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Syntheses and Reactions of Allylic and Homoallylic Pyrophosphate Tetraesters

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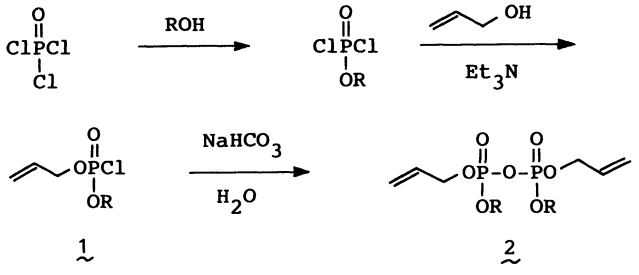
Pyrophosphate tetraesters possessing allylic and homoallylic side chains were synthesized. Reaction of alkyl allyl (and 3-methyl-3-butenyl) phosphorochloridates with sodium hydrogencarbonate gave P^1,P^2-dialkyl P^1,P^2-diallyl [and P^1,P^2-bis(3-methyl-3-butenyl)] pyrophosphates. Condensation of alkyl allyl (and 3-methyl-3-butenyl) phosphorochloridates with dialkyl phosphates gave trialkyl allyl (and 3-methyl-3-butenyl) pyrophosphates. Reactions of crotyl (2-butenyl) pyrophosphates with various nucleophiles such as phenolic ethers, aromatic amines, and nitrogen-containing heterocycles in the presence of boron trifluoride etherate gave good to moderate yields of crotylated products. The crotyl pyrophosphates were found to be much more reactive than the corresponding orthophosphate esters.

In our continuous studies on the reaction of allylic phosphate esters, it has been revealed that allylic phosphates are useful and versatile reagents in synthetic chemistry.[1] They possess several advantages over allylic halides in regard to reactivity, selectivity, and ease of preparation and handling. It is well-known that naturally occurring terpenoids are biosynthesized via allylic and homoallylic pyrophosphate esters in a regio- and stereospecific manner.[2] Therefore, the use of pyrophosphates in place of orthophosphate esters is expected to improve the reactivity and selectivity in synthetic reactions. In this connection, pyrophosphate monoester salts possessing an allylic polyprenyl residue have been successfully used for enzymatic transformation to natural products.[3] However, the use of such pyrophosphate salts in preparative-scale synthesis is strictly limited owing to the difficulties in manipulation and the poor solubility in organic solvents. From these viewpoints, we were interested in the syntheses and reaction behavior of allylic and homoallylic pyrophosphate tetraesters. Although a number of workers reported the syntheses and applications of tetraalkyl pyrophosphates,[4] pyrophosphate tetraesters bearing allylic and/or homoallylic side chains have been scarcely studied.[5] In this paper, we describe the syntheses of such pyrophosphate tetraesters and discuss their reactivities toward phenolic ethers, aromatic amines, and nitrogen-containing heterocycles in comparison with that of the corresponding orthophosphate ester.

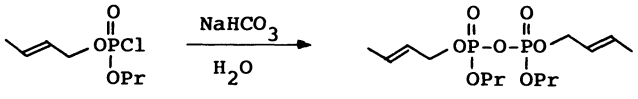


1 2

Scheme 1.

Results and Discussion

Syntheses. The synthesis of symmetrical P^1,P^2-dialkyl P^1,P^2-diallyl pyrophosphates (**2**) was achieved by the treatment of alkyl allyl phosphorochloridates (**1**) with sodium hydrogencarbonate in the presence of a catalytic amount of water.[6] The crude products were purified first by vacuum distillation and then by column chromatography on silica gel. The starting alkyl allyl phosphorochloridates (**1**) in turn were prepared by the triethylamine-induced condensation of alkyl phosphorodichloridates with allyl alcohol. The overall reaction scheme is as Scheme 1. Of the four pyrophosphate tetraesters prepared, P^1,P^2-diallyl P^1,P^2-dipropyl pyrophosphate (**2b**) is the most stable and the highest yield was achieved. The corresponding diethyl pyrophosphate **2a** is considerably unstable and all attempts to isolate P^1,P^2-diallyl P^1,P^2-dimethyl



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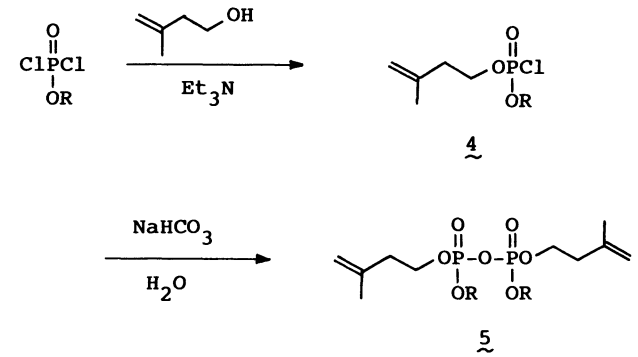
Scheme 2.



4 5

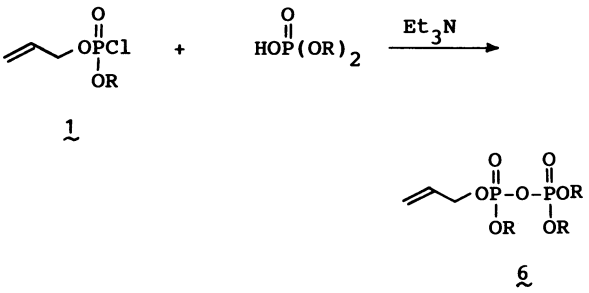
Scheme 3.

pyrophosphate failed owing to the rapid decomposition during purification. P^1,P^2-Di-2-butenyl (crotyl) P^1,P^2-dipropyl pyrophosphate (**3**) was similarly prepared from crotyl propyl phosphorochloridate in 86% yield (Scheme 2). The pyrophosphate is thermally labile and sensitive to silica gel, so it was used for next reactions without further purification.

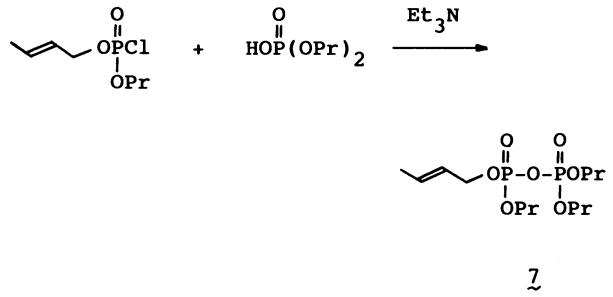
A series of symmetrical homoallylic pyrophosphates, P^1,P^2-dialkyl P^1,P^2-bis(3-methyl-3-butenyl) pyrophosphates (**5**) were also obtained by the same method (Scheme 3). Again, the maximum yield was achieved when R=propyl.

Condensation of alkyl allyl phosphorochloridates (**1**) with dialkyl phosphates in the presence of triethylamine furnished the second type of pyrophosphate tetraesters, trialkyl allyl pyrophosphates (**6**) (Scheme 4). By this method, crotyl tripropyl pyrophosphate (**7**) was synthesized in 76% yield (Scheme 5). Pyrophosphate tetraesters (**8**) of this type bearing a homoallylic 3-methyl-3-butenyl group were analogously prepared and isolated.

