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Chemistry of Phosphorus Ylides 21 New Route for the Synthesis of Azetidinones. Reaction of Phosphonium Ylides with Benzil-, *o*-Naphthoquinone-, and Triketonemonoanils

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ABSTRACT: *Active vinylidenetriphenylphosphoranes are nucleophilic reagents which can be considered as versatile synthons for the synthesis of new heterocycles. The active phosphacumulene ylides, namely N-phenylimino-***2a***, 2-oxo-***2b*** or 2-thioxovinylidenetriphenylphosphoranes (***2c***), react with benzil- (***1a,b***), o-naphthoquinone- (***8***), or triketonemonoanils (***11***), to give the corresponding phenylimino- (***3a, d, 9a, 12a***), oxo- (***3b, e, 9b, 12b***), or thioxoazetidinones (***3c, f, 9c, 12c***), respectively, which constitute an important class of organic compounds with medicinal and biological importance. On the other hand, quinone monoanils* **1a, 8, 11** *can be converted by reaction with the stabilized alkylidenephosphoranes (***5a–d***), namely acetylmethylene-* **5a**, *methoxycarbonylmethylene-* **5b**, *ethoxycarbonylmethylene-* **5c**, *and benzoylmethylenetriphenylphosphorane* **5d**, *into the phosphoranylidenes (***7a–d, 10a–d, 13a–d***). No reaction was observed between iminophosphorane (***14***) and the monoanil (***11***). The structures of the new products were assigned according to consistent analytical and spectroscopic data.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:476–483, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20144

Dedicated to Professor Dr. Hans Jurgen Bestmann on the ocassion of his 80th birthday.

For chemistry of other phosphorus ylides, please refer to [1].

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INTRODUCTION

Azetidinones and their derivatives constitute an important class of organic compounds with medicinal and biological importance. The most interesting aspects of these compounds are their antimicrobial [2,3], anticonvulsant [2,3], antiinflammatory [2], antidepressant [4], and antitumor properties [5]; besides their action on the central nervous system [6], sulfonated azetidinones are used as antibiotics [7] and are also useful for the preparation of the nocardicins and monobactams [7]. On the other hand, they possess insecticidal [8], herbicidal [9], gametocidal [10], dwarfing action [11], and are used as inhibitors of pollen fertility [12]. Moreover, they have industrial importance, since, they possess good corrosion inhibition effects [13].

Active phosphacumulenes are nucleophilic reagents which are shown to be versatile synthons for preparing new heterocycles [14–16]. It was therefore of interest to continue our studies [17–19] on the use of these reagents for the synthesis of new azetidinone derivatives. Therefore, we investigated the reaction of the active phosphacumulenes, namely (*N*-phenyliminovinylidene)- **2a**, (2-oxovinylidene)- **2b**, and (2-thioxovinylidene)-triphenylphosphorane (**2c**) with benzil (**1a,b**), *o*-naphthoquinone- (**8**), and

triketone-monoanils (**11**), and compared the reactivities of the active phosphacumulene ylides (**2a–c**), with those of the stabilized phosphonium ylides (**5a–d**), toward the above-mentioned monoanils (**1a, 8, 11**).

