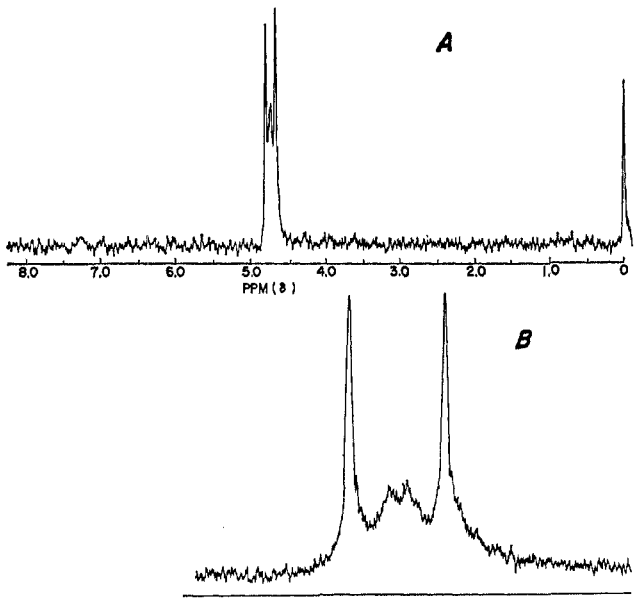

Figure 3—Sweep width (a) 500 cps; (b) 50 cps.

1030, 1010, 770, and 730 cm^{-1} (excluding C–H absorption concealed by the Nujol medium). The nmr spectrum in $CDCl_3$ appeared at first to be a single resonance line, but with higher resolution it was found to be a multiplet (Figure 3). The spectrum appears to be a $X_3AA'X'_3$ type with XX′ interaction, where A and A′ are phosphorus, and X_3 and X'_3 are protons. 1,6-Diphospha-HOD was very stable under the ionizing conditions in the mass spectrometer and *m/e* 236 (the molecular weight) was the most abundant ion in the spectrum; *m/e* 28 (CO), 29 (CHO), and 47 (PO) were also present. From the isotopic abundance ratio, the calculated value for *m/e* 237 is 6.7%. The experimental value obtained was 6.9%.

Attempts to improve the yield of 1,6-diphospha-HOD by changes in reaction times and temperatures or methods of isolation of the product were unsuccessful.

1,6-Diphospha-HOD was oxidized with hydrogen peroxide to give a product, presumably the phosphate, which sublimed about 100° higher. This material darkened at 350°, but did not melt up to 420°. The ir spectrum of this material showed bands at 1090, 1070, and 1010 cm^{-1} (Nujol mull). The region between 800 and 700 cm^{-1} showed no absorption.

Registry No.—II, 15955-20-1; III, 4922-14-9; IV, 4922-15-0.

Acknowledgment.—We are indebted to Dr. A. J. D'Eustachio for carrying out the microbiological oxidation of *myo*-inositol and to Dr. William H. Sharkey for advice and suggestions.

Reactions of Phosphorus Compounds. XIX. Reactions of 3-(*o*-Formylphenoxy)propyltriphenylphosphonium Bromide and 3-(*p*-Formylphenoxy)propyltriphenylphosphonium Bromide

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The preparation of 2,3-dihydrobenzoxepin (**7**) was accomplished in high yield from 3-(*o*-formylphenoxy)propyltriphenylphosphonium bromide (**6**). By changing the solvent, 2-methyl-2H-1-benzopyran (**8**) was prepared in high yield. Treatment of **6** with sodium methoxide in CH_3OD gave 2-methyl-2H-1-benzopyran-α,3-d_2 (**18**). Treatment of 3-(*p*-formylphenoxy)propyltriphenylphosphonium bromide (**20**) with sodium ethoxide in ethanol gave a polymer (**21**). A number of possible mechanisms for the formation of **8**, an unusual rearrangement product, are discussed and discarded on the strength of chemical evidence.

There are a number of reactions in the literature illustrating the usefulness of phosphoranes an intermediates in the preparation of cyclic systems. Carbocyclic systems have been prepared from (a) ketophosphoranes,[1] (b) ester phosphoranes,[2] (c) halophosphoranes,[3] (d) diphosphoranes and oxygen,[4] (e) vinyltriphenylphosphonium bromide and keto malonates,[5] and (f) diphosphoranes with dicarbonyl reagents.[6] Heterocyclic systems have been prepared from reagents paralleling d,[3b] e,[7] f,[8] and ketophosphoranes with azides.[9] One of the happy circumstances characterizing these reactions is that there are no apparent skeletal rearrangements occurring in the carbon chains. Maercker has noted this to be a common characteristic of the Wittig reaction.[10]

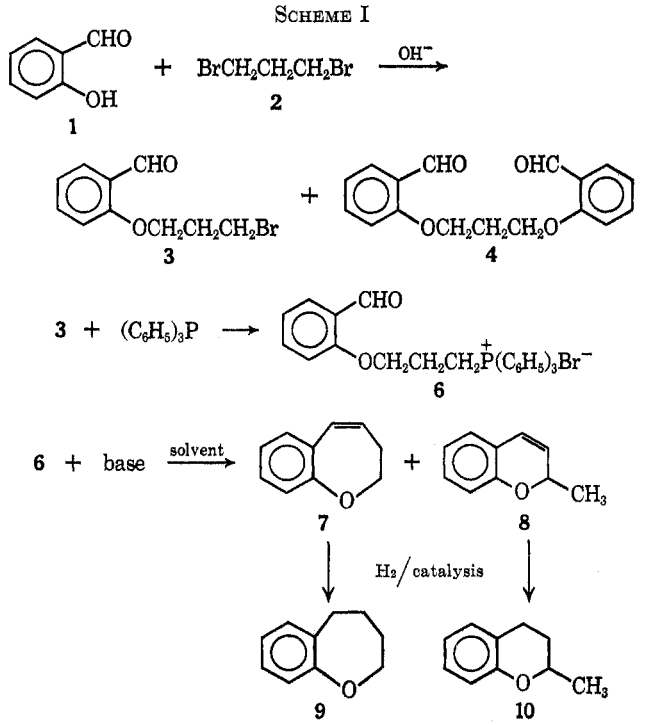
We wish to report[11] the preparation of 2,3-dihydro-1-benzoxepin, **7**, and 2-methyl-2H-1-benzopyran, **8** (Scheme I). Both heterocycles are formed by the Wittig reaction from 3-(*o*-formylphenoxy)propyltriphenylphosphonium bromide, **6**. The formation of benzopyran **8** is a rare example of a skeletal rearrangement in the Wittig reaction. Four mechanistic pathways for the formation of **8** from **6** are considered and are discarded because of evidence cited.

