Anal. Calcd for $C_{11}H_{25}CrN_7O_3S_5$: C, 24.18; H, 4.58; N, 17.95. Found: C, 25.08; H, 5.15; N, 18.19.

In a similar way, ethyl bis(2-diethylaminoethyl), ethyl bis(2-dimethylaminoethyl), and *n*-butyl bis(2-dimethylaminoethyl) phosphites were converted to the corresponding thiophosphoryl-2-aminoethanols. These results are summarized in Table II.

Preparation of Ethyl 2-Monomethylaminoethyl-2-dimethylaminoethyl Phosphite.—After a solution of 2-ethoxy-3-methyl-1,3,2-oxazaphospholidine (5.96 g, 0.04 mole) and 2-dimethylaminoethanol (3.00 g, 0.04 mole) in 50 ml of benzene was refluxed for 2 hr, the solvent was removed under reduced pressure. The vacuum distillation of the residue gave 6.7 g (70%) of ethyl 2-monomethylaminoethyl-2-dimethylaminoethyl phosphite (bp 70–89° at 1 mm).

Anal. Calcd for $C_9H_{23}N_2O_2P$: N, 11.76. Found: N, 11.61.

Preparation of Ethylthiophosphorylcholine from 2-Monomethylaminoethyl-2-dimethylaminoethyl Phosphite.—To a solution of ethyl 2-monomethylaminoethyl-2-dimethylaminoethyl phosphite (2.38 g, 0.01 mole) in 20 ml of benzene was added sulfur (0.32 g, 0.01 g-atom) in small portions with stirring at room temperature. After the mixture was allowed to stand overnight at room temperature, the solvent was removed under reduced pressure. The obtained viscous oily substance was heated at 95–105° for about 3 hr to give transparent resinous solid. The solid was dissolved in 20 ml of ethanol, and then 5 g of methyl iodide was added to the solution with stirring at room temperature. The precipitate of tetramethylpiperazinium diiodide (1.41 g, 57%) was collected by filtration. The filtrate was poured into a freshly prepared solution of ammonium reineckate (3.5 g) in 150 ml of ethanol with stirring. After the mixture was allowed to stand overnight at room temperature, it was filtered with suction. The precipitate was washed throughly with ethanol and water and then dried *in vacuo* over phosphorus pentoxide to a constant weight. Reprecipitation from acetone and ethanol gave 3.0 g (52%) of pure Reinecke salt of ethylthiophosphorylcholine (mp 182–184°), which was identified with an authentic sample.

Acknowledgment.—The authors wish to express their hearty thanks to Dr. Oyo Mitsunobu for his helpful suggestion and to Miss Keiko Nakamura for her microanalysis.

Reactions of Phosphorus Compounds. IX. Synthesis of a Series of 2H-1-benzopyrans and Determination of the Mechanism of Reaction

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A series of 2-alkyl and 2,2-dialkyl-2H-1-benzopyrans have been synthesized from substituted allyltriphenylphosphonium halides and sodium salicylaldehyde. The mechanism for this reaction has been shown to be one of initial attack on the aldehyde function to form the *cis* and *trans* Wittig products, followed by closure of the *cis* adduct to the 2H-1-benzopyran system.

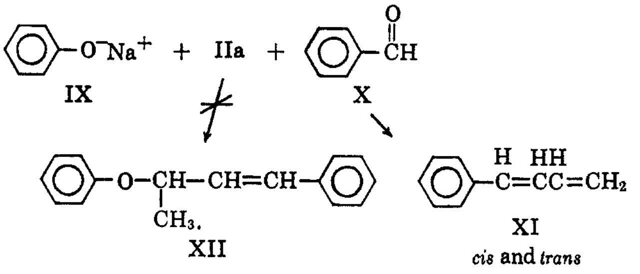
Continuing our interest in the reactions of phosphonium salts, it has been shown[1] that sodium salicylaldehyde (I) will react with substituted allyltriphenylphosphonium salts to give a series of 2H-1-benzopyrans.

Allyltriphenylphosphonium bromide (IIa) will react with I in dimethylformamide (DMF) to give 2-methyl-2H-1-benzopyran (IIIa) in up to 34% yield.

The previously reported[2] preparation of 2H-1-benzopyran from vinyltriphenylphosphonium bromide and I led to the initial assumption that the present reaction is the result of a base-catalyzed isomerization[3] of the allyl salt, IIa, to the corresponding propenyltriphenylphosphonium bromide (VIII) followed by ring closure as described in our earlier paper.[2] Keough and Grayson[3] have shown, however, that the characteristic phosphonioethylation reactions of vinylphosphonium salts do not occur with the propenyl salt, VIII.

We have also shown[1] that the reaction of sodium phenoxide (IX) and salt, IIa, in the presence of benzaldehyde (X) gives only the two geometric isomers of phenylbutadiene (XI). None of the phenoxy adduct (XII), which would be expected if the reaction were the result of an initial isomerization of IIa to VIII followed by a Michael-type addition of phenoxide and then a Wittig reaction with benzaldehyde, was observed. (See Scheme I.)

