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The Reaction of Active and Stabilized Phosphonium Ylides with α,β-Unsaturated Carbonyl Compounds [1]

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ABSTRACT

*The active ketenylidene-(**2a**) or thioketenylidenetriphenylphosphoranes (**2b**) react with 2-benzylidene-1,3-indandione (**1**), 5-benzylidenebarbituric acid (**11**), and 4-benzylidene-1,2-diphenyl-3,5-pyrazolidinedione (**16**) to give the corresponding pyranones and thioxopyranones (**3a,b, 12a,b**) and (**17a,b**), respectively. On the other hand, compounds **1** and **11** can be converted by reaction with the stabilized alkylidenephosphoranes **4a–e** into the phosphoranylidenes **6a–e** and **13a–e**. Moreover, the oxaphosphinins **8** or **14** and the oxazaphosphinins **10** or **15** were obtained when compounds **1** and **11** were allowed to react with the phosphorane **7** and the iminophosphorane **9**, respectively. Some of these new organophosphorus compounds are found to have insecticidal and molluscicidal properties against cotton leafworm Spodoptera littoralis larvae and Biomphalaria alexandrina snails.*
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INTRODUCTION

Bestmann reported on the reactions of phosphacumulenes with unsaturated centers, which are of particular preparative interest [2]. These phosphacumulenes are versatile nucleophilic reagents that have been utilized in heterocyclic synthesis [3]. This has prompted us to study the reaction of 2-benzylidene-1,3-indandione (**1**), 5-benzylidenebarbituric acid (**11**), and 4-benzylidene-1,2-diphenyl-3,5-pyrazolidinedione (**16**) with the active phosphacumulenes, ketenylidene-(**2a**) and thioketenylidenetriphenylphosphorane (**2b**). A comparative study on the behavior of **1** or **11** toward the stabilized alkylidenephosphoranes **4a–e** or **7** and the iminophosphorane **9** is also described.

RESULTS AND DISCUSSION

We have found that the reaction of 2-benzylidene-1,3-indandione (**1**) with ketenylidenetriphenylphosphorane (**2a**) proceeds in dry tetrahydrofuran at room temperature for 4 hours in the case of **2a** or 8 hours in the case of **2b** by addition with subsequent cyclization to give 3,4-dihydro-4-phenyl-3-(triphenylphosphoranylidene)indeno[1,2-b]pyran-2,5-dione (**3a**), which can be represented by the resonance structures **A** and **B**. Structural support for compound **3a** was based upon the following evidence: (a) There were correct elementary analyses and molecular weight determination (MS). (b) The IR spectrum of **3a** (in KBr, cm^{-1}) showed strong absorption bands at 1700 and 1660 (C=O), 1640 (P=C) [4] and 1440 (P-aryl) [5]. (c) The ^1H NMR spectrum of **3a** (in $CDC1_3$) showed the methine proton (pyran ring) as a doublet ($^3J_{H\text{-}P}$ = 8 Hz) centered at δ 4.1, and the ^{13}C NMR spectrum also showed a signal at δ 192 (C=O, indene) and δ 169 (C=O, pyran). (d) A signal at δ +23.92 was observed in the ^{31}P NMR spectrum of

