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.

Acknowledgment.—This work was supported by Grant PRF2032-Al from the Petroleum Research Fund of the American Chemical Society. E. E. S. and C. J. B. gratefully acknowledge this support.

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

E. E. SCHWEIZER, W. S. CREASY, K. K. LIGHT, AND E. T. SHAFFER

Department of Chemistry, University of Delaware, Newark, Delaware 19711

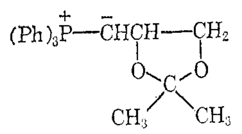
Received August 29, 1968

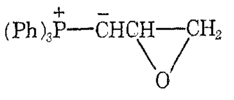
The triphenylphosphonium salts of furfuryl bromide and its fully and partially hydrogenated derivatives have been prepared and allowed to react in the Wittig manner. A reversible β elimination followed by an unusual internal ylidization reaction was observed with the tetrahydrofurfuryl salt.

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]

---

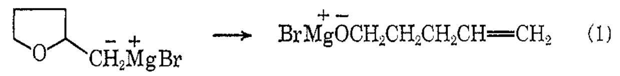
[1] Paper XIX: E. E. Schweizer, *et al.*, *J. Org. Chem.*, **34**, 207 (1969).

[2] (a) A. Maerker, *Org. Reactions*, **14**, 272 (1965). (b) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

[3] F. Bohlmann and P. Herbst, *Chem. Ber.*, **92**, 1319 (1959).

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

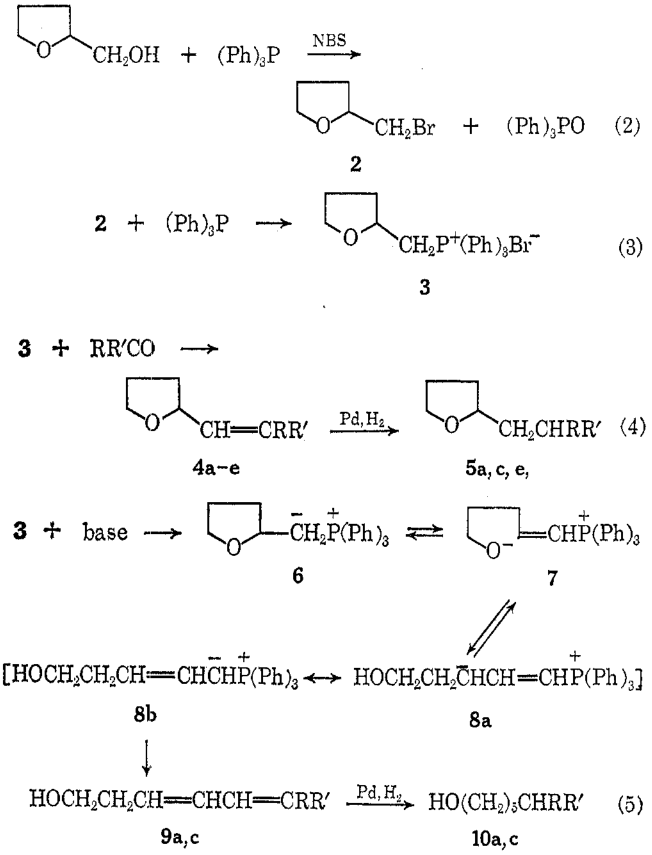
It is well known that β-halo ethers are cleaved to olefins and alkoxides by the action of metals such as sodium, magnesium, and zinc. Boord[5] has used this method in the preparation of olefins that bears his name. Robinson and Smith[6] and later Amstutz[7] have investigated the behavior of magnesium on tetrahydrofurfuryl bromide (see eq 1). The product was



not the normal Grignard reagent, but a ring-opened species obtained through β elimination, thus supporting the ionic nature of the magnesium–carbon bond.

A study was undertaken of the reactions of tetrahydrofurfuryl triphenylphosphonium bromide, **3**, in order to compare the results with those shown in eq 1. Some of the corresponding reactions of the dihydro- and unsaturated furan salts were also examined.

Tetrahydrofurfuryl bromide, **2**, was prepared from tetrahydrofurfuryl alcohol (92% yield) employing a technique used earlier by Trippett[8] (eq 2). Salt **3** was prepared by allowing bromide **2** to react with triphenylphosphine (eq 3). Salt **3** was then allowed to react with benzaldehyde and other carbonyl species under a variety of conditions in the hopes of isolating ring-opened products.



a, R = Ph; R′ = H (*cis*)
b, R = Ph; R′ = H (*trans*)
c, R = R′ = C_5H_{10}
d, R = Ph; R′ = CH_3
e, R = $(CH_3)_2CH$; R′ = H

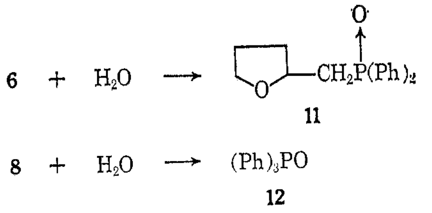
When **3** and benzaldehyde were dissolved in dimethylformamide (DMF), NaH was added, and the mixture was allowed to react at 110° (48 hr) under anhydrous conditions, only *cis*- and *trans*-2-styryltetrahydrofuran, **4a** and **4b**, were obtained in a 65/35 ratio, respectively (eq 4). If, however, **3** was added to a solution of benzaldehyde in the presence of ethanolic sodium ethoxide and allowed to react, six products were observed by glpc. These products could be separated into a mixture of **4a** and **4b** and another mixture of the four possible isomers of 6-hydroxy-1-phenylhexa-1,3-diene, **9a** (eq 5). The glpc of the original mixture showed the ratio of **4a–b** to **9a** to be 4/96, respectively. Hydrogenation of a mixture of **4a** and **4b** gave 2-(β-phenylethyl)tetrahydrofuran, **5a**. Hydrogenation of isomers **9a** gave only 6-phenylhexanol, **10a**.

This is, as far as we know, the only example of an ylide undergoing a simple reversible β elimination to form an oxy anion which then may act intramolecularly[9] as a base to pluck off the α proton from a β-substituted vinylic phosphonium salt forming an allyl ylide.

Initially, serious doubts were entertained as to the reversibility of steps **6–8** on the basis of the following experiments.

I.—When furfuryltriphenylphosphonium bromide, **3**, was allowed to reflux in a variety of solvent–base pairs (NaOEt–EtOH, PhLi–benzene, *n*-BuLi–Et_2O), followed by cooling and quenching with anhydrous HBr, only the starting salt **3** resulted (90–95% yield recovered). There was no evidence (by ir, nmr, or tlc) that any open-chain salt was present.

