Reactions of Phosphorus Compounds. 33. Preparation of Heterocyclic Species from α-Substituted Vinyl Phosphonium Salts. Anomalous Products from Isopropenylphosphonium Halides[1]

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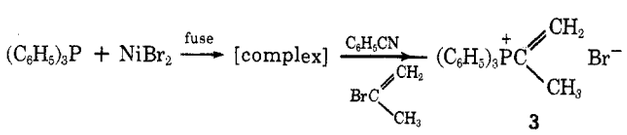
The synthetic utility of isopropenylmethyldiphenylphosphonium iodide (**2**), isopropenyltriphenylphosphonium bromide (**3**), and 1-phenylvinyltriphenylphosphonium bromide (**4**) is compared with that of the unsubstituted vinyltriphenylphosphonium salt, **1**, with respect to the preparation of heterocyclic and chain-extended species. An inner phosphonium zwitterion (**10**) can also be isolated from **2**. Under fusion conditions, 2-methyl-2*H*-1-benzopyran (**13**) is also formed from salts **2** and **3** with no inner zwitterion isolated in either case. A mechanism is proposed for the latter reaction.

Vinyltriphenylphosphonium bromide (**1**) has been shown to be a versatile reagent for the preparation of cyclic and chain-extended products.[2] This reaction has been postulated as one involving an initial conjugate addition followed by a Wittig reaction.[3] To date only one series of reactions, involving this Michael–Wittig sequence, has been reported using substituted vinyltriphenylphosphonium salts.[4]

In order to expand the scope of this synthetic technique, we have prepared[5] a number of substituted vinylphosphonium salts and have investigated their reactivity *vis-a-vis* the unsubstituted vinyl salt **1** in the Michael–Wittig reaction sequence. Thus, isopropenylmethyldiphenylphosphonium iodide (**2**), isopropenyltriphenylphosphonium bromide (**3**), and 1-phenylvinyltriphenylphosphonium bromide (**4**) were subjected to a representative sampling of the previously demonstrated reactions of **1**, in order to compare the reactivity and synthetic utility of these new salts with the parent compound. Anomalous reactions are reported for salts **2** and **3**, and mechanisms are proposed.

It should be noted that, contrary to our previous report,[5] salt **3** may in fact be prepared readily utilizing a modification of the Horner[6] procedure. Fusion of triphenylphosphine with nickel bromide (anhydrous), followed by addition of dry benzonitrile solvent, 2-bromopropene, and heating of the resultant mixture, furnishes salt **3** in 50–60% yield.



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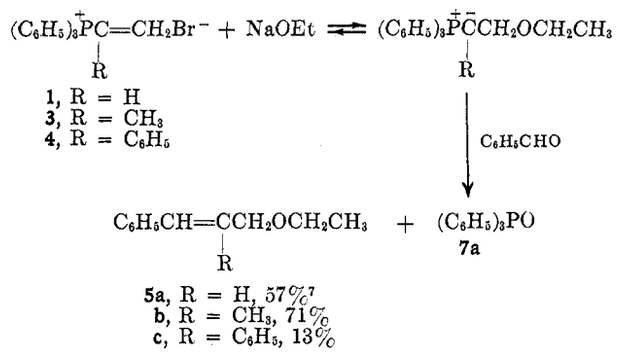
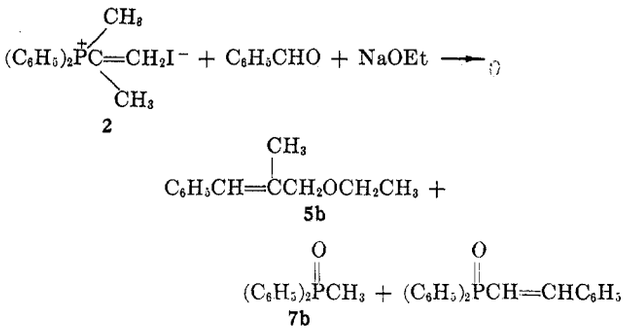
Vinylphosphonium salts **1**, **3**, and **4**, when treated with sodium ethoxide and benzaldehyde, produced the corresponding chain-extended cinnamyl ethyl ether and triphenylphosphine oxide (**7a**).

Salt **2**, when treated similarly, produced the expected 1-phenyl-2-methyl-4-oxa-1-hexene (**5b**) in 38% yield, as well as methyldiphenylphosphine oxide (**7b**)



5a, R = H, 57%[7]
b, R = CH_3, 71%
c, R = C_6H_5, 13%

(28%) and 2-phenylvinyldiphenylphosphine oxide (13%).

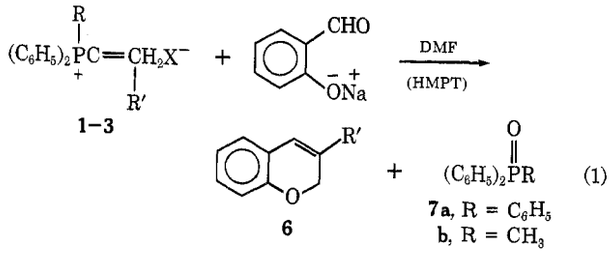


Salts **1–3** gave the expected products of Michael–Wittig cyclization reactions[8–10] when treated with bases containing a carbonyl moiety. The reactions are illustrated in eq 1–3.

In this reaction there are three expected steps: Michael addition, betaine formation, and betaine decomposition. Assuming that the betaine decomposition is the rate-determining step[11] for the reactions of salts **1**, **2**, and **3**, then one would expect the formation of olefinic species to be less favorable with salts containing a phosphonium moiety which is less electrophilic. Thus, the reactions of salt **2** were expected to be less favorable than the reactions of salt **1** and **3**, as found.