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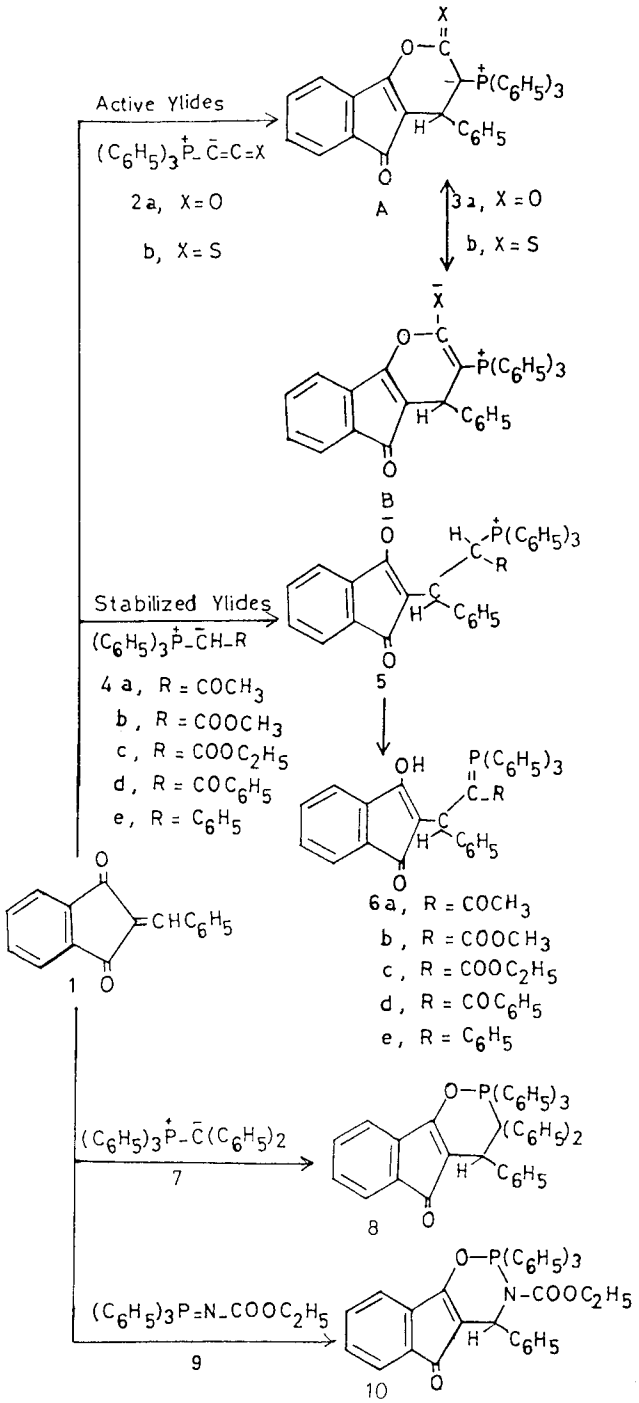
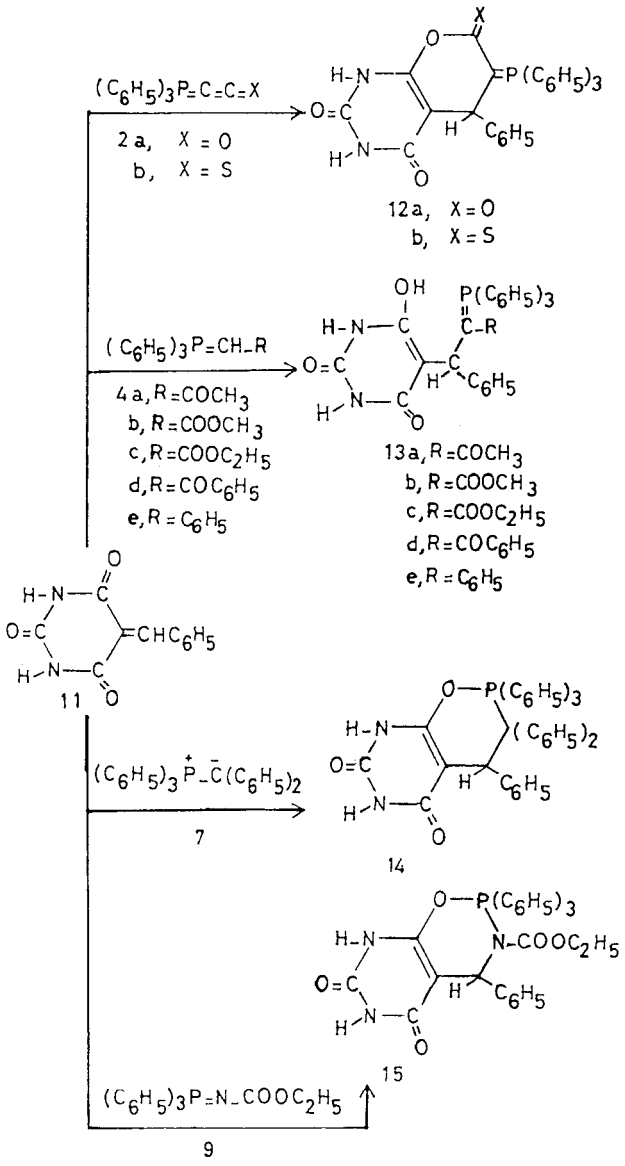
3a, which supports structure **3** and excludes a four-membered ring structure conceivably formed by addition with cyclization [6]. (e) In the MS of **3a**, *m/e* = 536 (M^+). When compound **1** was allowed to react with thioketenylidenetriphenylphosphorane (**2b**), under the same experimental conditions, 3,4-dihydro-4-phenyl-2-thioxo-3-(triphenylphosphoranylidene)indeno[1,2-b]pyran-5(2H)-one (**3b**) was obtained. Its elemental analyses and molecular weight determination (MS) agreed with the molecular formula, $C_{36}H_{25}O_2PS$. Its IR spectrum (in KBr, cm^{-1}) showed absorption bands at 1700 (C=O), 1640 (P=C), 1440 (P-aryl), and 1255 (C=S) [7]. Its ^1H NMR spectrum showed the methine proton (pyranthione ring) as a doublet ($^3J_{H\text{-}P}$ = 7 Hz) at δ 4.6. Moreover, a signal at δ 16.99 was observed in its ^{31}P NMR spectrum, and, in the mass spectra, *m/e* = 552 (M^+) (Scheme 1).