II.—Similar reactions followed by cooling and treatment with water gave only tetrahydrofurfuryldiphenylphosphine oxide, **11**. None of the triphenylphosphine oxide, **12**, which would be expected on hydrolyzing the semistabilized ylide, **8**, was found. However, the elimination–addition possibilities of a β-alkoxy ylide were supported by the reaction of 2-methoxyethyltriphenylphosphonium bromide, **13**, with benzaldehyde in ethanolic sodium ethoxide to give only the ethyl ether of cinnamyl alcohol, **14** (none of the methyl ether was observed). The most conclusive argument in favor of the **6** to **8** reversibility is an examination of the tetrahydrofurfuryldiphenylphosphine oxide, **11**, obtained from the reaction of salt, **3**, in EtOD–NaOEt, followed by quenching in D_2O. In this case the hot alcoholic solution was quenched with D_2O and the ring-closed tetrahydrofurfuryldiphenylphosphine oxide was shown (nmr) to have structure **15**. The exchange of the



$$\underset{\mathbf{13}}{MeOCH_2CH_2P^+(Ph)_3Br^-} + PhCHO \xrightarrow[NaOEt]{EtOH} \underset{\mathbf{14}}{EtOCH_2CH{=}CHPh}$$

---

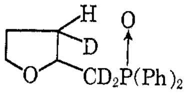
(5) C. G. Schmitt and C. E. Boord, *J. Amer. Chem. Soc.*, **54**, 758 (1932).

(6) R. Robinson and L. H. Smith, *J. Chem. Soc.*, 195 (1936).

(7) E. D. Amstutz, *J. Org. Chem.*, **9**, 310 (1944).

(8) S. Trippett, *J. Chem. Soc.*, 2337 (1962).

(9) This may be the result of an intermolecular reaction; however, the over-all effect is as described.



15

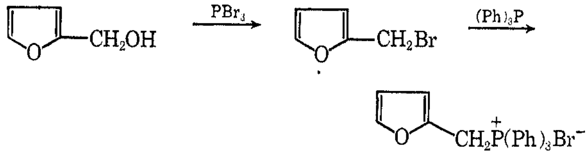
protons in the 3 position on the tetrahydrofuran ring could only come about by deuteration of species **8a** on the road to **15** *via* γ-deuterated **7**. Thus the reversibility of the β-elimination sequence was firmly established.

We were interested to note that on quenching the hot ylide–alcohol mixture with water (or D_2O) both **11** (or **15**) and **12** were formed. This latter bit of information (in direct contrast to the exclusive formation of **11** on quenching a cold alcoholic solution) supports the expected high degree of reactivity of the unstabilized ylide, **6**, compared with that of the semistabilized ylide, **8b**.

The results of reactions with cyclohexanone, acetophenone, isobutyraldehyde, and benzaldehyde are given in Table I.

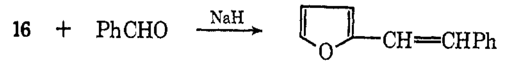
The reactions of furfuryltriphenylphosphonium bromide, **16**, were then investigated in order to compare these with the tetrahydrofurfuryl salt, **3**, as far as the *cis/trans* ratio of products was concerned. No ring-opening compounds were expected.

Furfuryl bromide was prepared according to Zanetti[10] and allowed to react with triphenylphosphine to give **16** (eq 6a). Salt **16** was then allowed to react under the conditions that gave ring opening in the case of salt, **3**. When **16** was allowed to react with benzaldehyde, two products were isolated from the reaction and shown to be *cis*- and *trans*-2-styrylfuran, **17**, in 39 and 61% yield, respectively (eq 6b). A higher percentage of *trans*-product is obtained where the ylide is highly stabilized (*i.e.*, from salt **16**). These results are in agreement with the findings of House[11] and coworkers.



(6a)

16

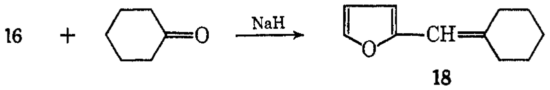


(6b)

17a, *cis*
b, *trans*

Wadsworth[12] has obtained only the *trans*-2-styrylfuran by the reaction of diethyl 2-furylmethylphosphate with benzaldehyde in NaOMe and DMF. Using the corresponding Wittig reaction offers a means of obtaining the *cis* as well as the *trans* product.

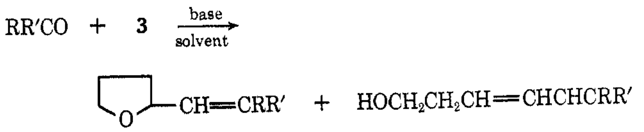
The reaction of **16** with cyclohexanone, under conditions that gave ring-opened product in the case of **3**, gave only the expected furfurylidene cyclohexane **18** in 54% yield (eq 7).



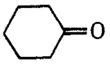
(7)

18

TABLE I

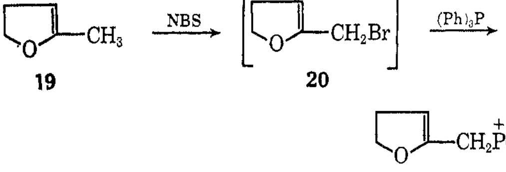


9

					Olefins 4 and 9	
Carbonyl	Solvent	Base	Temp, °C	Time, hr	Yield, %	Ratio of **4/9**
$PhCHO^a$	DMF	NaH	110	48	70	100/0
$PhCHO^b$	DMF	NaH	110	48	71	23/77
PhCHO	EtOH	NaOEt	Reflux	15	49	3/97
PhCHO	Benzene	NaH	Reflux	12	26	9/91
$PhCHO^d$	DMSO	NaH	90	12	41	8/92
$(CH_3)_2CHCHO^d$	EtOH	NaOEt	Reflux	48	80	8/92
$(CH_3)_2CHCHO^a$	DMF	NaH	110	12	74	28/72
$C_6H_5COCH_3^d$	EtOH	NaOEt	Reflux	12	56	0/100
	DMF	NaH	100	48	43	0/100
	DMF	NaH	30	48	35	0/100
	DMF	NaH	0	48	0	
	THF	PhLi	Reflux	48	27	0/100
	DMF	NaH	110^c	13	56	6/94

[a] Added before NaH. [b] Added after NaH; ratio of **4/9** based on ratios of hydrogenated species. [c] Addition was made as soon as ylide color appears on addition of NaH to salt–DMF mixture. Temperature raised to reflux then immediately lowered to 110° for 13 hr. [d] Added after 6-hr reflux of salt **3**.

Finally, 4,5-dihydrofurfuryltriphenylphosphonium bromide, **21**, was prepared and its reaction with benzaldehyde observed (eq 8).