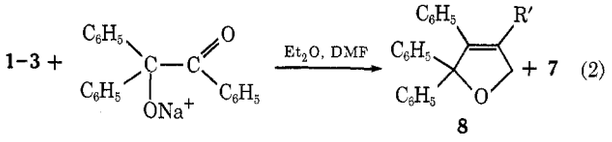
The high reactivity of the unsubstituted salt **1** in comparison to **2** and **3** may be due to the steric in-

(1) E. E. Schweizer, C. S. Kim, C. S. Labaw, and W. P. Murray, *Chem. Commun.*, 7 (1973), paper number 32 in this series.
(2) E. E. Schweizer and C. M. Kopay, *J. Org. Chem.*, **37**, 1561 (1972), and references cited therein.
(3) E. E. Schweizer, *J. Amer. Chem. Soc.*, **86**, 2744 (1964).
(4) E. E. Schweizer and W. S. Creasy, *J. Org. Chem.*, **36**, 2244 (1971).
(5) E. E. Schweizer and A. T. Wehman, *J. Chem. Soc. C*, 343 (1971).
(6) L. Horner, G. Mummenthey, H. Moser, and P. Beck, *Chem. Ber.*, **99**, 2782 (1966).
(7) E. E. Schweizer, L. D. Smucker, and R. J. Votral, *J. Org. Chem.*, **31**, 467 (1966).
(8) E. E. Schweizer and J. G. Liehr, *J. Org. Chem.*, **33**, 583 (1968).
(9) (a) E. E. Schweizer and K. K. Light, *J. Amer. Chem. Soc.*, **86**, 2963 (1964); (b) E. E. Schweizer and K. K. Light, *J. Org. Chem.*, **31**, 870 (1966).
(10) E. E. Schweizer and J. G. Thompson, procedure submitted to *Org. Syn.*
(11) G. Wittig and U. Schoellkopf, *Chem. Ber.*, **87**, 1318 (1954).



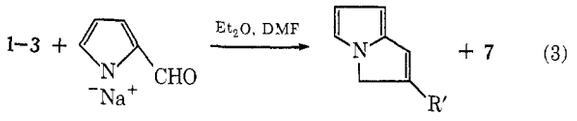
1–3 6 7a, R = C_6H_5; b, R = CH_3 (1)

From 1, 6 (R′ = H); 54–58%[10]
From 2, 6 (R′ = CH_3); 30%
From 3, 6 (R′ = CH_3); 35%



8 (2)

From 1, 8 (R′ = H); 71%[8]
From 2, 8 (R′ = CH_3); 36%
From 3, 8 (R′ = CH_3); 47%



9 (3)

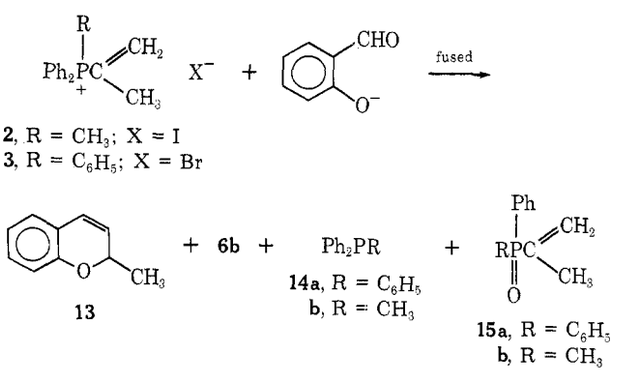
From 1, 9 (R′ = H); 87%[9]
From 2, 9 (R′ = CH_3); 25%
From 3, 9 (R′ = CH_3); 67%

hibition, which would be expected[12] to slow down the initial conjugate addition step of the reaction.

The first anomalous product was observed on allowing the phosphonium iodide (**2**) to react in solution; apart from the expected products it also yielded the isolable inner phosphonium zwitterion whose formation may be rationalized as shown in Scheme I.

The salicyloxide undergoes conjugate addition to the vinyl salt **2**; proton transfer leads to the methylene ylide **11b**, which attacks the aldehyde group to give the betaine **12**. Protonation of the betaine oxygen with β elimination of the phenoxide and dehydration would give the zwitterion **10**.

Reactions of salts **2** and **3** under fusion conditions yielded the isomeric 2-methyl-2*H*-1-benzopyran (**13**) as the major product with only a small amount of the expected 3-methyl isomer, **6** (R′ = CH_3). The tertiary phosphine **14** and the phosphine oxide **15** were also formed.

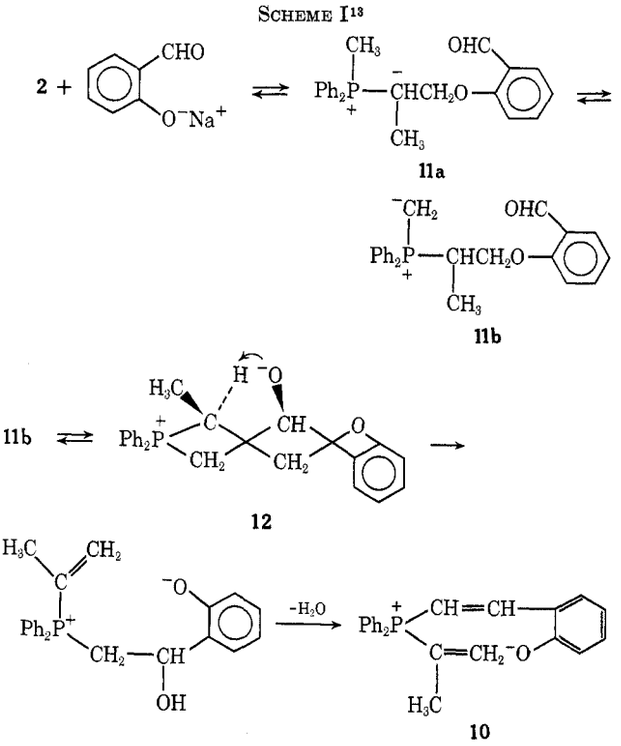


2, R = CH_3; X = I
3, R = C_6H_5; X = Br

13 **14a**, R = C_6H_5; **b**, R = CH_3 **15a**, R = C_6H_5; **b**, R = CH_3

(12) E. D. Bergmann, D. Ginsburg, and R. Rappo in "Organic Reactions," Vol. 10, Wiley, New York, N. Y., 1959, pp 182–187.