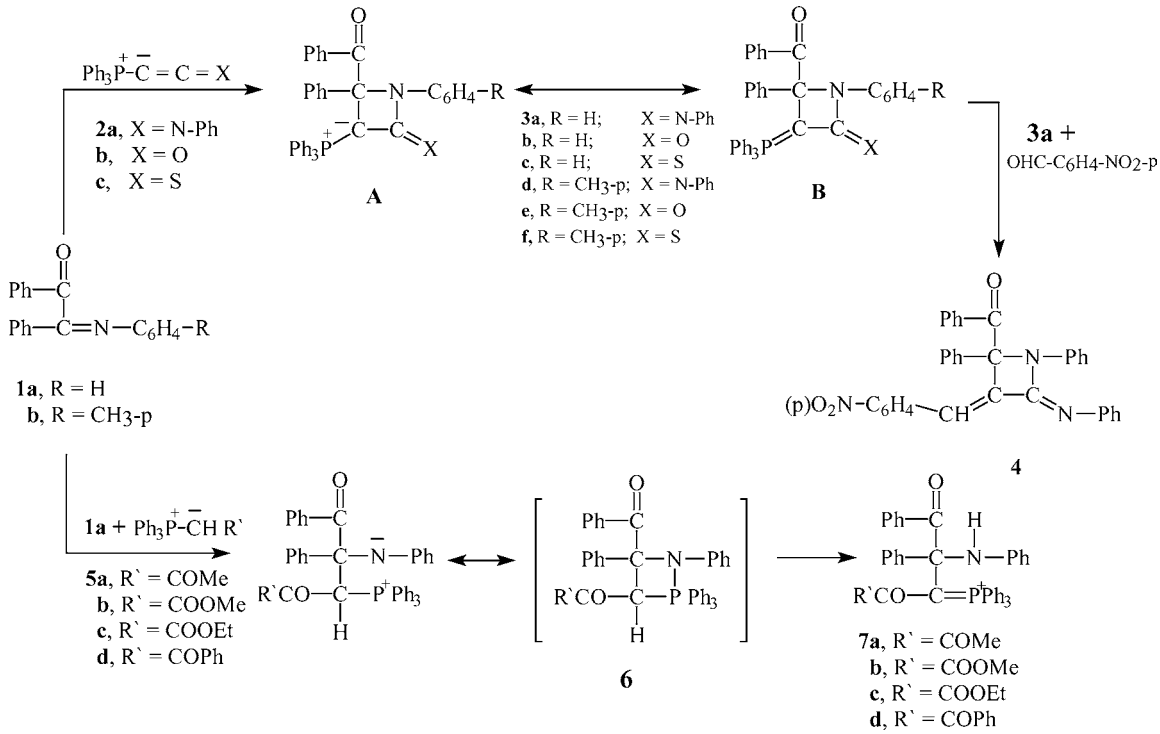
RESULTS AND DISCUSSION

We have found that the reaction of benzil monoanil (**1a**) with one equivalent of (*N*-phenyliminovinylidene)triphenylphosphorane (**2a**) proceeds in dry tetrahydrofuran at room temperature in 5 h to give the new four-membered ring compound, namely 1,2-diphenyl-4-(phenylimino)-3-(triphenylphosphoranylidene)-azetidin-2-yl phenyl ketone (**3a**), which can be represented by the resonance structures **A** and **B**, by addition with subsequent cyclization. Carrying out the reaction using 2 mole equivalents of the active phosphacumulene **2a** instead of 1 led to the formation of the same product **3a**. The ^{31}P-NMR data support structure **3a** and fit with a phosphorane with a four-membered ring [20,21]. On the other hand, when compound **1a** was allowed to react with (2-oxovinylidene)triphenylphosphorane (**2b**) for 8 h, under the same experimental conditions, 1,2-diphenyl-4-oxo-3-(triphenylphosphoranylidene)-azetidin-2-yl phenyl ketone (**3b**) was obtained. From the point of preparing heterocyclic compounds with a thioxo group, the behavior of benzil monoanil (**1a**) toward (2-thioxovinylidene)triphenylphosphorane (**2c**) was also investigated. Thus, 1,2-diphenyl-4-(thioxo)-3-(triphenylphosphoranylidene) azetidin-2-yl phenyl ketone (**3c**) was isolated (Scheme 1). The structures of compounds **3a–c** were verified through elemental analysis and spectroscopic results.

The structure of compound **4** was also chemically verified. When the Wittig reaction was carried out on the phenyliminoazetidinone derivative **3a**, using *p*-nitrobenzaldehyde, 4-(phenylimino)-3-[(4-nitrophenyl) methylene]-1,2-diphenylazetidin-2-yl phenyl ketone (**4**) together with triphenylphosphine oxide was isolated. The structure of the new exocyclic olefin **4** was assigned from its combustion analysis, IR, and MS spectral data.

In addition, when 2-phenyl-2-(*p*-tolylimino)-acetophenone (**1b**) was allowed to react with the active phosphacumulenes (**2a–c**) under the same experimental conditions, the new azetidinone derivatives (**3d–f**) were isolated.

Next, when *o*-naphthoquinone monoanil (**8**) was treated with (*N*-phenyliminovinylidene)- **2a**, (2-oxovinylidene)- **2b**, or (2-thioxovinylidene)-triphenylphosphorane (**2c**) in tetrahydrofuran at 20°C for 4 h in the case of **2a**, 6 h with **2b** revive 8 h when **2c** was used, the adducts **9a–c** were isolated. Compounds **9a–c** were equally obtained, irrespective of whether 1 or 2 mole equivalents of the active phosphacumulene ylides **2a–c** were used.

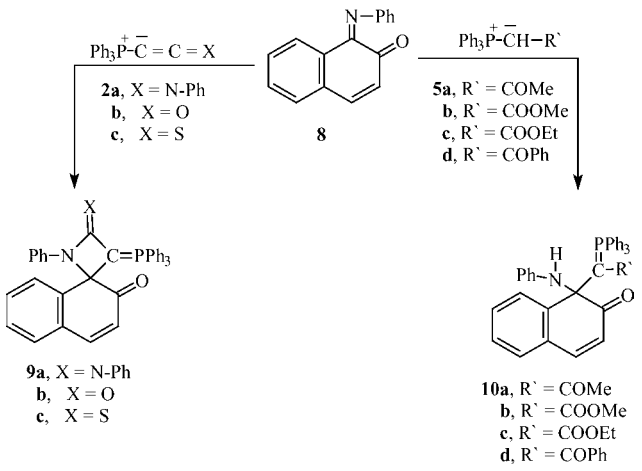


SCHEME 1

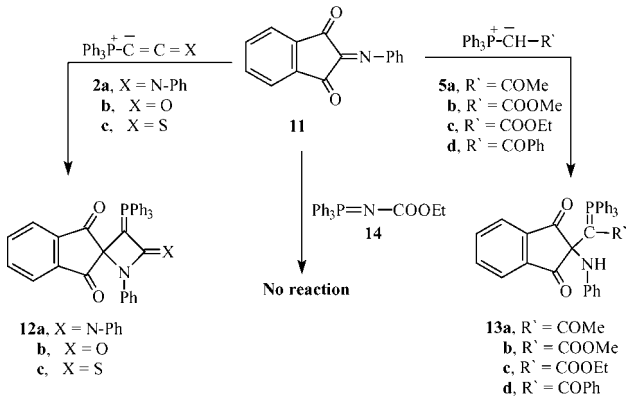
Their elemental analyses and spectroscopic results were consistent with the assigned structures, namely 1-phenyl-2-(phenylimino)-3-(triphenylphosphoranylidene)spiro[azetidine-2,1′(2′H)-naphthalen]-2′-one (**9a**), 1-phenyl-2-(oxo)-3-(triphenylphosphoranylidene)spiro[azetidine-2,1′-(2′H)-naphthalen]-2′-one (**9b**), 1-phenyl-2-(thioxo)-3-(triphenylphosphoranylidene)spiro[azetidine-2,1′-(2′H)-naphthalen]-2′-one (**9c**) (Scheme 2).