Large scale preparation of pure 2,3-dihydrobenzoxepin, **7**, was accomplished (70% yield)[12] by adding sodium methoxide (0.95 equiv) in dimethylformamide (DMF) to **6** in DMF under dilute conditions.

Preparation of 2-methyl-2H-1-benzopyran, **8**, was accomplished (88% yield) by adding excess sodium

(1) T. I. Bieber and E. H. Eisman, *J. Org. Chem.*, **27**, 678 (1962).
(2) H. O. House and H. Babad, *ibid.*, **28**, 90 (1963).
(3) (a) A. Mondon, *Ann.*, **603**, 115 (1957); (b) H. J. Bestmann and H. Haberlein, *Z. Naturforsch.*, **17b**, 787 (1962).
(4) H. J. Bestmann, H. Haberlein, H. Wagner, and O. Kratzer, *Ber.*, **99**, 2848 (1966).
(5) E. E. Schweizer and J. G. O'Neill, *J. Org. Chem.*, **30**, 2032 (1965).
(6) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).
(7) (a) E. E. Schweizer and J. Liehr, *J. Org. Chem.*, **33**, 583 (1968); (b) E. E. Schweizer, J. Liehr, and D. Monaco, *ibid.*, **33**, 2416 (1968).
(8) J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 5080 (1967).
(9) G. R. Harvey, *J. Org. Chem.*, **31**, 1587 (1966).
(10) A. Maercker, *Org. Reactions*, **14**, 272 (1965).
(11) An initial report of these results appeared in E. E. Schweizer and R. Schepers, *Tetrahedron Lett.*, No. 15, 979 (1963).
(12) We wish to thank Mr. Russell H. Bowers, Jr., National Science Foundation Summer High School Trainee.

SCHEME I



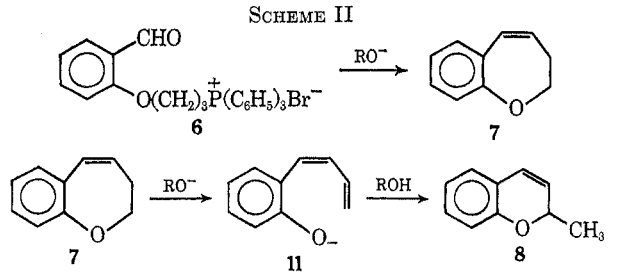
methoxide to **6** in refluxing methanol. Both benzoxepin **7** and benzopyran **8** were hydrogenated quantitatively to 2,3,4,5-tetrahydro-1-benzoxepin, **9**, and 2-methylchroman, **10**, respectively. The analytical and spectral data of **9** and **10** support their assigned structures.[11] The hydrogenated benzoxepin, **9**, was identical with an authentic sample prepared from *o*-bromoanisole according to a procedure of Cagniant.[13]

The starting phosphonium salt, **6**, was prepared (84% yield) by mixing 3-(*o*-formylphenoxy)propyl bromide, **3**, and triphenylphosphine, **5**, in refluxing chlorobenzene. Bromide **3** was prepared (64% yield) by allowing salicylaldehyde, **1**, to react in aqueous base with an excess of 1,3-dibromopropane, **2**, the dialdehyde, **4**, being an isolated side product.

The strong solvent dependence of the reaction may be appreciated by perusing Table I. Clearly the solvent polarity is not the critical factor for the rearrangement to benzopyran **8**. Instead, what appears to be necessary is a strong proton donating solvent.

The mechanism which one would at first suspect for the formation of benzopyran **8** involves the initial production of the expected benzoxepin **7** followed by base-catalyzed rearrangement to **8** as shown in Scheme II.

SCHEME II



Four experiments provide strong evidence against Scheme II as the route whereby the bulk of benzo-

(13) P. Cagniant, *C. R. Acad. Sci., Paris*, **229**, 889 (1949). We wish to thank Mr. B. L. Horowitz (National Science Foundation summer undergraduate fellow) for the preparation of this sample.

TABLE I

SOLVENT DEPENDENCY OF THE BENZOXEPIN **7** TO BENZOPYRAN **8** RATIO[a]

Expt	Solvent	ϵ_{25}[b]	7	8
1	Dioxane	2.2	98	2
2	DMSO[b]	46.6	98	2
3	DMF[c]	37.8	97	3
4	*t*-Butyl alcohol	17.7	96	4
5	Ethanol	24.3	18	82
6	Pyrrole[d]	7.5	15	85
7	Methanol	32.6	2	98

[a] Salt **6** (0.0083 mol) was added all at once to solvent (150 ml) + sodium methoxide (0.0091 mol) under dry nitrogen and allowed to reflux 24 hr. Ratios were determined by vpc. [b] Reaction mixture maintained at 50°. [c] Reaction mixture maintained at 80°. [d] Reaction mixture maintained at 50°. Dielectric constant, ϵ, at 18°.

pyran **8** is formed when the phosphonium salt, **6**, is allowed to react in alcoholic alkoxide.

