

of II-g-i was treated with 2 mL of phenylhydrazine and heated on the water bath for 2 h and evaporated. The residue was crystallized from the proper solvent. See Table II. Compounds III gave the color reactions characteristic of pyrazolines (10, 13).

**8-Aryl-6,7,8,9,10,11-hexahydro-5H-benzo[3,4]cyclohepteno[2,1-d]pyrimidene-10-thiones (IV).** (A) A mixture of 0.01 mol of the arylmethylene derivative (II) and 1 g of thiourea was heated in a metal bath at 170 °C (bath temperature), until the mixture melted. The viscous mass was stirred with a glass rod and the temperature of the bath was allowed to rise to 180 °C during 0.5 h and then to 190 °C. The product was crystallized from the proper solvent.

(B) A mixture of 0.02 mol of II, 1.5 g of thiourea, and 2 g of potassium hydroxide in 100 mL of absolute ethanol was heated on a water bath for 4 h and left overnight. The product was filtered off and washed with water until free from alkali. See Table II.

**8-Aryl-6,7,10,11-tetrahydro-5H,8H-benzo[3,4]cyclohepteno[2,1-d]thiazolo[3,2-a]pyrimidin-10-ones (V).** A mixture of 0.02 mol of IV, 3.2 g of chloroacetic acid, and 8 g of fused sodium acetate, in 40 mL of acetic acid and 20 mL of acetic anhydride was refluxed for 4 h, cooled, and poured into water. The solid (V) that separated was collected, washed with water and crystallized from the proper solvent. The products did not dissolve in sodium carbonate nor in sodium hydroxide solutions. See Table II.

**8-Aryl-11-arylmethylene-6,7,10,11-tetrahydro-5H,8H-benzo[3,4]cyclohepteno[2,1-d]thiazolo[3,2-a]pyrimidin-10-ones (VI).** (A) A mixture of 1 g of V, an equimolecular amount of the aldehyde, and a few drops of piperidine was heated at 150 °C for 0.5 h and cooled, and the product was crystallized.

(B) A mixture of 0.005 mol of IV, 1 g of chloroacetic acid, 2 g of fused sodium acetate, an equimolecular amount of the ap-

propriate aldehyde in 15 mL of acetic acid, and 10 mL of acetic anhydride was refluxed for 4 h. The reaction mixture was cooled and poured onto ice. The precipitate formed was collected and crystallized. See Table III.

**8-Aryl-6,7,10,11-tetrahydro-5H,8H-benzo-3,4-cyclohepteno[2,1-d]thiazolo[3,2-a]pyrimidine-10,11-dione 11-Arylhydrazones (VII).** A cold diazonium salt solution (prepared in the usual way from 0.002 mol of the amine) was gradually added with stirring to a cooled solution of 0.002 mol of V in 10 mL of pyridine. The reaction mixture was cooled for 0.5 h and poured into 100 mL of water. The precipitate formed was collected and crystallized. See Table IV.

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Received for review March 21, 1977. Accepted July 12, 1977.

## Exocyclic Olefins: Reactions of Some Semistabilized Phosphonium Ylides with Substituted Fluorenones

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**The reactions of some semistabilized phosphonium ylides with 2,7-disubstituted fluorenones have been reported to give exocyclic olefins, 9-arylidene-2,7-disubstituted-fluorenones (compounds 4a-5k). The structural assignments of the products were based on IR and NMR spectral evidence.**

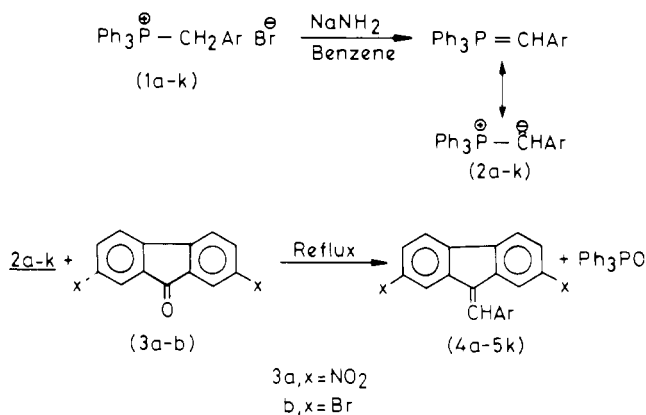
The reactions of nonstabilized phosphonium ylides with cyclic ketones have been extensively studied to give cyclic olefins (7, 9, 10, 12, 19). However, the stabilized phosphonium ylides with cyclic ketones were found to be successful under forcing conditions (6, 7, 9, 13, 14) and in some cases failure was observed (8). But, little attention has been paid toward the reactions involving interaction of semistabilized phosphonium ylides with cyclic ketones (15, 20). Recently, we have reported the utility of some semistabilized ylides in the syntheses of various acyclic (16, 17) and exocyclic (17, 18) olefins. In the present work, the reactions of two substituted fluorenones with a series of sem-

stabilized phosphonium ylides have been studied with a view to examine their synthetic potentiality in the carbonyl olefination of substituted fluorenones.