Reactions. We have reported that allylic orthophosphate esters readily allylate phenolic ethers in the presence of boron trifluoride etherate.[7] In order to compare the reactivity of allylic pyrophosphates with that of allylic orthophosphates, the reactions of crotyl pyrophosphates **3** and **7** with various phenolic ethers were carried out and the yields were compared with those of the reactions of crotyl dipropyl phosphate (**9**) under the same reaction conditions. The Friedel–Crafts type alkenylations were conducted at 0—−23 °C using five-fold excess of phenolic ethers to avoid polycrotylation. Yields and product distributions were determined by GLC analysis. Results are shown in Table 1. The reactions of **3**, **7**, and **9** with anisole gave all possible four regio (α and γ) and positional isomers (ortho and para). There were no important differences in the product distributions of

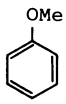
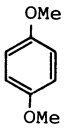
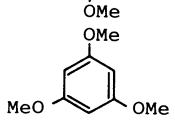
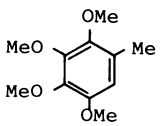
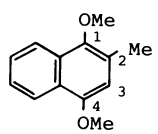


Scheme 4.



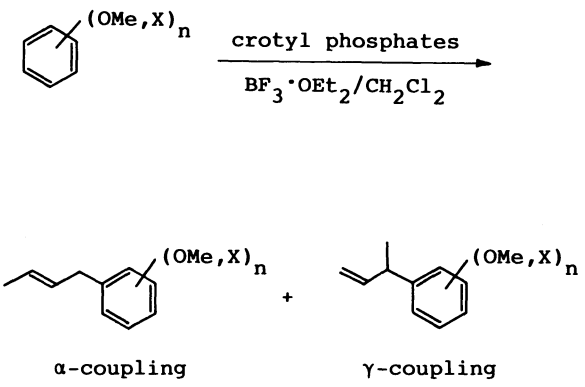
Scheme 5.

Table 1. Crotylation of Phenolic Ethers by Crotyl Phosphates (**3**, **7**, and **9**)

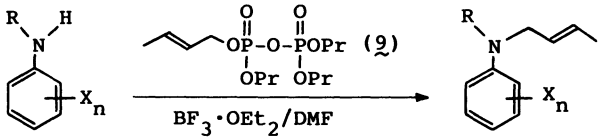
Phenol ether	Phosphate	Reaction conditions	Total yield[a]/%	Product ratio[b]/α : γ
	**3**	0 °C, 3.5 h	91	81 (29/57) : 14 (3/11)
	7	0 °C, 3.5 h	82	88 (30/58) : 12 (3/ 9)
	9	0 °C, 3.5 h	49	87 (38/49) : 13 (3/10)
	**3**	−23 °C, 4 h	76	83 : 17
	7	−23 °C, 4 h	54	84 : 16
	9	−23 °C, 4 h	4	72 : 28
	**3**	−23 °C, 4 h	97	86 : 14
	7	−23 °C, 4 h	89	91 : 9
	9	−23 °C, 4 h	27	84 : 16
	**3**	0 °C, 3 h	53	69 : 31
	7	0 °C, 3 h	61	69 : 31
	9	0 °C, 3 h	10	71 : 29
	**3**	0 °C, 4 h	95	100 : 0[c]
	7	0 °C, 4 h	86	100 : 0[c]
	9	0 °C, 4 h	75	88 : 12[c]

a) Glc yield. b) Figures in parentheses refer to *o*/*p* ratio. c) The alkenylation occurred exclusively at the 3-position of the naphthalene.

the three reactions, but the yield using the orthophosphate (**9**) was largely depressed compared to those of pyrophosphate cases. It must be noted that only one crotyl group of the dicrotyl pyrophosphate (**3**) was used for alkenylation of phenolic ethers under the reaction conditions employed. The results obtained here clearly show that pyrophosphate residues are excellent leaving groups and hence the reactivity of the pyrophosphates **3** and **7** are markedly higher than that of the orthophosphate (**9**).



Scheme 6.

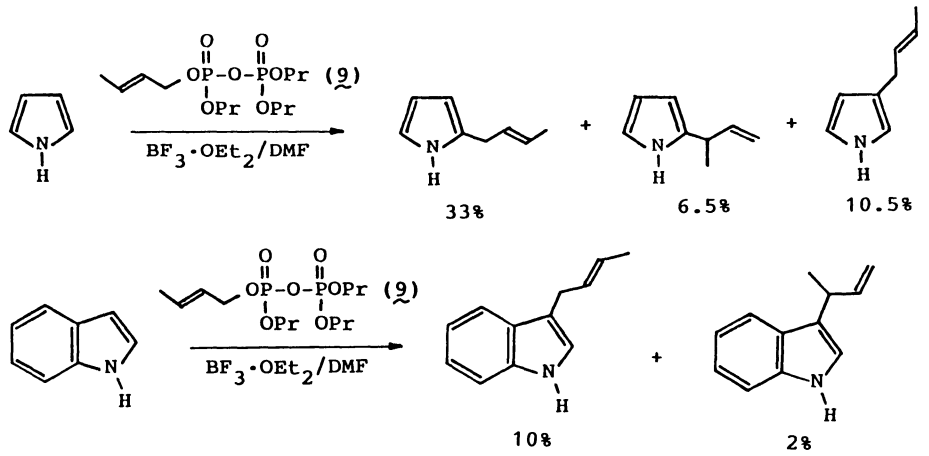


Scheme 7.

Crotyl tripropyl pyrophosphate (**7**) also allylated aromatic amines in *N,N*-dimethylformamide (DMF) in the presence of boron trifluoride etherate at room temperature. As shown in Table 2, *N*-crotylation occurred predominantly and the corresponding amines were isolated in moderate yields. In the cases of diphenylamine and 1-naphthylamine, trace amounts of nucleus-crotylated products were also obtained. Under the reaction conditions employed, crotyl orthophosphate (**9**) gave, if any, only poor yields of *N*-crotylamines,[8] owing to the lower reactivity of **9** than **7**.

Pyrrole and indole reacted with crotyl pyrophosphate (**9**) to give nucleous-crotylated products. In these reactions, *N*-crotylated products could not be found. Again, no reactions occurred when orthophosphate (**9**) was used in place of **7**.

In summary, it has been shown that allylic pyrophosphates have much higher reactivity toward various nucleophiles than the corresponding orthophosphate and that they serve as useful allylating reagents in synthetic chemistry.



Scheme 8.

Table 2. Reaction of Crotyl Tripropyl Pyrophosphate (**7**) and Aromatic Amines

Run	Aromatic amine	Product	Yield[a]/%
1	$PhNH_2$	$PhNH(CH_2CH{=}CHCH_3)$	57 (0)
		$PhN(CH_2CH{=}CHCH_3)_2$	9 (0)
2	$Ph(CH_3)NH$	$Ph(CH_3)N(CH_2CH{=}CHCH_3)$	30 (7)
3	$4\text{-}MeOC_6H_4NH_2$	$4\text{-}MeOC_6H_4NH(CH_2CH{=}CHCH_3)$	18 (0)
		$4\text{-}MeOC_6H_4N(CH_2CH{=}CHCH_3)_2$	35 (0)
4	Ph_2NH	$Ph_2N(CH_2CH{=}CHCH_3)$	9 (0)
		$Ph_2N[CH(CH_3)CH{=}CH_2]$	5 (0)
		$PhNHC_6H_4(CH_2CH{=}CHCH_3)$	1 (0)
5	$(1\text{-Naphthyl})NH_2$	$(1\text{-Naphthyl})NH(CH_2CH{=}CHCH_3)$	22 (4)
		$(2\text{-Crotyl-1-naphthyl})NH_2$	1 (0)

a) Figures in parentheses refer to yields of the reaction with crotyl dipropyl phosphate (**9**).