In addition, the reaction of active ylides **2a–c** was also performed using the triketone monoanil (**11**). When 2-phenylimino-1,3-indandione (**11**) was allowed to react with phosphacumulene ylides (**2a–c**), in molar ratio 1:1, in dry boiling toluene for 4 h in the case of **2a**, 7 h with **2b,** and/or 10 h when **2c** was used, the corresponding **12a–c** were isolated, namely 1-phenyl-2-(phenylimino)-3-(triphenylphosphoranylidene)spiro-[azetidine-2,2′-(2H)indene]-1′,3′-dione (**12a**), 1-phenyl-2-(oxo)-3-(triphenylphosphoranylidene)spiro[azetidine-2,2′-(2H)-indene]1′,3′-dione (**12b**), and 1-phenyl-2-(thioxo)-3-(triphenylphosphoranylidene)spiro[azetidine-2,2′-(2H)-indene]-1′,3′-dione (**12c**) (Scheme 3).

The behavior of the stabilized phosphonium ylides (**5a–d**) toward the previously mentioned monoanils (**1a, 8, 11**) was also studied to determine the site of attack. We have found that methylene triphenylphosphoranes, namely acetylmethylene- **5a**, methoxycarbonylmethylene- **5b**, ethoxycarbonylmethylene- **5c**, and benzoylmethylenetriphenylphosphorane (**5d**) react with benzil monoanil (**1a**) (Scheme 1), in dry boiling toluene over a period of 12 h to give yellow 1:1 adducts (**7a–d**). Compounds (**7a–d**) are equally obtained whether 1 mole equivalent or 2 mole equivalents of the Wittig reagents **5** were used with respect to 1 mole equivalent of **1a**. The elemental analysis, IR, ^{1}H-, ^{13}C-,



SCHEME 2



SCHEME 3

and ^{31}P-NMR were reasons for assigning structure **7a**. 1,2-Diphenyl-2-(phenylamino)-3-(triphenylphosphoranylidene)pentane-1,4-dione (**7a**), taken as an example, showed bands at 3400 (NH), 1685 (br, Ph—C=O, CH_3—C=O) and 1436 (P-aryl) cm^{-1} in its IR spectrum. In the ^{1}H-NMR spectrum, signals at δ 2.1 (3H, CH_3, s), 4.8 (NH, exchangeable with D_2O), and 7.6 (30H, aromatics, m) were observed. In the ^{31}P-NMR spectrum of **7a**, a signal at δ 14.9 ppm was observed which supports ylidene-phosphorane structure [22,23] (Scheme 1).

In the same way, *o*-naphthoquinone monoanil (**8**) reacts with the stabilized Wittig reagents **5a–d**, in dry boiling tetrahydrofuran over 15 h to give the phosphoranylidenes **10a–d** (Scheme 2).

We also have found that when 2-phenylimino-1,3-indandione (**11**) reacted with the stable phosphonium ylides (**5a–d**), in dry boiling xylene over 20 h, compounds **13a–d** were isolated, respectively (Scheme 3).

The reaction of phosphinimines is often analogous to those of phosphonium ylides. But in their activity iminophosphoranes are inferior to phosphine alkylidenes [24–26]. We have found that triketone monoanil (**11**) is inactive against ethoxycarbonyltriphenylphosphinimine (**14**), even when the reactants were boiled in toluene for a long time; they were recovered practically unchanged.

The results of the present investigation show that the reaction course of benzil- (**1a,b**), *o*-naphthoquinone- (**8**), and/or triketone-monoanils (**11**) with active phosphacumulenes (**2a–c**) differs markedly from that of the respective stabilized phosphonium ylides (**5a–d**) and the phosphinimine (**14**). Although the initial step in these reactions is nucleophilic attack by the carbanion center of the phosphoranes, preferentially at the electron-deficient carbon nitrogen double bond [27–29], rather than the carbonyl group of the bifunctional monoanils, even

when we used 2 moles of the phosphoranes **5**, the consequences of the initial step varied markedly according to the structure of these phosphoranes. In the case of the reaction of active phosphacumulenes, *N*-phenylimino- (**2a**), 2-oxo- (**2b**), and 2-thioxovinylidene-triphenylphosphorane (**2c**), the phenylimino azetidinones (**3a, d, 9a,** or **12a**), the oxoazetidinones (**3b,e, 9b,** or **12b**), and thioxoazetidines (**3c,f, 9c,** or **12c**) were produced. Moreover, the difference in the nucleophilic character of (*N*-phenyliminovinylidene)- **2a**, (2-oxovinylidene)- **2b**, and (2-thioxovinylidene)- triphenylphosphorane (**2c**) can be noticed too (**2a** > **2b** > **2c**) [30]. While, **2a** reacts smoothly with monoanils (**1a,b, 8,** or **11**) [30], the oxo- and thioxo-analogues react less rapidly.