#### Results and Discussion

The reactions of ylides (compounds 2a-k) with 2,7-dinitrofluorenone (compound 3a) and 2,7-dibromofluorenone (compound 3b) were carried out at reflux temperature for 25-40 h affording exocyclic olefins, i.e., 9-arylidene-2,7-dinitrofluorenones (compounds 4a-k), 9-arylidene-2,7-dibromofluorenones (compounds 4a-k), and 9-arylidene-2,7-dibromofluorenones (compounds 5a-k), respectively, in 25-65% yields (Scheme I). It is interesting to note that ketone 3b failed to react with ylides 2a-k at room temperature but reacted successfully at elevated temperature. Ketone 3a is more reactive than ketone 3b, since the ylides 2a-k reacted more readily with the former and afforded better yields of exocyclic olefins (compounds 4a-k) in less time, probably due to the electron-withdrawing nature of nitro groups. Our attempts to react the stabilized ylides (com-

## Scheme I



pounds **2**, Ar = COR, etc.) were unsuccessful even at reflux temperature probably due to the decreased nucleophilicity of ylides.

The various exocyclic olefins (compounds **4a-5k**) synthesized in the present study are listed along with the yields obtained in Table I. The applicability of ylides **2a-k** as versatile olefinating reagents is obvious from the inspection of Table I.

## Experimental Section

Melting points were determined on a Gallenkamp apparatus and are uncorrected. A Perkin-Elmer infracord spectrophotometer was used to record the IR spectra (KBr). The NMR

spectra (CDCl<sub>3</sub>) were run by the use of a Varian A-60 spectrometer with Me<sub>4</sub>Si as the internal standard. Column chromatography was done to purify the product, by the use of a glass column packed with neutral alumina. For thin-layer chromatography (TLC), glass microscope slides coated with silica Gel-G were used. The spots on these slides were detected by iodine.

Phosphonium salts (compounds **1a-k**) were prepared by the treatment of  $\alpha$ -bromo compounds with triphenylphosphine in benzene at reflux temperature (5).

The general procedure for preparation of 2,7-disubstituted-9-arylidene-fluorenes (compounds **4a-5k**) is as follows.

To a stirred suspension of phosphonium salt (compounds **1a-k**) (4 mmol) and sodamide (0.19 g, 5 mmol) in anhydrous benzene (100 mL) was added under nitrogen solution of ketone (compounds **3a-b**) in benzene (25 mL). The first reaction was run at room temperature for 2 h and then at reflux temperature for an additional 25-40 h. The residue containing triphenylphosphine oxide and unreacted sodamide was removed by filtration. Filtrate was concentrated on a steam bath under reduced pressure. The resulting mass was chromatographed on neutral alumina. The elution with benzene-petroleum ether (4:1) afforded the corresponding substituted fluorenes (compounds **4a-5k**). The products were crystallized from the suitable solvents in appreciable yields (Table I).

## Acknowledgments

The authors thank Dr. S. D. Shukla, Director, H.B.T.I., Kanpur, for providing facilities. One of the authors (K.C.G.) is thankful to

Table I. Structures and Physical Properties of 9-Arylidene-2,7-disubstituted-fluorenes (Compounds 4a-5k)