Experimental

General. Infrared spectra were recorded on a JASCO IRA-102 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-24A spectrometer (60 MHz) or on a Varian XL-200 spectrometer (200 MHz) with Me_4Si as an internal standard. ^{13}C NMR spectra were obtained on a Varian XL-200 spectrometer (50 MHz). Multiplicities refer to those of proton-decoupled spectra. Mass spectra (MS) were determined at 20 eV using a Hitachi M-52 or ESCO EMD-05B instrument. GLC analyses were performed on a Yanaco G1800 gas chromatograph. Elemental analyses were performed at the Elemental Analysis Center of Kyoto University. Dialkyl phosphates,[6] alkyl phosphorodichloridates,[9] and dialkyl phosphorochloridates[10] were prepared by the literature methods.

Alkyl Allyl (and 3-Methyl-3-butenyl) Phosphorochloridates (1 and 4). The following preparation of allyl ethyl phosphorochloridate represents the general procedure. To a solution of ethyl phosphorodichloridate (9.8 g, 60 mmol) in anhydrous ether (20 cm^3) was slowly added a mixture of allyl alcohol (3.6 g, 62 mmol) and triethylamine (6.4 g, 63 mmol) in ether (20 cm^3) with cooling in an ice-salt bath. The reaction mixture was stirred at that temperature for 4 h. Triethylammonium chloride which formed was filtered off and the filtrate was concentrated. The residue was distilled [bp 60—69 °C/1.1×10^{-3} Torr(1 Torr=133.322 Pa)] to give allyl ethyl phosphorochloridate (9.02 g, 81%) as a pale yellow liquid. Other alkyl allyl (and 3-methyl-3-butenyl) phosphorochloridates (**1** and **4**) were similarly prepared and purified by distillation. Crotyl propyl phosphorochloridate is thermally unstable, so the crude product was used for the next reactions without distillation.

Allyl ethyl phosphorochloridate (**1a**): 81% yield; bp 60—69 °C/1.1×10^{-3} Torr; IR (neat) 3100, 2990, 2950, 2930, 1650, 1415, 1395, 1370, 1300, 1165, 1030 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.40 (t, J=7 Hz, 3H, Me) 3.97—4.73 (m, 4H, CH_2), 5.17—5.52 (m, 2H, =CH_2), 5.68—6.30 (m, 1H, =CH); Found: C, 32.84; H, 5.67%. Calcd for $C_5H_{10}ClO_3P$: C, 32.54; H, 5.46%.

Allyl propyl phosphorochloridate (**1b**): 82% yield; bp 54—64 °C/6.1×10^{-4} Torr; IR (neat) 3080, 2980, 2950, 2910, 2890, 1650, 1465, 1425, 1300, 1150, 1020 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.01 (t, J=7 Hz, 3H, Me), 1.32—2.10 (m, 2H, CH_2), 3.79—4.36 (m, 2H, CH_2), 4.41—4.78 (m, 2H, CH_2), 5.10—5.54 (m, 2H, =CH_2), 5.59—6.30 (m, 1H, =CH); Found: C, 36.48; H, 6.31%. Calcd for $C_6H_{12}ClO_3P$: C, 36.29; H, 6.09%.

Allyl butyl phosphorochloridate (**1c**): 81% yield; bp 83—95.5 °C/1.3×10^{-4} Torr; IR (neat) 3100, 2980, 2950, 2890, 1650, 1465, 1430, 1385, 1300, 1160, 1150, 1030 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.98 (t, J=7 Hz, 3H, Me), 1.30—1.85 (m, 4H, CH_2), 3.98—4.73 (m, 4H, CH_2), 5.17—5.50 (m, 2H, =CH_2), 5.68—6.29 (m, 1H, =CH); Found: C, 40.60; H, 7.00%. Calcd for $C_7H_{14}ClO_3P$: C, 39.54; H, 6.64%.

Allyl isobutyl phosphorochloridate (**1d**): 75% yield; bp 85—93 °C/2.3×10^{-3} Torr; IR (neat) 3100, 2980, 2905, 2895, 1650, 1473, 1426, 1374, 1300, 1162, 1130, 1025 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.98 (d, J=6 Hz, 6H, Me), 1.59—2.28 (m, 1H, CH), 3.90 (dd, J_{HP}=8 Hz, J_{HH}=7 Hz, 2H, CH_2), 4.59 (dd, J_{HP}=10 Hz, J_{HH}=5 Hz, 2H, CH_2), 4.99—5.54 (m, 2H, =CH_2), 5.59—6.24 (m, 1H, =CH); Found: C, 39.77; H, 6.79%. Calcd for $C_7H_{14}ClO_3P$: C, 39.54; H, 6.64%.

Ethyl 3-methyl-3-butenyl phosphorochloridate (**4a**): 65% yield; bp 80 °C/1.5×10^{-3} Torr; IR (neat) 3070, 2980, 2940, 2910, 1640, 1445, 1390, 1375, 1295, 1165, 1025 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.40 (t, J=7 Hz, 3H, Me), 1.87 (s, 3H, Me), 2.43 (t, J=7 Hz, 2H, CH_2), 3.86—4.52 (m, 4H, CH_2), 4.78 (s, 2H, =CH_2); Found: C, 39.79; H, 6.87%. Calcd for $C_7H_{14}ClO_3P$: C, 39.54; H, 6.64%.

3-Methyl-3-butenyl propyl phosphorochloridate (**4b**): 73% yield; bp 87—95 °C/4×10^{-4} Torr; IR (neat) 3100, 2990, 2960, 2930, 1655, 1465, 1380, 1300, 1155, 1020 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.99 (t, J=7 Hz, 3H, Me), 1.51—2.00 (m, 2H, CH_2), 1.77 (s, 3H, Me), 2.41 (t, J=7 Hz, 2H, CH_2), 3.90—4.50 (m, 4H, CH_2), 4.75 (s, 2H, =CH_2); Found: C, 42.69; H, 7.35%. Calcd for $C_8H_{16}ClO_3P$: C, 42.39; H, 7.12%.

Butyl 3-methyl-3-butenyl phosphorochloridate (**4c**): 61% yield; bp 95—99 °C/4.8×10^{-4} Torr; IR (neat) 3080, 2970, 2940, 2880, 1650, 1470, 1380, 1295, 1150, 1120, 1030 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.93 (bt, J=6 Hz, 3H, Me), 1.18—2.00 (m, 4H, CH_2), 1.74 (s, 3H, Me), 2.39 (t, J=7 Hz, 2H, CH_2), 3.78—4.58 (m, 4H, CH_2), 4.74 (s, 2H, =CH_2); Found: C, 44.91; H, 7.70%. Calcd for $C_9H_{18}ClO_3P$: C, 44.92; H, 7.54%.

Isobutyl 3-methyl-3-butenyl phosphorochloridate (**4d**): 62% yield; bp 90—108 °C/8.5×10^{-4} Torr; IR (neat) 3090, 2990, 2930, 2890, 1655, 1470, 1380, 1305, 1185, 1170, 1130, 1030 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.98 (d, J=6 Hz, 6H, Me), 1.79 (s, 3H, Me), 1.90—2.23 (m, 1H, CH), 2.44 (t, J=7 Hz, 2H, CH_2), 3.77—4.42 (m, 4H, CH_2), 4.79 (s, 2H, =CH_2); Found: C, 45.55; H, 7.90%. Calcd for $C_9H_{18}ClO_3P$: C, 44.92; H, 7.54%.

Crotyl propyl phosphorochloridate: 88% yield; IR (neat) 2970, 2940, 2880, 2850, 1673, 1460, 1378, 1287, 1010 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.99 (t, J=7 Hz, 3H, Me), 1.32—2.12 (m, 2H, CH_2), 1.75 (d, J=5 Hz, 3H, Me), 3.82—4.27 (m, 2H, CH_2), 4.52 (dd J_{HP}=10 Hz, J_{HH}=5 Hz, 2H, CH_2), 5.22—6.12 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$) δ=9.9 (s, Me), 17.7 (s, Me), 23.3 (d, J=8 Hz, CH_2), 70.1 (d, J=6 Hz, CH_2), 71.3 (d, J=8 Hz, CH_2), 124.3 (d, J=7 Hz, =$\underline{C}$HCH$_2$), 133.3 (s, =$\underline{C}$HMe).

