was obtained which consisted of about 50% 3-isopropyl-2-nitrothiophene and 50% 4-isopropyl-2-nitrothiophene.

Anal. Calcd for $C_7H_9NO_2S$: C, 49.11; H, 5.30; N, 8.18; S, 18.72. Found: C, 49.48; H, 5.35; N, 8.20; S, 18.59.

The isomers were separated by preparative glpc (DEGS, 6 ft, 170°): 2-nitro-3-isopropylthiophene, nmr (CCl_4) δ 1.28 (d, 6, J = 7.0 Hz, CH_3), 3.98 (complex m, 1, methine H), 7.03 (d, 1, J = 5.5 Hz, aromatic H), and 7.38 (d, 1, J = 5 Hz, aromatic H); 2-nitro-4-isopropylthiophene, nmr (CCl_4) δ 1.27 (d, 6, J = 7.5 Hz, CH_3), 2.98 (complex m, 1, methine H), 7.19 [d (slightly split), 1, J = 2.0 Hz, 5 H), and 7.76 (d, 1, J = 2.0 Hz, 3 H), and uv (95% EtOH) 289 mμ (log ϵ 3.76) and 327 (3.80).

3-Cyclopropyl-2-phenylthiophene (22) was prepared by irradiating with a high pressure mercury lamp **21** (500 mg, 2 mmol) in 125 ml of benzene containing 1 mol % anhydrous $Na_2S_2O_3$. After 6 hr irradiation stopped. The benzene solution was washed repeatedly with aqueous $Na_2S_2O_3$ and then dried over $MgSO_4$. After removal of the solvents the residue was chromatographed over Al_2O_3 using benzene to give chiefly **22** (50% yield from glpc) which was purified by preparative glpc (F & M 700, 150°) to give a clear liquid: ir (neat) 1035, 1055 cm^{-1} (cyclopropyl); nmr (CCl_4) δ 0.5–1.0 (complex multiplet, 4, cyclopropylmethylene), 1.7–2.2 (complex multiplet, 1, *tert*-H), 6.55 [d, 1, J = 5.5 Hz, 4(?) H], 7.04 [d, 1, J = 5.5 Hz, 5(?) H], and 7.1–7.6 (complex multiplet, 5, phenyl). Too little sample was obtained for an elemental analysis.

Attempted Synthesis of 9 from Quaternary Iodide 7.—In a manner analogous to that described for **1**, condensation of 3-thiophenealdehyde with malonic acid gave 3-(3-thienyl)acrylic acid.[48] Reduction with $LiAlH_4$ gave 3-(3-thienyl)-1-propanol in 66% yield, bp 141–145° (12 mm). Treatment with tosyl chloride gave an oily tosylate which was not purified but allowed to react with dimethylamine to give 3(3-thienyl)-1-dimethylaminopropene in 32% yield based on alcohol: bp 104–107° (12 mm); $n^{18}D$ 1.5130. Treatment with methyl iodide gave in 90% yield the quaternary iodide (**7**), mp 167–169°.

Anal. Calcd for $C_{10}H_{18}SNI$: C, 38.59; H, 5.84; S, 10.30; N, 4.50; I, 40.78. Found: C, 38.45; H, 5.71; S, 10.30; N, 4.40; I, 40.73.

Attempted cyclization in liquid ammonia with sodium amide gave, after work-up, a liquid (about 30%), bp 60° (10 mm), which, besides some weak signals ultimately attributed to **9**, showed strong absorptions at δ 6.3–6.5 indicating vinyl protons presumed to arise from 3-(3-thienyl)-1-propene (**8**). The reaction mixture was not investigated further.