19 **20**

(8)

21

The 2-methyl-4,5-dihydrofuran[13] **19** was treated with N-bromosuccinimide (NBS) in benzene at 35°. After removal of the succinimide by filtration, the 4,5-dihydro-2-furfuryl bromide **20** was allowed to react *in situ* with triphenylphosphine in ethyl acetate. When no peroxides were used and the temperature of the reaction mixture was kept below 60° after addition of the triphenylphosphine, dihydro salt **21** could be isolated in 15% yield. When peroxides were added and the reaction temperature was taken to reflux, the furfuryltriphenylphosphonium bromide, **16**, was isolated. Somewhat similar results were obtained by Korte[14] when he attempted to brominate a dihydrofuran system with NBS and was unable to isolate the corresponding bromide. Only the furan derivative was obtained.

Salt **21** was then allowed to react with benzaldehyde using NaH as the base in DMF. The work-up of the reaction mixture yielded only two volatile products which were shown to be *cis*- and *trans*-2-styrylfuran, **17**, by infrared spectra and glpc retention times.

Hydrolysis of **21** with KOH in aqueous ethanol gave a mixture of two products in 65% yield. These were

---

[10] J. E. Zanetti, *J. Amer. Chem. Soc.*, **61**, 2249 (1939).

[11] H. O. House, V. K. Jones, and G. A. Frank, *J. Org. Chem.*, **29**, 3327 (1964).

[12] D. H. Wadsworth, O. E. Schupp, III, E. J. Seus, and J. A. Ford, Jr., *J. Org. Chem.*, **30**, 680 (1965).

[13] Obtained from Aldrich Chemical Co., Milwaukee, Wis.

[14] F. Korte, R. Heinz, and D. Scharf, *Chem. Ber.*, **94**, 825 (1961).

shown to be 2-methyl-4,5-dihydrofuran, **19**, and 2-methylfuran, **22**, in the ratio of 15/85, respectively.

From the above results, one might wonder if in reality salt **21** was impure **16**. It can be shown that the two salts are not the same.

Both salts gave sharp melting points with decomposition. Salt **16** melted at 270–271° and salt **21** melted at 246–247°. A mixture melting point of the two was broad and finished melting at about 220°. The infrared and nmr spectra of the two were totally different. Thus there was no doubt that the two salts, **16** and **21**, were not identical.

Thus a novel reversible ring-opening reaction has been observed, in the case of tetrahydrofurfuryl salt **3**, which may be followed by Wittig reaction. Furfuryl salt **16** gave the expected normal Wittig reaction products. 4,5-Dihydro-2-furfuryl salt **21** was oxidized under the conditions of the Wittig reaction and gave products identical with those obtained from **16**.

Experimental Section

All ir 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 standard. The vpc data were obtained using a column of 20% SE-30 Gas-Pack W, 60/80 mesh on a Matronic instrument. All melting points were uncorrected and obtained on a Fisher-Johns melting point apparatus. Analyses were by Micro-Analysis, Inc., Wilmington, Del.

Tetrahydrofurfuryl Bromide, 2.—To a mixture of 81.6 g of tetrahydrofurfuryl alcohol (Aldrich) and 230 g of triphenylphosphine in a 1-l. three-necked flask fitted with reflux condenser and mechanical stirrer was added 130 g of N-bromosuccinimide very slowly with continuous stirring. The addition of NBS required a total of 1.5 hr, during which time a considerable exothermic reaction was observed. As soon as the addition was completed, the reflux condenser was replaced with a distillation column, thermometer, water-jacketed condenser, and vacuum take-off and the pure bromide distilled under reduced pressure; bp 85–87° (24 mm): yield, 152 g of clear distillate (92%), shown to be tetrahydrofurfuryl bromide by comparison of its ir and nmr spectra with those of an authentic sample.

Tetrahydrofurfuryltriphenylphosphonium Bromide, 3.—To a 500-ml round-bottomed flask fitted with reflux condenser was added 131 g (0.5 mol) of triphenylphosphine. To this was added slowly 83 g (0.5 mol) of tetrahydrofurfuryl bromide, **2**. This mixture was heated on a steam bath for 48 hr. The solid mass that formed was broken out of the flask, ground into a fine powder, refluxed for 12 hr in ethyl acetate, filtered, and dried under vacuum at 80° for 6 hr, giving 159.7 g (75% yield) of a solid (one product by tlc): mp 232–234°; ir ν (KBr) 1610, 1500, 1450, 1110, 1050, 840 cm^{-1}; nmr δ (CDCl$_3$) 2.20 (m, 4, CH$_2$), 3.50–4.50 (m, 5, CH$_2$ and CH), 7.75 ppm (m, 15, C$_6$H$_5$).

Anal. Calcd for $C_{23}H_{24}BrOP$: C, 64.64; H, 5.66; Br, 18.70. Found: C, 64.73; H, 5.59; Br, 18.69.

2-Styryltetrahydrofuran, 4a and 4b.—To a 500-ml round-bottomed flask fitted with reflux condenser and stirrer were added 40 g (0.10 mol) of **3** and 11 g (0.10 mol) of benzaldehyde in 250 ml of dimethylformamide (DMF). To this was added under nitrogen and with stirring 5.6 g (0.10 mol) of 54% NaH. The temperature was brought to 110° over a period of 1 hr and held for 48 hr. The mixture was then added to 1 l. of water and extracted with ether. The ether layer was washed with water, dried over MgSO$_4$, concentrated, and short-path distilled to give 11.5 g (70% yield) of product, bp 70–150° (1.0 mm). Glpc showed two major products in the ratio of 65% (shown to be *cis* isomer) to 35% (shown to be *trans* isomer).

An attempt was made to separate the isomers **2a** and **2b** by gas chromatography. The individual isomers could be obtained in only 90% purity. A 60/40 *cis*/*trans* mixture of the two was analyzed.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 83.00; H, 7.96.

***cis*-2-Styryltetrahydrofuran, 4a.**—A 90% pure sample of this isomer gave the following spectra: ir ν (neat) 3000, 2980, 1640, 1600, 1580, 1480, 1440, 1050, 770, 700 cm^{-1}; nmr δ (CDCl$_3$) 1.80–2.08 (m, 4, CH$_2$), 3.70 (m, 2, CH$_2$), 4.6 (m, 1, CH), 5.50–6.65 (m, 2, -CH=CH- *cis* pattern), 7.25 ppm (m, 5, C$_6$H$_5$).

***trans*-2-Styryltetrahydrofuran, 4b.**—A 95% pure sample of this isomer gave the following spectra: ir ν (neat) 3000, 2990, 1650, 1580, 1480, 1420, 1040, 960, 750, 690 cm^{-1}; nmr δ (CDCl$_3$) 1.60 (m, 4, CH$_2$), 3.80 (m, 2, CH$_2$), 4.30 (q, 1, CH), 5.80–6.80 (m, 2, -CH=CH- *trans* pattern), 7.25 ppm (m, 5, C$_6$H$_5$).

