stirred for 1 hr. The reaction mixture was cooled in an ice bath and 3 ml of 20% sodium hydroxide solution was carefully added. Stirring was continued for another hour at room temperature and the white precipitate was removed by filtration. The filtrate was dried with magnesium sulfate and the ether was removed. Chromatography of the residue on a thin layer plate (1.5 mm silica gel eluted with 10% ether in benzene) gave 0.119 g of benzil (yield 37%), nmr ($CDCl_3$) τ 1.9–2.8 (only aromatic hydrogens), mp 94–95° (lit.[12] 94°), and 0.177 g of 2,3-diphenyl-1,4-diethyl-1,4-diaza-1,3-butadiene (**8**): yield 44%; mp 37–39°; nmr ($CDCl_3$) τ 2.1–2.35 and 2.55–2.85 (m, 10 H), 3.61 (q, 4 H), and 8.75 (t, 6 H); ir (KBr) 1630, 1580, 1450, 775, and 700 cm^{-1}. A small amount of 2,3-diphenylpyrazine (0.022 g) is also produced.

1,4-Diethyl-2,3-diphenyl-1,4-diaza-1,3-butadiene (8).—The method of imine synthesis by Weingarten[9] was modified as described below.

Benzil (4.2 g, 0.02 mol) was placed in a 250-ml flask and mixed with a solution of 100 ml of ether containing 15 ml of anhydrous ethylamine at −10°. A solution of 20 ml of pentane containing 3.6 ml of $TiCl_4$ (6.2 g, 0.0326 mol) was then added over 45 min. After all of the $TiCl_4$ was added, the material was allowed to warm up to room temperature over 1 hr, then heated to reflux for 0.5 hr. The solvent was removed and 4.0 g of **8** was obtained (76% yield). The analytical sample was purified by recrystallization from ether: mp 37–39°; nmr ($CDCl_3$) τ 2.1–2.35 and 2.55–2.85 (m, 10 H), 3.61 (q, 4 H), and 8.75 (t, 6 H); ir (KBr) 1630, 1580, 1450, 775, and 700 cm^{-1}.

Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.77; H, 7.63; N, 10.60. Found: C, 81.61; H, 7.77; N, 10.62.

Reduction of 6a.—To 0.3 g of lithium aluminum hydride in 21 ml of anhydrous ether was slowly added 0.48 g (0.0015 mol) of 2,3-diphenyl-1,4-diacetyl-1,4,5,6-tetrahydropyrazine (**6a**) and the mixture was stirred for 1 hr. The reaction mixture was cooled in an ice bath and 3 ml of 20% sodium hydroxide was carefully added. Stirring was continued for another hour at room temperature and the white precipitate was removed by filtration. The filtrate was dried with magnesium sulfate and the ether was removed. The residue was crystallized on standing and recrystallized from ethyl acetate: mp 100–102°; 0.43 g (98% yield); nmr ($CDCl_3$) τ 2.65–3.06 (m, 10 H), 7.03 (s, 4 H), 7.33 (q, 4 H), and 9.0 (t, 6 H); ir (KBr) 2970, 2850, 1590, 1445, 1380, 1128, 755, and 700 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.14; H, 8.27; N, 9.58. Found: C, 82.28; H, 8.43.

Registry No.—**5a**, 32174-84-8; **6a**, 32174-85-9; **6b**, 32174-86-0; **7**, 1588-89-2; **8**, 32174-88-2; **10**, 32174-89-3.

Acknowledgment.—We are indebted to the Research Foundation of the State University of New York, The Research Corporation, and the National Science Foundation (GP-20099) for financial support of this work.

(12) "Handbook of Chemistry and Physics," 40th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1958–1959, p 844.

Reactions of Phosphorus Compounds. 28. Mechanism of the Formation of 2-Methyl-2*H*-1-benzopyran by the Reaction of 3-(*o*-Formylphenoxy)propylphosphonium Salts in Alcoholic Alkoxide

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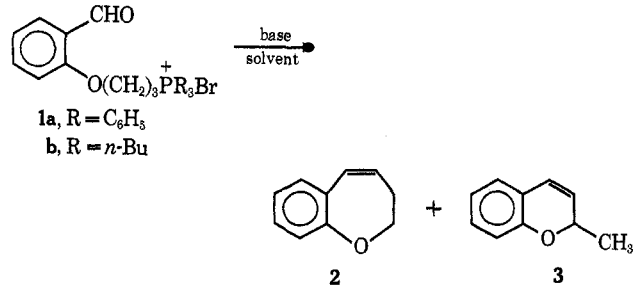
A mechanism is proposed for the formation of 2-methyl-2*H*-1-benzopyran (**3**) by the reaction of 3-(*o*-formylphenoxy)propylphosphonium salts (**1**) in alcoholic alkoxide. 2,3-Dihydro-1-benzoxepin-4-tri-*n*-butylphosphonium bromide (**17b**) and 2-methyl-2*H*,1-benzopyran-3-triphenylphosphonium bromide (**15a**) were prepared using catalytic amounts of base in alcoholic solvent and their reactions were observed. The reaction of *o*-vinyloxybenzaldehyde (**10**) with methylene triphenylphosphorane (**11**) yielded 1-phenyl-2-(*o*-vinyloxyphenyl)ethyldiphenylphosphine oxide (**13**).