SCHEME I



Further work has shown that the mechanism for the formation of the substituted 2H-1-benzopyrans consists of an initial Wittig reaction with the aldehyde function of I, followed by addition to the butadiene system.

If the salt, IIa, is allowed to react with I in DMF at 0°, two products are formed. These products cannot be isolated owing to polymerization and ring closure, but, when the mixture of the two is hydrogenated, 2-*n*-butylphenol (VIa) is isolated as the only product. This shows that the two intermediates must have been *cis*- and *trans*-O-(1,3-butadienyl)phenol (IVa and Va).

When the allyl salt, IIa, is allowed to react in refluxing ethanol with I, followed by neutralization of the reaction mixture with gaseous HBr, 1-vinyl-2-(O-hydroxyphenol)vinyltriphenylphosphonium bromide (XII) can be isolated.

One may postulate the formation of XIII as shown in Scheme II.

When the allyl salt, IIa, is allowed to react with I in $DOCH_3$, the product obtained is the 2-deuteriomethyl-3-deuterio-2H-1-benzopyran (XIV) (9% yield). This shows that there is indeed a base-catalyzed equilibrium in the salt giving XV before Wittig reaction (Scheme III).

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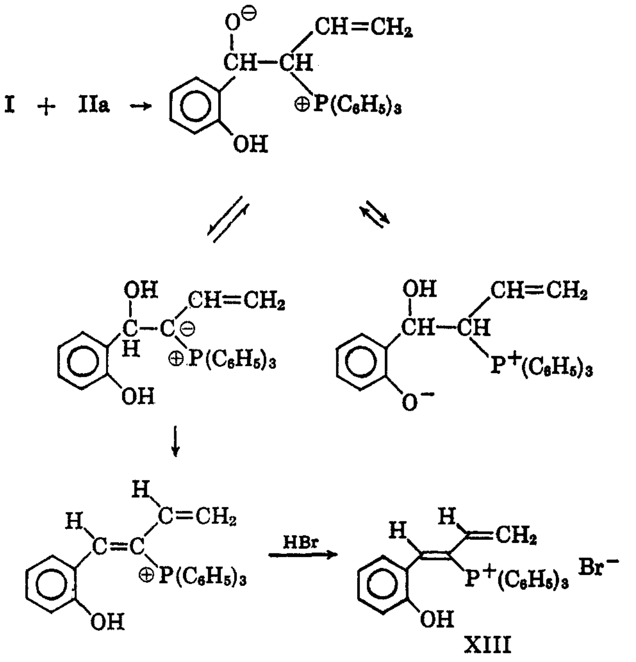
[1] E. E. Schweizer and C. J. Berninger, *Chem. Comm.* (London), 92 (1965).

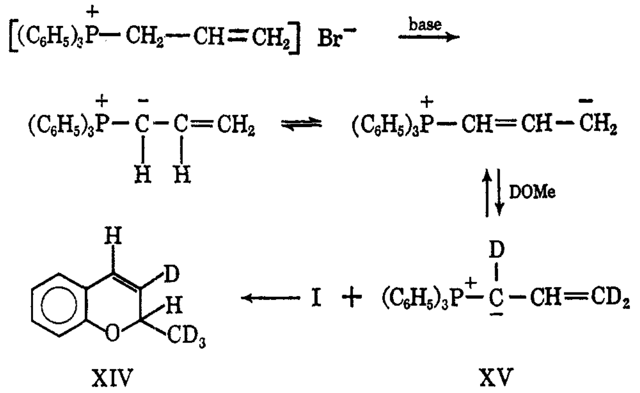
[2] E. E. Schweizer, *J. Am. Chem. Soc.*, **86**, 2744 (1964).

[3] P. T. Keough and M. Grayson, *J. Org. Chem.*, **29**, 631 (1964).

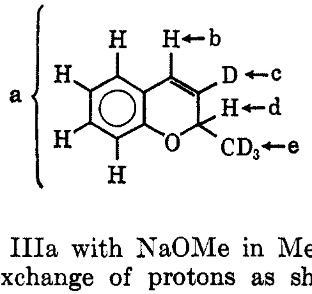
SCHEME II



SCHEME III



Complete conversion of all the α- and γ-protons in IIa to deuterium (in XV) was not apparent under the reaction conditions since nmr spectra shows proton ratios of a = 4, b = 1, c = 0, d = 1, e = 0.5 in compound XIV.



Reaction of IIIa with NaOMe in MeOD gives essentially no exchange of protons as shown by nmr ratios of a = 4, b = 1, c = 1, d = 0.9, e = 3.

Reactions have been carried out using the propenyl salt, VIII, to form the benzopyran, IIIa. In each case, the pyran system was formed, but in a lower yield than that given by the corresponding allyl salt run under the same conditions. (See Scheme IV and Table I.)