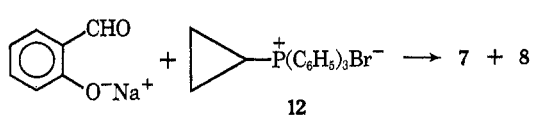
1.—Table II shows that benzoxepin **7** is converted into benzopyran **8**. However, at 24 hr the **7**/**8** ratio is 99/1, whereas **6** gives a ratio of 18/82 under the same conditions (see Table I, expt 5).

2.—When **6** was allowed to react in the presence of 0.8 equiv of benzoxepin **7** in base a 93% yield of **7** was recovered unchanged (see Table III, expt 2).

3.—When *o*-(*cis*-butadienyl)phenol, **11**, was heated in neutral refluxing methanol[14] for 24 hr, only an 18% yield of benzopyran **8** was formed; the rest of butadienylphenol **11** was recovered unchanged. Under similar conditions (see Table I, expt 7), a 98% yield of benzopyran **8** was obtained from **6**.

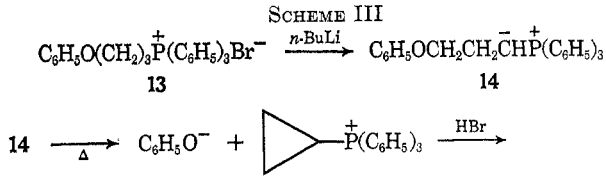
4.—When the sodium salt of **11** was heated in refluxing methanol[14] for 24 hr, the yield of **8** was reduced to 2%. When phosphonium salt **6** was allowed to react under basic conditions in the presence of **11**, 95% of butadienylphenol **11** was recovered unchanged (see Table III, expt 3). Therefore, benzoxepin **7** is not an intermediate in the formation of the benzopyran **8**, and Scheme II must be rejected.

It was shown[15] that benzoxepin **7** and benzopyran **8** could be prepared in 54% yield (35/65 ratio, respectively) by a fusion reaction of the sodium salt of salicylaldehyde, **1**, and cyclopropytriphenylphosphonium salt, **12**. Similarly[15] phenol and phosphonium salt **12**



were prepared (19% yield) from 3-phenoxypropy triphenylphosphonium bromide, **13**, on forming the ylide **14** first, then allowing the phenoxide to eliminate, and later quenching with hydrogen bromide (Scheme III). These experiments suggest a new mechanism,

SCHEME III

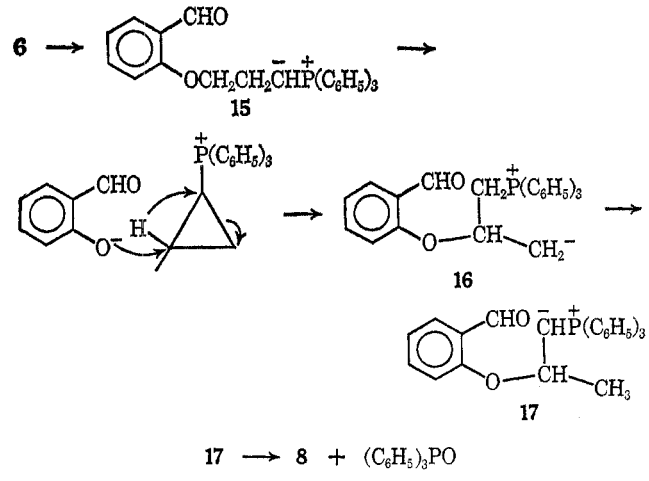


(14) The synthesis, proof of structure of **11**, and the mechanism for the formation of **8** from **11** is elaborated in detail in a companion article in press.

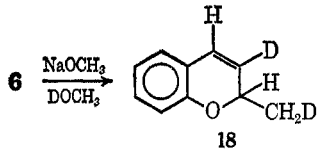
(15) E. E. Schweizer, C. J. Berninger, and J. C. Thompson, *J. Org. Chem.*, **33**, 336 (1968).

Scheme IV, for the formation of benzopyran **8** from phosphonium salt **6**.

SCHEME IV



Further support for Scheme IV besides that already documented may be found in the reaction of phosphonium salt **6** in CH_3OD and sodium methoxide which forms 2-methyl-2H-1-benzopyran-α,3-d_2, **18**.



However, two experiments provide evidence against Scheme IV being the sequence whereby most of **8** is formed when the phosphonium salt, **6**, reacts in sodium methoxide methanol.

1.—Cyclopropyltriphenylphosphonium bromide, **12**, and the sodium salt of **1** were allowed to react in refluxing ethanol for 8 days (with and without catalytic amounts of sodium methoxide), and the vpc showed no **7** or **8**. When 1 equiv of sodium methoxide was added under the same conditions, only 1% of a mixture of **7** and **8** were observed by vpc.

2.—The phosphonium salt, **20**, was allowed to react in refluxing sodium ethoxide ethanol, and a 98% yield of the polymer **21** was obtained. Analysis showed n to be approximately 9, and no $>CHCH_3$ groups were evident in the nmr spectrum. The preparation of the salt, 3-(*p*-formylphenoxy)propyltriphenylphosphonium bromide, **20**, was accomplished as shown in Scheme V below.