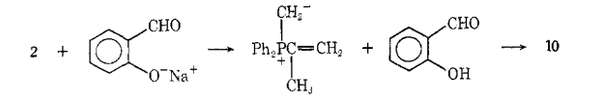
SCHEME I[13]



Attempts to isomerize **6** (R′ = CH_3) to **13** either thermally or by basic catalysis only resulted in the isolation of the starting material. Therefore, one is led to the proposition that rearrangement of the original phosphonium compound prior to the Wittig reaction must be the pathway to the isomeric product (Scheme II).

Under fusion conditions, the sodium salicyloxide, acting as a base, removes a proton from the isopropenyl group to produce the resonance-stabilized carbanion **16**, whose formation is demonstrated in an isolated experiment by the formation of equal amounts of deuterated sites at both the methyl and methylene groups. Reaction by path A would lead to the formation of allene (not isolated) and the isolated tertiary phosphine (**14a,b**) *via* an elimination reaction. Reaction by path B, involving an internal nucleophilic displacement on phosphorus, would result in the formation of a vinyl carbanion, which could give either the allylphosphorane **17** by proton transfer or allene and the tertiary phosphine **14a,b**. This allylic phosphorane is known[14] to react with sodium salicyloxide to produce 2-methyl-2*H*-1-benzopyran (**13**). Another possibility, the formation of a cyclopropylphosphorane, has been ruled out because it is known that this phosphorane reacts with sodium salicyloxide to produce 2,3-dihydro-1-benzoxepin[15] as well as the 2-methyl-2*H*-1-

(13) Both referees suggest the simpler pathway

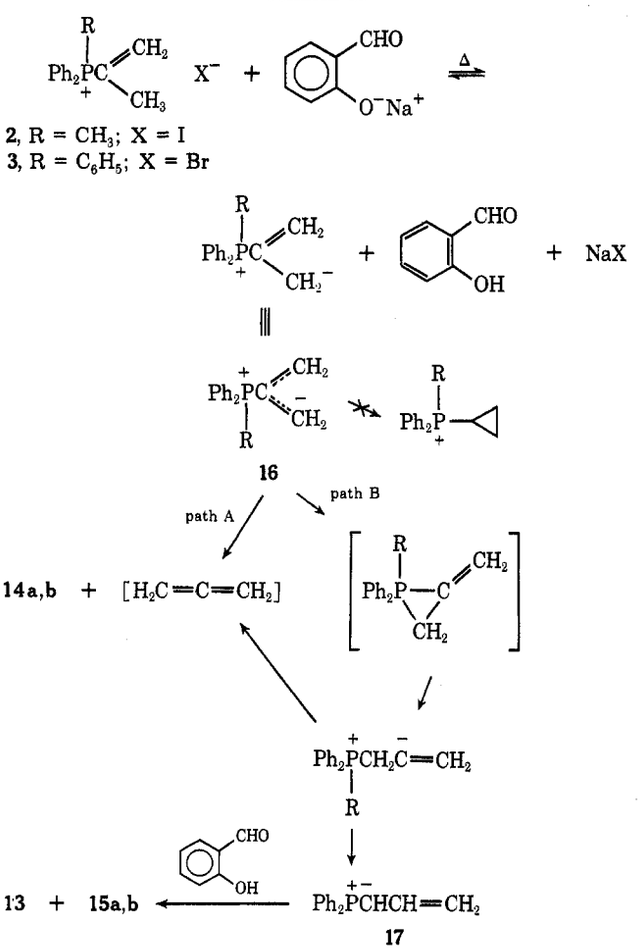


However, numerous attempts by Nycz to obtain a reaction between the sodium salicyloxide and ethyltriphenylphosphonium salts were shown to be unsuccessful (Nycz, unpublished results).

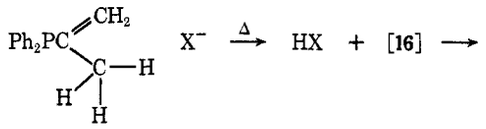
(14) E. E. Schweizer, E. T. Shaffer, C. T. Hughes, and C. J. Berninger, *J. Org. Chem.*, **31**, 2907 (1966).

(15) E. E. Schweizer, C. J. Berninger, and J. G. Thompson, *J. Org. Chem.*, **33**, 336 (1968).

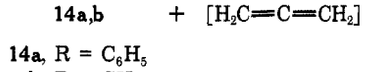
SCHEME II



benzopyran, and no benzoxepin has been observed in the reactions reported here. Furthermore, it was found that both of the isopropenylphosphonium halides, **2** and **3**, produced tertiary phosphines (**14a,b**) when



2, R = CH_3; X = I
3, R = C_6H_5; X = Br

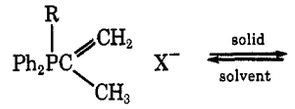


14a, R = C_6H_5
b, R = CH_3

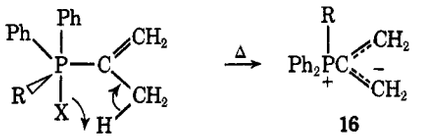
heated alone at 225° under vacuum. In this latter case, it is assumed that the halide ion must be acting as the base.