When 5-benzylidenebarbituric acid (**11**) was treated with ketenylidene-(**2a**) or thioketenylidene-triphenylphosphorane (**2b**) in THF, yellow adducts **12a,b** were isolated in good yields. Compounds **12a,b** were obtained in the same yields irrespective of whether 1 or 2 mole equivalents of the phosphacumulenes (**2a,b**) were used. Correct elemental analyses and molecular weight determinations (MS) were obtained for both products (**12a,b**). The IR spectrum of 5,6-dihydro-5-phenyl-6-(triphenylphosphoranylidene)(2H)pyrano[2,3-d]pyrimidine-2,4,7(1H, 3H)trione (**12a**) revealed the presence of strong absorption bands at 3200 (N–H broad), 1660, 1700 (C=O), 1620 (P-acyl), and 1440 cm^{-1} (P-aryl). Presence of carbonyl groups in (**12a**) was also attested by signals at δ 164, 162.8, and 161.6 (C=O), in its ^{13}C NMR spectrum. Moreover, the methine proton (pyran ring) resonated at δ 4.11 (d, $^3J_{H\text{-}P}$ = 8 Hz). The ^{31}P NMR shift recorded for compound **12a** was δ +22.74. On the other hand, absorption bands shown by the IR spectrum of 1,5,6,7-tetrahydro-5-phenyl-7-thioxo-6-(triphenylphosphoranylidene)-2H-pyrano-[2,3-d]pyrimidine-2,4-(3H)-dione (**12b**), at 3220, 1700 (broad), 1640, 1455, 1280, are attributed to the N–H, C=O, C=P, P-aryl, and C=S groups, respectively. The ^1H NMR spectrum of **12b** disclosed the presence of signals at δ 10.7 (s, 1H, N–H), 7.1 (s, 1H, N–H) broad (exchangeable with D_2O), and 4.1 (d, 1H, C–H, $^3J_{H\text{-}P}$ = 7 Hz). The ^{31}P NMR shift recorded for the product **12b** was δ +17.95 (Scheme 2).

When 1,2-diphenyl-3,4-pyrazolidinedione (**16**) was allowed to react with the phosphacumulenes **2a** or **2b**, under the same experimental conditions described above, 1,2,4,5-tetrahydro-1,2,4-triphenyl-5-(triphenylphosphoranylidene)pyrano[2,3-c]pyrazole-3,6-dione (**17a**) or 1,4,5,6-tetrahydro-1,2,4-triphenyl-6-thioxo-5-(triphenylphosphoranylidene)-pyrano[2,3,-c]pyrazole-3(2H)-one (**17b**) was isolated. The IR spectrum of compound **17a** showed peaks at 1720, 1670 (C=O), 1600 (C=P), and 1440 cm^{-1} (P-aryl). Its ^1H NMR spectrum exhibits a doublet at δ 4.2 (d, 1H, $^3J_{H\text{-}P}$ = 8 Hz pyran-methine).