SCHEME V

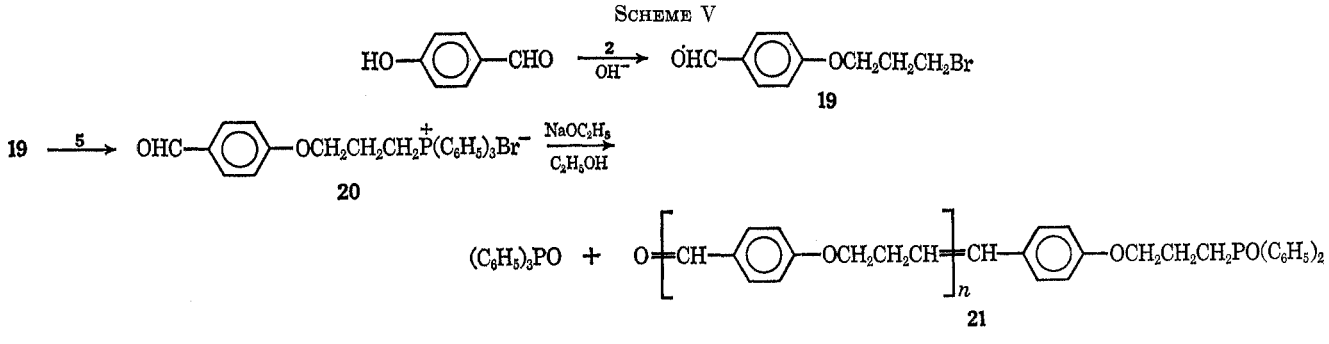


TABLE II

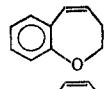
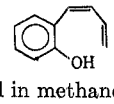
Benzoxepin **7** $\xrightarrow[\text{solvent, time}]{\text{base}}$ benzopyran **8**

7, mol	Base (moles)	Solvent (ml)	Ratio of **7**/**8** at 0 hr	1 hr	2 hr	24 hr	48 hr	1 week
0.007	NaOEt (0.022)	EtOH (100)[a]	100/0	100/0	100/0	99/1	94/6	
0.023	NaOEt (0.008)	EtOH (7.6)[a]	100/0					83/17
0.023	NaOEt (0.008)	EtOD (7.6)[a]	100/0					83/17[c]
0.027	NaH (0.1)	Pyrrole (30)[b]	100/0				98/2	

[a] Reflux. [b] 80°. [c] Product shows no exchange of any protons in benzoxepin **7**. Benzopyran **8** is present only as α-d_1-2-methyl-2H-1-benzopyran (as shown by nmr), suggesting an E2 (nonreversible) step from **7** to **11** in Scheme II.

TABLE III

REACTION OF PHOSPHONIUM SALT **6** WITH ADDED INTERMEDIATES

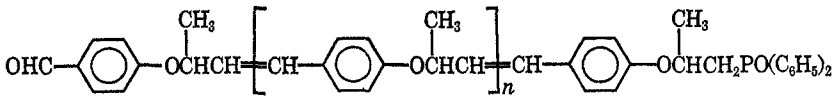
Intermediate added[a]	Amt, equiv	Ratio of product[b] **8**	**7**	**11**
1. None		100	Trace	0
2. 	0.8	55	45	0
3. 	0.8	45	Trace	55

[a] All in methanol at reflux for 24 hr under nitrogen with 0.039 mol of sodium methoxide (4.44 equiv) and 0.0083 mol of **6**. [b] Determined by vpc.

The singularly poor yields of benzoxepin **7** and benzopyran **8** from cyclopropyl salt **12** compared to the yields of **7** and **8** from the original salt **6** under similar conditions leads us to the conclusion that Scheme IV is inoperative. This conclusion is supported by the fact that the *para* salt, **20**, gave none of the polymer, **22**, which would be expected if a mechanism parallel to Scheme IV were operative in the reaction of salt **20**. Thus, Scheme IV must be eliminated.

An alternative but more complicated mechanism, Scheme VI, was examined recently[16] by Schweizer, *et al.* These authors found that benzopyran **8** was always

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



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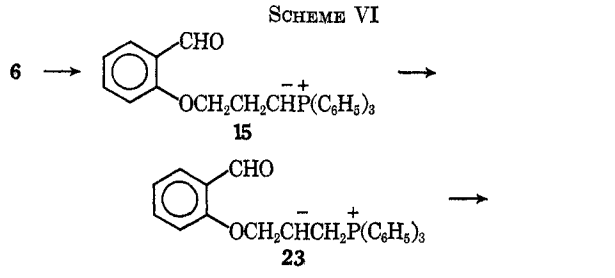
formed in lower yields when the propenyl salt, **25**, rather than the corresponding allyl salt, **24**, was used. With this observation and results from deuterium labeling experiments, they concluded that the allyl salt is in

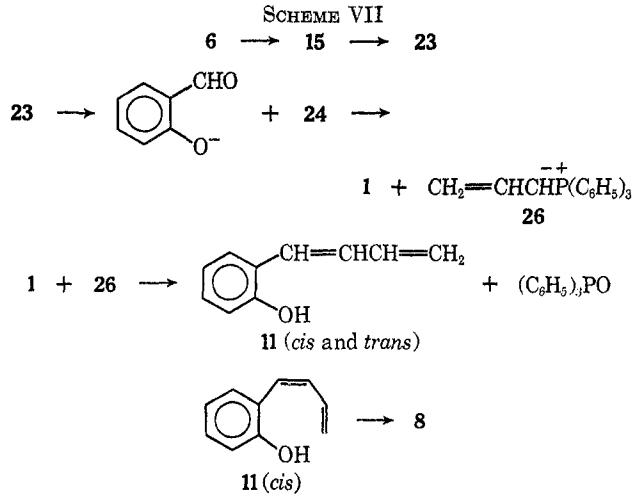
SCHEME VI



equilibrium with the propenyl salt but that the formation of **8** takes place through the allyl moiety, not by initial formation of **17** *via* propenyl salt **25**. Therefore, Scheme VI must be eliminated.

