13 (7.28)	5.84 (5.95)

a) Protons due to the phenyl and vinyl groups appeared at 6.5—8.0 as multiplets.

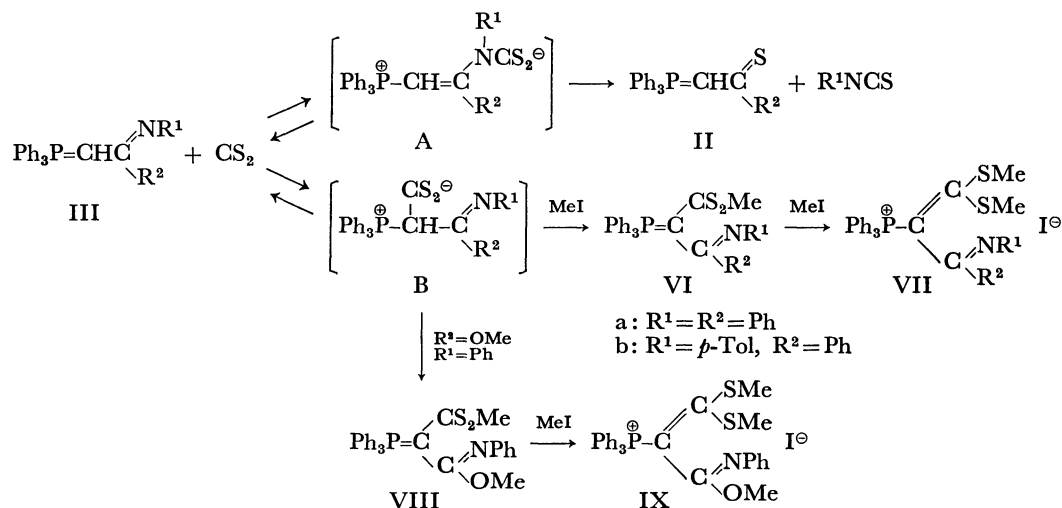
The reactivity decreases with the decrease in pK_a values (Tables 2 and 5). Considering the results obtained, we assumed equilibria between III, A, and B, followed by the kinetically controlled decomposition of A and B, depending on the nature of the substituents, R¹ and R² (Scheme 1). The A formed from IIIk, l, p, and r and carbon disulfide gave II and isothiocyanate, while the B from IIIp, r gave VIa and b in the presence of methyl iodide. On the other hand, IIIn reacted slowly with carbon disulfide to give the product, VIII, from B via the intermolecular nucleophilic attack of the thiolate anion on the methyl group of IIIIn. The thiocarbonyl ylides, VI and VIII, can be easily identified because of their high reactivity with methyl iodide to yield two *S*-methylation products, VII and IX, as was observed for the II ylides.²⁾

The Reaction of III with Aldehydes, X. The Wittig reaction of III with the aldehydes, X, gave α,β -unsaturated ketimines, XI, in fairly good yields (Table 6). The products were confirmed by MS, NMR, and acid hydrolysis. XI (R¹=R²=R³=Ph) and XI (R¹= p -Tol, R²=R³=Ph) gave chalcone on hydrolysis with 1M-HCl in 30% aqueous ethanol. Although the NMR spectra of XI (Table 6) showed the presence of stereo isomers, no effort was made to effect their isolation at this stage.

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Scheme 1.

with amines to give not imines, but β -amino ketones.¹²⁾ The Wittig reaction of III seems to be a useful method for the preparation of α,β -unsaturated ketimines, XI.

N-Tosyl-substituted ylides IIIb and h showed no reactivity toward aldehydes even when heated at 80 °C for 10 h in benzene or chloroform.

Experimental

Preparation of Imidoyl Chlorides, Imidates, and Thioimides.

The formimidates, Va, u, v, and w were prepared by the condensation of ethyl orthoformate and amide or amine according to the literature.^{13,14)} The new compound, Vu, had a mp of 84–85 °C (ethanol); M^+ , 255.

The other imidoyl chlorides and imidates were prepared by the known methods shown in the literature.¹⁵⁾ New compounds were checked by MS. Vd: mp 62–63 °C (ethanol); M^+ , 363. Vf: mp 84–85 °C (ethanol); M^+ , 273. Vg: mp 76 °C (ethanol); M^+ , 287. Vi: mp 60–62 °C (ethanol); M^+ , 272. Vh: bp 110–113 °C/3 mmHg; M^+ , 225. Vm: bp 136–138 °C/3 mmHg; M^+ , 253.