Registry No.—**1**, 26019-23-8; **2**, 29481-20-7; **3**, 29481-21-8; **4**, 29481-22-9; **5**, 29481-23-0; **6**, 29481-24-1; **7**, 29481-25-2; **9**, 29576-51-0; **10**, 29481-26-3; **11**, 29481-27-4; **12**, 29481-28-5; **14**, 29481-29-6; **15**, 29576-52-1; **16**, 29481-30-9; **17**, 29481-31-0; **19**, 29481-32-1; **20**, 29481-33-2; **21**, 29481-34-3; **22**, 29481-35-4; **23**, 29481-36-5; **24**, 29481-37-6; 4-isopropylpyridine, 696-30-0; 3-(2-thienyl)-1-propanol, 19498-72-7; 3-(2-thienyl)-1-propyl tosylate, 29488-39-9; 3-(2-thienyl)-*n*-propyldimethylamine, 23711-40-2; 2-isopropyl-3-nitrothiophene, 29488-41-3; 3-(5-phenyl-2-thienyl)-propenoic acid, 29488-42-4; 3-(5-phenyl-2-thienyl)-1-propanol tosylate, 29488-43-5; dimethyl-*n*-[3-(5-phenyl-2-thienyl)]propylamine, 29488-44-6; 3-(5-cyclopropyl-2-thienyl)propenoic acid, 29488-45-7; dimethyl-*n*-[3-(5-cyclopropyl-2-thienyl)]-propylamine, 29488-46-8; 4-isopropyl-2-nitrothiophene, 29488-47-9; 3-(3-thienyl)-1-propanol, 20905-98-0; 3-(3-thienyl)-1-dimethylaminopropane, 29488-48-0; 4-cyclopropylpyridine, 4904-21-6.

Acknowledgment.—We are extremely indebted to Miss N. Gjøs and Professor S. Gronowitz of the University of Lund, Sweden, for providing samples of nitrated phenylthiophenes. Helpful discussions with Professors Hans Wynberg and M. J. Janssen of this department are gratefully acknowledged. A portion of this work was initiated at Hope College, Holland, Mich.

Reactions of Phosphorus Compounds. XXVI. Preparation and Reactions of 3- and 4-Substituted 5-Benzoyl-2,2,2,5-tetraphenyloxa-2-phospholanes[1]

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Received January 5, 1971

Substituted (1- and 2-) vinylphosphonium salts reacted with the sodium salt of benzoin in DMSO to give 3- and 4-substituted 5-benzoyl-2,2,2,5-tetraphenyloxa-2-phospholanes, respectively. Methyl-substituted oxaphospholanes were separated into diastereoisomers while 3- and 4-phenyl-substituted oxaphospholanes were isolated as single isomers. Diastereomeric mixtures of oxaphospholanes substituted at C_3 tended to isomerize to one stable isomer while those substituted at C_4 did not isomerize. Reaction of 1- and 2-substituted vinylphosphonium salts with the sodium salt of benzoin in acetonitrile gave 2,5-dihydrofurans in all cases except 1-phenylvinyltriphenylphosphonium bromide which gave only the oxaphospholane. Pyrolysis of the oxaphospholanes gave benzil, triphenylphosphine, and an olefin.

In a previous article[2] we described the preparation and reactions of 5-benzoyl-2,2,2,5-tetraphenyloxa-2-phospholane (**5**) formed by attack of the benzoin enolate carbanion **1a** on vinyltriphenylphosphonium bromide (**2**) in dimethyl sulfoxide (DMSO). In contrast, the dihydrofuran **3** was exclusively formed when acetonitrile was used as solvent (Scheme I).[2]

We now wish to report the reactions of **1** with 1- and 2-substituted vinylphosphonium salts which yield oxaphospholanes and dihydrofurans. The basis for the stereochemical assignments of the oxaphospholanes obtained is discussed. The fusion reaction products of the oxaphospholanes are also examined.

Previous workers have had variable success in obtaining products from conjugate additions to propenyltriphenylphosphonium bromide[3] **6**. When **1** was allowed to react with this salt in DMSO, a 40% yield of oxaphospholanes was realized, which was easily separated into two diastereomeric oxaphospholanes **7a,b** by selective extraction with chloroform and fractional crys-