The allyl salt mechanism, Scheme VII, was more

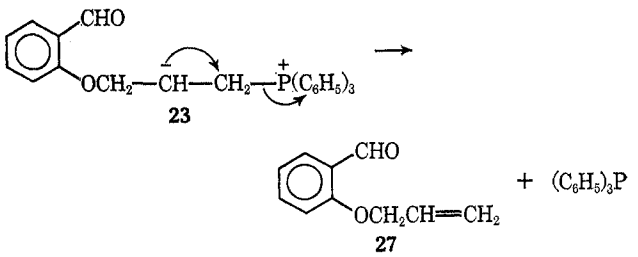
SCHEME VII



difficult to eliminate. There is some evidence that a reaction sequence involving the allyl salt, **24**, as an intermediate in the formation of benzopyran **8** from phosphonium salt **6** may be plausible. Allyl salt **24** does yield benzopyran **8** (38%) upon mixing **24** with the sodium salt of **1** and refluxing in ethanol for 8 days.[16] The other product was *trans-o*-butadienylphenol **11**.

However, results from three experiments refute Scheme VII as the sequence for the formation of benzopyran **8** from phosphonium salt **6**.

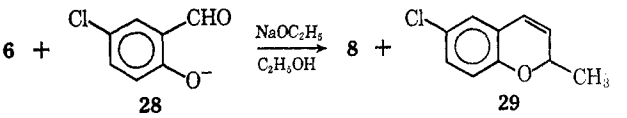
1.—All attempts to isolate the intermediates in the sequence have been uniformly unsuccessful. Allyl salt **24** has never been detected even when starting material was recovered. Neither *cis*- nor *trans*-butadienylphenol **11** has been isolated under conditions where they are known to be stable.[14] Furthermore, allyl ether **27**, which one would expect as a side product from this sequence, has never been observed.



2.—A low yield of benzopyran **8** (38%) was obtained from allyl salt **24** and the sodium salt of **1** when they were allowed to react in ethanol for 8 days.[14] Compare this result with the 88% yield of benzopyran **8** from the phosphonium salt **6** in 1 day.

3.—*cis*-Butadienylphenol **11** does yield benzopyran **8** (18%) on refluxing in methanol under neutral conditions.[14] However, when **11** was allowed to react with **6** in an excess of sodium methoxide, 95% of **11** was recovered unchanged (see Table III, expt 3). It has been shown[16] that *cis*-butadienylphenol **11** is an intermediate in the formation of benzopyran **8** from the sodium salt of **1** and allyl salt **24**.

One final experiment that casts doubt on Schemes IV, VI, and VII as pathways for the formation of **8** from **6** is an attempted crossover experiment. These three pathways are essentially intermolecular reactions. If an intermediate phosphorane separates from salicylaldehyde, it should be trapped by placing a more electrophilic aldehyde in the system. Chlorosalicylaldehyde **28** was added to phosphonium salt **6** during reaction and no chlorobenzopyran, **29**, was found in the product by ir or vpc.



In summary, it has been shown that 2,3-dihydro-1-benzoxepin, **7**, and 2-methyl-2H-1-benzopyran, **8**, may be prepared in high yield from **3** (*o*-formylphenoxy)-propyltriphenylphosphonium bromide, **6**. The ratio of **7** to **8** is strongly dependent on the solvent system employed. Four mechanistic pathways (Schemes II, IV, VI, and VII) were examined for the unusual skeletal rearrangement in a Wittig reaction whereby **8** is formed from **6**. These pathways were discarded on the basis of the experimental evidence obtained.

Experimental Section

General.—Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer and nmr spectra on a Varian A-60A spectrometer using tetramethylsilane (TMS) as internal reference. Vapor phase chromatography was performed on a Wilkins Aerograph Model A-90P instrument using a 20% Ucon Polar on Firebrick (60–80 mesh, 10 ft × 0.25 in.) column, a 15% Carbowax 20M on Chromosorb W (60–80 mesh, 10 ft × 0.25 in.) column, or a 10% UC-W98 (silicone) on Chromosorb W (DMCS, AW; 60–80 mesh, 10 ft × 0.025 in.) column. Ascending thin layer

chromatography (tlc) was effected using 2 × 8 in. glass plates coated with silica gel G (Brinkmann). Anhydrous conditions in a dry nitrogen atmosphere were used except where indicated. Melting points and boiling points are uncorrected. Analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

Reaction of Salicylaldehyde, 1, and 1,3-Dibromopropane, 2.—A mixture of 172 g (1.43 mol) of salicylaldehyde, 353 g (1.75 mol) 1,3-dibromopropane, and 100 ml of water was placed in a 3-l. three-necked (Morton) flask. After flushing with dry nitrogen, a 10% aqueous solution of sodium hydroxide (57 g, 1.43 mol) was added, with vigorous stirring, over an 8-hr period under reflux. The mixture was allowed to continue refluxing and stirring under a pad of nitrogen 16 hr. The mixture was cooled, the layers were separated, and the aqueous layer was washed with two 250-ml portions of chloroform. The nonaqueous layers were combined, washed with four 300-ml portions of 10% aqueous sodium hydroxide, once with 300 ml of 10% HCl, and with two 300-ml portions of water. The organic layer was dried ($MgSO_4$), concentrated, and distilled yielding 219 g (64%) of 3-(*o*-formylphenoxy)propyl bromide, **3**, bp 130–134° (1 mm), and a black residue.

3-(*o*-Formylphenoxy)propyl bromide, 3, was purified by distillation to give an analytically pure sample: bp 131–132° (0.4 mm); $n^{24.5}D$ 1.5735; nmr ($CDCl_3$) δ 2.33 (quintet, 2), 3.57 (t, 2), 4.16 (t, 2), 6.8–7.8 (m, 4, aromatic), 10.34 ppm (s, 1, -CHO).

Anal. Calcd for $C_{10}H_{11}BrO_2$: C, 49.40; H, 4.56; Br, 32.87. Found: C, 49.25; H, 4.53; Br, 32.75.