Since the 2-methyl isomer **13** was never isolated nor detected (nmr or vpc) in the reactions run in solution (DMF or HMPT over an 80–200° temperature range), one is led to the suggestion that the SNi rearrangement may be emanating from the pentavalent form of **2** (or **3**), **18a,b**, which would not be present in the highly polar solvents used otherwise.

1-Phenylvinyltriphenylphosphonium bromide (**4**), whose preparation has already been described,[5] was also subjected to ring synthesis reaction conditions with extremely limited success. The reaction of salt **4** with sodium salicyloxide in DMF solvent produced no



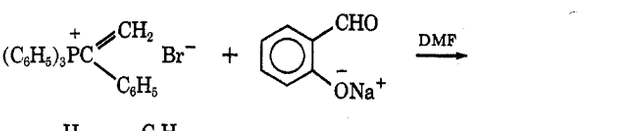
2, R = CH_3; X = I
R = C_6H_5; X = Br



18a, R = C_6H_5; X = Br
b, R = CH_3; X = I

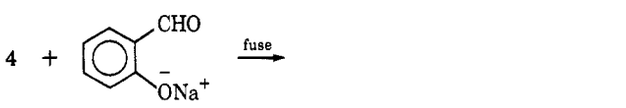
16

3-phenyl-2*H*-1-benzopyran. Instead, an open-chain compound (**19**) was formed in 40% yield, along with triphenylphosphine oxide (**7a**, R = C_6H_5, 50%), and the reduced 1-phenylethyltriphenylphosphonium bromide[5] (**20**) in 10% yield.



19 **7a** **20**

3-Phenyl-2*H*-1-benzopyran (**6d**, R′ = C_6H_5) could be produced in 8% yield only under fusion conditions; 21% **19**, 28% **7a**, and 23% triphenylphosphine (**14a**) were also formed.



6d

Compound **19** is presumably formed *via* the reduced salt **20**, since it too leads to **19** (57% yield) when treated with sodium salicyloxide. Reactions involving **4** have invariably resulted in the isolation of salt **20**.[5]

The reason for the low yields of expected products from the reactions of **4** is unclear, but might be due to a combination of increased bulk at the carbon α to phorphorus as well as to the intermediacy of a semistabilized ylide formed by the initial Michael addition. The effect of the formation of the semistabilized ylide would be to decrease the rate of betaine formation, thus allowing side reactions to occur (*e.g.*, reduction).[5] The effect of bulk at the α carbon might be demonstrated by the reaction of **4** with the sodium salt of pyrrolaldehyde, wherein no **9** (R = C_6H_5) is formed,

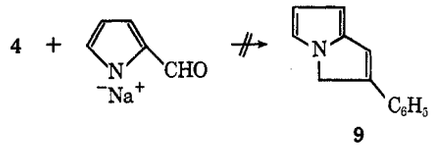


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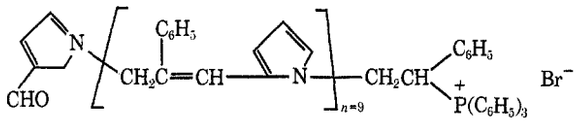
TABLE I

PREPARATION OF CINNAMYL ETHYL ETHERS 5

Salt (mol)	NaOEt, mol	C_6H_5CHO, mol	Yield, % 7	Yield, % 5	Isolation method	5 Analysis Calcd	5 Analysis Found
1 (0.08)	0.08	0.08		57	a	ref 6	
3 (0.03)	0.03	0.03	73	71	a	C 81.75	C 81.41
						H 9.15	H 9.14 (vpc)
4 (0.03)	0.03	0.03	48	12.5	b	C 85.72	C 85.40
						H 7.62	H 7.36 (vpc)



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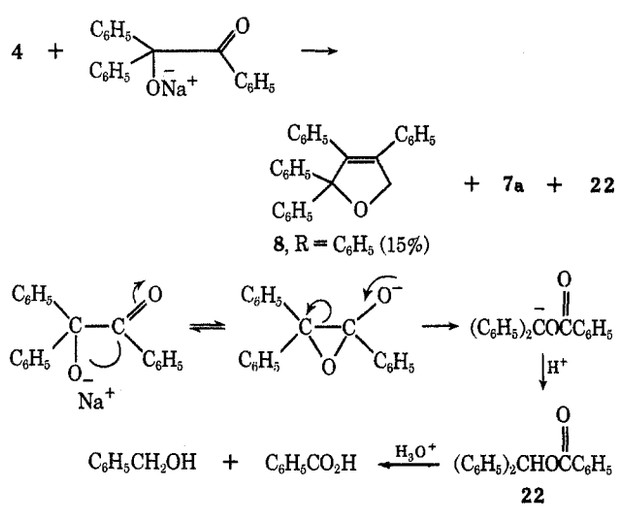
and thus an intermolecular reaction resulting in polymer **21** is more facile than ring formation.

When the anion of phenylbenzoin is employed, the excessive bulk both at the α carbon of the ylide and at the carbonyl does not permit reaction to any great extent, but the entropically more favored ring formation proceeds to a small degree. There is also produced a 48% yield of benzhydrylbenzoate (**22**), which can be rationalized by a rearrangement of the sodium salt of phenylbenzoin, facilitated by the lower reactivity of the phosphonium salt **4**. Support for this rearrangement lies in the fact that when the sodium salt of phenylbenzoin is treated under the reaction conditions in the absence of **4**, rearrangement proceeds to the extent of 80%. The utility of the Michael–Wittig reaction sequence is thus expanded through the use of substituted vinylphosphonium salts.