SCHEME IV

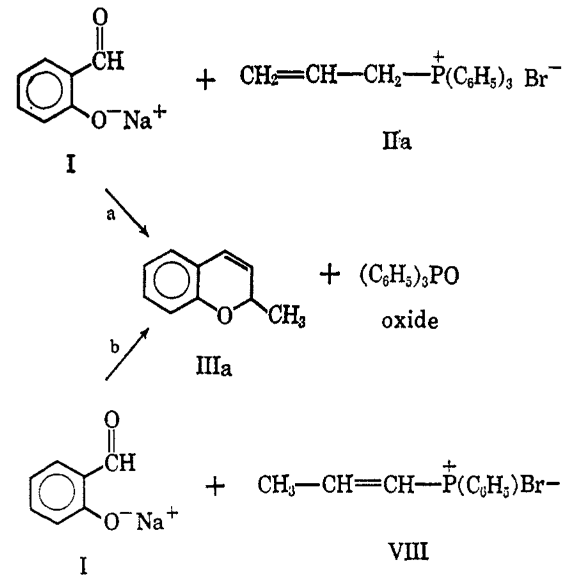


TABLE I

2-METHYL-2H-1-BENZOPYRAN FROM (a) ALLYL SALT, IIa + I, AND (b) PROPENYL SALT, VIII + I

Reagents	Solvent	Time	Product	
			IIIa, %	Oxide, %
a	C_2H_5OH	8 days	18	36
b	C_2H_5OH	9 days	0	. .
a + NaI	DMF	24 hr	34	70
b + NaI	DMF	24 hr	3	32
a	Fuse	. . .	30	63
b	Fuse	. . .	10	37

The above results show that the allyl salt, IIa, is in equilibrium with the propenyl salt, VIII, but that the Wittig reaction takes place through the allyl moiety.

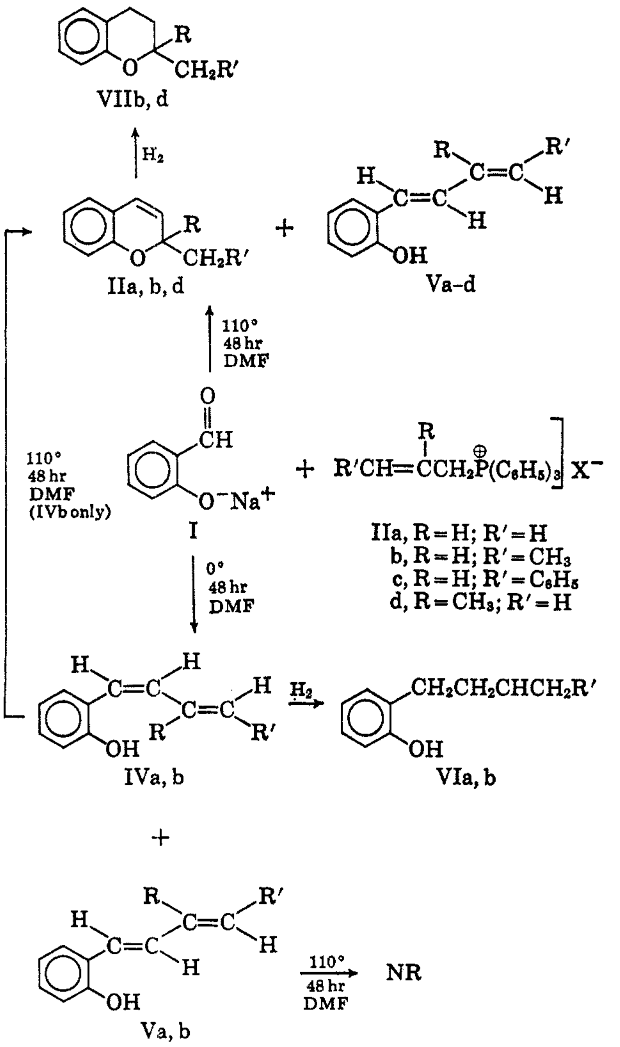
Similar reactions were carried out using the analogous 2-butenyltriphenylphosphonium chloride (IIb). The salt, IIb, was allowed to react with I at 110° in DMF for 48 hr to give two products. These products are 2-ethyl-2H-1-benzopyran (IIIb) and what was shown to be *trans,trans*-O-(4-methyl-1,3-butadienyl)phenol (Vb) (Scheme V).

The salt, IIb, was then allowed to react with I at 0° in DMF for 48 hr. The pyran product was removed from the phenolic products by extraction of the latter with dilute NaOH. The neutralized extraction residue showed two peaks on the gas chromatograph. The two products were separated by a spinning-band distillation at high vacuum. Both showed a strong OH band in the infrared at 3500 cm^{-1}. Both showed a *trans* olefinic band at 990 cm^{-1}, but the band was much stronger in the higher boiling product than in the lower boiling.

A mixture of the two was hydrogenated to give as the only product, 2-*n*-pentylphenol (VIb). The hydrogen uptake was 2 moles for each mole of isomer. This shows that the two products are isomeric forms of O-(4-methyl-1,3-butadienyl)phenol (IVb, Vb) and that there is at least one *trans* bond present in each of the isomers.