1,3-Bissalicyloxypropane, 4, was obtained pure, from a similar experiment, by pouring the dark residue from the distillation, reported in the first experiment, into 100 ml of carbon tetrachloride. A crystalline product formed slowly. The precipitate was washed five times with 50 ml of CCl_4 and then recrystallized from CCl_4 to yield 19 g (14%) of **4**, an analytically pure sample with mp 99–100°; nmr ($CDCl_3$) δ 2.4 (quintet, 2), 4.3 (t, 4), 6.8–7.9 (m, 8, aromatic), 10.52 ppm (s, 2, -CHO).

Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.83; H, 5.82.

3-(*o*-Formylphenoxy)propyltriphenylphosphonium Bromide, 6.—A solution of 243 g (1 mol) of compound **3**, 262 g (1 mol) of triphenylphosphine (recrystallized from ether), and 1 l. of dry chlorobenzene was heated at reflux for 3 days under a blanket of dry nitrogen. The product which crystallized on cooling and stirring overnight was washed with six 500-ml portions of chlorobenzene and ten 500-ml portions of anhydrous ether and gave (after drying) 424 g (84%) of salt **6**: mp 160–161°; nmr ($CDCl_3$) δ 2.30 (broad, 2), 4.18 (broad t, 2), 4.55 (t, 2), 6.8–8.2 (m, 19, aromatic), 10.30 ppm (s, 1, -CHO).

Anal. Calcd for $C_{28}H_{26}BrO_2P$: C, 66.54; H, 5.19. Found: C, 66.53; H, 5.23.

2-Methyl-2H-1-benzopyran, 8. A. Preparation.—Into a 250-ml three-necked flask containing 150 ml of dry methanol and 2.0 g (0.036 mol) of sodium methoxide (Fischer) was added 4.1 g (0.0083 mol) of phosphonium salt **6**. The solution was refluxed for 18 hr, poured into 500 ml of water, and extracted with four 30-ml portions of ether. The combined ether extracts were washed with water (30 ml), dried ($MgSO_4$), and concentrated on the rotary evaporator. The oil was poured in 150 ml of distilled pentane to give 1.49 g of a white solid (triphenylphosphine oxide). After removal of the pentane 1.04 g (88%) of benzopyran **7** was obtained.

An analytical sample was obtained by distillation: bp 34° (0.2 mm); $n^{25}D$ 1.5658; nmr ($CDCl_3$)[17] δ 1.40 (d, 3, J_{cd} = 7 Hz), 4.9 (m, 1), 5.56 (d of doublets, 1, J_{bc} = 3 Hz, J_{ab} = 10 Hz), 6.31 (d of doublets, 1, J_{ac} = 2 Hz, J_{ab} = 10 Hz), 6.4–7.2 ppm (m, 4).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.15; H, 6.90. Found: C, 82.25; H, 6.84.

B. Preparation with Added 2,3-Dihydro-1-benzoxepin, 7.—Stoichiometry and conditions were exactly the same as the preparation above with 0.96 g (0.8 equiv) of benzoxepin **7** added. The pentane concentrate was 2.0 g. Nmr integration showed benzoxepin **7** added. The pentane concentrate was 2.0 g. Nmr integration showed benzoxepin was 45% or 0.9 g (93% recovered).

C. Preparation with Added *o*-(*cis*-Butadienyl)phenol, 11.—Stoichiometry and conditions were exactly the same as the preparation above with 0.95 g (0.8 equiv) of butadienylphenol **11** added. The pentane concentrate was 1.63 g. Nmr integration showed butadienylphenol **11** was 55% or 0.9 g (95% recovered).

2,3-Dihydro-1-benzoxepin, 7, Preparation.—To a solution of 79.1 g (0.157 mol) of salt **6** in 2 l. of DMF was added dropwise over a period of 15 min a suspension of 8.2 g (0.152 mol) of sodium methoxide in 500 ml of DMF. The solution was vigorously stirred at room temperature under nitrogen for 8 hr; then the temperature was raised to 60° for 14 hr. The solution was cooled and added to 4 l. water, and in batches extracted with five 100-ml portions of ether. The combined ether layers were washed with four 100-ml portions of water, dried ($MgSO_4$), and concentrated to obtain 22.2 g of crude product (shown to be 76.7% **7**, 19.0% triphenylphosphine oxide, and 4.3% diethyl ether.) Oxepin **7** was short-path distilled at 55° (0.5 mm) to yield 15.6 g of pure product (68.5%).

An analytically pure sample of 2,3-dihydro-1-benzoxepin, **7**, from another experiment was shown to have bp 35° (0.07 mm); $n^{23.5}D$ 1.5926; nmr ($CDCl_3$) δ 2.6 (m, 2), 4.18 (t, 2, J_{cd} = 5 Hz), 5.85 (d of triplets, 1, J_{bc} = 4 Hz, J_{ab} = 11 Hz), 6.30 (d of triplets, 1, J_{ac} = 1 Hz, J_{ab} = 11 Hz), 6.7–7.2 ppm (m, 4).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.15; H, 6.90. Found: C, 82.15; H, 6.88.

Reaction of Salt 6 in the Presence of 5-Chlorosalicylaldehyde, 28.—Dry ethanol (200 ml) was distilled into a three-necked flask and allowed to react with 1.58 g (0.0686 mol) of sodium. Phosphonium salt **6** (17.3 g, 0.0343 mol) and 5.4 g (0.0343 mol) of 5-chlorosalicylaldehyde, **28**, were added and the solution was refluxed for 4 days with mechanical stirring. The ethanol was removed and the residue extracted with three 100-ml portions of dry ether. The ether was stripped to give 2.1 g (42% $C_{10}H_{10}O$) of a yellow oil with an infrared spectrum identical with that of a mixture of **7** and **8**. Vpc peak enhancement also indicated the presence of **7** and **8** and the absence of any other compounds. The 6-chloro-2-methyl-2H-1-benzopyran, **29**, has been prepared[7b] and was shown not to be present.