On the other hand, the formation of phosphoranylidenes (**7a-d, 10a-d**, and **13a-d**) by the reaction of the stabilized 2-oxoalkylidenephosphoranes (**5a–d**), with benzil- (**1a**), *o*-naphthoquinone- (**8**), and triketone-monoanils (**11**) can be explained as follows: The R′ moieties in the stabilized phosphonium ylides (**5a–d**), which are electron withdrawing in nature, stabilize the formation of the phosphoranylidenes, via migration of the α-proton of the first formed phosphonium betaine, such as **6**, to the electron-rich center of the molecule. However, no reaction was observed between the above-mentioned monoanil (**11**) and the iminophosphorane (**14**).

The new reactions supply a novel and direct route for the synthesis of nitrogen heterocycles, especially phenylimino-, oxo-, and thioxo-azetidinones.

EXPERIMENTAL

All melting points are uncorrected. The solvents were dried and distilled by usual techniques. Reactions were carried out under a nitrogen atmosphere. Elemental analyses were carried out at the Microanalysis Department of National Research Center. The IR spectra were measured in KBr on a Perkin-Elmer infracord spectrometer model 157 (grating). The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian spectrometer at 90 MHz, using TMS as an internal reference. ^{31}P-NMR was run, relative to external H_3PO_4 (85%), with a Varian FT-80 spectrometer; mass spectra were obtained on a Varian MAT CH-4B instrument.

*Reaction of Benzil Monoanil (***1a***) with the Active Phosphacumulene Ylides* **2a–c***. Preparation of Azitidinone Derivatives (***3a–c***)*

To a solution of benzil monoanil (**1a**) (0.01 mol) in 20 mL of tetrahydrofuran was added dropwise, with stirring at room temperature, a solution of (*N*-phenyliminovinylidene)- **2a** [32], (2-oxovinylidene)- **2b** [33], and/or (2-thioxovinylidene)-triphenylphosphorane (**2c**) [33] (0.01 mol) in 30 mL of THF. The reaction mixture was stirred for 5 h in the case of **2a**, 8 h with **2b,** and/or 10 h with **2c**. The precipitate that had formed was filtered off and crystallized from a specify solvent.

When the reaction was performed using 1 mole of the benzil monoanil (**1a**) and 2 moles of the phosphacumulenes **2a–c**, the same azetidinone derivatives **3a–c** were obtained respectively.

Yields, analytical, and physical data of compounds **3** are shown in Table 1.

*Wittig Reaction of 1,2-Diphenyl-4-(phenlimino)-3-triphenylphosphoranylidene)azetidin-2-yl Phenyl Ketone (***3a***) with p-Nitrobenzaldehyde*

A mixture of compound **3a** (0.001 mol), *p*-nitrobenzaldehyde (0.0011 mol) and toluene (20 mL) was refluxed for 6 h. Toluene was distilled off, and the residue that remained was crystallized from benzene to give exocyclic olefin **4** as greenish crystals.

The benzene filtrate afforded, upon concentration and addition of *n*-hexane, colorless precipitate crystals of triphenylphosphine oxide, with mp and mixed mp 151° (40%) [34].

*Reaction of 2-Phenyl-2-(p-tolylimino)-acetophenone (***1b***) with Phosphacumulene (***2a***). Preparation of Azetidinone Derivative* **3d**

To a solution of 2-phenyl-2-(*p*-tolylimino) acetophenone(**1b**) [29] (0.01 mol) in 20 mL of tetrahydrofuran was added a solution of (*N*-phenyliminovinylidene)triphenylphosphorane (**2a**) (0.01 mol) in 15 mL of THF. The reaction mixture was stirred for 7 h at 20°C until no starting material could be detected (TLC). After THF was distilled off under reduced pressure, the residue that remained was redissolved in 50 mL of acetone and evaporated to dryness in the presence of silica gel (5 g). The mixture was then added to a column previously charged with silica gel in light petroleum. The column was developed with light petroleum followed by the same eluent containing increasing amounts of acetone. The fraction eluted with (70:30 v/v) light petroleum: acetone yielded azetidinone derivative **3d** as orange crystals.

*Reaction of 2-Phenyl-2-(p-tolylimino)acetophenone (***1b***) with Phosphacumulenes (***2b,c***). Synthesis of Azetidinone Derivatives* **3e,f**

A mixture of 2-phenyl-2-(*p*-tolyl-imino) acetophenone (**1b**) (0.01 mol), and (2-oxovinylidene)- **2b**

TABLE 1 Physical and Analytical Data for *N*-Phenylimino- (**3a, d, 9a, 12a**), 2-Oxo- (**3b,e, 9b, 12b**), 2-Thioxoazetidinones (**3c, f, 9c, 12c**), and Phosphoranylidenes (**7a–d, 10a–d**, and **13a–d)**