8, R = C_6H_5 (15%)

Experimental Section

General.—Infrared (ir) spectra were obtained on a Perkin-Elmer 137, ultraviolet (uv) spectra on a Perkin-Elmer 237 spectrophotometer, nuclear magnetic resonance (nmr) on a Varian A-60A or a Perkin-Elmer R-12b using tetramethylsilane as internal standard, and mass spectra on a CEC 21-110B double focusing spectrometer utilizing an ionizing potential of 70 eV.

Vapor phase chromatography (vpc) was accomplished on a Wilkens Aerograph A-90 P instrument employing a column of 10% UC-W98 on Chromosorb W (60–80 mesh, 10 ft × 0.25 in.), and thin layer chromatography (tlc) was accomplished by the ascending technique utilizing 2 × 8 in. plates coated with silica gel G of 0.25-mm thickness.

Melting points are corrected and were taken on a Fisher-Johns melting point apparatus. Analyses were performed by MHW Laboratories, Garden City, Mich., or Microanalysis, Inc., Wilmington, Del.

All reactions were run under an atmosphere of dry nitrogen. When products of known identity were obtained, their presence was proven by the use of two or more of the following methods: ir and nmr spectra, vpc retention time and coinjection with authentic material, and melting point and mixture melting point with an authentic sample. Purity of the compounds was determined by tlc, vpc, melting point, and nmr spectra.

Preparation of Isopropenyltriphenylphosphonium Bromide (3).—A mixture of 69 g (0.262 mol) of triphenylphosphine and 57.2 g (0.262 mol) of anhydrous nickel bromide was heated in a flask until fusion was complete and the deep green color was uniform. Benzonitrile (150 ml) was added and the solution was heated while water was removed with a Dean-Stark trap until the temperature had reached 200°. After cooling to *ca.* 50°, 36 g (0.30 mol) of 2-bromopropene was added dropwise. The reaction mixture was stirred at 50–80° overnight and then heated slowly, over a period of 2 days, until the temperature reached 200° once more. The flask and contents were cooled and steam distilled, and the distillate was discarded (benzonitrile–water). The residue was cooled and filtered to remove a black, insoluble material and the filtrate was extracted with CH_2Cl_2. The organic extract was dried over $MgSO_4$ and concentrated while EtOAc was added to precipitate a gummy solid which was recrystallized from CH_2Cl_2–EtOAc to furnish 55 g (55%) of **3**, mp 197–197.5° (lit.[16] mp 196.5–197.5°), ir and nmr in agreement with those reported.

Reaction of Vinylphosphonium Salts with Sodium Ethoxide and Benzaldehyde. Chain Extension Reaction.—Reaction was run as previously described.[7] Data are found in Table I.

1-Phenyl-2-methyl-4-oxa-1-hexene (5b) (*Z* isomer) had ir (neat) ν 2940, 2830 (CH), 1480, 1440 (CC), 1090 (COC), 745, 690 cm^{-1} (aromatic); nmr ($DCDl_3$) δ 1.23 (t, 3, J = 7 Hz, CH_3-CH_2), 1.88 (d, 3, J = 1.4 Hz, CH_3), 3.50 (q, 2, J = 7 Hz, CH_2CH_3), 3.99 (d, 2, J = 1.0 Hz, CH_2), 6.51 (qt, 1, J = 1.4 Hz, 1.0, vinyl), 7.28 (s, 5, C_6H_5).

The *E* isomer had ir (neat) ν 2950, 2840 (CH), 1485, 1435 (CC), 1110 (COC), 740, 700 cm^{-1} (aromatic); nmr ($CDCl_3$) δ 1.20 (t, 3, J = 7 Hz, CH_2CH_3), 1.98 (d, 3, J = 1.4 Hz, CH_3), 3.45 (q, 2, CH_2CH_3), 4.10 (d, 2, J = 0.8 Hz, CH_2), 6.51 (qt, 1, J = 1.4 Hz, 0.8, vinyl), 7.28 (s, 5, C_6H_5).

1,2-Diphenyl-4-oxa-1-hexene (5c) had ir (neat) ν 3010, 2940, 2820 (CH), 1600 (C=C), 1490, 1440 (CC), 1090 (COC), 760, 690 cm^{-1} (aromatic); nmr ($CDCl_3$) δ 1.22 (t, 3, J = 7 Hz, CH_2CH_3), 3.48 (q, 2, J = 7 Hz, CH_2CH_3), 4.62 (s, 2, CH_2), 7.11 (s, 1, vinyl), 7.1–7.6 (m, 10, C_6H_5).

Preparation of 2*H*-1-Benzopyrans (6) (Eq 1).—A mixture of 1 equiv of vinylphosphonium salt and 2 equiv of sodium salicyloxide[10] was weighed into a dry flask. Dry DMF was added, and the mixture was stirred and heated at reflux for 2 days. The reaction mixture was poured into water and extracted with ether and CH_2Cl_2. Both organic extracts were washed with dilute NaOH solution and water and then dried over $MgSO_4$. From the ether extract was obtained the 2*H*-1-benzopyran, phosphines, and phosphine oxides (Table II). The CH_2Cl_2 extracts provided phosphonium salts.