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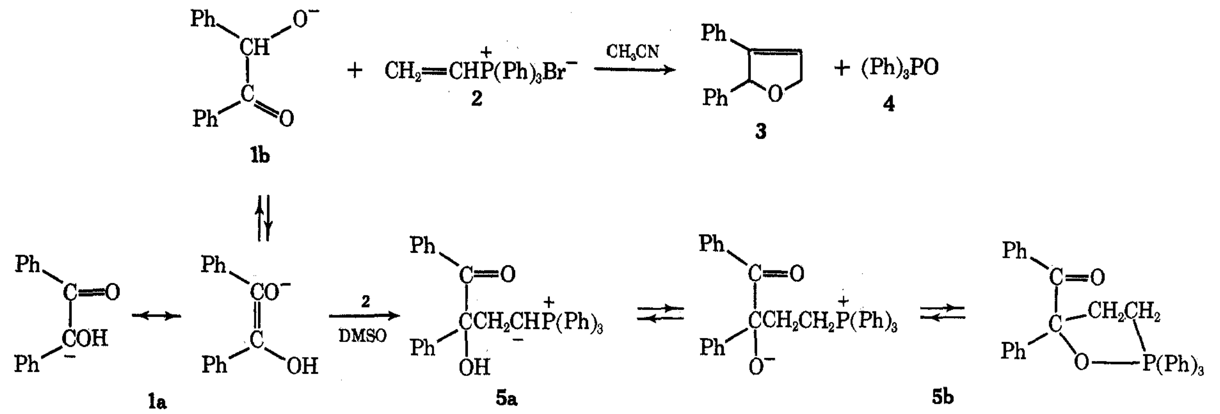
[1] E. E. Schweizer and W. S. Creasy, *J. Org. Chem.*, **36**, 2379 (1971).

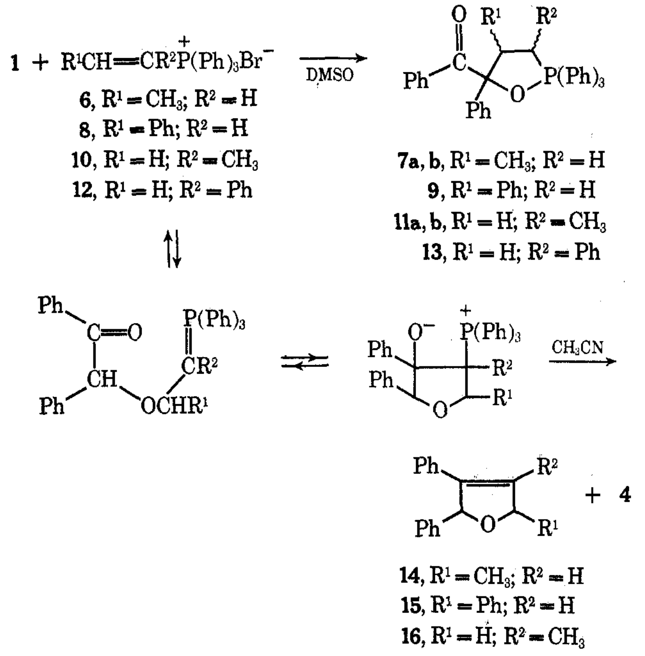
[2] E. E.Schweizer, W. S. Creasy, J. G. Liehr, M. E. Jenkins, and D. L. Dalrymple, *ibid.*, **35**, 601 (1970).

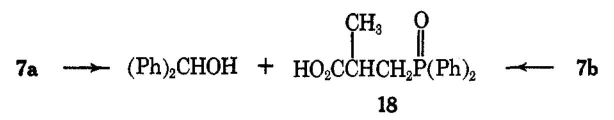
[3] (a) P. Keough and M. Grayson, *ibid.*, **29**, 631 (1964); (*b*) D. Seyferth and J. Fogel, *J. Organometal. Chem.*, **6**, 205 (1966).

SCHEME I



tallization. The structural identity of these two compounds was related by basic hydrolysis to identical mixtures of the same products.[4] Infrared spectra of **7a** and **7b** are identical but the methyl absorptions in the

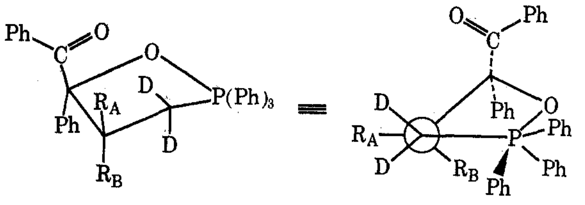




$$\mathbf{7a} \longrightarrow (Ph)_2CHOH + HO_2C\overset{CH_3}{C}HCH_2\overset{O}{\overset{\|}{P}}(Ph)_2 \longleftarrow \mathbf{7b}$$