					Analysis Calcd/ Found (%)				
Comp. No.	*Solvent of Cryst.*	*m.p. (°C)*	*Yield (%)*	*Mol. Formula (M. wt.)*	*C*	*H*	*N*	*P*	*S*
3a	Acetone/light pet.	198	75	$C_{46}H_{35}N_2OP$	83.38	5.28	4.22	4.68	–
				(662)	83.62	5.40	4.43	4.32	–
3b	Chloroform/light pet.	165	72	$C_{40}H_{30}NO_2P$	81.77	5.11	2.38	5.28	–
				(587)	81.43	5.35	2.54	5.43	–
3c	Chloroform/light pet.	175	78	$C_{40}H_{30}NOPS$	79.60	4.97	2.32	5.14	5.30
				(603)	79.43	4.62	2.66	5.02	5.11
3d	Acetone/light pet.	162	68	$C_{47}H_{37}N_2OP$	83.43	5.47	4.14	4.58	–
				(676)	83.62	5.13	4.00	4.22	–
3e	Acetone/*n*-hexane	147	70	$C_{41}H_{32}NO_2P$	81.86	5.32	2.32	5.15	–
				(601)	81.65	5.10	2.01	5.30	–
3f	CH_2Cl_2/*n*-hexane	170	72	$C_{41}H_{32}NOPS$	79.74	5.18	2.26	5.02	5.18
				(617)	79.52	5.32	2.42	5.21	5.32
4	Chloroform/light pet.	175	68	$C_{35}H_{25}N_3O_3$	78.50	4.67	7.85	–	–
				(535)	78.62	4.75	7.63	–	–
9a	Acetone/*n*-hexane	192	70	$C_{42}H_{31}N_2OP$	82.62	5.08	4.59	5.08	–
				(610)	82.41	5.35	4.66	5.32	–
9b	Acetone/*n*-hexane	288	78	$C_{36}H_{26}NO_2P$	80.74	4.85	2.61	5.79	–
				(535)	80.86	4.92	2.42	5.52	–
9c	Acetone/*n*-hexane	186	75	$C_{36}H_{26}NOPS$	78.40	4.72	2.54	5.63	5.80
				(551)	78.62	4.85	2.65	5.45	5.32
12a	Acetone/light pet.	263	65	$C_{41}H_{29}N_2O_2P$	80.39	4.74	4.58	5.06	–
				(612)	80.26	4.52	4.65	5.21	–
12b	Et. acetate/*n*-hexane	232	77	$C_{35}H_{24}NO_3P$	78.21	4.47	2.60	5.77	–
				(537)	78.53	4.55	2.42	5.54	–
12c	Et. acetate/*n*-hexane	210	79	$C_{35}H_{24}NO_2PS$	75.95	4.34	2.53	5.61	5.79
				(553)	75.65	4.22	2.62	5.32	5.55
7a	CH_2Cl_2/light pet.	137	78	$C_{41}H_{34}NO_2P$	81.59	5.64	2.32	5.14	–
				(603)	81.40	5.42	2.10	5.00	–
7b	$CHCl_3$/light pet.	130	75	$C_{41}H_{34}NO_3P$	79.48	5.49	2.26	5.00	–
				(619)	79.20	5.25	2.02	5.15	–
7c	$CHCl_3$/light pet.	160	78	$C_{42}H_{36}NO_3P$	79.62	5.69	2.21	4.89	–
				(633)	79.50	5.43	2.01	4.53	–
7d	$CHCl_3$/light pet.	175	78	$C_{46}H_{36}NO_2P$	83.00	5.41	2.10	4.66	–
				(665)	83.20	5.20	2.32	4.52	–
10a	Acetone/*n*-hexane	178	65	$C_{37}H_{30}NO_2P$	80.58	5.44	2.54	5.62	–
				(551)	80.72	5.30	2.76	5.33	–
10b	Et. acetate/*n*-hexane	180	65	$C_{37}H_{30}NO_3P$	78.30	5.29	2.46	5.46	–
				(567)	78.45	5.46	2.65	5.66	–
10c	Et. acetate/*n*-hexane	188	66	$C_{38}H_{32}NO_3P$	78.48	5.50	2.41	5.33	–
				(581)	78.69	5.21	2.01	5.65	–
10d	Acetone/*n*-hexane	196	65	$C_{42}H_{32}NO_2P$	82.21	5.22	2.28	5.05	–
				(613)	82.46	4.99	2.00	5.42	–
13a	Acetone/light pet.	176	72	$C_{36}H_{28}NO_3P$	78.12	5.06	2.53	5.60	–
				(553)	78.53	5.45	2.66	5.72	–
13b	Acetone/light pet.	203	78	$C_{36}H_{28}NO_4P$	75.92	4.92	2.46	5.44	–
				(569)	75.53	4.70	2.60	5.65	–
13c	Acetone/light pet.	163	75	$C_{37}H_{30}NO_4P$	76.15	5.15	2.40	5.31	–
				(583)	76.52	5.63	2.12	5.00	–
13d	Et. acetate/light pet.	198	77	$C_{41}H_{30}NO_3P$	80.00	4.87	2.28	5.04	–
				(615)	80.26	4.66	2.23	4.52	–

or (2-thioxovinylidene)-triphenylphosphorane (**2c**) (0.01 mol) in toluene (40 mL) was refluxed for 8 h when **2b** was used, for 10 h with **2c**. Toluene was distilled off, and the precipitate that formed was crystallized from the specify solvent to give the azetidinones **3e,f** respectively. The starting materials were recovered unchanged when reactions were done in THF.