***P*^{1},*P*^{2}-Dialkyl *P*^{1},*P*^{2}-Diallyl [and *P*^{1},*P*^{2}-Bis(3-methyl-3-butenyl)] Pyrophosphates (2 and 5).** The following preparation of *P*^{1},*P*^{2}-diallyl *P*^{1},*P*^{2}-diethyl pyrophosphate (**2a**) represents the general procedure. A mixture of allyl ethyl phosphorochloridate (**1a**) (736 mg, 4 mmol), sodium hydrogencarbonate (373 mg, 4.4 mmol) and a catalytic amount (ca. 10 mol%) of water (7 mg, 0.39 mmol) was stirred for 2 h at room temperature. After sodium chloride which formed was filtered, the reaction mixture was distilled (bp 137—142 °C/4.3×10^{-3} Torr) and then column chromatographed on silica gel (eluant: ether) to give *P*^{1},*P*^{2}-diallyl *P*^{1},*P*^{2}-diethyl pyrophosphate (**2a**) (139 mg, 22%) as a viscous colorless oil. Other dialkyl diallyl [and bis(3-methyl-3-butenyl)] pyrophosphates (**2** and **5**) were similarly prepared and purified. *P*^{1},*P*^{2}-Dicrotyl *P*^{1},*P*^{2}-dipropyl pyrophosphate (**3**) is unstable and used for the next reactions without further purification.

P^1,*P*^{2}-Diallyl *P*^{1},*P*^{2}-diethyl pyrophosphate (**2a**): 22% yield; bp 137—142 °C/ 4.3×10^{-3} Torr; IR (neat) 3080, 2980, 2925, 2905, 1645, 1367, 1290, 1160, 1100, 1024, 967 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.34 (t, J=7 Hz, 6H, Me), 3.80—4.80 (m, 8H, CH_2), 4.80—5.60 (m, 4H, =CH_2), 5.60—6.40 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$) δ=15.9 (m, Me), 65.4 (m, CH_2), 69.2

(m, CH_2), 118.8 (s, $=CH_2$), 131.8 (m, =CH); MS *m/z* (rel intensity) 314 (M^+, 11), 189 (100); Found: C, 37.71; H, 6.66%. Calcd for $C_{10}H_{20}O_7P_2$: C, 38.22; H, 6.42%.

P^1,P^2-Diallyl P^1,P^2-dipropyl pyrophosphate (**2b**): 54% yield; bp 130—135 °C/7.7×10^{-5} Torr; IR (neat) 3080, 2975, 2945, 2910, 2880, 1650, 1465, 1425, 1295, 1155, 1025, 960 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.99 (t, *J*=6 Hz, 6H, Me), 1.30—2.09 (m, 4H, CH_2), 3.83—4.38 (m, 4H, CH_2), 4.38—4.83 (m, 4H, CH_2), 5.06—5.63 (m, 4H, $=CH_2$), 5.63—6.28 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$) δ=9.9 (s, Me), 23.5 (m, CH_2), 69.2 (m, CH_2), 70.8 (m, CH_2), 118.8 (s, $=CH_2$), 132.0 (m, =CH); MS *m/z* (rel intensity) 342 (M^+, 7), 217 (100); Found: C, 41.83; H, 7.18%. Calcd for $C_{12}H_{24}O_7P_2$: C, 42.11; H, 7.07%.

P^1,P^2-Diallyl P^1,P^2-dibutyl pyrophosphate (**2c**): 20% yield; bp 145—150 °C/1.5×10^{-4} Torr; IR (neat) 3090, 2970, 2945, 2880, 1650, 1470, 1425, 1385, 1295, 1155, 1030, 960 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.95 (bt, *J*=6 Hz, 6H, Me), 1.18—1.88 (m, 8H, CH_2), 3.86—4.39 (m, 4H, CH_2), 4.39—4.83 (m, 4H, CH_2), 5.07—5.58 (m, 4H, $=CH_2$), 5.58—6.33 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$) δ=13.5 (s, Me), 18.6 (s, CH_2), 32.1 (m, CH_2), 69.1 (m, CH_2), 69.2 (m, CH_2), 118.8 (s, $=CH_2$), 131.9 (m, =CH); MS *m/z* (rel intensity) 370 (M^+, 0.8), 99 (100); Found: C, 45.70; H, 7.62%. Calcd for $C_{14}H_{28}O_7P_2$: C, 45.41; H, 7.62%.

P^1,P^2-Diallyl P^1,P^2-diisobutyl pyrophosphate (**2d**): 23% yield; bp 146—150 °C/4.1×10^{-3} Torr; IR (neat) 3090, 2970, 2900, 2880, 1650, 1470, 1370, 1290, 1023, 960 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.97 (d, *J*=6 Hz, 12H, Me), 1.70—2.35 (m, 2H, CH), 3.60—4.04 (m, 4H, CH_2), 4.30—4.90 (m, 4H, CH_2), 4.90—5.60 (m, 4H, $=CH_2$), 5.60—6.35 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$) δ=18.5 (s, Me), 29.0 (m, CH), 69.2 (m, CH_2), 118.8 (s, $=CH_2$), 131.9 (m, =CH); MS *m/z* (rel intensity) 370 (M^+, 24), 259 (100); Found: C, 45.24; H, 7.72%. Calcd for $C_{14}H_{28}O_7P_2$: C, 45.41; H, 7.62%.

P^1,P^2-Diethyl P^1,P^2-bis(3-methyl-3-butenyl) pyrophosphate (**5a**): 26% yield; bp 140—150 °C/1.0×10^{-3} Torr; IR (neat) 3085, 2990, 2940, 2920, 1645, 1445, 1395, 1375, 1295, 1166, 1040, 985, 960 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.35 (t, *J*=7 Hz, 6H, Me), 1.75 (s, 6H, Me), 2.39 (t, *J*=6 Hz, 4H, CH_2), 3.90—4.50 (m, 8H, CH_2), 4.75 (s, 4H, $=CH_2$); ^{13}C NMR ($CDCl_3$) δ=16.0 (m, Me), 22.4 (s, Me), 38.1 (m, CH_2), 65.3 (m, CH_2), 67.1 (m, CH_2), 112.9 (s, $=CH_2$), 140.7 (s, $-\overset{|}{C}=$); MS *m/z* (rel intensity) 370 (M^+, 0.8), 235 (100); Found: C, 45.18; H, 7.73%. Calcd for $C_{14}H_{28}O_7P_2$: C, 45.41; H, 7.62%.

P^1,P^2-Dipropyl P^1,P^2-bis(3-methyl-3-butenyl) pyrophosphate (**5b**): 66% yield; bp 135—140 °C/4.2×10^{-5} Torr; IR (neat) 3070, 2975, 2940, 2900, 1650, 1460, 1375, 1290, 1020, 960 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.00 (t, *J*=7 Hz, 6H, Me), 1.40—2.10 (m, 4H, CH_2), 1.75 (s, 6H, Me), 2.40 (t, *J*=7 Hz, 4H, CH_2), 3.70—4.55 (m, 8H, CH_2), 4.73 (s, 4H, $=CH_2$); ^{13}C NMR ($CDCl_3$) δ=9.9 (s, Me), 22.4 (s, Me), 23.5 (m, CH_2), 38.1 (m, CH_2), 67.1 (m, CH_2), 70.7 (m, CH_2), 112.9 (s, $=CH_2$), 140.7 (s, $-\overset{|}{C}=$); MS *m/z* (rel intensity) 398 (M^+, 0.7), 179 (100); Found: C, 48.40; H, 8.32%. Calcd for $C_{16}H_{32}O_7P_2$: C, 48.24; H, 8.10%.