In a previous paper[1] we have discussed and discarded a number of possible mechanisms for the unexpected formation of 2-methyl-2*H*-1-benzopyran (**3**) from 3-(*o*-formylphenoxy)propyltriphenylphosphonium bromide (**1a**) under normal Wittig[2] reaction conditions. An alternate mechanism (Scheme I) has recently been proposed.[3] It is supported by (a) the data[1] which indicate that the rearrangement of **1** to **3** is favored in more highly protonic solvents, *i.e.*, inhibiting decomposition of betaine **5** to the expected benzdihydrooxepin (**2**) by protonation of **5** to **6**; (b) the β elimination (**6** → **7**) which would also be favored by a more electrophilic phosphonium species, *i.e.*, **1a** *vs.* **1b** (see Table I).



(1) E. E. Schweizer, C. J. Berninger, D. M. Crouse, R. A. Davis, and R. S. Logothetis, *J. Org. Chem.*, **34**, 207 (1969); E. E. Schweizer and R. Schepers, *Tetrahedron Lett.*, 979 (1963).

(2) A. Maercker, *Org. Reactions*, **14**, 272 (1965).

(3) Proposed by Professor H. T. Bestmann at the Chemical Societies International Symposium on Ylides, Leicester, England, July 14, 1970. Although Professor Bestmann did not really believe that this would be the right mechanism, we felt compelled to find supporting evidence or disprove it.

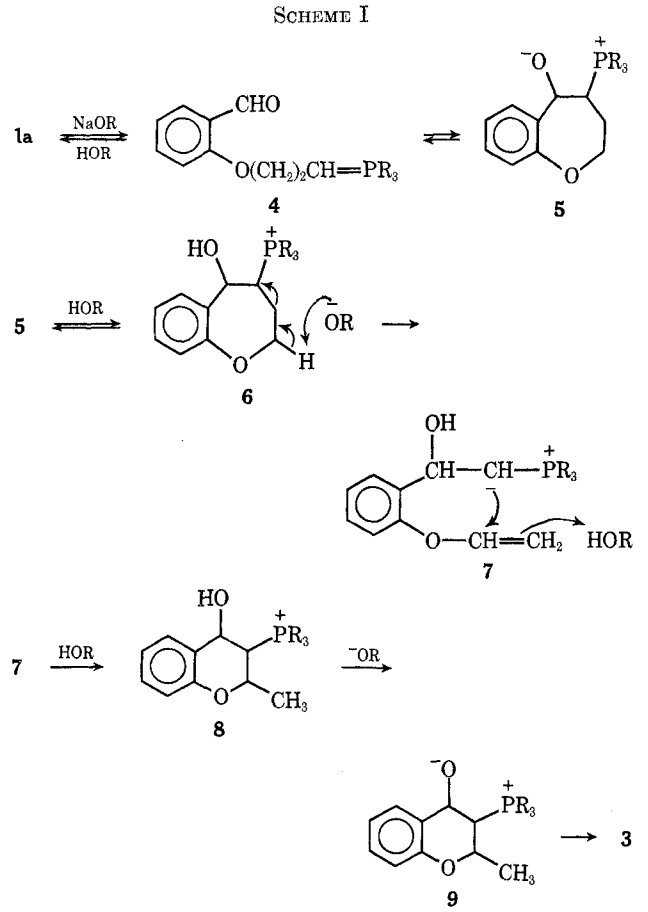
TABLE I

SOLVENT AND PHOSPHORUS SUBSTITUENT EFFECTS ON RATIOS OF 2 AND 3 FROM SALTS 1[a]

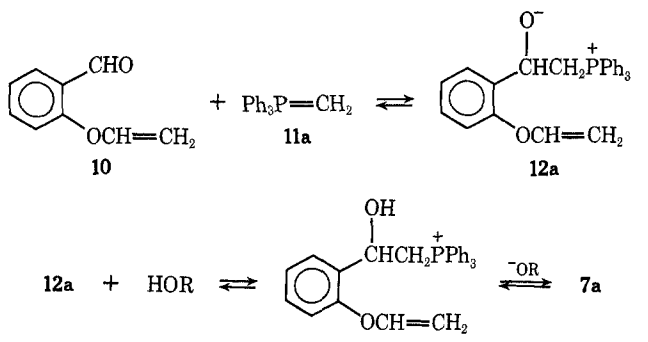
R in salt 1	Solvent	Overall yield of 2 + 3, %	Ratio of 2:3
Ph	DMF	70	100:0
n-Bu	DMF	43	48:52
Ph	MeOH	65	0:100
Ph	MeOH[b]	88	0:100
n-Bu	MeOH[c]	0	
n-Bu	MeOH[b,c]	0	
n-Bu	MeOH–DMF 20:80	10	1:99
n-Bu	MeOH–DMF 10:90	31	4:96
n-Bu	DMF[d]	50	78:22

[a] At 64° for 24 hr under N_2 with 1.0 equiv of NaOMe except as noted. [b] As in *a* except 4.44 equiv of NaOMe. [c] Only starting salt 1 and **17b** recovered on work-up after HBr neutralization. [d] Base used is NaH.