TABLE 2 NMR and IR Data for Azetidinones (**3a–f, 4, 9a–c**, and **12a–c**) and Phosphoranylidenes (**7b–d, 9a–c, 10a–d**, and **13a–d**)

Comp. No.	*IR (cm^{-1})*	*NMR*		
		^{1}H-NMR	*^{31}P-NMR*	*^{31}C-NMR*
3a	1670 (C=O), 1610 (C=N), and 1439 (P-aryl) [31]	δ 7.13 (m, 35H, Ar)	δ 26.20	δ 206.89 (C=O)
3b	1722 (N–C=O), 1641 (Ph–C=O), 1436 (P-aryl)	δ 7.57 (m, 30H, Ar)	δ 14.69	δ 179.0 (Ph–C=O), δ 169.0 (N–C=O), δ 143 (C=P)
3c	1660 (C=O), 1438 (P-aryl), and 1210 (C=S) [31]	δ 7.77 (m, 30H, Ar)	–	δ 209.5 (C=S), δ 190.0 (C=O), δ 158 (C=P)
3d	1670 (C=O), 1606 (C=N), and 1438 (P-aryl)	δ 1.42 (s, 3H, CH_3), δ 7.23 (m, 34H, Ar)	–	δ 206.1 (C=O), δ 28.3 (CH_3)
3e	1646 (C=O, Ph), 1610 (C=O, –N), 1490 (P-aryl)	δ 2.34 (s, 3H, CH_3), δ 7.15 (m, 29H, Ar)	–	δ 198.5 (N–C=O), δ 191.5 (Ph–C=O), δ 22.3 (CH_3)
3f	1662 (C=O), 1448 (P-aryl), and 1211 (C=S)	δ 2.1 (s, 3H, CH_3), δ 7.45 (m, 29H, Ar)	–	δ 198.5 (C=S), δ 194.5 (C=O), δ 24.4 (CH_3), δ 135 (C=P)
4	1662 (C=O), and 1620 (C=N), 1440 (P-c).	–	–	–
7b	3500 (NH), 1730 (br, Ph–C=O, C=O, ester), and 1470 (P-aryl)	δ 3.5 (s, 3H, O CH_3), δ 7.0 (s, 1H, NH), δ 7.45 (m, 30H, Ar)	δ 29.24	–
7c	3450 (NH), 1702 (Ph–C=O), 1627 (C=O, ester), and 1435 (P-aryl)	δ 1.1 (t, 3H, CH_3CH_2), δ 4.1 (q, 2H, CH_3CH_2), δ 4.75 (s, 1H, NH), δ 7.6 (m, 30H, Ar)	δ 27.70	–
7d	3400 (NH), 1720; 1620 (Ph–C=O), and 1436 (P-aryl)	δ 4.9 (s, 1H, NH), δ 7.64 (m, 35H, Ar)	δ 17.2	–
9a	1727 (C=O), 1620 (C=N), 1440 (P-aryl)	δ 7.35 (m, 31H, Ar)	δ 17.18	δ 168.0 (C=O), δ 162 (C=N), δ 154 (C=P)
9b	1720 (C=O, naphthalenone), 1640 (C=O, azetidinone), and 1440 (P-aryl)	δ 7.2 (m, 26H, Ar)	δ 16.1	δ 192.0 (C=O azetidinone), δ 163.0 (C=O naphthalenone), δ 150.5 (C=P)
9c	1650 (C=O), 1440 (P-aryl), and 1240 (C=S)	δ 7.4 (m, 26H, Ar)	δ 22.52	–
10a	3357 (NH), 1700 (C=O, naphthalenone), 1621 (C=O, acetyl), and 1440 (P-aryl)	δ 7.1 (m, 26H, Ar), δ 4.25 (s, 1H, NH), δ 2.63 (s, 3H, CH_3)	δ 13.32	δ 180.6 ($OCOCH_3$), δ 171.7 (C=O naph-), δ 30.0 (CH_3), δ 150 (C=P)
10b	3400 (NH), 1720 (C=O, naphtha-), 1640 (C=O, ester), and 1457 (P-aryl)	δ 3.8 (s, 3H, O CH_3), δ 4.75 (s, 1H, NH), δ 7.3 (m, 26H, Ar)	δ 29.58	δ 177.5 (C=O, naph), δ 166.3 (C=O, OCO–C_2H_5), δ 16.59 (CH_3)
10c	3400 (NH), 1720 (C=O, naphtha-), 1640 (C=O, ester), and 1440 (P-aryl)	δ 1.15 (t, 3H, CH_3CH_2), δ 3.4 (q, 2H, CH_3CH_2), δ 4.8 (s, 1H, NH), δ 7.9 (m, 26H, Ar)	δ 29.72	–
10d	3300 (NH), 1700 (C=O, naphtha-), 1640 (Ph–C=O), and 1436 (P-aryl)	δ 4.2 (s, 1H, NH), δ 7.8 (m, 31H, Ar)	δ 18.01	–
12a	1706 (C=O), 1604 (C=N), and 1438 (P-aryl)	δ 7.57 (m, 29H, Ar)	δ 27.6	δ 200.60 (C=O), δ 152 (C=N), δ 148 (C=P)
12b	1702 (C=O, indanone), 1621 (C=O azetidinone), and 1440 (P-aryl)	–	δ 22.39	–
12c	1710 (C=O), 1440 (P-aryl) 1232 (C=S)	–	δ 21.52	δ 203.4 (C=S), δ 200 (C=O), δ 148 (C=P)
13a	3357 (NH), 1700 (C=O, indanone), 1621 (C=O, acetyl), and 1434 (P-aryl)	δ 2.1 (s, 3H,CH_3), δ 3.65 (NH), and δ 7.04 (m, 24H, Ar)	δ 15.35	δ 199.5 (C=O, indanone), δ 189.7 (C=O, acetyl), δ 145(C=P), δ 27.8 (CH_3)
13b	3367 (NH), 1706 (C=O, indanone), 1654 (C=O, ester), and 1405 (P-aryl)	δ 3.63 (s, 3H, OCH_3), δ 3.75 (s, 1H, NH), δ 7.3 (m, 24H, Ar)	δ 29.95	δ 200.3 (C=O, indanone), δ 180.5 (C=O, ester), δ 146 (C=P) δ 23.8 (CH_3)
13c	3330 (NH), 1702 (C=O, indanone), 1623 (C=O, ester), and 1436 (P-aryl)	δ 1.25 (t, 3H, CH_3 CH_2), δ 4.2 (q, 2H, CH_3CH_2), δ 4.75 (s, 1H, NH), δ 7.27 (m, 24H, Ar)	δ 26.67	δ 200.6 (C=O, indanone), δ 181.3 (C=O, ester), δ 66.2 (CH_2), δ 14.5 (CH_3)
13d	3360 (NH), 1700 (C=O, indanone), 1620 (C=O, Ph), and 1436 (P-aryl)	δ 3.68 (s, 1H, NH), δ 7.3 (m, 29H, Ar)	δ 17.64	δ 199.4 (C=O, indanone), δ 183 (C=O, Ph), δ 146 (C=P)