When the lower boiling isomer, IVb, is allowed to react with I in DMF for 48 hr at 110°, a 70% yield of IIIb is obtained. There is also a 15% conversion to the higher boiling isomer, Vb. This shows that the structure of IVb must be *cis,trans*-O-(4-methyl-1,3-

Scheme V



butadienyl)phenol, because only the *cis* isomer would allow the butadiene portion of the molecule to be close enough to the phenolic OH to experience ring closure.

When the higher boiling isomer, Vb, is allowed to react with I in DMF for 48 hr at 110°, there is no closure and there is no conversion to IVb. This indicates that the α double bond is *trans* and that isomer Vb is the more stable of the two isomers. Ultraviolet data of IVb [λ_{max}^{MeOH} 266 mμ (ϵ 17,200)] and Vb [λ_{max}^{MeOH} 279 mμ (ϵ 18,500)] also would indicate that Vb is a *trans,trans* system as opposed to a *cis,trans* system of IVb.[4]

The mechanism for the formation of the 2H-1-benzopyran is then clearly one in which the aldehyde function of the sodium salicylaldehyde, I, suffers initial attack to form the *cis* and *trans* Wittig adducts. The *cis* isomer will then close to give the 2H-1-benzopyran by way of a Michael-type addition of the phenolate anion to the double bond. The *trans* isomer, due to its geometry, will not close.

Other examples of the formation of 1,3-butadienes *via* a Wittig reaction have been published by Wittig[5] and Plieninger.[6]

The last step in this mechanism involves ring closure by reaction between phenolic hydroxyl and olefin functional groups. Examples of this reaction have been reported by Bartz[7] and Shulgin.[8]

One might expect starting with a *cis,trans* mixture of 2-butenyltriphenylphosphonium chloride (IIb) that the intermediates isolated would be *cis,cis*-, *cis,trans*-, *trans,cis*-, and *trans,trans*-O-(4-methyl-1,3-butadienyl)-phenol. The fact that only two intermediates are isolated leads us to the following proposal.

We have shown that under basic conditions the allyl salt, IIa, equilibrates between the allyl anion and the propenyl anion, and that reaction takes place by way of the allyl anion. It could be, therefore, reasoned that a similar equilibrium is established in the 2-butenyl salt, IIb, as shown in Scheme VI.

Of the four possible equilibrium structures (C, D, E, and F), structures E and F would be the more stable because of the close proximity of unlike charges. Of the two, E would be reasoned to be the more stable because of a lesser steric interaction between the methyl and phenyl groups. If E is then concluded to be the more stable, the equilibrium would tend to be shifted toward the formation of E. Structure E would then in turn convert to G to give the observed *cis,trans*- and *trans,trans*-O-(4-methyl-1,3-butadienyl)phenol (IVb and Vb).

The 2H-1-benzopyrans that have been prepared from the phosphonium salts (shown in Scheme V) follow.

(a) R, R' = H; yield 34%, IIIa
(b) R = H, R' = CH_3; yield 30%, IIIb
(d) R = CH_3, R' = H; yield 45%, IIId

The intermediate phenol was isolated, but the 2H-1-benzopyran was not formed where

(c) R = H, R' = C_6H_5; yield 45%, Vc

Compound Vc was shown to be the only product by thin layer chromatography. This is to be expected because highly stabilized ylids have been shown to give predominantly *trans* products.[9]

Research is continuing in this area. The results of these studies will be reported in future publications.

Experimental Section

All infrared spectra were obtained on a Perkin-Elmer Infracord 137 and nmr spectra were obtained on a Varian A-60 analytical nmr spectrometer using tetramethylsilane as a standard. The vapor phase chromatographic data were obtained using a column of 20% S.E.-30 Gas-Pack W, 60-80 mesh on a Matronic instrument. All melting points were uncorrected and obtained on a Fischer-Johns melting point apparatus. Analyses were by Micro-Analysis, Inc., Wilmington, Del.

General Procedure.—To a dried, three-necked, 500-ml round-bottomed flask, fitted with a reflux condenser, stirrer, and pressure-equalizing dropping funnel, was added 2 moles of sodium salicylaldehyde (I) dissolved in 200 ml of DMF. To this was added dropwise 1 mole of the phosphonium salt dissolved in 200 ml of DMF. The total addition took about 1 hr. The reactions were run under dry N_2. The temperature was held at 110 or 0° for 48 hr, at which time the reaction mixture was added to 1 l. of water. The water-DMF mixture was then extracted with ether. The ether extraction was washed with water, washed with sodium bisulfite, and again with water, then finally dried over $MgSO_4$ (anhydrous).

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[4] A. Sandoval and L. J. Zechmeister, *J. Am. Chem. Soc.*, **69**, 553 (1947).

[5] G. Wittig and U. Scholkopf, *Ber.*, **87**, 1318 (1954).