Reactions to Show Solvent Dependency of 7/8 Ratio.—Salt **6** (4.1 g, 0.0083 mol) was added, all at once, to a solution of 0.5 g (0.009 mol) of $NaOCH_3$ in 150 ml of solvent (see Table I). The solution was heated (Table I) for 24 hr, poured into 150 ml of water, and then extracted with two 50-ml portions of dry ether. The combined ether extracts were washed with 25 ml of water, dried ($MgSO_4$), and concentrated under vacuum on a rotary evaporator at room temperature. The glpc values were taken and the results are recorded in Table I.

Preparation of 2,3,4,5-Tetrahydro-1-benzoxepin, 9.—2,3-Dihydro-1-benzoxepin, **7** (0.7 g), was hydrogenated quantitatively over platinum catalyst at room temperature in anhydrous ether. Filtration and short-path distillation gave a pure sample of **9**: ir and nmr spectra and vpc identical with those of authentic sample prepared according to Cagniant;[13] nmr ($DCCl_3$) δ 1.2–2.0 (broad m, 4, H_b and H_c),[17] 2.8 (m, 2, H_a), 3.9 (m, 2, H_a), 6.7–7.3 ppm (broad m, 4, aromatic).

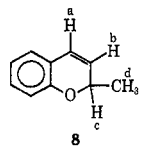
Preparation of 2-Methylchroman, 10.—2-Methyl-2H-1-benzopyran, **8** (2.5 g), was hydrogenated quantitatively over 10% Pd on charcoal at room temperature in anhydrous ether. Filtration and distillation gave an analytically pure sample of **10**: bp 72° (3.2 mm); $n^{25}D$ 1.5316 [lit.[18] bp 223–226° (762 mm)]; nmr ($CDCl_3$) δ 1.29 (d, 3, methyl, J_{cd} = 6 Hz), 1.5–2.0 (broad m, 2, H_b), 2.5–2.9 (broad m, 2, H_a), 4.0 (m, 1, H_c), 6.65–7.2 ppm (broad m, 4, aromatic).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.17. Found: C, 80.98; H, 8.07.

Rearrangment of Benzoxepin 7 to Benzopyran 8. A. With Sodium Ethoxide in Ethanol.—Benzoxepin **7** (1 g, 0.007 mol) was placed in 100 ml of refluxing absolute ethanol in which (0.5 g, 0.022 g-atom) of sodium had previously been dissolved. Drawing out 0.3-ml aliquots at the times indicated, the ratios of **7/8** were obtained by vpc and are shown in Table II.

B. With Sodium Hydride–Pyrrole.—Benzoxepin **7** (3.32 g, 0.027 mol) was placed in a solution of sodium hydride (0.1 mol) and pyrrole (30 ml) (which had been allowed to react 1 hr previously) and heated at 80° for 24 hr. The solution was quenched by adding it to 250 ml of H_2O. The aqueous mixture was ex-

(17) The nmr values refer to protons in the following positions.



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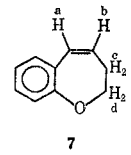

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(18) C. D. Harries and G. T. Busse, *Ber.*, **28**, 502 (1895).

tracted with two 50-ml portions of ether; the ether extracts were washed with two 100-ml portions of H_2O and dried ($MgSO_4$). Rotary evaporation at room temperature and analyses showed the benzoxepin **7** to benzopyran **8** ratio to be 98/2.

C. With Sodium Ethoxide in EtOD.—Benzoxepin **7** (0.023 mol) was allowed to reflux for 1 week in 7.6 ml of ethanol-*d*, with sodium ethoxide (0.008 mol) present. Work-up in the manner listed above in the previous experiment gave a **7**/**8** ratio of 83/17 (by vpc). The nmr spectrum of the mixture was a combination of the spectrum for **7** (with ratio of $a/b/c/d^{16}$ = 1/1/2/2) and **8** (ratio $a/b/c/d^{16}$ = 1/1/1/2).

Reaction 3-(*o*-Formylphenoxy)propyltriphenylphosphonium Bromide, 6, with $NaOCH_3$ in CH_3OD.—Salt **6** (6.9 g, 0.014 mol) was added to a solution of 0.014 mol of $NaOCH_3$ in 20 g of CH_3OD and allowed to reflux for 2.5 hr. The solvent was stripped and the residue short-path distilled (0.3 mm) to give 0.6 g (30%) of 2-methyl-2H-1-benzopyran-α,3-d_2: nmr (neat) δ 1.30 (d, 2, J_{cd} = 7 Hz), 4.90 (broad triplet, 1, H_c), 6.30 (s, 1, H_a), 6.77–7.42 ppm (broad m, 4, aromatic).

Reactions of Cyclopropyltriphenylphosphonium Bromide, 12.

A.—Salts **1** and **12**, and $NaOCH_3$, in equimolar (0.0078 mol) ratios, were allowed to reflux in 50 ml of absolute ethanol for 8 days. Concentration and vpc of the crude mixture showed peaks in the areas (checked by spiking experiments) expected for **7** and **8** in approximately equal amounts with an over-all yield of less than 1%.

B.—Similar experiments were run with only **1** and **12** [or **1**, **12**, and a catalytic amount of $NaOCH_3$ (0.0008 mol)] with no apparent reaction to make **7** and **8** observed.