*Reaction of o-Naphthoquinone Monoanil (***8***) with Phosphacumulene Ylides* **2a–c**. *Preparation of Azetidinone Derivatives (***9a-c***)*

A solution of *o*-naphthoquinone monoanil (**8**) (0.01 mol) in 50 mL of tetrahydrofuran was added drop by drop with stirring at room temperature, to a solution of phosphacumulene ylides (**2a–c**) (0.011 mol) in 50 mL THF. The reaction mixture was stirred for 4 h in the case of **2a**, 6 h with **2b**, and/or 9 h with **2c**, during which color changed from deep yellow to deep red. After THF was distilled off under reduced pressure, the residue was triturated with ether, filtered, and crystallized from specify solvents to give the new azetidinones **9a–c**.

*Reaction of 2-Phenylimino-1,3-indandione (***11***) with Phosphacumulenes (***2a–c***). Synthesis Azetidinone derivatives* **12a–c**

A mixture of 2-phenylimino-1,3-indandione (**11**) (0.01 mol), phosphacumulene ylides (**2a–c)** (0.01 mol), and toluene (40 mL) was boiled for 8 h when **2a** was used, for 10 h with **2b,** and/or 11 h in the case of **2c** until no starting material could be detected. Toluene was removed under vacuum, and the residue that remained was crystallized from the specify solvents to give azetidinones **12a–c** respectively. No reaction was observed between the phosphacumulenes (**2a–c**) and the compound **11** when the reactions were performed in THF.

*Reaction of Benzil Monoanil (***1a***) with Methylenetriphenylphosphoranes* **5a–d**. *Preparation of the Phosphoranylidenes* **7a–d**

To a solution of benzil monoanil (**1a**) (0.01 mol) in 20 mL of dry toluene was added a solution of methylenetriphenylphosphoranes **5a–d** (0.011 mol) in 30 mL of toluene, and the reaction mixture was refluxed for 12 h until all the benzil monoanil was consumed; the reactions were monitored by TLC. After the solvent was distilled off under reduced pressure, the residue was crystallized from the appropriate solvents to give the phosphoranylidenes (**7a–d**).

*Reaction of o-Naphthoquinone Monanil (***8***) with the Stabilized Wittig Reagents* **5a–d**. *Preparation of the Novel Phosphoranylidenes (***10a-d***)*

A solution of *o*-naphthoquinone monoanil (**8**) (0.01 mol) in 20 mL of THF was added to a solution of the 2-oxoalkylidenephosphoranes (**5**) [35,36] (0.01 mol) in 20 mL of THF and drops of triethylamine (1 mL) as a basic catalyst. The reaction mixture was refluxed for 15 h until no reactants could be detected (TLC). After removal of the solvent, the residue was chromatographed on the silica gel with *n*-hexane containing increasing amounts of ethyl acetate as eluent. Fractions eluted with 80:20 v/v *n*-hexane: ethyl acetate yielded phosphoranylidenes **10a–d**, which were recrystallized from the specify solvents.

*Reaction of 2-Phenylimino-1,3-indandione (***11***) with Stabilized Phosphonium Ylides (***5a–d***)*

To a solution of **11** (0.011 mol) in dry xylene (30 mL) was added a solution of the stabilized phosphonium ylides (**5a–d**) in the same solvent (20 mL) containing drops of triethylamine (1 mL) as a catalyst; the reaction mixture was refluxed till no reactants could be detected (TLC). The reaction mixture was then evaporated at 60°C under reduced pressure. The residue was redissolved in methanol (100 mL) and evaporated to dryness in the presence of silica gel (5 g). The mixture was then added to a column previously charged with silica gel in petroleum ether (br. 60–80°C). The column was developed with petroleum ether followed by the same eluent containing increasing amount of acetone. Fractions eluted with 65:35 v/v petroleum ether: acetone yielded phosphoranylidene derivatives **13a–d**, which were recrystallized from the specify solvents.

*Attempted Reaction of 2-Phenylimino (***11***) with Ethoxycarbonyl Triphenylphosphinimine (***14***)*

No reaction was observed between 2-phenylimino-1,3-indandione (**11**) and phosphinimine **14** [37] even when the reactants were boiled in THF and/or toluene for a long time, and they were recovered unchanged.