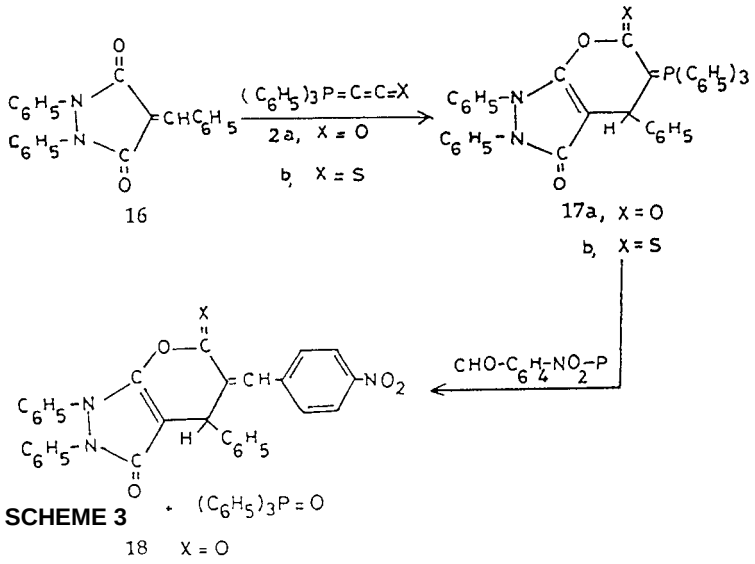
SCHEME 1



SCHEME 2

Compound **17a** gave M^+ at 642 and the ^{31}P NMR resonance at δ 23.11. On the other hand, the IR spectrum of its thioanalogue, **17b**, showed absorption bands at 1740 (C=O), 1660 (C=P), 1220 (C=S; pyran), and 1440 cm^{-1} (P-aryl). In the ^1H NMR spectrum of **17b**, a doublet was observed at δ 4.1 (d, 1H, C–H, pyran, $^3J_{H\text{-}P} = 7$). The ^{31}P NMR shift recorded for **17b** was δ 26.85 and the *m/e* was found at 658 (M^+) in the mass spectra.

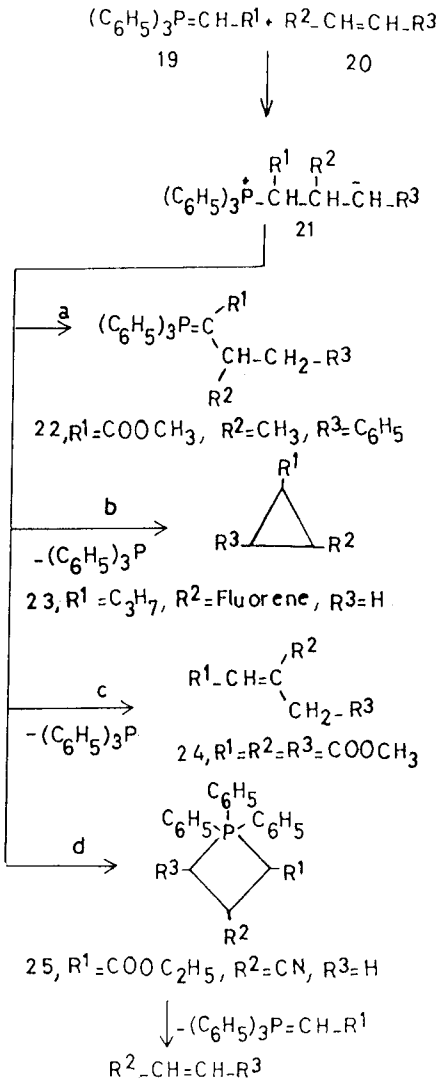
When the Wittig reaction was carried out on the pyranone derivative **17a**, using *p*-nitrobenzaldehyde, the new exocyclic olefin **18**, together with triphenylphosphine oxide, was obtained. The structure of compound **18** is assignable from its analyses, IR, ^1H NMR, and MS spectral data. The IR spectrum shows a strong band at 1740 and lacks the presence of a peak around 1440 cm^{-1} for (P–C) (Scheme 3).



SCHEME 3

It is well known that a phosphonium ylide (**19**) will react with α,β-unsaturated ketones (**20**) either at the carbonyl function to give olefins [8] or add to the activated carbon–carbon double bond to give an intermediate betaine (**21**). This latter zwitterion may then decompose in one of four ways, depending upon the substituents present on the reactants and produce the new stable ylide (**22**) [9] cyclopropane derivatives (**23**) [10], olefinic components (**24**) [11], or the phosphetane (**25**), which gives again the phosphonium ylide (**19**) and the α,β-unsaturated compound (**20**) [12] (Scheme 4).