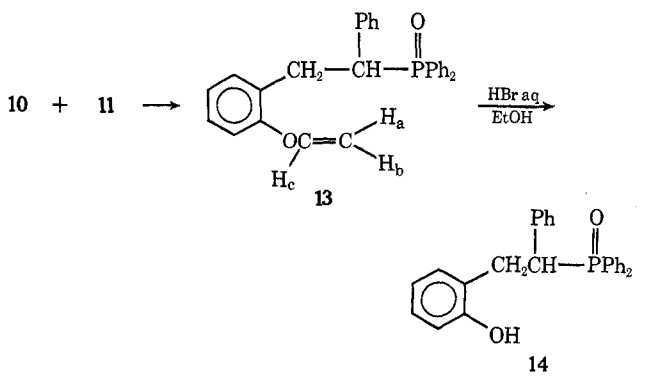
SCHEME I



If the mechanism in Scheme I is feasible, one would expect to be able to produce **3** from *o*-vinyloxybenzaldehyde (**10**) and methylene triphenylphosphorane (**11**), since the proposed intermediate **7** would be in equilibrium with the betaine **12** which would be formed from the reaction of **10** and **11**.



The reaction of **10** and **11** was allowed to take place and the product was shown to contain no trace of 2-



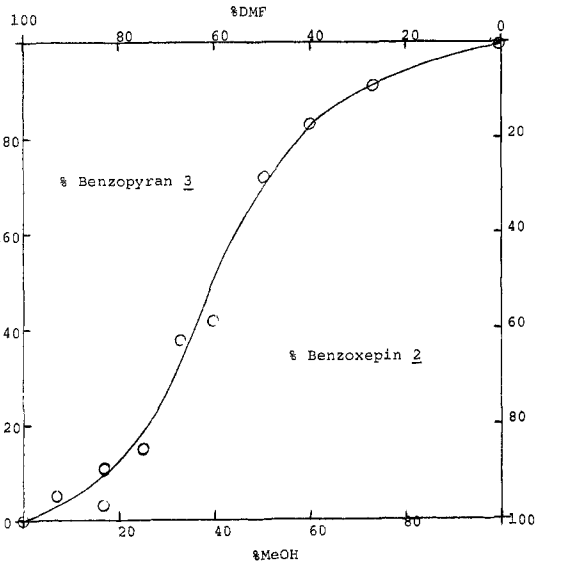


Figure 1.—Phosphonium salt (**1a**) decomposition in mixed solvents.

methyl-2*H*-1-benzopyran (**3**) (by vpc) and only 1-phenyl-2-(*o*-vinyloxyphenyl)ethyldiphenylphosphine oxide (**13**) was found in 70% yield.

The formation of the oxide **13** is consistent with some alcoholic alkoxide reactions of phosphonium salts with aldehydes;[4,5] however, it is not consistent with the mechanism shown in Scheme I. The structure of **13** was also supported by obtaining and characterizing **14** as its hydrolysis product.

It has been shown that the reaction of salt **1a** to give **3** is highly solvent dependent[1] and that more acidic solvents enhance the formation of the rearranged product **3**. The results obtained by using a variable ratio of only two solvents (DMF–MeOH) with the triphenylphosphonium salt (**1a**), sodium methoxide as a base, are shown in Figure 1.

The tri-*n*-butylphosphonium salt (**1b**) (prepared in the same manner as **1a**[1]) was significantly more sensitive to the effects of MeOH in DMF than the salt **1a**. If pure DMF was used as solvent with NaOMe as the base (thus 1 equiv of MeOH would be present per 1 equiv of ylide formed) the ratio of **2** to **3** was 48:52 (Table I). Elimination of all of the MeOH by employing NaH as a base gave mainly the expected 2,3-dihydrobenzoxepin (**2**). Using pure MeOH (no DMF) as solvent, none of the cyclized products **2** or **3** were observed, and on work-up only the starting material **1b** and a vinyl phosphonium salt (**17b**) were recovered. Thus a reduction of the electrophilic nature of the phosphonium moiety both reduced the overall yield of the reaction and increased the ratio of the 2-methyl-2*H*-1-benzopyran (**3**) to **2** formed.