2-(β-Phenylethyl)tetrahydrofuran, 5a.—A mixture of **4a** and **4b** (1 g, 0.006 mol) was dissolved in 50 ml of methanol and shaken in a hydrogen atmosphere over 10% Pd–C catalyst. After 90% of the theoretical amount of hydrogen was consumed (1 hr), the reaction was stopped, filtered, and concentrated. Distillation gave 0.81 g (80% yield) of **5a**: bp 67° (0.1 mm); n^{25}D 1.5124; ir ν (neat) 3010, 2990, 1600, 1490, 1450, 1060, 750, 700 cm^{-1}; nmr δ (neat) 1.40 (m, 6, CH$_2$), 2.35 (t, 2, CH$_2$), 3.30 (m, 3, CH$_2$ and CH), 6.80 ppm (m, 5, C$_6$H$_5$).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.68; H, 9.50.

6-Phenylhexanol, 10a, and 5a *via* Ring Opening of 3.—To a 500-ml round-bottomed flask fitted with stirrer and condenser was added 30 g (0.07 mol) of **3** dissolved in 200 ml of DMF. To this was added under N$_2$ 3.2 g (0.07 mol) of a 54% NaH dispersion. As soon as the deep red ylide color formed, 7.4 g (0.07 mol) of benzaldehyde in 100 ml of DMF was added dropwise. The temperature was then brought to 110° and held for 48 hr. The reaction mixture was then added to 1 l. of water and extracted with ether. The ether was washed with H$_2$O, dried over MgSO$_4$, concentrated, and short-path distilled to give 8.55 g (71% yield) of products. The glpc showed five major and one minor peak to be present (isomeric $C_{12}H_{14}O$). This mixture was dissolved in 100 ml of methanol and shaken in a hydrogen atmosphere over 10% Pd–C catalyst for 10 hr. The reaction was then stopped, filtered, and concentrated; glpc showed only two peaks present. These were separated by vacuum distillation to give 5.5 g (77%) of a product whose infrared spectrum was identical with that of **5a** and 1.72 g (23%) of a product which was shown to be 6-phenylhexanol **10a**: bp 89–91° (0.10 mm); n^{25}D 1.5076; ir ν (neat) 3400, 3050, 2950, 1610, 1500, 1460, 920, 750, 700 cm^{-1}; nmr δ (neat) 1.10 (m, 8, CH$_2$), 2.25 (t, 2, CH$_2$), 3.30 (t, 2, CH$_2$), 4.55 (S, 1, -OH), 6.80 ppm (m, 5, -C$_6$H$_5$).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.67; H, 10.23.

5-Cyclohexylidene-3-pentenol, 9c, *via* 3 in DMF at 110°.—To a 500-ml round-bottomed flask fitted with stirrer and condenser was added, under N$_2$, 3.14 g (0.056 mol) of NaH (54% dispersion). To this were added 50 ml of DMF and then 24 g (0.056 mol) of **3** in 200 ml of DMF. As soon as the red ylide color formed, 5.5 g (0.056 mol) of cyclohexanone in 100 ml of DMF was added dropwise. The temperature was then brought to 100° and held for 48 hr. The reaction mixture was added to 1 l. of water and extracted with ether. The combined ether extracts were washed with water, dried over MgSO$_4$, concentrated, and short-path distilled under vacuum to give 4.03 g (43% yield) of product. This was shown to be one major product by glc. The product was fractionally distilled under vacuum to give **9c**: bp 89° (0.2 mm); n^{25}D 1.5322; ir ν neat 3350, 2900, 1650, 1440, 1340, 1230, 965, 855 cm^{-1}; $\lambda_{\max}^{\mathrm{MeOH}}$ 243 mμ (ε 81,000); nmr δ (neat) 0.80–2.35 (m, 12, CH$_2$), 3.30 (t, 2, CH$_2$), 4.35 (s, 1, OH), 5.00–6.50 ppm (m, 3, =CH).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.41; H, 10.91. Found: C, 79.40; H, 10.90.

5-Cyclohexylpentanol, 10c.—A 1.2-g (0.007 mol) sample of **9c** was dissolved in 50 ml of methanol and shaken in a hydrogen atmosphere over 10% Pd–C catalyst. After 90% of the theoretical amount of H$_2$ was consumed (3 hr), the reaction was stopped, filtered, and concentrated. Vacuum distillation gave 1.04 g (85% yield) of **10c**: bp 78° (0.20 mm); n^{25}D 1.466 [lit.[15] bp 118–119° (4.0 mm); n^{25}D 1.464]; ir ν (neat) 3390, 2900, 1450, 1260, 890, 850 cm^{-1}; nmr δ (neat) 0.80–1.90 (m, 19, CH$_2$'S and CH), 3.40 (t, 2, CH$_2$), 4.70 ppm (s, 1, OH).

5-Cyclohexylidene-3-pentenol, 9c, *via* 3 in DMF at 30°.—This reaction was run in the same manner as the preceding reaction using 20.0 g (0.047 mol) of **3** and 4.6 g (0.047 mol) of cyclohexanone in DMF. The temperature was held at 30° for 48 hr. After the usual work-up procedure, 2.73 g (35% yield) of product was

---

[15] G. S. Hiers and R. Adams, *J. Amer. Chem. Soc.*, **48**, 2388 (1926).

isolated. This was shown to be **11c** by comparison of its infrared spectrum with that of the analytical sample.

5-Cyclohexylidene-3-pentenol, 9c, *via* 3 in DMF at 0°.—This reaction was run in the same manner as the preceding reaction using 20 g (0.47 mol) of **3** and 4.6 g (0.47 mol) of cyclohexanone in DMF. The temperature was held at 0° for 48 hr. After the usual work-up procedure, 2.4 g (31% yield) of product was isolated. This was shown to be **9c** by comparison of its infrared spectrum with that of the analytical sample.

5-Cyclohexylidene-3-pentenol, 9c, *via* 3 in THF at Reflux.—This reaction was run in the same manner as the preceding one using 10 g (0.023 mol) of **3** and 2.3 g (0.023 mol) of cyclohexanone in tetrahydrofuran. The temperature was brought to reflux and held for 48 hr. After the usual work-up procedure, 1.03 g (27% yield) of product was isolated. This was shown to be **9c** by comparison of its ir spectrum with that of the analytical sample.

Reaction of 3 with Benzaldehyde in Ethanol at Reflux. I.—To 200 ml of absolute ethanol was added Na (1.1 g) under nitrogen. When this had dissolved, 7.4 g (0.07 mol) of freshly distilled benzaldehyde was added and then 20 g (0.047 mol) of **3**. The reaction mixture was allowed to reflux 15 hr under N_2, cooled, and added to 500 ml of water, extracted with four 125-ml portions of ether, dried ($MgSO_4$), concentrated, and short-path distilled to give a crude mixture of **4a** and **4b** and **9c**, 3.4:96.6, respectively, by vpc. This mixture was then fractionally distilled to give 3.9 g of **9c**: bp 122–124° (0.6 mm); 48% isolated yield; ir ν (neat) 3360 (s), 2930 (s), 1600 (m), 1490 (s), 1450 (s), 1050 (s), 1030 (s), 910 (w), 745 (s), 697 cm^{-1} (s); nmr δ (CCl_4) 7.20 (m, 5, $-C_6H_5$), 6.65–5.45 (diene pattern, 4, –CH=CHCH=CH–), 3.60 (t, 2, $-CH_2O-$), 2.32 (q, 2, $-CH_2-$), 1.92 ppm (s, 1, –OH).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.62; H, 7.85.