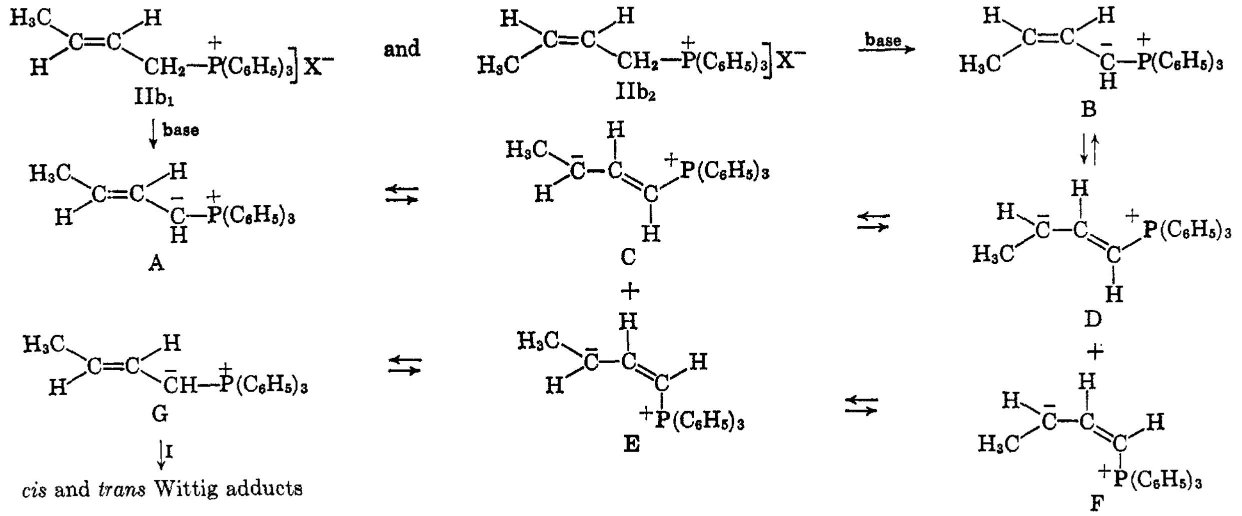
[6] H. Plieninger, M. Hobel, and V. Lude, *ibid.*, **96**, 1618 (1963).

[7] Q. R. Bartz, R. F. Miller, and R. Adams, *J. Am. Chem. Soc.*, **57**, 371 (1935).

[8] A. T. Shulgin and A. W. Baker, *J. Org. Chem.*, **28**, 2468 (1963).

[9] H. O. House, V. K. Jones, and G. A. Frank, *ibid.*, **29**, 3327 (1964).

SCHEME VI



The dried ether extract was concentrated and the residue distilled *in vacuo*.

2-Methyl-2H-1-benzopyran (IIIa).—To a solution of 6.4 g (0.04 mole) of I was added 8.5 g (0.02 mole) of allyl triphenylphosphonium bromide (IIa), prepared according to Grayson,[10] and the general procedure was followed. The final ether was extracted with dilute NaOH, washed with water, and dried over $MgSO_4$ (ether I). The NaOH layer was neutralized with dilute HCl, extracted with ether, and dried (ether II). Ether II was concentrated and an attempt made to distil the product under vacuum. The product polymerized. Ether I was concentrated and vacuum distilled to give 1.2 g (31% yield) of IIIa: bp 45° (0.5 mm); $n^{25}D$ 1.5670; ν 3090, 3000, 2990, 1670, 1650, 1610, 1460, 1235, 1040, 775, 754 cm^{-1}; $\delta = 0.90$ (d, 3, CH_3), 4.50 (m, 1, H), 5.05 (split d, 1, =CH), 5.85 (split d, 1, $-\overset{|}{C}=CH$), 6.8–6.2 ppm (m, 4, C_6H_4) [lit.[11] bp 34° (0.2 mm), $n^{25}D$ 1.5658].

2-*n*-Butylphenol (VIa).—To a solution of 12.5 g (0.09 mole) of I was added 16.75 g (0.04 mole) of IIa and the general procedure was followed. The reaction was run at 0°. The ether extract was washed with NaOH; the NaOH portion was neutralized with dilute HCl and extracted with ether. The ether was then washed with water and dried over $MgSO_4$. Gas chromatography showed two products present in the ether, *cis*- and *trans*-O-(1,3-butadienyl)phenol, IVa and Va. The mixture was hydrogenated over 10% Pd–C catalyst. After 4 hr the ether was filtered, concentrated, and distilled to give 0.4 g (6.1% yield) of VIa (one product by gc): bp 62° (0.05 mm); $n^{25}D$ 1.5184; ν 3400, 3040, 2950, 2890, 1600, 1580, 1450, 1370, 1230, 750 cm^{-1}; $\delta = 0.65$ (t, 3, CH_3), 1.15 (m, 4, CH_2's), 2.30 (t, 2, CH_2), 5.80 (s, 1, OH), 6.2–6.9 ppm (m, 4, C_6H_4) [lit.[12] bp 75° (1 mm), $n^{25}D$ 1.5182].

An attempt was made to isolate the *cis*- and *trans*-O-(1,3-butadienyl)phenol. These products could be seen on the gc, but attempts to vacuum distil them resulted in polymerization.