18

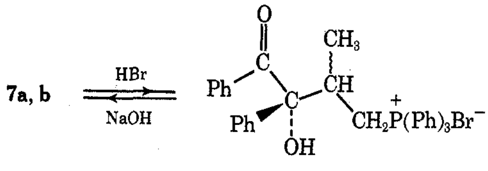
proton nmr are significantly different. That of **7b** appears at 0.6 ppm, considerably shielded with respect to the absorption observed in **7a** (1.1 ppm). Compound **7b** undergoes a deuterium for proton exchange at C_3 when a sample in $CDCl_3$ is shaken with D_2O (requiring 48 hr), a reaction similarly reported for **5**.[2] The remaining methine proton, on C_4, then appears as a doublet of quartets at δ 3.4 ppm with a vicinal P–H coupling constant of 34 Hz. This agrees very well with data reported for H_A in compound **5**, with the relatively large coupling constant indicating an anti relationship to phosphorus.[5] Methyl should then occupy the same position as H_B in compound **5** and is shielded, accordingly, due to proximity of the phenyl group on C_5. Although **7a** was insufficiently soluble for determination of proton nmr fine structure, it may very well be the other diastereoisomer as indicated. The predominance of **7a** is probably a reflection, then, of the pseudoaxial position of methyl on the oxaphospholane ring of **7b**.



5, $R_A = H_A$; $R_B = H_B$
7a, $R_A = CH_3$; $R_B = H_B$
7b, $R_A = H_A$; $R_B = CH_3$
9, $R_A = Ph$; $R_B = H_B$

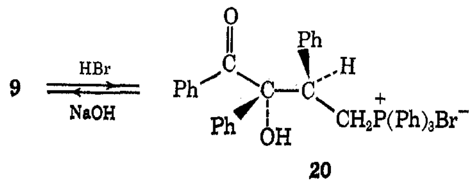
Reaction of benzoin (**1**) and 2-phenylvinyltriphenylphosphonium bromide (**8**) gave only one diastereoisomer **9**. The C_4 methine proton of **9** after deuterium exchange had δ 4.6 ppm and $J_{HCCP} = 11$ Hz, indicating a gauche relationship to phosphorus. Compound **9** then corresponds in structure to **7a**. Phenyl would be expected to have steric requirements similar to methyl with respect to protons.

Compounds **7a**, **7b**, and **9** were allowed to react with hydrobromic acid to give the corresponding hydroxyphosphonium bromides **19a**, **19b**, and **20**, respectively.



19a, b

There were only very small changes in position of the nmr methyl absorptions when **7a** and **7b** were converted to their salts. These salts, therefore, retain the basic geometry of the oxaphospholanes from which they are



20

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[4] A mechanism for this reaction has been proposed in ref 2.

[5] (a) J. G. Verkade, R. W. King, and C. W. Heitsch, *Inorg. Chem.*, **3**, 886 (1964); (b) J. G. Verkade and R. W. King, *ibid.*, **1**, 948 (1962).

derived. On basification good reconversion to the parent oxaphospholanes was observed with no destruction of the stereochemistry of the ring, *i.e.*, no conversion to the opposite isomer.

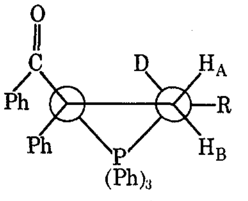
Reaction of **1** and 1-methylvinyltriphenylphosphonium bromide (**10**) afforded 70% of a 1:1 mixture of two diastereomeric oxaphospholanes, **11a,b**, separated by fractional crystallization. Compound **11a** had methyl absorption at δ 1.4 ppm (d d) and compound **11b** showed an identical pattern centered at δ 1.2 ppm. Both patterns collapsed to doublets on shaking the sample with D_2O and absorptions due to methylene protons on C_4 appear as shown in Table I.

TABLE I

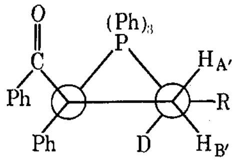
PROTON NMR SPECTRA OF 5-BENZOYL-3-METHYL-2,2,2,5-TETRAPHENYLOXA-2-PHOSPHOLANES

11a			11b		
Proton	δ, ppm	J_{HCCP}, Hz	Proton	δ, ppm	J_{HCCP}, Hz
H_A	3.4	35	$H_{A'}$	3.3	20
H_B	2.3	9	$H_{B'}$	2.0	27

Oxaphospholane **11a** exhibits proton nmr patterns and coupling constants quite similar to **5**. However, the magnitudes of P–H coupling constants for protons of **11b** differ from other oxaphospholanes described, although there is little difference in chemical shifts between protons of **11a** and **11b**. A reasonable explanation is as follows. The methyl in **11a** is pseudoequatorial on the ring which is conformationally similar to **5**. However, to accommodate the methyl group in an equatorial position, the ring of **11b** must undergo a conformational change which then places $H_{A'}$ essentially gauche and $H_{B'}$ anti to phosphorus, resulting in larger P–H coupling to the higher field proton $H_{B'}$. Notably, the sum of P–H coupling constants in **11b** (44 Hz) is identical with that in **11a** (44 Hz).