As a continuation of our interest in the reactions of stabilized phosphonium ylides with α,β-unsaturated carbonyl compounds [13], we have examined the reactivity of acylmethylenetriphenylphosphoranes toward 2-benzylidene-1,3-indandione (**1**), or 5-benzylidenebarbituric acid (**11**), to determine the preferential site of attack. We have found that acetylmethylene-(**4a**), methoxycarbonylmethylene-(**4b**), ethoxycarbonylmethylene-(**4c**), or benzoylmethylenetriphenylphosphorane (**4d**) reacts with compound **1** (Scheme 1), or **11** (Scheme 2), in dry boiling toluene for 12 hours to give colorless 1:1 adducts formulated as **6a–d** and **13a–d**, respectively. Compounds **6a–d** and **13a–d** are obtained in equal yields whether 1 mole equivalent or 2 mole equivalents of the Wittig reagents **4** were used with respect to 1 mole equivalent of **1** or **11**. In the same sense, compounds **1** or **11** reacted with phenylmethylenetriphenylphosphorane in ethanol in the presence of so-



SCHEME 4

dium ethoxide (**4e**), at room temperature, to give the phosphoranes **6e** or **13e**, respectively. Structures **6** and **13** were proved from elementary analyses and spectroscopic data. The IR spectrum of ethyl *β*-phenyl-3-hydroxy-1-oxo-*α*-(triphenylphosphoranylidene)indene-2-propionate (**6c**), taken as an example, showed bands at 3400 (OH), 1720, 1670 (C=O), and 1620 cm^{-1} (P=C). Its ^1H NMR spectrum showed signals at δ 1.4 (3H, ethoxy-CH_3, t), 3.1 (2H, ethoxy-CH_2, q), and 4.1 (1H, for the exocyclic methine proton, d, $^3J_{H\text{-}P}$ = 6 Hz). In the ^{31}P NMR spectrum of **6c**, a signal at δ +23.42 was observed that supports the ylidenephosphorane structure [14], and its MS showed the peak at *m/e* 582 (M^+).

In the same sense, diphenylmethylenetriphenylphosphorane (**7**) reacted with 2-benzylidene-1,3-indandione (**1**), or 5-benzylidenebarbituric acid (**11**), in ethanol to give the corresponding oxaphosphinins **8** or **14**. The elemental microanalyses, IR, ^1H and ^{31}P NMR data agree with the proposed structures. Signals at δ +22.68 and +22.16 were observed in the ^{31}P NMR spectra of compounds **8** and **14**, respectively, which are in accord with oxaphosphinins [15].

Iminophosphoranes are the nitrogen analogues of phosphorus ylides. They undergo reactions with electrophiles that correspond to those of phosphorus ylides giving C=N bonds rather than C=C. The reactivity of iminophosphoranes results from the polarity of the P–N bond, which is influenced by the substituents, particularly on the nitrogen atom [16].

We have now examined the reaction of ethoxycarbonyltriphenylphosphinimine (**9**) with the *α*-*β*-unsaturated carbonyl compounds, **1** or **11**. The iminophosphorane **9** reacted with compounds **1** or **11** in the molar ratio 1:1 at 25°C in tetrahydrofuran for 12 hours to give the oxazaphosphinins **10** and **15**, respectively. The IR and ^1H NMR spectra as well as the elemental analyses were consistent with structures **10** and **15**. The IR spectrum of **10** showed strong absorption bands at 1720 (C=O) and 1410 cm^{-1} (P-aryl). In its ^1H NMR spectrum, signals at δ 1.4 (3H, CH_3, t), 3.5 (2H, CH_2, q), and 4.9 (methine proton of the oxazaphosphinin ring) appeared.

CONCLUSIONS

It has been shown from the results of this investigation that the phosphoranes **2**, **4**, **7**, and **9**, behave toward the *α*,*β*-unsaturated carbonyl compounds **1**, **11**, and **16**, in different manners. Although the initial step in all of these reactions is nucleophilic attack by the carbanion center of the phosphoranes at the electron-deficient exoconjugated system, the consequences of the initial step vary markedly according to the structure of the phosphorane. In the cases of the reactions of active phosphacumulenes **2a,b** with compounds **1**, **11**, or **16**, the oxoindenopyranones **3a**, **12a**, or **17a** and thioxoindenopyranones **3b**, **12b**, or **17b** were produced. Furthermore, the R moiety in the stabilized phosphoranes, **4**, if it is electron-withdrawing in nature, stabilizes the formation of phosphoranylidenes **6** and **13**, via migration of the *α*-proton of the phosphonium betaine, such as **5**, to the electron-rich center of the molecule. On the other hand, diphenylmethylenetriphenylphosphorane afforded the oxaphosphoranes **8** and **14** on reaction with the *α*,*β*-unsaturated carbonyl compounds **1** and **11**, respectively. Moreover, the oxazaphosphinins **10** and **15** were isolated from the reactions of the iminophosphorane **8** with compounds **1** or **11**. The pres-