The search for a vinyl salt as a possible intermediate in the reaction of **1** was pursued by lowering the concentration of the base used (Table II). Isolation of large quantities of vinyl salt **17b** (90% yield) and **15a** (76%) were accomplished by using 0.25 equiv or less of base per 1 equiv of the corresponding salt **1**.

When salt **15a** was treated with 1 equiv of NaOH in anhydrous MeOH, 2-methyl-2*H*-1-benzopyran (**3**) was

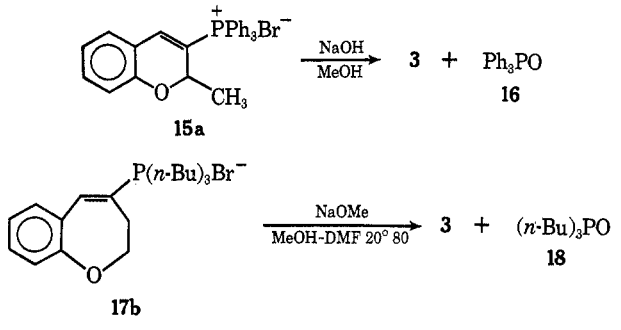
(4) E. M. Richards and J. C. Tebby, *Chem. Commun.*, 494 (1969); S. Trippett and B. J. Walker, *J. Chem. Soc. C*, 887 (1966).
(5) E. E. Schweizer, unpublished results.

TABLE II

REACTION OF 3(*o*-FORMYLPHENOXY)PROPYLPHOSPHONIUM SALTS (1) WITH SODIUM METHOXIDE

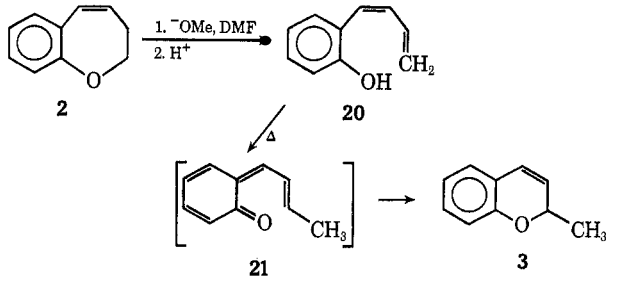
R in 1	Solvent	Ratio of NaOMe:1	Yield of 2 + 3, %	Ratio of 2:3	Yield of 15a, %[a]	Ratio of 1b:17b
Ph	MeOH	4.0	88[a]	*b*		
Ph	MeOH	1.0	65[a]	*b*		
Ph	MeOH	0.40	31[a]	*b*	53	
Ph	MeOH	0.23	15[c]	8:92[d]	77	
Ph	MeOH	0.10	9[c]	44:56[d]	76	
n-Bu	MeOH	1.0				83:17[c]
n-Bu	MeOH	0.8				83:17[c]
n-Bu	MeOH	0.62				81:19[c]
n-Bu	MeOH	0.39				94:6[c]
n-Bu	MeOH–DMF 20:80	1.1	9[d]	4:96[d]		0:87[a]
n-Bu	MeOH–DMF 20:80	0.25	4[d]	64:36[d]		0:90[a]

[a] Isolated and purified. [b] 100% of 3. [c] Yields based on nmr; accuracy ±2% for salts 1b:17b. [d] Ratio determined by vpc.