11a, R = CH_3
13, R = Ph

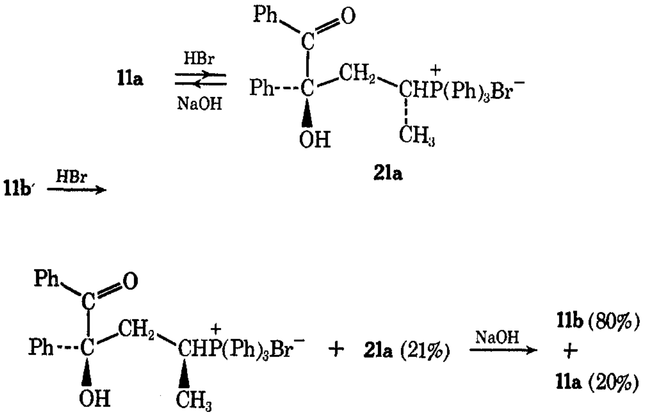


11b, R = CH_3

Furthermore, **11a** was found to isomerize slowly to **11b** on standing in chloroform. Conversion was 50% after 24 hr and required more than 1 week to reach the limits of nmr sensitivity. The compounds are relatively stable in the solid state but have identical melting points and mixture melting point, suggesting rapid isomerization at elevated temperatures.

The observance of interconversion further confirms earlier observations concerning the presence of the phosphonium ylide in equilibrium with the oxaphospholane,[2] although ^{31}P nmr spectra consistently indicate that the latter form is predominant at 25° in chloroform.

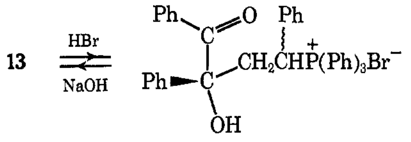
Reaction of **11a** with hydrobromic acid yielded one pure salt **21a**, which was converted into pure **11a** by aqueous base (85% overall) with no apparent isomerization. Similar treatment of **11b** gave, however, a mixture of salts containing 21% of **21a**, which gave on treatment with alkali a mixture consisting of 20% of **11a** and 80% of **11b** (78% overall). The impurity must arise from selective protonation since **11b** showed no tendency to isomerize to **11a**.



21b

The oxaphospholane **13**, formed from reaction of **1** and 1-phenylvinyltriphenylphosphonium bromide (**12**), is isolated as a single diastereoisomer. The methylene protons on C_4 exhibit coupling constants and patterns similar to **5**, after deuterium exchange (rapid). The low-field proton (δ 4.1 ppm) had J_{H_ACCP} = 38 Hz and the high-field proton (δ 2.55 ppm) had J_{H_BCCP} = 10 Hz. Compound **13** is, therefore, one isomer as opposed to a rapidly equilibrating mixture and corresponds in structure to **11a**.

Reaction of **13** with hydrobromic acid afforded an apparent 1:1 mixture of phosphonium salts **22a,b** which could not be separated into two components but which was converted to one pure salt, **22a**, on boiling in benzene or warming with a catalytic amount of potassium *tert*-butylate in DMSO (quantitative recovery). Basic treatment of either the mixture or pure **22a** gave pure **13** (74 and 67%, respectively), indicating that **13** is probably the more stable of the two possible isomers formed by the reaction of **1** and **12**, the other isomerizing rapidly upon formation. These results suggest the phosphonium ylide is the form of **13** which undergoes protonation and that this oxaphospholane possesses significantly more ylide character than other oxaphospholanes examined. Indeed, the ^{31}P nmr absorption at +43.4 ppm is the smallest positive shift reported here, consistent with the lowest pentavalent phosphorus character. The increased acidity of benzylphosphonium salts as compared to ethyl and propyl salts[6] is undoubtedly responsible for the observed behavior of **13**.