3-Methyl-2*H*-1-benzopyran had bp 64–65° (0.2 mm); ir (neat) ν 3020, 2950, 2900, 2810 (CH), 1570 (C=C), 1470, 1420 (CC), 1105 (COC), 835, 755 cm^{-1} (aromatic); nmr (CCl_4) δ 1.70 (dt, 3, J = 1.3, 1.3 Hz, CH_3), 4.57 (dq, 2, J = 1.2, 1.3 Hz, CH_2), 6.0 (qt, 1, J = 1.3, 1.2 Hz, vinyl), 6.5, 7.0 (m, 4, C_6H_4).

Reaction of Isopropenylphosphonium Salts with Sodium Salicyloxide. A. In DMF.—The reaction was run as previously described. When salt **2** was used, the phosphonium zwitterion **10** was isolated from the CH_2Cl_2 extraction by concentrating the

(16) D. Seyferth and J. Vogel, *J. Organometal. Chem.*, **6**, 205 (1966).

TABLE II

PREPARATION OF 2*H*-1-BENZOPYRANS (6) (EQ 1)

Salt (mol)	Sodium salicyloxide, mol	DMF, ml	Yield, % 6	Yield, % 7	6 Analysis Calcd	6 Analysis Found
1 (0.1)	0.2	125	54–58	55–72	ref 10	
2 (0.05)	0.10	150	30	29.5	C 82.71 H 6.93	C 82.52 H 6.77 (vpc)
3 (0.025)	0.05	75	35	40		

solvent, leaving a viscous oil. This oil was then slowly poured into 500 ml of anhydrous ether and the solid was filtered off, giving a 10% yield of **10**: mp 247–248°; ir (Nujol) 1570 (C=C), 1100 (*P*-phenyl), 1005 cm^{-1} (P salt); mass spectrum *m/e* 344, 303, 267, 226, 108, 77; nmr ($CDCl_3$) δ 2.17 (split d, 3, J = 13.5 Hz, CH_3), 5.91 (split d, 1, J = 22 Hz, isopropenyl vinyl cis to P), 6.74 (split d, 1, J = 46 Hz, isopropenyl (vinyl trans to P), 6.6–8.0 ppm (m, 16, vinyl and C_6H_5); uv max ($CHCl_3$) 246 nm (ϵ 70,801), 289 (17,000), 254 (8200). The zwitterion was then treated with HBr and formed the phosphonium bromide, mp 192–194°.

Anal. Calcd for $C_{23}H_{22}BrOP$: C, 64.92; H, 5.21. Found: C, 65.34; H, 5.26.

B. In HMPT.—The same procedure as A was followed. The only differences observed were in the yield of the 3-methyl-2*H*-1-benzopyran when the temperature was varied, and in the rate of development of the characteristic color change of the reaction mixture when the phosphorus ylide forms at the start of the reaction.[16] This color change occurs only after 30–40 min in DMF, but occurs after only 5 min in HMPT.

The yields of the 3 isomer were as follows: 80°, 14%; 160°, 30%; 200°, 0%.[17]

C. Fusion Method.—An intimate mixture of 1 equiv of either salt **2** or **3** and 2 equiv of sodium salicyloxide was placed in a dry flask equipped with a short path distilling head leading to a Dry Ice cooled receiver. Vacuum was applied to the system; the mixture was heated until fusion took place and distillation had ceased.

From salt **2**, fusion produced **6** (R′ = CH_3) (4%), **13** (11%), and diphenylmethylphosphine (12%).

From salt **3**, fusion resulted in the formation of **6** (R′ = CH_3) (9%), **13** (14%), and triphenylphosphine (15%).

Attempted Isomerization of 6 (R′ = CH_3) to 13.—A sample of redistilled **6** (R′ = CH_3), approximately 1.0 g, was heated in a flame-dried flask containing a small amount of sodium salicyloxide. The mixture was heated at 210° for 3 hr under nitrogen. A nmr spectrum of the mixture showed the presence of a small amount of some decomposition products, but no **13**. Further heating, followed by distillation, again showed no rearranged product by nmr or vpc.

Deuterium Exchange Studies.—Pure samples of both phosphonium halides **2** and **3** were placed into nmr tubes and dissolved in DMSO-d_6. An nmr spectrum was then taken of each (T' = 0) and ten integrations were run with the help of a Hewlett-Packard DC digital voltmeter, Model 405Br. A catalytic amount of potassium *tert*-butoxide was then added to each and another spectrum with ten integrations was run (T = 0). The nmr tubes were then placed in a sand bath at 160°. At various times, the nmr tubes were removed from the bath and additional spectra were run. With both salts, the phenyl protons were used as an internal standard for the integration. After 25 hr salt **3** showed a reduction of the methylene and methyl proton of 25 and 23%, respectively. Similarly the salt **2** showed a reduction of these protons of 20 and 17%, respectively.

Preparation of 2,5-Dihydrofurans (8) (Eq 2).—The procedure employed was essentially that of Schweizer and Liehr.[8] Pertinent data are reported in Table III.

2,2,3-Triphenyl-4-methyl-2,5-dihydrofuran had mp 149–150° (MeOH); ir (Nujol) 1605 (C=C), 1055 (COC), 760, 700 cm^{-1} (aromatic); nmr ($CDCl_3$) δ 1.78 (t, 3, J = 1.1 Hz, CH_3), 4.87 (q, 2, J = 1.1 Hz, CH_2), 6.7–7.4 (m, 15, C_6H_5); uv $\lambda_{max}^{CHCl_3}$ 263 mμ (ϵ 6820).

Preparation of 3*H*-Pyrrolizines (9) (eq 3).—Following the procedure of Schweizer and Light,[9] 3*H*-pyrrolizines **9** were prepared as indicated in Table IV.

(17) At this temperature, the HMPT decomposed and left an unseparable tar.