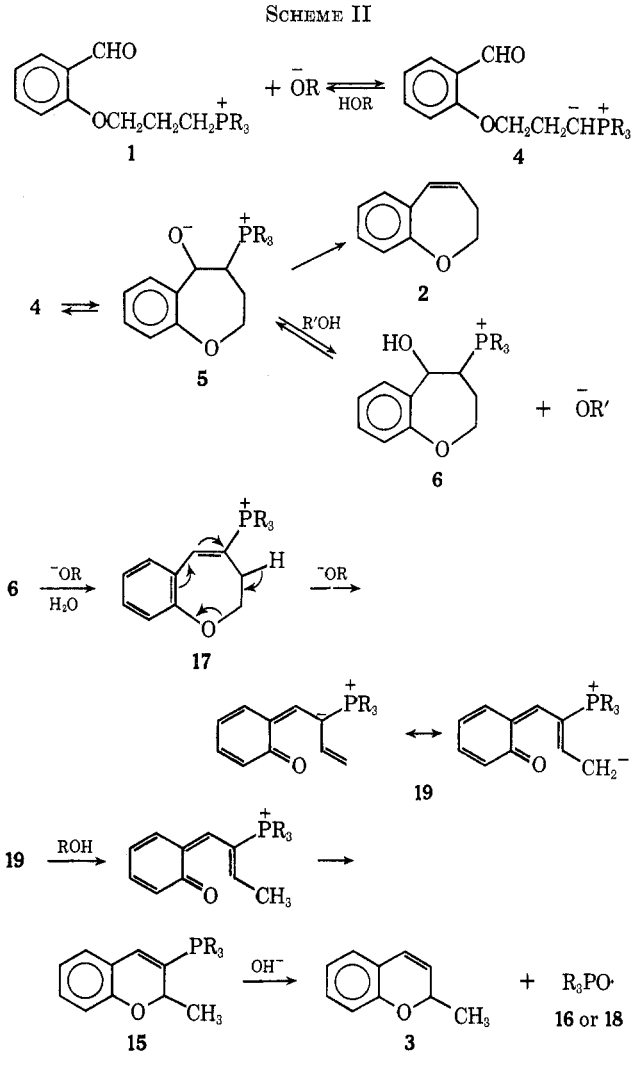


isolated in 82% yield and triphenylphosphine oxide **16** was isolated in 92% yield, whereas aqueous NaOH gave **3** and **16** in 88 and 97% yields, respectively. These data compel us to write the mechanism shown in Scheme II for the formation of **3** from **1**.

The postulation is that the initial reaction is that of a phosphonium salt under basic conditions giving an ylide (**4**) which forms the normal "Wittig" betaine (**5**). The expected collapse of the betaine (**5**) yields the 2,3-dihydrobenzoxepin-1 (**2**). However, the more acidic the solvent system becomes,[1] the more the alkoxide in **5** is protonated to afford **6**. The hydroxyphosphonium salt is readily dehydrated to give the conjugated vinylphosphonium salt (**17**).[4,5] The lower electrophilicity of the tri-*n*-butylphosphonio group in salt **1b** allows us to stop the reaction at the *non*ring-contracted salt **17b** (Table II), whereas in the reaction of **1a** the β-elimination step that initiates the sequence converting **17a** to **15a** must be faster than the conversion of **6a** to **17a**, since we have been unable to obtain **17a**. Even without the assistance of the phosphonium moiety, 2,3-dihydrobenzoxepin-1 (**2**) has been found to be readily converted to **20**.[6] The conversion of **20** to **3** occurs[6,7]



SCHEME II



via an allylidenecyclohexadienone intermediate **21** as shown in the conversion of **17** to **15** *via* **19**.

The aqueous (or methanolic) hydrolysis of **17b** with NaOH produces 2-methyl-2*H*-1-benzopyran (**3**) and salicylaldehyde, but never any of the expected oxepin **2** (Table II). The lack of **2** shows that the ring contraction of **17b** to **15b** must be considerably faster than the hydrolysis of **17b** to **2**. It also indicates that, although the *n*-butyl groups (instead of phenyl) on the phosphorus lower the electrophilicity of phosphorus so that hydroxide attack is slower at that site, the predominant

(6) E. E. Schweizer, D. M. Crouse, and D. L. Dalrymple, *Chem. Commun.*, 354 (1969).

(7) R. Hug, H. J. Hansen, and H. Schmid, *Chimia*, **23**, 108 (1969).

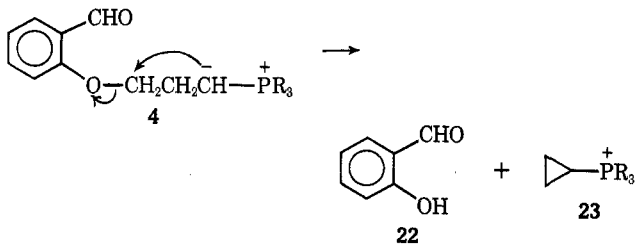
TABLE III

AQUEOUS ALKALINE HYDROLYSIS OF PHOSPHONIUM SALTS

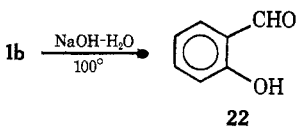
Salt	Ratio (equiv) of NaOH:salt	Solvent	Temp, °C	Time, hr	Products (yield, %)[a]
15a	1	MeOH	64	24	**3** (82) + **16** (92)
15a	2	H_2O	100	4	**3** (88) + **16** (97)
17b	1	MeOH	64	24	**3** (5) + **17b** (75)
17b	2	H_2O	100	4	**3** (trace) + **22** (26) + **17b** (64)
17b	2	H_2O	100	18	**3** (4) + **22** (40) + **17b** (37)
1b	2	H_2O	100	4	**22** (8) + **18** (5) + **1b** (68)
1b	2	H_2O	100	18	**22** (16) + **18** (7) + **1b** (65)
1b	2	H_2O	100	45	**22** (61) + **18** (24) + **1b** (25) + **3** (9)

[a] Yields based on nmr of isolated materials.

reaction of **17b** with hydroxide is undoubtedly a reversal of the pathway back to **4** which then gives salicylaldehyde, probably as shown below (Table III). Previous



work from this group has shown that this is a common reaction.[8] We have also shown that treatment of **1b** with aqueous NaOH gives salicylaldehyde as the main identifiable product (Table III).