This product was hydrogenated in methanol, with PtO_2 catalyst, for 2 hr under an H_2 pressure of 30–40 psi. The product matched the aforementioned 6-phenylhexanol by vpc and nmr.

II.—To 300 ml of absolute ethanol was added Na (1.38 g) under nitrogen. When this had completely reacted, 25.62 g (0.06 mol) of **3** was added and the mixture stirred under reflux for 6 hr. Benzaldehyde (6.36 g, 0.06 mol) was then added dropwise; the mixture refluxed an additional 12 hr under nitrogen and worked up as above. Yield was 62%; the ratio of **9c** to **4a** and **b** was 96/4, respectively, by vpc.

Other reactions of **3** and benzaldehyde are listed in Table I along with the experimental conditions. Work-up procedures were essentially the same as reported here in all cases.

2-Cyclohexylidenemethyltetrahydrofuran, 4c.—To a solution of 8.54 g of **3** in 75 ml of anhydrous DMF in a three-necked flask fitted with reflux condenser, thermometer, and magnetic stirrer was added 0.95 g of a 54% dispersion of NaH in mineral oil. After 10 min at 25–30°, 5.0 g (twofold excess) of cyclohexanone was added quickly. The temperature was then rapidly taken to reflux and lowered to 110° for 13 hr. After this time the reaction mixture was diluted with 500 ml of water and extracted with two 200-ml portions of ether, dried ($MgSO_4$), concentrated, and short-path distilled to give a product mixture consisting of 94% **9c** and 6% **4c**, by vpc, in 56% over-all yield based on cyclohexanone. The first product peak was collected from the vpc (10 ft × 3/8 in. VC-W98 DMCS on 60/80 Firebrick column) and short-path distilled to give an analytical sample of **4c**: ir ν (neat) 2980 (s), 1655 (w), 1450 (m), 1060 (m), 1045 cm^{-1} (m); nmr δ (CCl_4) 5.80 (m, 1, –CH=C<), 3.50 (q, 2, $-CH_2O-$), 3.2–2.9 (m, broad, 1, –CH), 2.5–2.0 (m, 4, $-CH_2CH_2-$), 2.01–1.2 ppm (m, 10, $-C_5H_{10}$).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.67; H, 10.92.

Reaction of 3 with Acetophenone. 6-Hydroxy-1-phenyl-1-methyl-1,3-hexadiene, 9d.—To a dry three-necked flask containing 150 ml of absolute ethanol was added Na (0.69 g) under nitrogen. When this had dissolved, 12.9 g (0.03 mol) of **3** was added and the red solution allowed to reflux 6 hr. Then 3.6 g of freshly distilled acetophenone in 30 ml of ethanol was added dropwise and the mixture refluxed another 12 hr. After this time the reaction mixture was added to 1 l. of water and extracted with two 200-ml portions of ether, dried ($MgSO_4$), and concentrated. The liquid was short-path distilled until the head temperature rose to 200° (1.0 mm). Vpc of the distillate showed four product peaks, shown by ir and nmr to be the four possible isomers of **9d**, 56% over-all yield based on acetophenone. Fractional distillation gave 3.38 g of **9d**, bp 120–143° (0.8 mm), which was purified by vpc and short-path distillation to give an analytical sample: ir ν (neat) 3190 (s), 2920 (m), 2850 (s), 1600 (m), 1490 (m), 1440 (s), 1370 (m), 1190 (w), 1060 (s), 978 (s), 925 (w), 890 (m), 770 (s), 705 (s); nmr δ (CCl_4) 7.25 (s, 5, $-C_6H_5$), 5.3–6.6 (diene pattern, 3, –CH=CHCH=C<), 3.55 (q, 2, $-CH_2O-$), 2.78 (s, 1, –OH), 2.6–2.2 (m, 2, $-CH_2-$), 2.09 ppm (s, 3, $-CH_3$).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.96; H, 8.27.

Reactions of 3 with Isobutyraldehyde. 6-Hydroxy-1-isopropyl-1,3-hexadiene, 9c.—To 200 ml of absolute ethanol in a three-necked flask fitted with reflux condenser and magnetic stirrer was added 1.38 g of Na (0.06 mol). When this had dissolved 25.6 g (0.06 mol) of **3** was added and the solution allowed to reflux 6 hr under nitrogen. Then 4.32 g (0.06 mol) of isobutyraldehyde in 30 ml of ethanol was added dropwise and the mixture refluxed an additional 12 hr. The solution was then added to 1 l. of water and extracted with three 150-ml portions of ether, dried ($MgSO_4$), and concentrated to give a crude mixture of **4c** and **9c**, 8/92, respectively, by vpc. Fractional distillation of the crude concentrate gave 6.6 g of **9c** (79%), bp 63–78° (0.6 mm). Over-all yield was 82% by vpc (**9c** plus **4c**). An analytically pure sample of **9c** (*cis* and *trans*) was obtained by vpc followed by short-path distillation) **4c** was isolated from the following reaction and identified): **9c**, ir ν (neat) 3180 (s), 2850 (s), 1670 (m), 1460 (s), 1370 (w), 1380 (w), 1055 (s), 990 (m), 955 (m), 752 cm^{-1} (w); nmr δ (CCl_4) 6.4–5.1 (diene pattern, 4, –CH=CHCH=CH–), 3.63 (t, 2, $-CH_2O-$), 3.35 (s, 1, –OH), 3.1–2.7 (m, broad, 1, –CH), 2.6–2.1 (m, 2, $-CH_2-$), 1.12 (d, 3, $-CH_3$), 1.02 ppm (d, 3, $-CH_3$).

Anal. Calcd for $C_9H_{16}O$: C, 77.02; H, 11.50. Found: C, 76.99; H, 11.37.