TABLE III

PREPARATION OF 2,5-DIHYDROFURANS (8) (EQ 2)

Salt (mol)	Yield, % 8	Yield, % 7	8 Analysis Calcd	8 Analysis Found
1 (0.04)	71		ref 8	
2 (0.03)	36	39	C 88.39 H 6.45	C 88.36 H 6.56
3 (0.03)	47	52		

TABLE IV

PREPARATION OF 3*H*-PYRROLIZINES 9 (EQ 3)

Salt (mol)	Sodium pyrrolaldehyde, mol	Yield, % 9	Yield, % 7	9 Analysis Calcd	9 Analysis Found
1 (0.215)	0.183	87		ref 9	
2 (0.075)	0.075	25	27	C 80.61 H 7.61	C 80.90 H 7.64 (vpc)
3 (0.075)	0.075	67	69		

3-Methyl-3*H*-pyrrolizine[18] had bp 66–67° (0.3 mm); mp 29–30°; ir (neat) 3020, 2860, 2810 (CH), 1605 (C=C), 940, 700 cm^{-1} (pyrrole ring); nmr (CCl_4) δ 1.95 (d, 3, J = 1.0 Hz, CH_3), 4.18 (d, 2, J = 0.8 Hz, CH_2), 5.50 (d, 1, J = 3.0 Hz, 6-H), 5.92 (t, 1, J = 3.0 Hz, 5-H), 6.0 (d, 1, J = 3.0 Hz, 4-H), 6.40 (dd, J = 1.0, 0.8 Hz, 1-H); uv λ_{max}^{EtOH} 219 mμ (ϵ 3660), 295 (7250).

Reaction of 1-Phenylvinyltriphenylphosphonium Bromide (4) with Sodium Salicyloxide. A. In DMF Solvent.—Into a dry flask equipped with mechanical stirrer and reflux condenser was placed 13.4 g (0.03 mol) of salt **4**, 8.65 g (0.06 mol) of sodium salicyloxide, and 125 ml of dry DMF. The mixture was stirred at room temperature for 1 day and then heated at 100° for 1 day. After cooling, the reaction mixture was worked up by pouring into water and extracting with ether and CH_2Cl_2. The extracts were dried over $MgSO_4$.

The ether extract provided, by column chromatography, 3.62 g (57.5%) yield of olefin **19** and 3.4 g (41% yield) of triphenylphosphine oxide (**7a**). The CH_2Cl_2 extract was poured into ether to yield 1.5 g (11%), of salt **20**.

B. Fusion Method.—A blended mixture of 13.4 g (0.03 mol) of salt **4** and 7.2 g (0.05 mol) of sodium salicyloxide was placed in a 250-ml one-necked flask equipped with magnetic stirrer and short-path distillation head leading to a Dry Ice–acetone cooled receiver. The flask was immersed in an oil bath and heating was begun, until fusion occurred (160–165°). Vacuum was applied and volatiles were distilled over a period of 1 hr. Vpc analysis of the volatiles showed the presence of salicylaldehyde (3.4 g for a 56% recovery) and styrene (0.4 g, 14% yield).

The residue from the fusion was taken up in DMF, poured into water, and extracted with ether. The ether extract was washed with water and dried ($MgSO_4$), and then chromatographed on silica gel to furnish, in order of elution (solvent), triphenylphosphine (hexane–15% benzene), 23%; 3-phenyl-2*H*-benzopyran (**6**) (R′ = C_6H_5) (hexane–20% benzene), 8%; **19** (benzene), 21%; triphenylphosphine oxide (**7a**) (EtOAc), 28%.

Compound 19 had mp 79–80° (MeOH); ir (KBr) 3400 (OH), 1600 (C=C), 1490, 1450 (CC), 760, 690 cm^{-1} (aromatic); nmr ($CDCl_3$) δ 2.07 (d, 3, J = 1.2 Hz, CH_3), 5.33 (br s, 1, OH), 6.74 (q, 1, J = 1.2 Hz, vinyl), 6.8–7.6 (m, 9, C_6H_5).

Anal. Calcd: C, 85.70; H, 6.71. Found: C, 85.93; H, 6.56.

Reaction of Salt 20 with Sodium Salicyloxide.—Into a flame-dried 250-ml flask equipped with reflux condenser and mechanical

(18) Material darkened very rapidly.

stirrer was placed 22.4 g (0.05 mol) of salt **20**, 14.4 g (0.10 mol) of sodium salicyloxide, and 150 ml of dry DMF, and the mixture was stirred at reflux for 2 days. It was worked up by pouring into water, acidifying, and extracting with ether. The dry ($MgSO_4$) organic extract was short path distilled; volatiles showed only solvents and salicylaldehyde. The distillation residue was column chromatographed to furnish 6.0 g (50% yield) of **19** and 9.3 g (67%) of triphenylphosphine oxide (**7a**).

Reaction of Salt 4 with the Sodium Salt of Pyrrolaldehyde.—To a flask containing 150 ml of dry ether and 3.16 g (0.075 mol) of 57% sodium hydride dispersion (Alfa) was added 7.15 g (0.075 mol) of pyrrolaldehyde. When hydrogen evolution had ceased (*ca.* 2 hr), 33.4 g (0.075 mol) of salt **4** was added and the mixture was refluxed for 10 hr. DMF (50 ml) was added, and the red-brown mixture was refluxed for an additional 12 hr. After cooling, the reaction mixture was poured into dilute aqueous acid and filtered, providing 18.2 g of purple solid **21**. The filtrate was extracted with ether and dried ($MgSO_4$). Evaporation of the ether left a mixture of **7a** and **21**, from which 12.5 g (60% yield) of triphenylphosphine oxide (**7a**) could be isolated by digestion with hot hexane. Compound **21** was dissolved in $CHCl_3$ and reprecipitated into ether for analysis, mp >300°.