Thus a mechanism has been proposed, which is supported by all of the data, for the conversion of 3-(*o*-formylphenoxy)propylphosphonium salt (**1**) to 2-methyl-2*H*-1-benzopyran (**3**). Also of considerable interest is the first isolation of vinylphosphonium salts in a reaction of a phosphorane with a carbonyl reagent, thus showing a pathway (in protonic solvents) which is not that of a normal Wittig[2] reaction to give olefins.[4]

Experimental Section

Preparation of *o*-Formylphenyl Vinyl Ether (10).—A mixture of 22.9 g (0.1 mol) of *o*-formylphenyl β-bromoethyl ether and 6.7 g (0.12 mol) of KOH was refluxed for 24 hr in 40 ml of ethanol. After ethanol was removed, the residue was distilled to give 4.25 g (28.7%) of **10**: bp 59° (0.3 mm); ir ν 1680 (C=O) and 1640 cm^{-1} (-OCH=CH_2); nmr (CCl_4) δ 4.5 (dd, 1 H, J_{bc} = 6.3 Hz, H_b), 4.75 (dd, 1 H, J_{ac} = 13.7 Hz, H_a), 6.65 (dd, 1 H, H_c); 6.85–7.87 (m, 4 H, phenyl protons), 10.30 (s, 1 H, aldehyde proton).

Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 73.05; H, 5.33.

Reaction of 10 with Triphenylmethylenephosphorane (11).—Sodium metal (0.58 g, 0.025 g-atom) was added to a refluxing solution of 8.93 g (0.025 mol) of methyltriphenylphosphonium bromide dissolved in 100 ml of anhydrous MeOH. To this was added dropwise 3.70 g (0.025 mol) of vinyl ether **10** dissolved in 50 ml of MeOH. The reaction mixture was allowed to reflux for 24 hr under dry N_2. After MeOH was removed, the residue was poured into 300 ml of H_2O and extracted with benzene. The benzene extract was washed with water, dried over $CaSO_4$, and evaporated to give 7.50 g (70%) of **13**: ir (KBr) ν 1640 (C=C), 1435 (P-C), 1220 (Ph-O), 1180 cm^{-1} (P=O); nmr ($CDCl_3$) δ 3.13–3.58 (m, 2 H, $-CH_2CPhHPPh_2$), 3.75–4.17 (m, 1 H, $-CH_2CPhHPPh_2$), 4.41 (dd, 1 H, J_{bc} = 5.4 Hz, H_b), 4.67 (dd, 1 H, J_{ac} = 13.4 Hz, H_a), 6.50 (dd, 1 H, H_c), 6.63–8.30 (m, 19 H, phenyl protons); mass spectrum (75 eV) *m/e* 424.

Anal. Calcd for $C_{28}H_{25}O_2P$: C, 79.23; H, 5.94; P, 7.29. Found: C, 79.47; H, 5.69; P, 7.09.

Hydrolysis of 13.—Hydrobromic acid (48%), 1 ml, was added to a solution of **13** (1.06 g, 2.5 mmol) in 35 ml of ethanol. The solution was refluxed for 22 hr. After the ethanol was removed by distillation, the residue was dissolved in 100 ml of methylene chloride. The methylene chloride extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to give 0.90 g (91%) of product **14** as white crystals. The analytical sample was prepared by recrystallization from benzene–alcohol to give white crystals: mp 213–214°; ir (KBr) ν 3000 cm^{-1} (OH); nmr (CD_3SOCD_3) δ 2.90–3.40 (m, 3 H, OH and methylene, one D_2O exchangeable proton), 4.08–4.62 (m, 1 H, methine), 6.25–8.35 (m, 19 H, phenyl).

Anal. Calcd for $C_{26}H_{23}O_2P$: C, 78.38; H, 5.82; P, 7.78. Found: C, 78.62; H, 5.69; P, 7.66.

Standard Reaction Procedure (for Figure 1).—Into a 250-ml, flame-dried, three-necked flask fitted with reflux condenser, mechanical stirrer (sometimes a magnetic stirrer), and glass stopper and containing 4.1 g (0.0083 mol) of triphenylphosphonium salt **1a** in 150 ml of dried solvent was added 0.5 g (0.0091 mol) of NaOMe. The reaction mixture was heated at 64° for 24 hr under nitrogen, then poured into 300 ml of distilled water and extracted four times with ether. The combined ether extracts (150 ml) were washed two times with water, dried ($MgSO_4$), filtered, and concentrated at room temperature on a rotary evaporator to give an oil. Glc of the oil yielded the values for Figure 1.