2-Deuteriomethyl-3-deuterio-2H-1-benzopyran (XIV).—To a solution of 4.5 g (0.031 mole) of I dissolved in 25 ml of DOMe was added 6.18 g (0.016 mole) of IIa dissolved in 25 ml of DMF; then the solution was allowed to react following the general procedure. The temperature was held at 96°. The reaction mixture was poured into 200 ml of water and extracted as in the general procedure. The ether was concentrated to give 0.2 g (9% yield) of XIV: bp 43° (0.3 mm); $n^{25}D$ 1.5653; ν 3050, 2920, 2830, 2240, 1640, 1610, 1570, 1450, 755 cm^{-1}; $\delta^{DCCl_3} = 4.80$ (s, 1, H), 6.25 (s, 1 =CH), 7.2–6.5 ppm (m, 4, C_6H_4).

Treatment of 2-Methyl-2H-1-benzopyran, IIIa, with Sodium Methoxide and Deuteriomethanol.—A 0.9-g (0.006 mole) sample of IIIa was put in a 50-ml round-bottom flask containing 0.006 mole of NaOMe in 25 ml of DOMe. The mixture was allowed to reflux for 48 hr, at which time the mixture was worked up according to the general procedure to give 0.3 g (34%) recovery of IIIa. There was no exchange of hydrogen for deuterium as seen by comparison with nmr from IIIa starting materials.

Reaction of Allyltriphenylphosphonium Bromide, IIa, with Benzaldehyde in the Presence of Sodium Phenoxide.—To a 1-l., 3-necked flask provided with mechanical stirring, condenser, and nitrogen pad was added 500 ml of DMF. Sodium hydride (8.9 g of a 54% by weight dispersion in mineral oil, 0.1 mole) was added and then 9.41 g (0.1 mole) of phenol (added slowly). After the salt had been formed a mixture of 38.3 g (0.1 mole) of IIa and 10.61 g (0.1 mole) of benzaldehyde was slowly added. After refluxing for 24 hr the brown mixture was poured into water and extracted with ether. The ether was washed with NaOH and water and dried over $MgSO_4$. Distillation gave 2.1 g (0.016 mole) of *cis*-1-phenyl-1,3-butadiene (16%) and 1.3 g (0.01 mole) of *trans*-1-phenyl-1,3-butadiene (10%) (infrared spectra were respectively superimposable with those given[13]).

Triphenylphosphine oxide (melting point and mixture melting point identical with authentic sample), 9 g (33%), was obtained from the residue. None of the fractions obtained in the distillation or the residue showed absorption attributable to a phenyl–O–C– linkage.

Propenyltriphenylphosphonium Bromide (VIII).—To 100 ml of acetonitrile (dried over P_2O_5) was added 38.4 g (0.1 mole) of IIa, and refluxed for 24 hr. Work-up gave 38.4-g (0.1 mole) yield of VIII (100%). This was shown to be pure material by thin layer chromatography and comparison of infrared spectrum with that of an authentic sample.[3]

2-Methyl-2H-1-benzopyran, IIIa, *via* Allyltriphenylphosphonium Bromide, IIa, and the Sodium Salt of Salicylaldehyde, I, in DMF with NaI.—A 200-ml portion of reagent grade DMF was placed in 1-l., 3-necked flask provided with mechanical stirring, condenser, and N_2 cover. A mixture of 14.4 g (0.1 mole) of I, 38.3 g (0.1 mole) of IIa, and 15 g (0.1 mole) of NaI was refluxed for 24 hr and then added to 600 ml of water. The mixture was extracted and worked up according to the general procedure to give 5.1 g (34%) of IIIa (identified by comparison of gc and infrared spectrum with those of an authentic sample) and 19.3 g (70%) of triphenylphosphine oxide (identified by comparison of melting point, mixture melting point, and infrared spectrum of an authentic sample).

2-Methyl-2H-1-benzopyran, IIIa, *via* Propenyltriphenylphosphonium Bromide, VIII, and Sodium Salicylaldehyde, I, in DMF with NaI.—This experiment was conducted in the same manner as the above. The yield of IIIa was 3% and the yield of triphenylphosphine oxide was 32%.

2-Methyl-2H-1-benzopyran, IIIa, *via* Fusion of IIa and I.—A 1.97-g (0.014 mole) portion of I and 5.25 g (0.014 mole) of IIa were mixed and put in a 50-ml, 1-necked flask. The flask was provided with a distillation head, a receiver, and vacuum was applied to the apparatus (0.4 mm). When the bath temperature reached 180°, the solids melted into a red liquid and distillation began. After 2 hr the distillate was dissolved in ether and distilled to give 0.6 g (30%) yield of IIIa (identified by gc and infrared spectrum comparison with authentic sample). The residue

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(10) M. Grayson and P. T. Klough, *J. Am. Chem. Soc.*, **82**, 3919 (1960).

(11) E. E. Schweizer and R. Schepers, *Tetrahedron Letters*, **No. 15**, 979 (1963).

(12) G. G. S. Dutton, T. I. Briggs, B. R. Brown and R. K. Powell, *Can. J. Chem.*, **31**, 837 (1953).

(13) O. Grummitt and F. J. Christoph, *J. Am. Chem. Soc.*, **73**, 3479 (1951).

was distilled (0.4 mm, 150°-200°) to give 2.4 g (63%) triphenylphosphine oxide (identified by melting point, mixture melting point, and infrared).