Preparation of Tetrahydrofurfuryldiphenylphosphine Oxide, 11.—Salt **3** (2.0 g) was placed in 80 ml of aqueous NaOH (10% solution) and refluxed 1 hr. The solution was cooled and added to 250 ml of water, extracted with two 50-ml portions of methylene chloride, dried ($MgSO_4$), and concentrated to give 1.15 g of crude phosphine oxide **11** (85%). This was recrystallized from hexane to give the pure product: mp 122–124°; ir ν (KBr) 3090 (w), 3000 (m), 2900 (m), 1595 (w), 1490 (w), 1460 (w), 1440 (s), 1410 (w), 1370 (w), 1180 (s), 1120 (m), 1100 (m), 1060 (m), 1045 (m), 1000 (w), 945 (w), 920 (w), 805 (m), 750 (m), 740 (s), 718 (s), 697 cm^{-1} (s); nmr δ ($CDCl_3$) 8.0–7.3 (m, 10, $-C_6H_5$), 4.35–3.95 (m, 1, –CH), 3.95–3.50 (q, 2, $-CH_2O-$), 2.90–2.30 (m, 2, $-CH_2P$), 2.13–1.45 ppm (m, 4, $-CH_2CH_2-$).

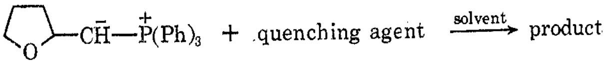
Anal. Calcd for $C_{17}H_{19}O_2P$: C, 71.31; H, 6.70; P, 10.82. Found: C, 71.24; H, 6.63; P, 10.90.

Quench Reactions of Tetrahydrofurfurylidenetriphenylphosphorane.—To a dry 100-ml three-necked flask equipped with reflux condenser and mechanical stirrer was added 70 ml of absolute ethanol and 0.23 g of Na. When the Na had dissolved, 4.27 g (0.01 mol) of **3** was introduced in about 20 ml of ethanol, and the reaction mixture allowed to reflux for 6 hr under nitrogen. After this time the solution was cooled and anhydrous HBr gas bubbled in until well after the ylide color had disappeared. The solution was then dropped slowly into 1 l. of vigorously stirring anhydrous ether and filtered. The white solid recovered was identified as salt **3** by its ir and nmr spectra, recovered in 90% yield.

Similar quenching of the ylide in ethanol with H_2O was accomplished by quickly adding the cooled solution to 500 ml of water and extracting the resulting phosphine oxide with methylene chloride, drying ($MgSO_4$), and concentrating. The crude residue was then analyzed by tlc, vpc, and nmr to determine the product ratios. In quenching the ylide hot, 5 ml of water was introduced quickly into the refluxing ethanolic solution, and the product(s) were worked up as above (see Table II for product ratios and yields in the quench reactions studied). Conditions were essentially the same as described here except where noted otherwise.

D_2O Quench of 3 in CH_3OD.—To 25 ml of CH_3OD was added 0.15 g of Na. When this had dissolved, under nitrogen, 2.18 g (0.005 mol) of **3** was added and the solution refluxed 72 hr under nitrogen. Then 2 ml of D_2O was added to the refluxing solution. The reaction cooled and was added to 100 ml of water, extracted with two 50-ml portions of methylene chloride, dried ($MgSO_4$), and concentrated. The residue was dried under vacuum (1 hr, 80°), analyzed by tlc, ir, and nmr, and shown to contain **12** and **15** 40:60, respectively, by nmr. The mixture gave the following spectra: ir ν ($CHCl_3$) 3020 (m), 2930 (m), 2860 (m), 2320 (w), 2200 (w), 2130 (w), 1595 (w), 1480 (m), 1440 (s), 1310 (w), 1280

TABLE II



Quenching agent	Solvent	Base	Products (%)	Yield, %
HBr gas	C_2H_5OH	Na	**3** (100)	90
HBr gas	C_6H_6	PhLi	**3** (100)	95
CH_3I	C_2H_5OH	Na	**3** (100) (iodide salt)	90
H_2O	C_2H_5OH	Na	**11** (100)	92
H_2O[a]	DMF	NaH	**11** (47) **12** (41) Ph_3P (12)	88
H_2O[b]	C_2H_5OH	Na	**11** (67) **12** (33)	90
D_2O[b]	CH_3OD	Na	**15** (60) **12** (40)	90

[a] Refluxed for 2 hr before quench. [b] Quenched hot.

(w), 1175 (s), 1110 (m), 1070 (m), 1000 (w), 925 (w), 793 (m), 740 (s), 710 (s), 692 cm^{-1} (s); nmr δ ($CDCl_3$) 8.1–7.25 (m, 17, $-C_6H_5$), 4.35–3.95 (m, 1, >CH), 3.95–3.50 (q, 2, $-CH_2O-$), 1.93–1.45 ppm (m, 3, $-CH_2CHD-$).

Reaction of Methoxyethyltriphenylphosphonium Bromide,[4] 13, with Benzaldehyde.—To 100 ml of absolute ethanol was added 0.5 g of Na, under nitrogen. When this had dissolved, 7.6 g (0.018 mol) of **13**[4] was added and stirred under reflux for 6 hr. Then 2.2 g of benzaldehyde (0.02 mol) was added; the mixture, refluxed under nitrogen an additional 12 hr, was added to 500 ml of water, extracted with two 200-ml portions of ether, dried ($MgSO_4$), and concentrated. This was then short-path distilled to give ethyl cinnamyl ether (0.3 g), **14**, as the sole Wittig product. The yield was 19% (along with 42% of benzyl alcohol). The product was identified by its nmr spectrum and by comparison of its vpc retention time with that of an authentic sample. No methyl cinnamyl ether could be detected in the vpc of the product mixture by comparison with an authentic sample.

Furfuryltriphenylphosphonium Bromide, 16.—To a 500-ml round-bottomed flask fitted with condenser and stirrer was added 20 g (0.204 mol) of fresh furfuryl alcohol in 200 ml of ether (dried over Na). To this was added dropwise with stirring and ice-bath conditions 20 g of phosphorous tribromide in 30 ml of dry ether. The total addition took 0.5 hr. The ice bath was then removed, the mixture stirred for several moments, and allowed to stand at room temperature for 1 hr. The ether was decanted into a clean flask, treated (with cooling) with a 40% NaOH solution, and stirred for 10 min. The ether was decanted off again and dried over NaOH pellets. After filtration, the ether solution of the bromide was added to a 1-l. flask and treated with 53 g (0.204 mol) of triphenylphosphine in 400 ml of ether (under N_2). The triphenylphosphine solution was added dropwise over a period of 0.5 hr. The temperature was brought to reflux and held for 48 hr, at which time the reaction was stopped and the salt filtered to give 57 g (66%) of **16**: mp 269–271° dec; ir ν (Nujol) 1590, 1370, 1150, 1100, 970, 755, 740, 730, 690 cm^{-1}; nmr δ ($CDCl_3$) 5.60 (d, 2, CH_2), 6.30 (m, 1, =CH), 6.55 (t, 1, =CH), 7.35 (m, 1, =CH), 7.75 ppm (m, 15, C_6H_5).

Anal. Calcd for $C_{23}H_{20}BrOP$: C, 65.26; H, 4.76; P, 7.32; Br, 18.88. Found: C, 65.55; H, 4.73; P, 7.48; Br, 18.66.