3-(*o*-Formylphenoxy)propyltri-*n*-butylphosphonium Bromide (1b).—Tri-*n*-butylphosphine (110 g, 0.36 mol) was dissolved in 600 ml of acetonitrile. While mechanically stirring under nitrogen, 88 g (0.36 mol) of 3-(*o*-formylphenoxy)propyl bromide was added dropwise (20 min). The yellow solution was refluxed for 24 hr. The solvent was removed under aspirator vacuum. After cooling, *ca.* 500 ml of anhydrous ether was added with fast stirring. In 5 min the semiliquid crystallized, causing the ether to reflux. After decanting the ether and adding 500 ml of fresh anhydrous ether, the salt was stirred overnight. Filtering and recrystallizing from methylene chloride–ethyl acetate gave 151 g (78%) of **1b**: mp 107–108°; ir (Nujol) 1680 (C=O), 1240 cm^{-1} (C-O-C); nmr ($CDCl_3$) δ 0.97 (t, 9, $-CH_3$), 1.2–1.9 (broad, 12), 2.1–3.1 (broad, 10), 4.30 (t, 2, $-OCH_2-$), 6.8–7.8 (m, 4, aromatic), 10.43 ppm (s, 1, -CHO).

Anal. Calcd for $C_{22}H_{38}BrO_2P$: C, 59.32; H, 8.59; Br, 17.71. Found: C, 59.48; H, 8.74; Br, 17.65.

General Procedure for the Reaction of 3-(*o*-Formylphenoxy)-propylphosphonium Salt (1) with NaOMe (Data for Table II).—To a solution of 0.432 g (8 mmol) of sodium methoxide in 100 ml of dried MeOH was added 3.60 g (8 mmol) of phosphonium salt **1b**. The reaction was allowed to stir at the MeOH refluxing temperature for 24 hr under dry N_2. After the reaction mixture was cooled to room temperature, it was neutralized with hydrobromic acid. The alcoholic solution was poured into 350 ml of H_2O and extracted with ether (four 150-ml portions) and CH_2Cl_2 (four 150-ml portions), respectively. The ether and the methylene chloride extractions were washed with water and dried over $CaSO_4$. No product was detected in the ether extraction.

(8) E. E. Schweizer, C. J. Berninger, and J. G. Thompson, *J. Org. Chem.*, **33**, 336 (1968); E. E. Schweizer and J. G. Thompson, *Chem. Commun.*, 666 (1966).

The methylene chloride extraction was concentrated until 50 ml of solvent remained.

The concentrated solution was added to 1 l. of anhydrous ether to give 3.0 g of a white precipitate. The precipitate (80% yield) was identified as a mixture of the starting material **1b** (83%) and the contracted product **17b** (17%) by nmr. Data was entered in Table II.

This technique was also used to obtain salt **15a**, with the yield and ratio of **2** and **3** coming from examination of the ether extract.

Reaction of 3-(*o*-Formylphenoxy)propyltributylphosphonium Bromide (1b) with NaOMe in MeOH–DMF.—Sodium metal (0.10 g, 4.35 g-atoms) was placed into 40 ml of anhydrous MeOH. After the evolution of hydrogen gas stopped, 160 ml of anhydrous DMF was added to the NaOMe solution. Then 8.20 g (18.5 mmol) of phosphonium salt **1b** was added to the NaOMe solution in MeOH–DMF. The reaction was allowed to stir at 64° for 24 hr under dry Na. The work-up followed was that used in the general procedure for the reaction of phosphonium salt with NaOMe in MeOH. Vinylphosphonium salt **17b** (7.10 g, 90%) and 0.25 g of a mixture of benzopyran **3** (1.44%), benzoxepine **2** (2.56%), and tributylphosphine oxide (4%) were obtained. All compounds were identified by comparison with authentic samples.

2,3-Dihydro-1-benzoxepin-4-tri-*n*-butylphosphonium Bromide (17b).—The salt from experiment 10 in Table II was recrystallized from methylene chloride–ethyl acetate, giving an analytically pure sample: mp 157–158°; ir (KBr) 1220 (C–O–C) and 1130 cm^{-1} (C–P); nmr ($CDCl_3$) δ 1.00 (t, 9, $-CH_3$), 1.23–2.10 (broad, 12), 2.35–3.16 (broad, 8), 5.52 (t, 2, J_{HH} = 6 Hz), 6.78–7.72 (m, 4, aromatic), 8.10 ppm (d, 1, J_{PH} = 18 Hz, vinyl); mass spectrum (70 eV) *m/e* 347.

Anal. Calcd for $C_{22}H_{38}BrOP$: C, 61.82; H, 8.49; P, 7.24; Br, 18.69. Found: C, 62.20; H, 8.67; P, 7.38; Br, 18.45.

Hydrolysis of Vinylphosphonium Salt 17b in Methanol.—Dried NaOH (0.32 g, 8 mmol) was added to a solution of 3.42 g (8 mmol) of phosphonium salt **17b** in 80 ml of dried MeOH and the mixture was allowed to stir at 64° for 24 hr under dry Na. The work-up followed the procedure of the reaction of phosphonium salt **1b** with NaOH. The ether extract gave 0.15 g of the mixture of benzopyran **3** (5%) and tributylphosphine oxide (16%) by nmr. The methylene chloride extract afforded 2.55 g (74.5%) of the unreacted starting salt **17b**. All compounds were identified by comparison with authentic samples.