P^1,P^2-Diisopropyl P^1,P^2-bis(3-methyl-3-butenyl) pyrophosphate (**5c**): 54% yield; bp 130 °C/9.2×10^{-5} Torr; IR (neat) 3090, 2990, 2950, 1655, 1470, 1455. 1380, 1290, 1185, 1145, 1110, 1010, 960 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.32 (d, *J*=7 Hz, 12H, Me), 1.76 (s, 6H, Me), 2.39 (t, *J*=7 Hz, 4H, CH_2) 3.99—4.33 (m, 4H, CH_2), 4.42—4.92 (m, 6H, CH and $=CH_2$); ^{13}C NMR ($CDCl_3$) δ=22.5 (s, Me), 23.5 (s, Me), 38.1 (m, CH_2), 66.9 (m, CH_2), 74.6 (m, CH), 112.8 (s, $=CH_2$), 140.8 (s, $-\overset{|}{C}=$); MS *m/z* (rel intensity) 398 (M^+, 0.8), 179 (100); Found: C, 48.08; H, 8.05%. Calcd for $C_{16}H_{32}O_7P_2$: C, 48.24; H, 8.10%.

P^1,P^2-Dibutyl P^1,P^2-bis(3-methyl-3-butenyl) pyrophosphate (**5d**): 50% yield; bp 140—150 °C/7.0×10^{-5} Torr; IR (neat) 3080, 2970, 2920, 2880, 1650, 1465, 1380, 1295, 1150, 1120, 1030, 965 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.95 (bt, *J*=6 Hz, 6H, Me), 1.21—2.02 (m, 8H, CH_2), 1.75 (s, 6H, Me), 2.39 (t, *J*=7 Hz, 4H, CH_2), 3.82—4.42 (m, 8H, CH_2), 4.76 (s, 4H, $=CH_2$); ^{13}C NMR ($CDCl_3$) δ=13.5 (s, Me), 18.6 (s, CH_2), 22.4 (s, Me), 32.1 (m, CH_2), 38.1 (m, CH_2), 67.1 (m, CH_2), 68.9 (m, CH_2), 112.9 (s, $=CH_2$), 140.6 (s, $-\overset{|}{C}=$); MS *m/z* (rel intensity) 426 (M^+, 0.5), 179 (100); Found: C, 50.52; H, 8.72%. Calcd for $C_{18}H_{36}O_7P_2$: C, 50.70; H, 8.51%.

P^1,P^2-Diisobutyl P^1,P^2-bis(3-methyl-3-butenyl) pyrophosphate (**5e**): 64% yield; bp 130 °C/2.1×10^{-5} Torr; IR (neat) 3090, 2990, 2930, 2890, 1655, 1465, 1375, 1300, 1035, 965 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.94 (d, *J*=6 Hz, 12H, Me), 1.75 (s, 6H, Me), 1.85—2.17 (m, 2H, CH), 2.38 (t, *J*=7 Hz, 4H, CH_2), 3.85 (t, J_{HH}=J_{HP}=6 Hz, 4H, CH_2), 4.19 (dd, J_{HH}=J_{HP}=7 Hz, 4H, CH_2), 4.76 (s, 4H, $=CH_2$); ^{13}C NMR ($CDCl_3$) δ=18.5 (s, Me), 22.4 (s, Me), 29.0 (m, CH), 38.1 (m, CH_2), 67.1 (m, CH_2), 74.9 (m, CH_2), 112.9 (s, $=CH_2$), 140.6 (s, $-\overset{|}{C}=$); MS *m/z* (rel intensity) 426 (M^+, 1), 68 (100); Found: C, 50.86; H, 8.80%. Calcd for $C_{18}H_{36}O_7P_2$: C, 50.70; H, 8.51%.

P^1,P^2-Dicrotyl P^1,P^2-dipropyl pyrophosphate (**3**): 86% yield; IR (neat) 3040, 2980, 2950, 2900, 2870, 1677, 1460, 1380, 1278, 1018, 968 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.86—1.08 (m, 6H, Me), 1.54—1.86 (m, 10H, CH_2 and Me), 3.84—4.24 (m, 4H, CH_2), 4.36—4.72 (m, 4H, CH_2), 5.50—6.00 (m, 4H, =CH); MS *m/z* (rel intensity) 370 (M^+, 3), 141 (100).

Trialkyl Allyl (and 3-Methyl-3-butenyl) Pyrophosphates (6 and 8). The following preparation of allyl triethyl pyrophosphate (**6a**) represents the general procedure. To a mixture of diethyl hydrogenphosphate (466 mg, 3 mmol) and triethylamine (0.49 cm^3, 3.5 mmol) in anhydrous ether (10 cm^3) was slowly added a solution of allyl ethyl phosphorochloridate (583 mg, 3.2 mmol) in ether (10 cm^3) with cooling in an ice-salt bath. After the addition was complete, the reaction mixture was stirred at that temperature for 2 h and then triethylammonium chloride which formed was filtered. The filtrate was concentrated and the residue was distilled (bp 155 °C/3.0×10^{-4} Torr) to give an almost pure product. This was further purified by column chromatography on silica gel (eluant: ether) to afford pure allyl triethyl pyrophosphate (**6a**) (611 mg, 67%) as a colorless oil. Other trialkyl allyl (and 3-methyl-3-butenyl) pyrophosphates (**6** and **8**) were similarly prepared and purified. Crotyl tripropyl pyrophosphate (**7**) is thermally unstable, so the crude material was used for the next reactions without further purification.

Allyl triethyl pyrophosphate (**6a**): 67% yield; bp 155 °C/3.0×10^{-4} Torr; IR (neat) 3100, 3000, 2950, 2920, 2825, 1650, 1480, 1445, 1373, 1290, 1167, 1032, 963 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.38 (t, *J*=7 Hz, 9H, Me), 3.90—4.50 (m, 6H, CH_2), 4.55—4.90 (m, 2H, CH_2), 5.10—5.70 (m, 2H, $=CH_2$), 5.70—6.40 (m, 1H, =CH); ^{13}C NMR ($CDCl_3$) δ=16.0 (m, Me), 65.3 (m, CH_2), 69.2 (bt, 4 Hz, CH_2), 118.7 (s, $=CH_2$), 131.8 (bt, *J*=2 Hz, =CH); MS *m/z* (rel intensity) 302 (M^+, 6), 161 (100); Found: C, 35.65; H, 6.66%. Calcd for $C_9H_{20}O_7P_2$: C, 35.77; H, 6.67%.

Allyl tripropyl pyrophosphate (**6b**): 77% yield; bp 130—135 °C/1.4×10^{-5} Torr; IR (neat) 3090, 2980, 2950, 2920, 2890, 1650, 1465, 1425, 1380, 1295, 1155, 1030, 960 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.99 (t, J=7 Hz, 9H, Me), 1.32—2.12 (m, 6H, CH_2), 3.84—4.34 (m, 6H, CH_2), 4.35—4.74 (m, 2H, CH_2), 5.05—5.54 (m, 2H, =CH_2), 5.62—6.81 (m, 1H, =CH); ^{13}C NMR ($CDCl_3$) δ=9.9 (s, Me), 23.5 (m, CH_2), 69.2 (bt, J=3 Hz, CH_2), 70.6 (m, CH_2), 118.7 (s, =CH_2), 132.0 (bt, J=3 Hz, =CH); MS m/z (rel intensity) 344 (M^+, 10), 219 (100); Found: C, 41.88; H, 7.91%. Calcd for $C_{12}H_{26}O_7P_2$: C, 41.87; H, 7.61%.