2-Methyl-2H-1-benzopyran, IIIa, *via* Fusion of VIII and I.—This experiment was conducted in the same manner as the above to give 0.2 g (10%) 2-methyl-2H-1-benzopyran, IIIa, and 1.5 g (37%) of triphenylphosphine oxide.

1-Vinyl-2-(O-hydroxyphenyl)vinyltriphenylphosphonium Bromide (XIII).—A mixture of 22.2 g (0.15 mole) of I and 59 g (0.15 mole) of IIa was added to 350 ml of dry ethanol under N_2. The mixture was refluxed for 48 hr and then neutralized with gaseous HBr; the ethanol was distilled off. The residue was added to chloroform, filtered, and added dropwise to 1 l. of ether. This precipitation process was repeated again to give (after drying) 55.5 g of yellow solid. A 1-g sample of this solid was dissolved in 1 ml of chloroform and placed on a chromatographic column (silica gel G) and eluted with 20% methanol-chloroform (by volume) to give a yellow solid: yield (total) 75%; mp 265-270°; ν^{KBr} 3400, 3100, 1620, 1600, 1575, 1420, 1260, 1000, 840, 725, 690 cm^{-1}; λ_{max}^{MeOH} 362 mμ (ϵ 14,000); δ^{DMSO} = 3.40 (s, 1, OH), 8.0-6.5 ppm (m, 23, C_6H_5 and C=CH).

Anal. Calcd for $C_{28}H_{24}BrOP$: C, 69.08; H, 4.94; Br, 16.38; P, 6.32. Found: C, 69.10; H, 5.11; Br, 15.94; P, 6.32.

2-Ethyl-2H-1-benzopyran (IIIb).—To a solution of 5.4 g (0.04 mole) of I was added 6.5 g (0.02 mole) of 2-butenyltriphenylphosphonium chloride (IIb) made according to Bohlmann and Mannhardt.[14] The reaction was run at 110° using the general procedure. Vacuum distillation gave 0.87 g (0.006 m) of IIIb (yield 30%): bp 65° (0.5 mm); n^{25}_{D} 1.5569; ν 2980, 1640, 1600, 1480 cm^{-1}; δ = 0.55 (t, 3, CH_3), 1.20 (q, 2, CH_2), 4.30 (split t, 1, H), 5.10 (split d, 1, =CH), 5.85 (split d, 1 =CH), 6.8-6.2 ppm (m, 4, C_6H_4).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.20; H, 7.40.

2-Ethylchroman (VIIb).—A solution of 1.3 g (0.08 m) of IIIb dissolved in methanol was shaken in a hydrogen atmosphere over 10% Pd-C. After 94% of the theoretical amount of hydrogen was consumed (1 hr), the reaction was stopped. The catalyst was removed and the solution concentrated. The product was vacuum distilled to give 1.2 g of VIIb: bp 42° (0.1 mm); n^{25}_{D} 1.5256 [lit.[15] bp 116° (16 mm); n^{26}_{D} 1.5250]; ν 3020, 2950, 1610, 1490, 1460, 1380, 755 cm^{-1}; δ = 0.60 (t, 3, CH_3), 1.35 (m, 4, CH_2), 2.20 (q, 2, CH_2), 3.35 (m, 1, H), 6.8-6.2 ppm (m, 4, C_6H_4).

O-(4-Methyl-1,3-butadienyl)phenol (IVb and Vb).—To a solution of 9.8 g (0.068 mole) of I was added 12 g (0.034 mole) of IIb; the reaction was run according to the general procedure at 0°. Distillation gave 4.55 g (84% yield) of a mixture of IIIb, IVb, and Vb. The compounds IVb and Vb were removed by extraction with dilute NaOH. Compounds IVb and Vb were extracted from the neutralized water layer with ether, concentrated and separated by spinning-band distillation under vacuum.

***cis,trans*-O-(4-Methyl-1,3-butadienyl)phenol (IVb).**—This isomer had bp 80° (1 mm); n^{25}_{D} 1.5918; ν 3510, 3040, 2950, 1660, 1610, 1495, 1455, 1210, weak 990, 755 cm^{-1}; δ = 1.15 (d, 3, CH_3), 6.9-5.0 ppm (m, 9, C_6H_5, OH, and =CH); λ_{max}^{MeOH} 266 mμ (ϵ 17,200).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.47; H, 7.49. Found: C, 82.72; H, 7.39.

***trans,trans*-O-(4-Methyl-1,3-butadienyl)phenol (Vb).**—This isomer had bp 91° (1 mm); n^{25}_{D} 1.6325; ν 3500, 3050, 2950, 1650, 1600, 1460, 1410, 990 (s), 795, 754, 708 cm^{-1}; δ = 1.25 (s-d, 3, CH_3), 5.80 (s, 1, OH), 6.8-4.8 ppm (m, 8, C_6H_4 and =CH); λ_{max}^{MeOH} 279 mμ (ϵ 18,500), 320 mμ (ϵ 11,000).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.47; H, 7.49. Found: C, 82.53; H, 7.28.