Hydrolysis of Vinylphosphonium Salt 17b in Water.—Sodium hydroxide (0.64 g, 16 mmol) was added to a solution of 3.42 g (8 mmol) of phosphonium salt **17b** in 100 ml of water and the mixture was allowed to stir at 100° for 18 hr under a nitrogen atmosphere. The mixture was neutralized with aqueous hydrobromic acid and extracted with three 200-ml portions of ether and then three 300-ml portions of methylene chloride. The ether extract was washed with three 150-ml portions of water and dried ($CaSO_4$). A mixture of salicylaldehyde **5** (40%), benzopyran **3** (4%), and tributylphosphine oxide (3.6%) was obtained by removing ether (total wt 0.50 g). The methylene chloride was similarly washed with two 200-ml portions of water and dried ($CaSO_4$). The methylene chloride extract was concentrated until 50 ml of methylene chloride remained. The concentrated methylene chloride extract was added dropwise to 1 l. of anhydrous ether; 1.25 g (37%) of white crystals of salt **17b** were recovered. All compounds were identified by comparison with authentic samples.

2-Methyl-2*H*-1-benzopyran-3-triphenylphosphonium Bromide (15a).—The solid from experiment 5 listed in Table II, run in a manner similar to the reaction for the preparation of **17b**, was recrystallized from chloroform–ethyl acetate to give analytically pure **15a**: mp 264–266°; ir (KBr) 1210 (C–O–C), 1100 cm^{-1} (C–P); nmr ($CDCl_3$) δ 1.17 (d, 3, J_{HH} = 6 Hz, decoupled, $-CH_3$), 5.20 (pentuplet, 1, $J_{HH} = J_{HP}$ = 6 Hz, –OCH–), 6.9–8.1 (m, 19, aromatic), 8.30 ppm (d, 1, J_{PH} = 13 Hz, vinyl); mass spectrum (70 eV) *m/e* 262.

Anal. Calcd for $C_{28}H_{24}BrOP$: C, 69.00, H, 4.96; Br, 16.39; P. 6.36. Found: C, 68.80; H, 4.93; Br, 16.64; P, 6.17.

Hydrolysis of Phosphonium Salt 15a in MeOH.—Dried NaOH (0.40 g, 0.01 mol) was added to a solution of 4.87 g (0.01 mol) of phosphonium salt **15a** in 100 ml of dried MeOH and the reaction mixture was allowed to stir at reflux temperature for 24 hr under dry Na. The reaction mixture was poured into 2 l. of anhydrous ether. The ether was washed with water and dried over $CaSO_4$. After the solvent ether was removed under reduced pressure, the reaction product was distilled to give 1.20 g (82%) of 2-methyl-2*H*-1-benzopyran (**3**). The residue was chromatographed to give 2.55 g (92%) of triphenylphosphine oxide. Comparison with authentic samples provided positive identification.

Hydrolysis of Phosphonium Salt 15a in Water.—Sodium hydroxide (0.20 g, 5 mmol) was added to an aqueous solution of 1.22 g (2.5 mmol) of phosphonium salt **15a** dispersed in 50 ml of water and the reaction mixture was allowed to stir at 100° for 4 hr. The reaction mixture was cooled to room temperature and extracted with ether (four 100-ml portions). The ether extract was washed with water and dried over $CaSO_4$. After the solvent ether was removed under reduced pressure, 1.0 g of residue was obtained. It was shown to be a mixture of **3** (88%) and triphenylphosphine oxide (97%) by nmr.

Aqueous Hydrolysis of 3-(*o*-Formylphenoxy)propyltributylphosphonium Bromide (1b).—In a 250-ml flask equipped with magnetic stirrer, a mixture of phosphonium salt **1b** (4.44 g, 0.01 mol) and NaOH (0.80 g, 0.02 mol), dissolved in 100 ml of water, was allowed to stir at 100° for 18 hr under a nitrogen atmosphere. The mixture was cooled to room temperature and neutralized with aqueous HBr. The aqueous mixture was extracted with three 150-ml portions of ether and then three 150-ml portions of CH_2Cl_2. The ether extract gave a mixture (0.35 g) of salicylaldehyde **2** (16%) and tri-*n*-butylphosphine oxide **3** (7%), identified by comparison with authentic samples. The methylene chloride extract was concentrated to 50 ml and added dropwise into 1 l. of anhydrous ether. The starting phosphonium salt (2.90 g, 65%) was recovered (nmr showed a trace of impurity as a contaminant).

Registry No.—NaOMe, 124-41-4; **1a**, 17954-76-6; **1b**, 31600-73-4; **2**, 14949-49-6; **3**, 2513-24-8; **10**, 31600-76-7; **13**, 31600-77-8; **14**, 31600-78-9; **15a**, 31600-79-0; **17b**, 31600-80-3.

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