Compd <sup>a</sup>	X	Ar	% yield	Mp, °C	Crystn solvent	IR (KBr), cm <sup>-1</sup>		NMR (CDCl <sub>3</sub> ) $\delta$ (ppm)
						$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{H})^x$	
<b>4a</b>	NO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	55	233-34 <sup>b</sup>	AcOH	1590	952	
<b>4b</b>		2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	50	267-269 <sup>c</sup>	EtOH			
<b>4c</b>		3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	58	320-322 <sup>d</sup>		1597	443	7.35-8.08 (m, 10 H, aromatic); 7.30 (s, 1 H, olefinic)
<b>4d</b>		4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	65	325-327 <sup>e</sup>	AcOH	1592	977	7.30-8.35 (m, 10 H, aromatic); 7.20 (s, 1 H, olefinic)
<b>4e</b>		4-ClC <sub>6</sub> H <sub>4</sub>	60	270-272 <sup>f</sup>	CHCl <sub>3</sub> -EtOH			
<b>4f</b>		4-BrC <sub>6</sub> H <sub>4</sub>	50	256-258 <sup>g</sup>	EtOH			
<b>4g</b>		4-IC <sub>6</sub> H <sub>4</sub>	45	210-212 <sup>h</sup>	AcOH	1605	950	
<b>4h</b>		4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	40	294-296 <sup>i</sup>	EtOH			6.80-8.20 (m, 10 H, aromatic); 7.13 (s, 1 H, olefinic); 2.37 (s, 3 H, CH <sub>3</sub> )
<b>4i</b>		4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	40	303-305 <sup>j</sup>	CHCl <sub>3</sub> -EtOH	1613	971	6.80-8.20 (m, 10 H, aromatic); 7.00 (s, 1 H, olefinic); 3.85 (s, 3 H, OCH <sub>3</sub> )
<b>4j</b>		2-C <sub>10</sub> H <sub>7</sub>	40	252-254 <sup>k</sup>	AcOH	1585	948	7.30-8.40 (m, 13 H, aromatic); 7.25 (s, 1 H, olefinic)
<b>4k</b>		1-Br-2-C <sub>10</sub> H <sub>6</sub>	45	263-264 <sup>l</sup>	EtOH			
<b>5a</b>	Br	C <sub>6</sub> H <sub>5</sub>	38	96-96 <sup>m</sup>	AcOH			
<b>5b</b>		2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	35	198-200 <sup>n</sup>	CHCl <sub>3</sub>			
<b>5c</b>		3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	45	156-157 <sup>o</sup>	EtOH	1603	952	
<b>5d</b>	Br	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	48	196-198 <sup>p</sup>	EtOH	1600	952	
<b>5e</b>		4-ClC <sub>6</sub> H <sub>4</sub>	42	212-214 <sup>q</sup>	AcOH			
<b>5f</b>		4-BrC <sub>6</sub> H <sub>4</sub>	35	222-224 <sup>r</sup>	EtOH			
<b>5g</b>		4-IC <sub>6</sub> H <sub>4</sub>	30	208-210 <sup>s</sup>	AcOH			
<b>5h</b>		4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	35	136-138 <sup>t</sup>				7.60-8.40 (m, 10 H, aromatic); 7.52 (s, 1 H, olefinic); 2.47 (s, 3 H, CH <sub>3</sub> )
<b>5i</b>		4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	30	132-134 <sup>u</sup>	EtOH	1613	952	7.54-8.50 (m, 10 H, aromatic); 7.46 (s, 1 H, olefinic); 3.97 (s, 3 H, OCH <sub>3</sub> )
<b>5j</b>		2-C <sub>10</sub> H <sub>7</sub>	25	108-110 <sup>v</sup>	AcOH			
<b>5k</b>		1-Br-2-C <sub>10</sub> H <sub>6</sub>	32	106-108 <sup>w</sup>				7.35-8.48 (m, 12 H, aromatic); 7.25 (s, 1 H, olefinic)

<sup>a</sup> Satisfactory analytical data ( $\pm 0.4\%$  for C, H) were reported for all compounds listed in the table. <sup>b</sup> Lit. (2) mp 235-236 °C. <sup>c</sup> Lit. (3) mp 271 °C. <sup>d</sup> Lit. (3) mp above 310 °C. <sup>e</sup> Lit. (3) mp above 310 °C. <sup>f</sup> Lit. (2) mp 268-269 °C. <sup>g,h,i</sup> Unreported. <sup>j</sup> Lit. (4) mp 310-305 °C. <sup>k</sup> and <sup>l</sup> Reported. <sup>m</sup> Lit. (17) mp 98-99 °C. <sup>n</sup> Lit. (17) mp 201-202 °C. <sup>o</sup> Lit. (17) mp 154-155 °C. <sup>p</sup> Lit. (17) mp 195-196 °C. <sup>q</sup> Lit. (17) mp 211-212 °C. <sup>r</sup> Unreported. <sup>s</sup> Lit. (17) mp 207-208 °C. <sup>t</sup> Lit. (17) mp 140-141 °C. <sup>u</sup> Lit. (17) mp 132-133 °C. <sup>v</sup> and <sup>w</sup> Unreported. <sup>x</sup> C-H deformations attached to the exocyclic carbon carbon double bond (7). Key: m = multiplet, s = singlet.

U.G.C., New Delhi, for the award of a Teacher Fellowship and to Dr. B. B. Lal, Principal, D.V. (Postgraduate) College, Orai, for his constant encouragement.

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Received for review June 13, 1977. Accepted September 27, 1977.