TABLE 1 Physical and Analytical Data for Pyranones (**3,12,17a**), Thioxopyranones (**3,12,17b**), Phosphoranylidenes (**6a–e,13a–e**), Oxaphosphinins (**8,14**), and Oxazaphosphinins (**10,15**)

				Analysis		*Calcd/Found*		
Compd	*Yield %*	*Mp of Crystals C*	*Molecular Formula*	*C*	*H*	*N*	*P*	*S*
3a	86	190[a]	$C_{36}H_{25}O_3P$	80.59	4.66	—	5.78	—
		pale yellow	(536)	80.29	4.75	—	5.61	—
3b	96	169[a]	$C_{36}H_{25}O_2PS$	78.26	4.52	—	5.61	5.79
		yellow	(552)	78.61	4.19	—	5.28	5.61
12a	94	215[b]	$C_{31}H_{23}N_2O_4P$	71.81	4.44	5.40	5.98	—
		pale yellow	(518)	71.61	4.13	5.27	5.71	—
12b	96	208[b]	$C_{31}H_{32}N_2O_3PS$	69.66	4.30	5.24	5.80	5.99
		pale yellow	(534)	69.70	4.32	5.28	5.47	6.22
17a	92	160[b]	$C_{42}H_{31}N_2OP$	70.50	4.82	4.36	4.82	—
		orange	(610)	70.33	4.60	4.19	4.81	—
17b	64	185[b]	$C_{42}H_{31}N_2O_2PS$	76.82	4.72	4.26	4.72	4.87
		orange	(658)	76.53	4.54	4.46	4.52	4.43
18	75	203[a]	$C_{31}H_{21}N_3O_5$	72.23	4.07	8.15	—	—
		greenish	(515)	72.50	3.92	8.36	—	—
6a	60	103[a]	$C_{37}H_{29}O_3P$	80.43	5.25	—	5.61	—
		yellow	(552)	80.13	5.17	—	5.41	—
6b	90	131[a]	$C_{37}H_{29}O_4P$	78.16	5.10	—	5.47	—
		orange	(568)	78.32	5.20	—	5.80	—
6c	81	159[c]	$C_{38}H_{31}O_4P$	78.35	5.32	—	5.32	—
		yellowish green	(582)	78.37	5.31	—	5.62	—
6d	75	125[a]	$C_{42}H_{31}O_3P$	82.80	5.04	—	5.04	—
		yellow	(614)	82.53	5.09	—	4.92	—
13a	82	173[d]	$C_{32}H_{27}N_2O_2P$	77.19	5.05	5.42	5.80	—
		orange	(502)	71.20	4.92	5.17	5.74	—
13b	85	205[a]	$C_{32}H_{27}N_2O_5P$	69.69	4.95	5.81	4.59	—
		faint brown	(550)	69.53	5.16	5.77	4.78	—
13c	75	233[b]	$C_{33}H_{29}N_2O_5P$	70.21	5.14	4.96	5.41	—
		pale yellow	(564)	70.68	5.11	4.97	5.58	—
13d	75	210[b]	$C_{77}H_{29}N_2O_2P$	74.49	4.86	4.69	5.20	—
		brown	(564)	74.66	4.62	4.07	5.38	—
6e	75	130[b]	$C_{41}H_{31}O_2P$	83.95	5.29	—	5.46	—
		pale yellow	(586)	83.69	5.60	—	5.41	—
13e	86	280[e]	$C_{36}H_{29}N_2O_3P$	76.05	5.10	4.92	5.45	—
		pale yellow	(568)	76.42	5.18	4.52	5.36	—
8	75	170[a]	$C_{47}H_{35}O_2P$	85.19	5.28	—	4.68	—
		violet	(662)	85.39	5.35	—	4.61	—
14	81	285[b]	$C_{42}H_{33}N_2O_3P$	78.26	5.12	4.34	4.81	—
		yellow	(664)	78.54	5.12	4.21	4.98	—
10	60	143[a]	$C_{37}H_{30}NO_4P$	78.58	5.30	2.47	5.48	—
		yellow	(583)	78.96	5.21	2.34	5.69	—
15	64	330[b]	$C_{32}H_{28}N_3O_5P$	67.96	4.95	7.43	5.48	—
		pale yellow	(565)	68.01	4.05	7.31	5.62	—

[a]Crystallized from = chloroform/light pet-ether.
[b]Crystallized from = acetone/light pet-ether.
[c]Crystallized from = chloroform/*n*-hexane.
[d]Crystallized from = ethyl acetate/*n*-hexane.
[e]Crystallized from = acetone/*n*-hexane.