Allyl tributyl pyrophosphate (**6c**): 72% yield; bp 165—167 °C/2.0×10^{-4} Torr; IR (neat) 2975, 2950, 2925, 2890, 1650, 1467, 1383, 1293, 1153, 1120, 1033, 960 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.75—1.30 (bt, J=6 Hz, 9H, Me), 1.30—2.35 (m, 12H, CH_2), 3.85—4.39 (m, 6H, CH_2), 4.39—4.75 (m, 2H, CH_2), 5.01—5.57 (m, 2H, =CH_2), 5.57—6.29 (m, 1H, =CH); ^{13}C NMR ($CDCl_3$) δ=13.5 (s, Me), 18.5 (s, CH_2), 32.1 (m, CH_2), 68.8 (m, CH_2), 68.9 (bt, J=4 Hz, CH_2), 118.7 (s, =CH_2), 131.9 (bt, J=3 Hz, =CH); MS m/z (rel intensity) 386 (M^+, 3), 179 (100); Found: C, 46.66; H, 8.65%. Calcd for $C_{15}H_{32}O_7P_2$: C, 46.63; H, 8.35%.

Allyl triisobutyl pyrophosphate (**6d**): 81% yield; bp 157 °C/3.0×10^{-4} Torr; IR (neat) 3110, 3000, 2960, 2920, 2900, 1650, 1475, 1375, 1300, 1170, 1135, 1032, 970 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.98 (d, J=6 Hz, 18H, Me), 1.73—2.33 (m, 3H, CH), 3.84 (t, J_{HH}=J_{HP}=7 Hz, 6H, CH_2) 4.33—4.73 (m, 2H, CH_2), 5.03—5.53 (m, 2H, =CH_2), 5.53—6.13 (m, 1H, =CH); ^{13}C NMR ($CDCl_3$) δ=18.4 (s, Me), 28.9 (m, CH), 69.0 (bt, J=3 Hz, CH_2), 74.8 (m, CH_2), 118.6 (s, =CH_2), 131.9 (bt, J=3 Hz, =CH); MS m/z (rel intensity) 386 (M^+, 1), 219 (100); Found: C, 46.65; H, 8.53%. Calcd for $C_{15}H_{32}O_7P_2$: C, 46.63; H, 8.35%.

Triethyl 3-methyl-3-butenyl pyrophopshate (**8a**): 13% yield; bp 135—140 °C/4.0×10^{-5} Torr; IR (neat) 3080, 2990, 2940, 2920, 1650, 1480, 1445, 1395, 1370, 1295, 1065, 1030, 980, 960 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.35 (t, J=7 Hz, 9H, Me), 1.75 (s, 3H, Me), 2.38 (t, J=7 Hz, CH_2), 3.81—4.48 (m, 8H, CH_2), 4.72 (s, 2H, =CH_2); ^{13}C NMR ($CDCl_3$) δ=16.0 (m, Me), 22.4 (s, Me), 38.1 (bt, J=4 Hz, CH_2), 65.2 (m, CH_2), 67.1 (bt, J=3 Hz, CH_2), 112.9 (s, =CH_2), 140.7 (s, -C=); MS m/z (rel intensity) 330 (M^+, 2), 179 (100); Found: C, 39.90; H, 7.59%. Calcd for $C_{11}H_{24}O_7P_2$: C, 40.00; H, 7.33%.

3-Methyl-3-butenyl tripropyl pyrophosphate (**8b**): 85% yield; bp 140—145 °C/7.3×10^{-5} Torr; IR (neat) 3090, 2990, 2960, 2920, 2900, 1655, 1465, 1395, 1380, 1295, 1155, 1030, 965 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.99 (t, J=7 Hz, 9H, Me), 1.39—2.09 (m, 6H, CH_2), 1.77 (s, 3H, Me), 2.40 (t, J=7 Hz, 2H, CH_2), 3.88—4.44 (m, 8H, CH_2), 4.76 (s, 2H, =CH_2); ^{13}C NMR ($CDCl_3$) δ=9.9 (s, Me), 22.4 (s, Me), 23.5 (m, CH_2), 38.1 (m, CH_2), 67.1 (m, CH_2), 70.6 (m, CH_2), 112.9 (s, =CH_2), 140.7 (s, -C=); MS m/z (rel intensity) 372 (M^+, 2), 179 (100); Found: 45.27; H, 8.36%. Calcd for $C_{14}H_{30}O_7P_2$: C, 45.16; H, 8.12%.

Tributyl 3-methyl-3-butenyl pyrophosphate (**8c**): 66% yield: bp 150—155 °C/5.0×10^{-5} Torr; IR (neat) 3080, 2970, 2940, 2920, 2880, 1650, 1465, 1385, 1290, 1150, 1120, 1030, 965 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.97 (bt, J=6 Hz, 9H, Me), 1.23—2.08 (m, 12H, CH_2), 1.78 (s, 3H, Me), 2.40 (t, J=7 Hz, 2H, CH_2), 3.88—4.48 (m, 8H, CH_2), 4.77 (s, 2H, =CH_2); ^{13}C NMR ($CDCl_3$) δ=13.5 (s, Me), 18.6 (s, CH_2), 22.5 (s, Me), 32.1 (m, CH_2), 38.1 (m, CH_2), 67.1 (m, CH_2), 68.9 (m, CH_2), 112.9 (s, =CH_2), 140.7 (s, -C=); MS m/z (rel intensity) 414 (M^+, 1), 179 (100); Found: C, 49.16; H, 8.85%. Calcd for $C_{17}H_{36}O_7P_2$: C, 49.26; H, 8.76%.

Triisobutyl 3-methyl-3-butenyl pyrophosphate (**8d**): 42% yield; bp 120 °C/1.8×10^{-5} Torr; IR (neat) 3090, 2980, 2890, 1655, 1475, 1365, 1300, 1185, 1170, 1135, 1030, 965 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.95 (d, J=6 Hz, 18H, Me), 1.76 (s, 3H, Me), 1.87—2.19 (m, 3H, CH), 2.40 (t, J=7 Hz, 2H, CH_2), 3.84 (t, J_{HH}=J_{HP}=7 Hz, 6H, CH_2), 4.00—4.35 (m, 2H, CH_2), 4.74 (s, 2H, =CH_2); ^{13}C NMR ($CDCl_3$) δ=18.6 (s, Me), 22.4 (s, Me), 29.0 (m, CH), 38.1 (bt, J=4 Hz, CH_2), 67.1 (bt, J=3 Hz, CH_2), 74.9 (m, CH_2), 112.9 (s, =CH_2), 140.6 (s, -C=); MS m/z (rel intensity) 414 (M^+, 2), 179 (100); Found: C, 49.04; H, 8.86%. Calcd for $C_{17}H_{36}O_7P_2$: C, 49.26; H, 8.76%.

Crotyl tripropyl pyrophosphate (**7**): 76% yield; IR (neat) 2975, 2950, 2890, 2860, 1675, 1460, 1380, 1290, 1153, 1018, 957 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.97 (t, J=7 Hz, 9H, Me), 1.36—1.91 (m, 9H, CH_2 and Me), 3.78—4.25 (m, 6H, CH_2), 4.31—4.71 (m, 2H, CH_2), 5.31—6.01 (m, 2H, =CH); ^{13}C NMR ($CDCl_3$) 9.9 (s, Me), 17.7 (s, Me), 23.5 (m, CH_2), 69.4 (dd, J=3, 2 Hz, CH_2), 70.6 (m, CH_2), 125.1 (dd, J=4, 2 Hz, =CH), 132.3 (s, =CH); MS m/z (rel. intensity) 358 (M^+, 15), 179 (100).