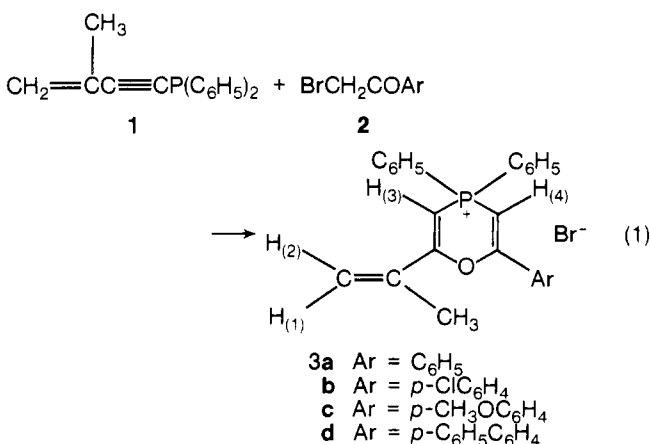
## Novel Organophosphorus Monomers: the 1,1-Diphenyl-3-aryl-4-oxa-5-(2-propenyl)-1-phosphoniacyclohexa-2,5-diene System

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**Synthesis of 1,1-diphenyl-3-aryl-4-oxa-5-(2-propenyl)-1-phosphoniacyclohexa-2,5-dienes has been described. These white crystalline phosphonium bromides have been characterized by their IR and NMR spectra.**

As a part of our general research program in the synthesis of new monomers and polymers, we wish to report a convenient route to the 1,1-diphenyl-3-aryl-4-oxa-5-(2-propenyl)-1-phosphoniacyclohexa-2,5-diene system **3** (eq 1). The compounds **3** constitute a new class of monomers which have not hitherto been described in the literature. The related syntheses previously reported have not been employed for the preparation of vinyl monomers (**1**, **3**–**5**). We have now found that diphenyl(3-methyl-3-en-1-butynyl)phosphine (**1**) reacts with  $\alpha$ -bromo ketones **2** to produce heterocycles **3** in good to excellent yields (eq 1).



The starting phosphine **1** was prepared by the reaction of 3-methyl-3-en-1-butynyllithium with diphenylphosphinous chloride. The infrared spectrum of **1** exhibited characteristic absorption bands at 1610 cm<sup>-1</sup> (C=C) and 2170 cm<sup>-1</sup> (C≡C). The structure of **1** was further supported by its NMR spectrum. The phosphine **1** upon treatment with ketones **2** produced heterocycles **3** as white crystals. The infrared spectra (KBr) of **3**

displayed characteristic (C=C) absorption bands at ~1625 and  $\delta$  ~1605 cm<sup>-1</sup>. In the NMR spectra of **3a**–**d**, the signal at  $\delta$  ~5.75 was assigned to the vinyl proton *cis* (H<sub>(1)</sub>) to the methyl group while the one at  $\delta$  ~6.25 was assigned to the vinyl proton *trans* (H<sub>(2)</sub>) to this methyl group (**2**). The downfield shift ( $\delta$  ~6.25) of the H<sub>(2)</sub> signal is probably due to deshielding by the "pseudo aromatic" heterocycle system (**3**, **4**). The quartet ( $J_{HH} = 3$ ,  $J_{PH} = 6$  Hz) at  $\delta$  ~6.70 was assigned to ring proton H<sub>(3)</sub>, while the quartet ( $J_{HH} = 3$ ,  $J_{PH} = 6$  Hz) at  $\delta$  ~7.2 was assigned to H<sub>(4)</sub>; this downfield shift of the H<sub>(4)</sub> signal is probably due to deshielding by the aryl group.

#### Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 453 spectrophotometer and the NMR spectra were obtained on a Bruker HX-60 spectrometer; the chemical shifts are described as  $\delta$  parts per million (ppm) from tetramethylsilane.

**Preparation of Diphenyl(3-methyl-3-en-1-butynyl)phosphine (1).** Freshly distilled 3-methyl-3-en-1-butyne (13.2 g, 0.2 mol) was dissolved in 500-mL of anhydrous diethyl ether and placed under nitrogen in a 2-L three-necked flask. The flask was cooled with dry ice and a 2.4 M hexane solution (85 mL) of *n*-butyllithium was added slowly (30 min) with continuous stirring. The reaction mixture was stirred for 1 h and then diphenylphosphinous chloride (44.0 g, 0.2 mol) was added dropwise with continuous stirring. The reaction mixture was stirred at this temperature for 2 h and then allowed to warm up to 0 °C. Saturated ammonium chloride solution (100 mL) was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with two 50-mL portions of diethyl ether; the combined extracts were washed with sodium bicarbonate solution and dried over anhydrous sodium sulfate. The dried solution was filtered and ether was evaporated to obtain 45 g of light brown oily product. Vacuum distillation was attempted using a portion of the product but rapid polymerization occurred at about 100 °C and no distillate could be obtained. The infrared spectrum (CHCl<sub>3</sub>) of the product displayed strong absorption bands at 2920, 2170 (C≡C), 1610 (C=C), 1430 (P–C<sub>6</sub>H<sub>5</sub>), 1270, 1120, 1090, 980, and 900 cm<sup>-1</sup>; the NMR spectrum exhibited a pair of doublets ( $J = 1$  Hz,  $\delta$  1.78, 3 H, CH<sub>3</sub>), a quartet ( $J = 1$  Hz,  $\delta$  5.15, 1