Preparation of III. A suspension of triphenylmethylphosphonium bromide (5.0 g, 14 mmol) and sodium amide (1.5 g) in 50 ml of dry benzene was stirred for 12 h in a stoppered flask at room temperature. After the separation of the precipitate, the ammonia was removed *in vacuo* to give a yellow solution of triphenylphosphonium methylide. To the solution we added imidoyl chloride (6 mmol) in 10 ml of benzene in one portion. The mixture was then allowed to stand for 1 h at room temperature and subsequently treated with charcoal (phosphonium chloride also separated) and condensed *in vacuo* to give a crystalline mass. Crystallization from appropriate solvents yielded III. The results are shown in Table 1.

Determination of pK_a of Ylides, III. The pK_a values were measured in 20% aqueous ethanol according to the literature.¹⁶⁾ The results are given in Table 2.

The Reaction of III with Carbon Disulfide. To a solution of IIIk, l, p, and r (1 mmol) in 20 ml of chloroform we added 1 ml of carbon disulfide in one portion. The resulting solution was heated at 40 °C or at room temperature for 1–2 day, and condensed *in vacuo*, thus separating the petroleum ether-soluble and -insoluble parts. The latter part gave triphenylphosphonium thiocarbonylmethylides, IIa, b, and c, whose physical properties have been previously reported by the present authors.²⁾

IIIp (1 mmol) was dissolved in 3 ml of carbon disulfide. Three minutes later methyl iodide (0.66 mmol) was added to the resulting red mixture. Then all the liquid was removed *in vacuo*, and a benzene-soluble product was separated. Crystallization from chloroform–hexane yielded VIa ($R^1=R^2=Ph$): mp 235–237 °C; NMR ($CDCl_3$) $\delta=2.64$ (3H, s, SMe), 6.8–8.0 (25H, m, Harom). Found: C, 74.51; H, 5.42; N, 2.44%; M^+ , 545. Calcd for $C_{34}H_{28}NPS_2$: C, 74.83; H, 5.17; N, 2.57%; M , 545. The methylation of VIa with methyl iodide in chloroform yielded VIIa ($R^1=R^2=Ph$) in a quantitative yield. VIIa: mp 162–164 °C; NMR ($CDCl_3$) $\delta=1.87$ and 2.00 (3H, s, 1:2, SMe), 2.69 and 2.82 (3H, s, 1:2, SMe), and 6.9–8.2 (25H, m, Harom). In the similar treatment of IIIr with carbon disulfide, VIb ($R^1=p-Tol$, $R^2=Ph$) was obtained in a 19% yield. VIb: mp 228–229 °C; NMR ($CDCl_3$) $\delta=2.38$ (3H, s, $CH_3C_6H_4$), 2.58 (3H, s, SMe), and 6.8–8.0 (24H, m, Harom). Found: C, 75.28; H, 5.24; N, 2.39%; M^+ , 559. Calcd for $C_{35}H_{30}NPS_2$: C, 75.10; H, 5.40; N, 2.50%; M , 559. VIIb ($R^1=p-Tol$, $R^2=$

Ph): mp 193–194 °C; NMR ($CDCl_3$) $\delta=1.90$ and 2.02 (3H, s, 1:2, SMe), 2.27 and 2.61 (3H, s, 1:2, $CH_3C_6H_4$), 2.71 and 2.84 (3H, s, 1:2, SMe), and 6.8–8.0 (24H, m, Harom).

The reaction of IIIn with carbon disulfide was run similarly to give VIII in a 75% yield. VIII: mp 242–245 °C (ethyl acetate–hexane); NMR ($CDCl_3$) $\delta=2.62$ (3H, s, SMe), 3.63 (3H, s, OMe), and 6.7–8.0 (20H, m, Harom). Found: C, 69.72; H, 5.33; N, 2.94%; M^+ , 497. Calcd for $C_{29}H_{26}NOPS_2$: C, 70.00; H, 5.27; N, 2.81%; M , 497. IX: oil; NMR ($CDCl_3$) $\delta=1.82$ (3H, s, SMe), 2.73 (3H, s, SMe), 3.56 (3H, s, OMe), and 6.7–8.0 (20H, m, Harom).

The Reaction of III with Aldehydes X. To a solution of III (1 mmol) in 10 ml of chloroform we added an equimolar amount of aldehyde, X. After 5 min the solution was condensed *in vacuo*, and the petroleum ether-soluble part (XI) and -insoluble part (phosphine oxide) were separated. By crystallization from ethanol XI substances were obtained in good yields (Table 6).

Hydrolysis of XI ($R^1=R^2=R^3=Ph$) and XI ($R^1=p-Tol$, $R^2=R^3=Ph$). A solution of XI (1 mmol) in 15 ml of 1M-HCl 30% aqueous ethanol was kept standing at room temperature for 12 h. The solution was quenched in 30 ml of water, yielding precipitates which, on crystallization from ethanol, gave chalcone in 70–80% yields.

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