3-(*p*-Formylphenoxy)propyl Bromide, 19.—The title compound, **19**, was prepared in exactly the same manner as that reported above for **3** (except for the use of *p*-hydroxybenzaldehyde). After stripping the chloroform, 132 g (38%) of 3-(*p*-formylphenoxy)propyl bromide, **19**, was obtained: bp 135° (0.15 mm); $n^{24}D$ 1.5820; ir (neat) 3000 w, 2875 w, 1700 s, 1610 s, 1520 s, 1180 s, 1025 s, 930 m, 835 s; nmr (CCl_4) δ 2.37 (quintet, 2, H_2), 3.77 (t, 2, H, $J_{1,2}$ = 7 Hz), 4.35 (t, 2, H_3, $J_{2,3}$ = 7 Hz), 7.35 (d, 2, H_{ortho}, $J_{o,m}$ = 9 Hz), 8.20 (d, 2, H_{meta}, $J_{o,m}$ = 9 Hz), 10.02 ppm (s, 1, CHO).

Anal. Calcd for $C_{10}H_{11}BrO_2$: C, 49.70; H, 4.46; Br, 32.77. Found: C, 49.67; H, 4.49; Br, 32.98.

3-(*p*-Formylphenoxy)propyltriphenylphosphonium Bromide, 20.—Triphenylphosphine, **5** (105 g, 0.4 mol), and bromide **19** (97 g, 0.4 mol) were allowed to reflux for 24 hr in 400 ml of dry ethyl acetate, then cooled with stirring another 24 hr. Filtration and stirring (of residue) in hot ethyl acetate (24 hr), filtration, and washing and drying of the residue gave 117 g (58%) of **20**. Recrystallization from acetone gave an analytically pure sample: mp 140–141°; ir (KBr) 3030 w, 2900 w, 1680 s, 1600 s, 1500 m, 1440 s, 1260 s, 1220 s, 850 m, 742 s, 720 s, 690 s; nmr ($CDCl_3$) δ 2.2 (broad, 2, H_2), 4 (broad, 2, H_1), 4.52 (broad t, 2, H_3), 7.09 (d, 2, H_{ortho}, $J_{o,m}$ = 9 Hz), 7.65–8.25 (broad, 17, aromatic), 9.87 ppm (s, 1, -CHO).

Anal. Calcd for $C_{28}H_{26}BrO_2P$: C, 66.63; H, 5.20. Found: C, 65.77; H, 5.64.

Reaction of 1-(*p*-Formylphenoxy)propyltriphenylphosphonium Bromide, 20, and Sodium Ethoxide in Ethanol.—Salt **20** (10.1 g, 0.02 mol) was allowed to reflux (24 hr) in a solution of sodium ethoxide (0.02 mol) in ethanol (50 ml). The mixture was carefully acidified with gaseous HBr and filtered; the residue was washed until the wash water gave a negative halogen test ($AgNO_3$). Concentration of the original mother liquors and crystallization from hexane gave 4 g (72%) of triphenylphosphine oxide (melting point and mixture melting point checked with an authentic sample). The halogen-free residue from the water wash, after washing with ethanol and drying, gave 2.9 g (98%) of a yellow solid, mp 130–135°. Crystallization from dimethylformamide gave a sample: mp 128–130; ir (KBr) 2080 w, 2980 w, 1620 s, 1580 s, 1520 s, 1480 m, 1243 s, 1035 s, 970 s, 843 m; nmr (pyridine-d_5) δ 2.58 (broad m, 2, $-CH_2CH=$), 4.05 (broad t, 2, $-OCH_2-$, J = 6 Hz), 6.2–7.0 (broad m, 2, $=CHAr$), 7.0–7.6 ppm (broad, 4, aromatic).

A correct analysis was obtained for the following structure: $OCHC_6H_4OCH_2CH_2CH[=CHC_6H_4OCH_2CH_2CH]_8=CHC_6H_4O-CH_2CH_2CH_2PO(C_6H_5)_2$, **21**.

Anal. Calcd for $C_{112}H_{111}O_{12}P$: C, 79.99; H, 6.67. Found: C, 80.15; H, 6.73.

Registry No.—**3**, 17954-11-9; **4**, 17954-12-0; **6**, 17954-76-6; **7**, 14949-49-6; **8**, 2513-24-8; **9**, 6169-78-4; **10**, 13030-26-7; **19**, 17954-81-3; **20**, 17954-82-4; **21**, 17954-83-5.

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Reactions of Phosphorus Compounds. XX. Reactions of Furfuryl-, Dihydrofurfuryl-, and Tetrahydrofurfuryltriphenylphosphonium Bromide

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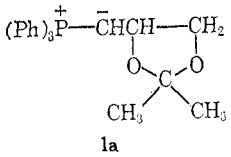
The triphenylphosphonium salts of furfuryl bromide and its fully and partially hydrogenated derivatives have been prepared and allowed to react in the Wittig manner. A reversible β elimination followed by an unusual internal ylidization reaction was observed with the tetrahydrofurfuryl salt.

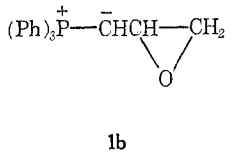
Continuing our interest in the reactions of phosphorous compounds,[1] we have studied the reactions of the furfuryl-, dihydrofurfuryl-, and tetrahydrofurfuryltriphenylphosphonium bromides under Wittig conditions with benzaldehyde and cyclohexanone.

The large volume of work in the past 10 years involving the Wittig reaction has shown[2] that this synthesis is relatively free of side reactions. Complications have arisen, however, if the initially formed ylide moiety contains a substituent in the β position to the phosphorus atom which may readily experience displacement.

Thus the ylides **1a** and **1b** have been shown by Bohlmann[3] to decompose very readily, as evidenced by the rapid disappearance of the ylide color. A similar



1a



1b

β elimination has been employed in the preparation of vinyltriphenylphosphonium bromide.[4]

(1) Paper XIX: E. E. Schweizer, *et al.*, *J. Org. Chem.*, **34**, 207 (1969).

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(4) E. E. Schweizer and R. H. Bach, *J. Org. Chem.*, **29**, 1746 (1964).