This same *trans,trans* isomer was also olated in 44% yield from the reaction of I and IIb run at 120°. Samples from the two different reactions were shown to be identical by comparison of infrared and nmr spectra.

2-*n*-Pentylphenol (VIb).—A mixture of IVb and Vb, 1 g (0.006 mole), was dissolved in 30 ml of methanol and shaken in a hydrogen atmosphere over 10% Pd-C. After 85% of the theoretical amount of hydrogen was consumed (2 hr), the reaction was stopped. Filtration, concentration, and distillation gave 0.8 g (yield 80%) of VIb: bp 69° (0.25 mm); n^{25}_{D} 1.5141 [lit.[12] bp 89° (1 mm); n^{25}_{D} 1.5141]; ν 3400, 2900, 1600, 1440, 1370, 1230, 1110, 750 cm^{-1}; δ = 0.85 (t, 3, CH_3), 1.40 (m, 6, CH_2), 2.60 (t, 2, CH_2), 5.95 (s, 1, OH), 7.2-6.5 ppm (m, 4, C_6H_4).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.29; H, 9.73.

2-Ethyl-2H-1-benzopyran (IIIb) from *cis,trans*-O-(4-Methyl-1,3-butadienyl)phenol (IVb).—To a solution of 0.6 g (0.004 mole) of I dissolved in 50 ml of DMF was added 0.334 g (0.002 mole) of IVb dissolved in 50 ml of DMF. The two were allowed to react at 110° for 48 hr under N_2. The reaction mixture was added to 100 ml of water, extracted with ether, washed with water, washed with $NaHSO_3$, and dried over $MgSO_4$. Concentration and distillation under vacuum gave IIIb in 70% yield. This sample was identical with the previously prepared sample of IIIb by nmr and gc. Also obtained was a 15% yield of Vb identified by comparison of gc with an authentic sample.

Attempted Ring Closure of *trans,trans*-O-(4-Methyl-1,3-butadienyl)phenol (Vb).—A solution of 0.5 g (0.004 mole) of I was heated at 120° with 0.5 g (0.003 mole) of Vb in 100 ml of DMF for 48 hr under dry N_2. Only starting materials were recovered (identified by gc and infrared) from this reaction (90% recovery of Vb). No IIIb and IVb were observed by gc.

2,2-Dimethyl-2H-1-benzopyran (IIId).—To a solution of 11 g (0.08 mole) of I dissolved in DMF was added 13.5 g (0.04 mole) of methylallyltriphenylphosphonium chloride (IId) prepared according to Hauser, *et al.*[16] The reaction was run at 110° according to the general procedure. The ether extract (ether I) was extracted with dilute NaOH; aqueous NaOH was neutralized with dilute HCl and extracted with ether to give ether II. Ether I and II were then washed with water and dried over $MgSO_4$. Ether II was concentrated; an attempt was made to isolate the product (one peak by gc). The product polymerized and could not be isolated. Ether I was concentrated and distilled under vacuum to give 2.8 g (0.017 mole) of IIId (45% yield): bp 84° (1.5 mm); n^{25}_{D} 1.5495; ν 3040, 2990, 2940, 1640, 1605, 1565, 1450, 1385, 1370, 1060, 770, 740 cm^{-1}; δ = 0.90 (s, 6, CH_3), 5.00 (d, 1, =CH), 5.80 (d, 1, =CH), 6.8-6.2 ppm (m, 4, C_6H_4).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.35; H, 7.41.

2,2-Dimethylchroman (VIId).—A 1-g (0.006 mole) sample of I was dissolved in 30 ml of methanol and shaken in a hydrogen atmosphere over 10% Pd-C catalyst. After 3 hr the catalyst was removed; the solution was concentrated and vacuum distilled to give 0.8 g (0.005 mole) of VIId (81% yield): bp 38° (0.1 mm); n^{25}_{D} 1.5247 (lit.[17] bp 224-226°; n^{25}_{D} 1.524); ν 3030, 2990, 2950, 1615, 1580, 1450, 1380, 1375, 1120, 758, 750 cm^{-1}; δ = 1.05 (s, 6, CH_3), 1.40 (t, 2, CH_2), 2.40 (t, 2, CH_2), 6.9-6.3 ppm (m, 4, C_6H_4).

O-(4-Phenyl-1,3-butadienyl)phenol (Vc).—To a solution of 35 g (0.24 mole) of I in DMF was added 50 g (0.12 mole) of cinnamyltriphenylphosphonium bromide (IIc) made according to Friedrich and Mirback[18] in DMF. The reaction was run according to the general procedure at 110°. The ether extract was concentrated; the residue was dissolved in chloroform and purified by chromatography (silica gel G column, eluted with benzene) to give 12 g (45% yield) of Vc: mp 164-165°; ν^{KBr} 3600, 1620, 1600, 1490, 1450, 1180, 980, 745, 725, 690 cm^{-1}; δ^{CDCl_3} = 7.5-6.5 ppm; λ_{max}^{MeOH} 341 (ϵ 33,500).

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.27; H, 6.55.

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