Reactions of P^1,P^2-Dicrotyl P^1,P^2-Dipropyl Pyrophosphate (3) and Crotyl Tripropyl Pyrophosphate (7) with Phenolic Ethers. Following reaction of P^1,P^2-dicrotyl P^1,P^2-dipropyl pyrophosphate (**3**) with anisole represents the general procedure. Into a mixture of anisole (1.1 cm^3, 10 mmol) and P^1,P^2-dicrotyl P^1,P^2-dipropyl pyrophosphate (**3**) (741 mg, 2 mmol) in anhydrous dichloromethane (7 cm^3) was added boron trifluoride etherate (0.25 cm^3, 2 mmol) at 0 °C, and the mixture was stirred at 0 °C for 3.5 h. The reaction was quenched by the addition of water and the products were extracted with dichloromethane. The extracts were washed with brine, and then dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was analyzed by GLC using p-methylanisole as an internal standard. Pure samples of the products were isolated by preparative GLC and the structures were deduced by their spectral data.

Reactions with other phenolic ethers were similarly carried out and the products were analyzed using adequate internal standards. The reaction conditions and the results are summarized in Table 1.

(E)-1-(2-Butenyl)-2-methoxybenzene:[11] ^{1}H NMR ($CDCl_3$) δ=1.68 (d, J=6 Hz, 3H, Me), 3.33 (d, J=6 Hz, 2H, CH_2), 3.85 (s, 3H, OMe), 5.41—5.75 (m, 2H, =CH), 6.81—7.01 (m, 2H, Ar), 7.11—7.29 (m, 2H, Ar); MS m/z (rel intensity) 162 (M^+, 100).

1-Methoxy-2-(1-methyl-2-propenyl)benzene:[12] MS m/z (rel intensity) 162 (M^+, 96), 147 (100).

(E)-1-(2-Butenyl)-4-methoxybenzene:[13] ^{1}H NMR ($CDCl_3$) δ=1.68 (d, J=5 Hz, 3H, Me), 3.27 (bd, J=5 Hz, 2H, CH_2), 3.80 (s, 3H, OMe), 5.40—5.74 (m, 2H, =CH), 6.87 (d, J=9 Hz, 2H, Ar), 7.14 (d, J=9 Hz, 2H, Ar); MS m/z (rel intensity) 162 (M^+, 100).

1-Methoxy-4-(1-methyl-2-propenyl)benzene:[12] ^{1}H NMR ($CDCl_3$) δ=1.34 (d, J=7 Hz, 3H, Me), 3.34—3.54 (m, 1H, CH), 3.80 (s, 3H, OMe), 4.96—5.16 (m, 2H, =CH_2), 5.84—6.12 (m, 1H, =CH), 6.88 (d, J=9 Hz, 2H, Ar), 7.16 (d, J=9 Hz, 2H, Ar).

(E)-2-(2-Butenyl)-1,4-dimethoxybenzene:[14] IR (neat) 3030, 3000, 2950, 2920, 2860, 2840, 1590, 1503, 1465, 1286, 1220, 1177, 1155, 1048, 1027, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.68

(d, J=6 Hz, 3H, Me), 3.30 (d, J=5 Hz, 2H, CH_2), 3.78 (s, 3H, OMe), 3.80 (s, 3H, OMe), 5.40—5.72 (m, 2H, =CH), 6.66—6.90 (m, 3H, Ar); MS m/z (rel. intensity) 192 (M^+, 100).

1,4-Dimethoxy-2-(1-methyl-2-propenyl)benzene:[14] ^1H NMR ($CDCl_3$) δ=1.31 (d, J=7 Hz, 3H, Me), 3.78 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.60—4.00 (m, 1H, CH), 5.00—5.16 (m, 2H, $=CH_2$), 5.94—6.16 (m, 1H, =CH), 6.60—6.88 (m, 3H, Ar); MS m/z (rel intensity) 192 (M^+, 100).

(*E*)-2-(2-Butenyl)-1,3,5-trimethoxybenzene: ^1H NMR ($CDCl_3$) δ=1.62 (d, J=6 Hz, 3H, Me), 3.26 (bd, J=5 Hz, 2H, CH_2), 3.82 (s, 9H, OMe), 5.35—5.71 (m, 2H, =CH), 6.17 (s, 2H, Ar); MS m/z (rel intensity) 222 (M^+, 100).

1,3,5-Trimethoxy-2-(1-methyl-2-propenyl)benzene: ^1H NMR ($CDCl_3$) δ=1.34 (d, J=7 Hz, 3H, Me), 3.80 (s, 6H, OMe), 3.81 (s, 3H, OMe), 3.98—4.18 (m, 1H, CH), 4.82—5.04 (m, 2H, $=CH_2$), 6.16 (s, 2H, Ar), 6.06—6.38 (m, 1H, =CH); MS m/z (rel. intensity) 222 (M^+, 54), 207 (100).

(*E*)-2-(2-Butenyl)-3,4,5,6-tetramethoxytoluene: IR (neat) 2960, 2940, 2860, 2830, 1645, 1463, 1350, 1258, 1195, 1073, 1040, 1010, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.64 (d, J=6 Hz, 3H, Me), 2.16 (s, 3H, Me), 3.32 (d, J=5 Hz, 2H, CH_2), 3.80 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.92 (s, 3H, OMe), 3,93 (s, 3H, OMe), 5.28—5.64 (m, 2H, =CH); MS m/z (rel intensity) 266 (M^+, 100).

2,3,4,5-Tetramethoxy-6-(1-methyl-2-propenyl)toluene: ^1H NMR ($CDCl_3$) δ=1.38 (d, J=7 Hz, 3H, Me), 2.18 (s, 3H, Me), 3.78 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.90 (s, 3H, OMe), 3,92 (s, 3H, OMe), 3.60—4.08 (m, 1H, CH), 4.92—5.12 (m, 2H, $=CH_2$), 6.02—6.26 (m, 1H, =CH); MS m/z (rel intensity) 266 (M^+, 100).

(*E*)-2-(2-Butenyl)-1,4-dimethoxy-3-methylnaphthalene: IR (neat) 3075, 3030, 2940, 2850, 1590, 1450, 1375, 1353, 1263, 1197, 1097, 1067, 1015, 970, 768 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.64 (dd, 3H, J=6, 1 Hz, Me), 2.40 (s, 3H, Me), 3.50—3.66 (m, 2H, CH_2), 3.88 (s, 3H, OMe), 3.91 (s, 3H, OMe), 5.28—5.54 (m, 1H, =CH), 5.54—5.78 (m, 1H, =CH), 7.44—7.58 (m, 2H, Ar), 8.00—8.18 (m, 2H, Ar); MS m/z (rel intensity) 256 (M^+, 100).

Reactions of Crotyl Tripropyl Pyrophosphate (7) with Aromatic Amines, Pyrrole, and Indole. Following reaction of crotyl tripropyl pyrophosphate (**7**) with aniline represents the general procedure. To a mixture of aniline (225 mg, 2.4 mmol) and crotyl tripropyl pyrophosphate (**7**) (866 mg, 2.4 mmol) in DMF (8 cm^3) was added boron trifluoride etherate (0.61 cm^3, 4.8 mmol) at room temperature and the reaction mixture was stirred overnight (20 h). Saturated sodium hydrogencarbonate was added and the products were extracted with hexane. The extracts were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residual oil was chromatographed on silica gel (eluant: benzene) to give *N*-crotylaniline (202 mg, 57%) and *N,N*-dicrotylaniline (21 mg, 9%).

Reactions for other aromatic amines, pyrrole, and indole were similarly carried out and the products were isolated by silica-gel column chromatography. The yields and physical data of the products are summarized in Table 2.