2-Styrylfuran, 17a and 17b.—To a 500-ml round-bottomed flask fitted with condenser and stirrer was added 10 g (0.024 mol) of **16** in 200 ml of DMF. To this was added, under N_2, 1.1 g (0.024 mol) of a 54% dispersion of NaH. As soon as the red ylide color formed, 2.52 g (0.024 mol) of benzaldehyde in 100 ml of DMF was added dropwise to the reaction mixture and the temperature brought to 110° and held for 48 hr. The reaction mixture was then added to 1 l. of water, extracted, washed, and dried in the above manner. The ether was then concentrated and short-path distilled under vacuum to give 3.9 g (95% yield) of products. This was shown to be two products, by vpc, in the ratio of 37/63 *cis/trans* isomer. These isomers were separated by vacuum distillation.

cis-2-Styrylfuran, **17a**, showed the following characteristics: bp 79–80° (0.5 mm); $n^{25}\mathrm{D}$ 1.6215; ir ν 3190, 1600, 1480, 1440, 1010, 880, 840, 740, 695 cm^{-1}; nmr δ (neat) 5.40–5.85 (m, 5, =CH), 6.50–7.10 ppm (m, 6, C_6H_5); $\lambda_{\max}^{\mathrm{MeOH}}$ 303 mμ ($\epsilon_{\max}$ 14,000).

Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.64; H, 6.05.

trans-2-Styrylfuran, **17b**, showed the following characteristics: bp 89° (0.5 mm); mp 49–50° (CH_3OH) [lit.[16] mp 49–51°; bp 150–165 (3 mm)]; ir ν (neat 1600, 1380, 1160, 1020, 960, 800, 740, 690 cm^{-1}; nmr δ ($DCCl_3$) 6.35 (m, 3, =CH), 6.90 (m, 2, =CH) 7.35 ppm (m, 5, C_6H_5); $\lambda_{\max}^{\mathrm{MeOH}}$ 318 mμ ($\epsilon_{\max}$ 32,000).

2-(β-Phenylethyl)tetrahydrofuran 5a *via* Hydrogenation of 17a and 17b.—A mixture of **17a** and **17b**, 1.7 g (0.01 mol), was dissolved in 50 ml of methanol and shaken in a hydrogen atmosphere over 10% Pd–C catalyst for 4 hr, at which time the reaction was stopped, filtered, concentrated, and short-path distilled, under vacuum, to give 1.4 g (81% yield) of a product whose infrared spectrum was identical with that of 2-(β-phenylethyl)tetrahydrofuran (**5d**).

Furfurylidenecyclohexane, 18.—To a 500-ml round-bottomed flask fitted with condenser and stirrer was added 10 g (0.024 mol) of **16** in 150 ml of DMF. To this was added, under N_2, 1.1 g (0.024 mol) of a 54% NaH dispersion. As soon as the red ylide color formed, 2.3 g (0.024 mol) of cyclohexanone in 100 ml of DMF was added dropwise to the reaction mixture and the temperature raised to 110° for 48 hr. Then the DMF solution was added to 1 l. of H_2O and worked up in the above manner. The ether was concentrated and short-path distilled under vacuum to give 2.05 g (54% yield) of the product, **18**. The product was distilled again to purify: bp 51–52° (0.30 mm); $n^{25}\mathrm{D}$ 1.5451; ir ν (neat) 2950, 2850, 1650, 1440, 1145, 1010, 840, 725 cm^{-1}; nmr δ (neat) 1.25 (m, CH_2), 1.85 (m, 2, CH_2), 2.30 (m, 2, CH_2), 5.6–6.0 (m, 3, =CH), 6.9 ppm (d, 1, =CH); $\lambda_{\max}^{\mathrm{MeOH}}$ 269 mμ ($\epsilon_{\max}$ 17,300).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.26; H, 8.59.

2-(Cyclohexylmethyl)tetrahydrofuran.—A sample of **18** (1 g, 0.006 mol) was dissolved in 50 ml of methanol and shaken in a hydrogen atmosphere over 10% Pd–C catalyst. After 85% of the theoretical amount of hydrogen had been consumed (3 hr), the reaction was stopped, filtered, and concentrated. Distillation under vacuum gave 0.8 g (78% yield) of **5c**: bp 45° (0.1 mm); $n^{20}\mathrm{D}$ 1.471 (lit.[17] $n^{20}\mathrm{D}$ 1.469); ir ν (neat) 2950, 2850, 1420, 1060, 1000, 980, 810 cm^{-1}; nmr δ (neat) 0.81–2.50 (m, 17, CH_2 and CH), 3.50–4.50 ppm (m, 3, CH_2 and CH).

4,5-Dihydrofurfuryltriphenylphosphonium Bromide, 21.—To a 250-ml, three-necked, round-bottomed flask fitted with stirrer and condenser was added 12 g (0.14 mol) of 2-methyl-4,5-dihydrofuran[13] in 100 ml of benzene. To this was added portionwise, keeping the temperature below 35°, 25 g (0.14 mol) of N-bromosuccinimide; the mixture stirred at room temperature for 0.5 hr, then cooled to 10°, and filtered. The benzene solution was then added to a 1-l. flask, diluted with 400 ml of ethyl acetate, and treated (under N_2) with 35 g (0.14 mol) of triphenylphosphine in 150 ml of ethyl acetate. The temperature was brought to 60° and held for 24 hr. Filtration gave 7.1 g (15% yield over both steps) of **21**: mp 246–247° dec; ir ν (KBr) 3000, 2950, 1620, 1490, 1440, 1180, 1150, 1110, 1030, 1000, 970, 940, 905, 885, 750, 725, 695 cm^{-1}; nmr δ ($DCCl_3$) 2.35 (m, 2, CH_2), 3.40 (m, 2, CH_2), 4.50 (t, 2, CH_2), 5.65 (d, 1, =CH), 7.75 ppm (m, 15, C_6H_5).

Anal. Calcd for $C_{23}H_{22}BrOP$: C, 64.95; H, 5.21; Br, 18.79; P, 7.28. Found: C, 65.04; H, 5.28; Br, 18.90; P, 7.51.

Isolation of 17a and 17b *via* Reaction of 21 with Benzaldehyde.—To a 251-ml round-bottomed flask was added 2.7 g (0.006 mol) of **21** in 150 ml of DMF. This was treated with 0.4 g (0.006 mol) of a 54% NaH dispersion under N_2. As the red ylide color formed, 0.68 g (0.006 mol) of benzaldehyde in 50 ml of DMF was added dropwise and the temperature brought to 110° for 48 hr. The reaction was then stopped and worked up in the previous manner. The concentrated ether solution was short-path distilled to give 0.40 g (37% yield) of two products by glpc in the ratio of 39/61 **17a**/**17b**. The two were separated by vacuum distillation to give samples whose infrared spectra were identical with those of **17a** and **17b**.