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REFERENCES

[1] Chemistry of Phosphorus Ylides 21; for part 20, cf. Soliman, F. M.; Khalil, Kh. M.; Said, M. M; Maigali, S. S. Heterocycl Commun 2002, 8(5), 451–458; for part 19, cf. Soliman, F. M.; El-Ansary, A.; Said, M. M.; Ramzy, F.; Maigali, S. S. Egypt J Bilhar (2005, in press); for part 18, cf. Soliman, F. M.; Said, M. M.; Maigali, S. S. J Monatsh Chem 2005, 136, 241–251.

[2] Srivastava, S. D.; Rawat, T. R. Indian J Chem, Sect B 1999, 38(5), 623–627.
[3] Srivastava, S. K.; Srivastava, S.; Srivastava, S. D. Indian J Chem, Sect B 1999, 38(2), 183–187.
[4] Szmuszkovicz, J. (Upjohn Co.). Eur Pat Appl EP 85, 811 (CI. Co7D205104), US Pat Appl. 1982, 347,127, 75; CA 1984, 100, 6311g.
[5] Izydore, R. A.; Zhong, Y.; Zhou, X.; Warren, E.; Wheaton, R.; Hall, H. Anticancer Res 2001, 21(1A).
[6] Testa, E.; Fontanella, L.; Aresi, V.; (Lepetit SPA, Milan) Ann 1964, 673, 60–70; CA 59, 7505a; 60, 10676h.
[7] Miller, J.; Atanu, B.; Krook, M. A. Tetrahedron 1983, 39(15), 2571– 2575; CA 1984.100.22466s.
[8] Shiono, Y.; Akiyama, K.; Hayashi, H. Biosci Biotechnol Biochem 2000, 64(7), 1519–1521.
[9] Chou, Ch.; Leu, Li. J Chem Ecol 1992, 18(12), 2285–2303.
[10] Mogensen, H. L.; Ladyman, J. A. R. Sex Plant Reprod 1989, 2(3), 173–183.
[11] Gale, M. D.; Salter, A. M.; Angus, W. J.; Maluszynski M. Adv Agric Biotechnol 1989, 24, 49–61.
[12] Cross, J. W.; Schulz, P. J. In Pollen Biotechnology for Crop Production and Improvement; Shivanna, K. R; Sawhney V. K. (Eds.); Cambridge University Press: Cambridge, UK, 1997; pp. 218–236.
[13] Kunitsugu, A. J Electrochem Soc 1971, 118(10), 1553–1558.
[14] Soliman, F. M.; Said, M. M. Z Naturforsch 1991, 46b, 1105.
[15] Soliman, F. M.; Said. M. M. Phosphorus Sulfur Silicon 1991, 61, 355.
[16] Soliman, F. M.; Khalil, Kh. M.; El-Naeam, Sh. Phosphorus Sulfur Silicon 1991, 60, 183.
[17] Soliman, F. M.; Yakout. E. M.; Said. M. M. Bull Chem Soc Jpn 1994, 2162.
[18] Said, M. M.; Maigali, S. S.; Soliman, F. M. Phosphorus Sulfur Silicon 1996, 108, 41–49.
[19] Soliman, F. M.; Said, M. M.; Maigali, S. S. Heteroatom Chem 1997, 8, 157.
[20] Bestmann, H. J.; Schmid, G.; Sandmeier, D.; Kisielowski, L. Angew Chem 1977, 89, 275; (b) Angew Chem, Int Ed Engl 1977, 16, 268.
[21] Bestmann, H. J.; Schmid, G.; Sandmeier, D.; Geismann, Ch. Tetrahedron Lett 1980, 2401.
[22] Johnson, A. Wm. Ylides and Imines of Phosphorus; Wiley: New York 1993.
[23] Grim. S.O.; McFarlane. W.; Marks T. J Chem Commun 1967, 1191.
[24] Appel, R.; Hauss, A. Chem Ber 1960, 93, 405.
[25] Appel, R.; Hauss, A. Z Anorg Alleg Chem 1961, 311, 240.
[26] Horner, L.; Hoffmann, H. Angew Chem 1956, 68, 473.
[27] Wieczorek, J. S.; Gancarz, R. Rocz Chem 1976, 50, 2171; CA 1977, 86, 171542.
[28] Sidky, M. M.; Zayed, M. F.; Praefcke, K.; Wong-Ng, W.; Nybuvg, S. C. Phosphorus Sulfur 1982, 13, 319.
[29] Sidky, M. M.; Mahran, M. R. H.; Abdou, W. M.; Hafez, T. S. Egypt J Chem 1984, 27(6), 809–816.
[30] Bestmann, H. J. Angew Chem 1977, 89(6), 361; Angew Chem, Int Ed Engl 1977, 16, 349.
[31] Williams, D. H.; Fleming, I. Spectroscopic Methods in Organic Chemistry; McGraw-Hill: Maidenhead, Berkshire, UK, 1987; p. 55.
[32] Bestmann, H. J.; Schmid, G.; Tetrahedron Lett 1975, 4025.
[33] Bestmann, H. J.; Sandmeier, D. Angew Chem, Int Ed Engl 1975, 14, 634.
[34] Michaelis, A.; Gleichmann, L. Chem Ber 1882, 15, 801.
[35] Ramirez, F.; Dershowitz, S. J Org Chem 1957, 22, 41.
[36] Bestmann, H. J.; Kratzer, O. Chem Ber 1962, 95, 1894.
[37] Wiegrabe, W.; Bock, H. Chem Ber 1968, 101, 1414.