Anal. Calcd for $C_{148}H_{126}BrN_{10}OP$, $n = 9$: C, 81.87; H, 5.95; N, 6.45. Found: C, 81.46; H, 6.07; N, 6.72.

Polymer **21** had ir (Nujol) 1600 (C=C), 920 (pyrrole), 760, 700 cm^{-1} (aromatic and pyrrole ring); nmr ($CDCl_3$) showed broad adsorptions at δ 1.8–4.2, 4.5–5.0, 5.8–6.3, 6.8–7.5; uv $\lambda_{max}^{CHCl_3}$ 242, 280, 350, 500 mμ; mol wt (osmometry) calcd 2171, found 2180.

Reaction of 4 with the Sodium Salt of Phenylbenzoin.—The sodium salt of phenylbenzoin was prepared by treating 8.65 g (0.03 mol) of phenylbenzoin dissolved in 100 ml of dry ether with 1.44 g (0.03 mol) of a 50% dispersion of sodium hydride. After stirring for 15 min, 13.4 g (0.03 mol) of salt **4**, dissolved in 100 ml of DMF, was added and the resultant mixture was stirred at ambient temperature for 2 days, then heated for 6 hr at 100°. The mixture was poured into water and extracted with ether. Chromatography of the dry ($MgSO_4$) ether extract on silica gel yielded (in order of elution) **22**, 4.1 g (47.5%); **8d**, 1.7 g (15%); **7a**, 4.4 g (52.8%).

2,2,3,4-Tetraphenyl-2,5-dihydrofuran (8d) had mp 109–110° (MeOH); ir (KBr) 1650, 1590 (C=C), 1480, 1330 (CC), 1230 (COC), 790, 770, 750, 690 cm^{-1} (aromatic); nmr ($CDCl_3$) δ 3.85 (s, 2, CH_2), 6.8–7.9 (m, 20, C_6H_5); uv $\lambda_{max}^{CHCl_3}$ 242 mμ (ϵ 10,000), 312 (9400).

Anal. Calcd: C, 89.78; H, 5.92. Found: C, 90.19; H, 6.11.

Rearrangement of the Sodium Salt of Phenylbenzoin.—A 5.76-g (0.02 mol) sample of phenylbenzoin in 100 ml of dry ether was treated with 0.96 g (0.02 mol) of a 50% dispersion of sodium hydride. When hydrogen evolution had ceased, 75 ml of dry DMF was added, and the mixture was heated at reflux for 2 hr, then stirred at room temperature for 24 hr. The mixture was poured into water and dilute acid was added until neutrality was reached. Extraction with ether resulted in the isolation of 4.7 g (81% yield) of benzhydryl benzoate (**22**), identical with an authentic sample. Hydrolysis in dilute acid furnished benzoic acid and benzhydrol (70% based on phenylbenzoin), identified by comparison of ir and nmr spectra and mixture melting point with authentic samples.

Registry No.—**2**, 30670-21-4; **3**, 7301-95-3; **4**, 30537-11-2; (*Z*)-**5b**, 38555-27-0; (*E*)-**5b**, 38555-28-1; **5c**, 38555-29-2; **6** (R′ = Me), 38555-30-5; **8** (R′ = Me), 38555-31-6; **8d**, 38555-32-7; **9** (R′ = Me), 38555-33-8; **10**, 38555-34-9; **10** bromide derivative, 33999-09-6; **19**, 38555-36-1; **20**, 30537-09-8; **21**, 38555-38-3; 2-bromopropene, 557-93-7.

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The Preparation, Thermolysis, and Photolysis of Phenylmaleoyl Peroxide

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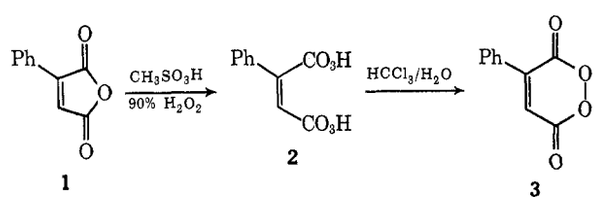
The decomposition of the cyclic monomeric peroxide derived from phenylmaleic acid generates carbon dioxide, phenylacetylene, and a carbonyl-containing polymeric substance. The yields of carbon dioxide and phenylacetylene are highest in a sensitized photolytic decomposition, and lowest in a thermolytic decomposition. These results are interpreted in terms of the nature of the likely intermediates in the decomposition sequence.

The chemistry of cyclic acyl peroxides has attracted the interest of organic chemists sporadically for many years. Phthaloyl peroxide was the first cyclic acyl peroxide to be investigated thoroughly.[1-5] More recently, cyclic malonyl peroxides have been the subject of several studies.[6,7] Cyclic acyl peroxides have also been implicated in the decomposition of dimeric and trimeric peroxides of cycloalkanones.[8] Cyclic diphenoyl peroxide has been prepared, but its chemistry has not been extensively explored.[9]

In this report, we wish to describe the synthesis, thermolysis and photolysis of phenylmaleoyl peroxide, **3**. This compound is the first monomeric cyclic maleoyl peroxide to be reported.

Results and Discussion

Synthesis.—Phenylmaleoyl peroxide (**3**) was generated in 38% yield when a heterogeneous mixture consisting of diperoxyphenylmaleic acid, **2**, chloroform, and water was agitated vigorously. The success of this



procedure depends upon the rapid cyclization of **2** to **3** in the polar aqueous phase, following which the less polar **3** is rapidly extracted into the inert chloroform phase, thereby preventing further hydrolysis to the monoperoxy acid.

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