(*E*)-*N*-(2-Butenyl)aniline: IR (neat) 3420, 3060, 3025, 2960, 2930, 2880, 2850, 1603, 1505, 1465, 1450, 1377, 1320, 1250, 964 cm^{-1}; ^1H NMR (CCl_4) δ=1.47—1.87 (m, 3H, Me), 3.34 (bs, 1H, NH), 3.47—3.87 (m, 2H, CH_2), 5.27—5.72 (m, 2H, =CH), 6.17—6.62 (m, 3H, Ph), 6.71—7.14 (t, J=7 Hz, 2H, Ph); MS m/z (rel intensity) 147 (M^+, 68), 93 (100).

(*E*)-*N,N*-Di(2-butenyl)aniline: IR (neat) 3100, 3070, 3040, 2970, 2930, 2860, 1720, 1600, 1507, 1450, 1380, 1353, 1260, 966, 862, 745, 692 cm^{-1}; ^1H NMR (CCl_4) δ=1.45—1.85 (m, 6H, Me), 3.35—4.05 (m, 4H, CH_2), 5.05—5.75 (m, 4H, =CH), 6.21—7.25 (m, 5H, Ph); MS m/z (rel intensity) 201 (M^+, 81), 77 (100).

(*E*)-*N*-(2-Butenyl)-*N*-methylaniline: IR (neat) 3090, 3060, 3020, 2930, 2920, 2875, 2850, 1665, 1598, 1505, 1446, 1368, 1350, 1250, 1030, 990, 960, 935, 857, 745, 687 cm^{-1}; ^1H NMR (CCl_4) δ=1.52—1.77 (m, 3H, Me), 2.78 (s, 3H, Me), 3.57—3.92 (m, 2H, CH_2), 5.26—5.57 (m, 2H, =CH), 6.27—6.66 (m, 3H, Ph), 6.72—7.14 (m, 2H, Ph); MS m/z (rel. intensity) 161 (M^+, 80), 120 (100).

(*E*)-*N*-(2-Butenyl)-*p*-anisidine: ^1H NMR ($CDCl_3$) δ= 1.72 (d, J=4 Hz, 3H, Me), 2.60—3.00 (bs, 1H, NH), 3.65 (d, J=4 Hz, 2H, CH_2), 3.76 (s, 3H, OMe), 5.54—5.84 (m, 2H, =CH), 6.63 (d, J=8 Hz, 2H, Ar), 6.82 (d, J=8 Hz, 2H, Ar); MS m/z (rel intensity) 177 (M^+, 15), 108 (100).

(*E*)-*N,N*-Di(2-butenyl)-*p*-anisidine: ^1H NMR ($CDCl_3$) δ= 1.68 (d, J=4 Hz, 6H, Me), 3.70—3.90 (m, 7H, CH_2 and OMe), 5.40—5.72 (m, 4H, =CH), 6.64—6.90 (m, 4H, Ar); MS m/z (rel intensity) 231 (M^+, 56), 122 (100).

(*E*)-*N,N*-Diphenyl-2-butenylamine: IR (neat) 3080, 3060, 3040, 3000, 2960, 2930, 2880, 2850, 1590, 1497, 1447, 1364, 1240, 962, 745, 690 cm^{-1}; MS m/z (rel intensity) 223 (M^+, 27), 77 (100).

N,N-Diphenyl-1-methyl-2-propenylamine: MS m/z (rel intensity) 223 (M^+, 25), 77 (100).

(*E*)-*N*-Phenyl-4(or 2)-(2-butenyl)phenylamine: ^1H NMR ($CDCl_3$) δ=1.66—1.84 (m, 3H, Me), 3.22—3.48 (m, 2H, CH_2), 5.48—5.73 (m, 2H, =CH), 6.86—7.42 (m, 9H, Ar).

(*E*)-*N*-(2-Butenyl)-1-naphthylamine: IR (neat) 3450, 3070, 2980—2870, 1580, 1520, 1370, 1340, 1270, 965, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.62—1.87 (m, 3H, Me), 3.72—4.00 (m, 2H, CH_2), 4.24 (bs, 1H, NH), 5.60—5.96 (m, 2H, =CH), 6.61 (d, J=7 Hz, 1H, Ar), 7.16—7.60 (m, 4H, Ar), 7.74—7.96 (m, 2H, Ar); MS m/z (rel intensity) 197 (M^+, 63), 115 (100).

(*E*)-2-(2-Butenyl)-1-naphthylamine: IR (neat) 3450, 3400, 3070, 3040, 2980, 2930, 2860, 1620, 1510, 1400, 970, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.66—1.83 (m, 3H, Me), 3.34—3.52 (m, 2H, CH_2), 3.60—4.40 (m, 2H, NH_2), 5.46—5.80 (m, 2H, =CH), 7.20—7.55 (m, 4H, Ar), 7.76—7.94 (m, 2H, Ar); MS m/z (rel intensity) 197 (M^+, 100).

(*E*)-2-(2-Butenyl)pyrrole:[15] IR (neat) 3400, 3110, 3040, 2980, 2950, 2930, 2900, 2860, 2830, 1567, 1438, 1470, 1380, 1092, 1040, 1025, 970, 790, 717 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.71 (d, J=4 Hz, 3H, Me), 3.22—3.46 (m, 2H, CH_2), 5.48—5.72 (m, 2H, =CH), 5.86—6.03 (m, 1H, pyrrole H^4), 6.10—6.24 (m, 1H, pyrrole H^3), 6.66—6.78 (m, 1H, pyrrole H^5), 7.98 (bs, 1H, NH); MS m/z (rel intensity) 121 (M^+, 100).

2-(1-Methyl-2-propenyl)pyrrole:[15] ^1H NMR ($CDCl_3$) δ= 1.38 (d, J=7 Hz, 3H, Me), 3.40—3.56 (m, 1H, CH), 5.00—5.20 (m, 2H, $=CH_2$), 5.72—6.04 (m, 2H, =CH and pyrrole H^4), 6.10—6.20 (m, 1H, pyrrole H^3), 6.66—6.78 (m, 1H, pyrrole H^5); MS m/z (rel intensity) 121 (M^+, 76), 106 (100).

(*E*)-3-(2-Butenyl)pyrrole:[16,17] IR (neat) 3410, 3040, 2980, 2950, 2930, 2860, 2850, 1557, 1435, 1380, 1066, 1053, 970, 770, 710 cm^{-1}; H NMR ($CDCl_3$) δ=1.69 (d, J=6 Hz, 3H, Me), 3.08—3.38 (m, 2H, CH_2), 5.40—5.72 (m, 2H, =CH), 6.00—6.20 (m, 1H, pyrrole H^4), 6.54—6.70 (m, 1H, pyrrole H^5), 6.70—7.84 (m, 1H, pyrrole H^2), 8.04 (bs, 1H, NH); MS

m/z (rel intensity) 121 (M^+, 100).

(*E*)-3-(2-Butenyl)indole: ^1H NMR ($CDCl_3$) δ=1.70 (d, *J*=6 Hz, 3H, Me), 3.46 (d, *J*=4 Hz, 2H, CH_2), 5.00—5.90 (m, 2H, =CH), 7.00 (s, 1H, indole H^2), 7.08—7.28 (m, 2H, indole H^5 and H^6), 7.38 (d, *J*=8 Hz, 1H, indole H^4), 7.64 (d, *J*=8 Hz, 1H, indole H^7), 7.84—8.10 (bs, 1H, NH); MS *m/z* (rel intensity) 171 (M^+, 100).

3-(1-Methyl-2-propenyl)indole: MS *m/z* (rel intensity) 171 (M^+, 54), 156 (100).

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