TABLE 2 ^{31}P NMR, ^{1}H NMR, and Spectral Data for Pyranones (**3,12,17a**), Thioxopyranones (**3,12,17b**), Phosphoranylidenes (**6a–e,13a–e**), Oxaphosphinins (**8,14**), and Oxazaphosphinins (**10,15**)

		NMR	
Compd	*IR*	*^{31}P NMR*	*^{1}H NMR*
6a	3450 (OH), 1720 (C=O) and 1640 (C=P)	22.51	2.15 (S, 3H, CH_3), 4.16 (d, 1H, exocylclic methine proton), and 7.55 (m, 24H, Ar–H)
6b	3400 (OH), 1710, 1670 (C=O), and 1630 (C=P)	22.23	2.45 (S, 3H, CH_3) and 7.5 (m, 24H, Ar–H)
6d	3430 (OH), 1690 (OH), and 1440 (P-aryl)	21.87	4.25 (d, 1H, exocyclic methine proton) and 7.65 (m, 29H, Ar–H)
13a	3370 (OH), 3200 (NH), 1680 (C=O), 1620 (C=P), and 1440 (P-aryl)	22.42	3.1 (S, 3H, CH_3), 4.5 (d, 1H, methline proton), and 8.855, 9.955 (2H, NH)
13b	3400 (OH), 3200 (NH), 1700 (C=O), 1610 (C=P), and 1410 (P-aryl)	22.29	3.15 (S, 3H, CH_3), 4.6 (d, 1H, methine), and 8.85, 9.9555 (S, 2H, NH)
13c	3400 (OH), 3200 (WH), 1720 (C=O), 1620 (C=P), and 1430 (P-aryl)	25.36	
13d	3420 (OH), 3250 (NH), 1700 (C=O), 1620 (C=P), and 1450 (P-aryl)	23.45	4.6 (d, 1H, methine) and 8.35, 9.95 (S, 2H, NH)
6e	3480 (OH), 1720 (C=O), and 1630 (C=P)	22.08	5.1 (d, 1H, methine)
13e	3400 (OH), 3240 (NH), and 1780, 1720 (C=O)	23.14	5.1 (d, 1H, methine)
8	1720 (C=O) and 1640 (C=P)	—	5.4 (d, 1H, methine)
14	3300 (NH) and 1720, 1680 (C=O)	—	—
15	3200 (NH) and 1720 (C=O)	—	1.2 (t, 3H, CH_3) and 3.5 (q, 2H, CH_2)

ent study shows the broad reaction spectrum of phosphoranes in heterocyclic syntheses, particularly concerning the synthesis of thioxopyranones.

The biological activities of the newly prepared organophosphorus compounds against the Egyptian cotton leafworm *Spodoptera littoralis* and the freshwater snail *Biomphalaria alexandrina* were studied. Only four compounds **10**, **12**, **19**, and **21** were found to be active and showed satisfactory results as insecticides. The stomach action of these compounds, however, was much higher than the contact one. On the other hand, the molluscicidal toxicity was more pronounced, as eight of these organophosphorus compounds **1**, **6**, **9**, **10**, **11**, **15**, **17**, and **21** displayed good effects in this respect. Although the toxicity of the prepared compounds varies greatly according to their structures and the test organism, they are still less active than various commercially available pesticides.

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", National Research Centre. 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 spectra were 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.

THE REACTION OF α,β-UNSATURATED CARBONYL COMPOUNDS **1**, **11**, *AND* **6** *WITH PHOSPHACUMULENES* **2a** *AND* **b**— *PREPARATION OF THE NEW PYRANONES* **3a**, **12a**, *AND* **17a** *AND THIOXOPYRANONE DERIVATIVES* **3b**, **12b**, *AND* **17b**

General Procedure

To a solution of 2-benzylidene-1,3-indandione (**1**) [17], 5-benzylidenebarbituric acid (**11**) [18], or 1,2-diphenyl-3,5-pyrazolidinedione (**16**) [19] (0.01 mole) in 20 mL of tetrahydrofuran was added dropwise, with stirring, at room temperature, a solution of the ketenylidene-(**2a**) [20] or thioketenylidnetriphenylphosphorane (**2b**) [20] (0.01 mole) in 30 mL of THF. The reaction mixture was left for 4 hours when **2a** was used and for 8 hours with **2b**. The precipitate

that had formed was filtered off and crystallized from an appropriate solvent.