Isolation of 5a *via* Reaction of 21.—A sample (1 g, 0.006 mol) of **17a** and **17b** obtained by the reaction of **21** with benzaldehyde as shown above was hydrogenated in the usual manner to give a 70% yield of **5a**, as shown by its glpc retention time and infrared spectrum.

---

(16) R. B. Woodward, *J. Amer. Chem. Soc.*, **62**, 1478 (1940).

(17) V. G. Bukharov and T. E. Pozdnyakova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 135 (1961).

Isolation of 16 *via* NBS Bromination of 2-Methyl-4,5-dihydrofuran with Peroxide.—To a 500-ml flask fitted with stirrer and condenser was added 25 g (0.03 mol) of 2-methyl-4,5-dihydrofuran in 200 ml of benzene. To this was added a small amount of benzoyl peroxide and then, with stirring, 53 g (0.3 mol) of N-bromosuccinimide (NBS) slowly, keeping the temperature below 35°. After stirring for 1 hr at room temperature, the mixture was cooled to 10°, filtered, diluted to 600 ml with ethyl acetate in a 1-l. flask, and treated with 79 g of triphenylphosphine in 200 ml of ethyl acetate, dropwise. The temperature was then brought to reflux and held for 24 hr. Filtration gave a solid which had mp 270–271° dec and was shown to be **16** by its infrared spectrum, tlc, and mixture melting point.

Hydrolysis of 21.—To a 250-ml flask fitted with stirrer and reflux condenser was added 7.0 g (0.017 mol) of **21** in 100 ml of aqueous ethanol. To this was added 0.9 g (0.017 mol) of KOH in aqueous ethanol. The mixture was refluxed for 12 hr, added to 500 ml of H_2O, and extracted with ether. The ether was washed, dried, and concentrated to give a 1.1 g (65% yield) of a mixture of 15/85 2-methyl-4,5-dihydrofuran and 2-methylfuran, respectively, as shown by vpc.

Registry No.—**3**, 18138-76-6; **4a**, 18138-77-7; **4b**, 18138-78-8; **4c**, 18138-79-9; **5a**, 2429-96-1; **9c**, 18138-81-3; **9d**, 18138-82-4; **9e**, 18138-83-5; **10a**, 2430-16-2; **11**, 18138-85-7; **16**, 18138-86-8; **17a**, 18138-87-9; **18**, 18138-88-0; **21**, 18153-52-1.

Acknowledgment.—This work was supported, in part, by a grant (PRF 2032-Al) from the Petroleum Research Fund of the American Chemical Society, by a Public Health Service Predoctoral Fellowship (to E. T. Shaffer), and by a Public Health Service Grant (9R01 CA 11000-04) for which we are most grateful.

Notes

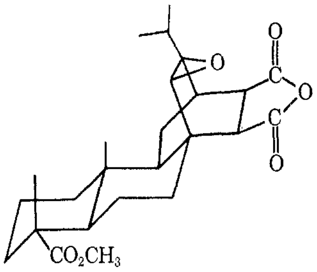
Bridged Ring Compounds.
XVI.[1] Stereoselectivity in Epoxidation of Bicyclic Anhydrides[2]

L. H. ZALKOW AND S. K. GABRIEL

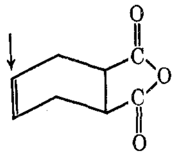
School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received June 24, 1968

Recently, we reported that, both on ozonlysis and on treatment with trifluoroperacetic acid, methyl maleopimarate gave the *syn*-epoxide I.[3] It was suggested that the stereospecificity observed might be due to formation of an intermediate cyclic peroxide, followed by intramolecular epoxidation. Such an explanation was first proposed by Henbest[4] for the *cis* epoxidation of *cis*-Δ^4-tetrahydrophthalic anhydride. However, others[5] have argued that in the latter case the observed stereospecificity arises because the cyclohexene ring in *cis*-Δ^4-tetrahydrophthalic anhydride exists as an "equatorial half-boat" (II) and *exo* attack occurs just as in norbornenyl anhydrides. Norbornenyl anhydrides and imides are reported to yield *exclusively exo*-epoxides.[5,6]

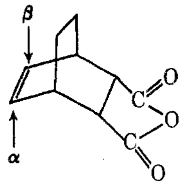


I

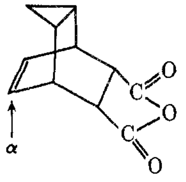


II

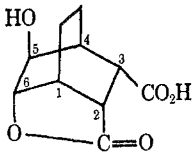
In order to obtain more information regarding intramolecular epoxidations we decided to study the epoxidation of bicyclo[2.2.2]-5-octene-2,3-*endo*,*cis*-dicarboxylic anhydride (III). During the course of our investigation, Fray, *et al.*,[7] reported that epoxidation of III paralleled that of bicyclo[2.2.1]-5-heptene-2,3-*endo*,-*cis*-dicarboxylic anhydride; that is, the *exo*-epoxide was exclusively obtained (β attack). On the other hand, anhydride IV gave the *endo*-epoxide (α attack). Fray, *et al.*,[7] therefore, concluded that the stereochemistry of epoxidation of these cyclic compounds is determined solely on steric grounds.



III

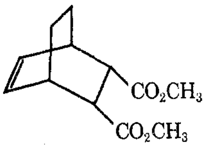


IV

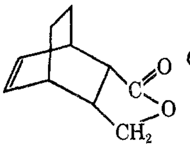


V

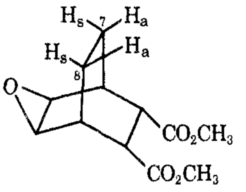
We have found that epoxidation of III under conditions similar to those reported by Fray[7] does in fact yield appreciable amounts of the *endo*-epoxide (Table I). Fray, *et al.*,[7] isolated the *exo*-epoxide of III in 48% yield by crystallization and apparently did not account for the remaining products.



VI



VII



VIII

All of the products mentioned in Table I were isolated in pure form and analytical and spectral data support

---

[1] Bridged Ring Compounds. XV: R. L. Hale and L. H. Zalkow, *Tetrahedron*, in press.

[2] Presented at the 19th Southeastern Regional Meeting of the American Chemical Society, Nov 1–3, 1967, Atlanta, Ga.

[3] L. H. Zalkow, M. V. Kulkarni, and N. N. Girotra, *J. Org. Chem.*, **30**, 1679 (1965).

[4] H. B. Henbest, *Proc. Chem. Soc.*, 159 (1963)

[5] A. P. Gray and D. E. Heitmeier, *J. Org. Chem.*, **30**, 1226 (1965).

[6] J. A. Berson and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 4341 (1958).

[7] G. I. Fray, R. J. Hilton, and J. M. Teire, *J. Chem. Soc., C*, 592 (1966).