When the reaction was performed using 1 mole of the α,β-unsaturated carbonyl compounds (**1**, **11**, and **16**) and 2 moles of the phosphacumulenes (**2a** and **b**), the same pyranones (**3a**, **12a**, and **17a**) and the thioxopyranones (**3b**, **12b**, and **17b**) were obtained as above. Yields, analytical, and spectroscopic data are presented in Tables 1 and 2.

The Reaction of Pyranone Derivative **17a** *with p-Nitrobenzaldehyde*

A mixture of the phosphorus compound **17a** (0.64 g, 0.001 mole), p-nitrobenzaldehyde (0.15 g, 0.0011 mole), and toluene (20 mL) was refluxed for 12 hours. Toluene was distilled off, and the residue was crystallized from benzene to give the exocyclic olefin, namely, 1,2,4,5-tetrahydro-1,2,4-triphenyl-5-(triphenylphosphoranylidene)pyrano[2,3-c]pyrazole-3, 6-dione (**18**) as greenish crystals, mp 203°C from chloroform/light petroleum (0.38 g, 75%). Anal. calcd for $C_{31}H_{21}N_3O_5$ C, 72.23; H, 4.07; N, 8.15. Found: C, 72.50; H, 3.92, N, 8.36.

The benzene filtrate afforded, upon concentration and addition of *n*-hexane, a colorless precipitate of triphenylphosphine oxide as white crystals, mp and mixed mp 151 [21] (0.19 g, 68%).

THE REACTION OF α,β-UNSATURATED CARBONYL COMPOUNDS **1** *OR* **11** *WITH ACYLMETHYLENETRIPHENYLPHOSPHORANES,* **4a–d**—*PREPARATION OF THE PHOSPHORANYLIDENES* **6a–d** *AND* **13a–d**

General Procedure

To a solution of 2-benzylidene-1,3-indandione (**1**) or 5-benzylidenebarbituric acid (**11**) (0.01 mole) in 20 mL of dry ethyl acetate was added a solution of the acylmethylenetriphenylphosphoranes **4a–d** [22, 23] (0.011 mole) in 30 mL of ethyl acetate, and the reaction mixture was refluxed for 15 hours. After the solvent was distilled off, the residue was crystallized from the appropriate solvent. Yields, analytical, and spectroscopic data are presented in Tables 1 and 2.

*THE REACTION OF 2-BENZYLIDENE-1,3-INDANDIONE (***1***) AND 5-BENZYLIDENEBARBITURIC ACID (***11***) WITH PHENYLMETHYLENETRIPHENYLPHOSPHORANE (***4e***) AND DIPHENYLMETHYLENETRIPHENYLPHOSPHORANE (***7***) AND SYNTHESIS OF THE PHOSPHORANYLIDENES* **6e** *AND* **13e** *AND THE OXAPHOSPHININ DERIVATIVES* **8** *AND* **14**

A solution of phosphonium ylides **4e** [24] or **7** [25] (prepared from the corresponding phosphonium salt and base) (0.01 mole) in 20 mL of absolute ethanol was added to a solution of the α,β-unsaturated carbonyl compounds **1** or **11**, in 30 mL of absolute ethanol, and the reaction mixture was stirred for 1 hour at 25°C. Ethanol was distilled off under reduced pressure, and the remaining solid residue was extracted with dry benzene. After the benzene extract had been concentrated, the phosphoranylidenes **6e** and **13e** and the oxaphosphorins **8** and **14** were precipitated. Yields, analytical, and spectroscopic data are presented in Tables 1 and 2.

Synthesis of the Oxazaphosphinins **10** *and* **15**

A solution of ethoxycarbonyltriphenylphosphinimine (**9**) [26] (0.011 mole) in 30 mL of dry toluene was added dropwise under stirring to a solution of 2-benzylidene-1,3-indandione (**1**) or 5-benzylidenebarbituric acid (**11**) (0.01 mole) in 30 mL of toluene. The reaction mixture was refluxed for 10 hours, during which the color changed to orange, and then it was kept in the refrigerator (5°C) for 12 hours. The precipitate that had formed was washed with dry ether, and the solvent was distilled off under vacuum. Yields, analytical, and spectroscopic data are presented in Tables 1 and 2 of compound **10** and **15**.

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