22a, b

Oxaphospholanes **7a**, **7b**, **9**, **11a**, **11b**, and **13** thermally decomposed to benzil (**23**), and triphenylphosphine (**24**) on a vpc column at temperatures between 150 and 250°. In addition, styrene was detected in the decom-

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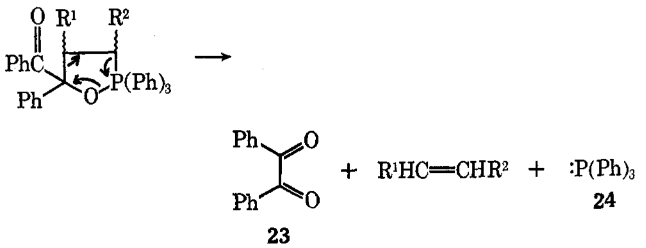
(6) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

position of **9** and **13**. The apparent mechanism involves fragmentation of the five-membered ring into two π systems and a neutral phosphine.



Similar results were obtained by pyrolysis of **5** in a hot tube pyrolysis apparatus.[7] The oxaphospholanes were relatively stable at temperatures of refluxing *tert*-butyl alcohol.

The vinylphosphonium salts **6**, **8**, **10**, and **12** were allowed to react with benzoin (**1**) in acetonitrile in order to prepare corresponding 4- and 5-substituted 2,3-diphenyl-2,5-dihydrofurans.[8] The results are shown in Table II.

TABLE II

PREPARATION OF 2,5-DIHYDROFURANS

Salt	Dihydrofuran (% yield)	Oxaphospholanes (%)
6	**14** (30)	**7a** + **7b** (32)
8	**15** (50)	**9** (8)
10	**16** (28)	**11a** + **11b** (34)
12	**17** (0)	**13** (76)

It is surprising that **15** was formed in highest yield since the Michael addition would be expected to encounter greatest hindrance in attack on **8**. Isolation of **13** only from reaction of **1** and **12** is probably a reflection of the decreased reactivity of the benzyl ylide (counterpart of **5a**) and greater hindrance to attack on the carbonyl, slowing intramolecular Wittig reaction and allowing effective competition for **12** by enolate **1a**. The latter observations are probably interrelated and provide valuable insight into the nature of the very complex interacting equilibria.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Infracord 137 proton nmr spectra on a Varian A-60A analytical nmr spectrometer using tetramethylsilane as standard and ^{31}P nmr spectra on a Varian HR-60 nmr spectrometer using an 85% phosphoric acid capillary as reference. Melting points are uncorrected and were obtained with a Thomas-Hoover capillary melting point apparatus. Analysis are by M-H-W Laboratories, Garden City, Mich. Unless otherwise indicated all reactions were undertaken in anhydrous conditions under a blanket of dry nitrogen. Sodium hydride used was a 52% dispersion in mineral oil obtained from Metal Hydrides, Inc., Beverly, Mass.

5-Benzoyl-4-methyl-2,2,2,5-tetraphenyloxa-2-phospholanes (7a and 7b).—To a prereacted (1 hr at 40°) mixture of NaH, 9.6 g (0.2 mol), and dry DMSO (200 ml) was added 4.4 g of benzoin (**1**, 0.2 mol). When frothing had essentially ceased, salt **6**, 77 g (0.2 mol), was introduced dropwise as a solution in DMSO with the green color giving way near the equivalence point to a light green precipitate. The reaction was stirred 6 hr at ambient temperature and filtered, and the residue washed with small amounts of DMSO, water, methanol, and ether to give 44.7 g of mixed oxaphospholanes **7a** and **7b**. Extraction of the mixture with chloroform followed by filtration gave a residue of **7a**, pure by nmr, and a solution containing **7b**. The latter was recovered in pure form by crystallization in two fractions from chloroform–hexane. Yields were 3.4 g of **7a** (34%), mp 206–206.5°, and 5.8 g (6%) of **7b**, mp 174–175°, mmp (between **7a** and **7b**) 174–187°.

5-Benzoyl-4-methyl-2,2,2,5-tetraphenyloxa-2-phospholane (7a): ir (Nujol) ν 1075 (s, COC), 1110 (m, CP), 1155 (m, POC), 1235 (s), 1655 cm^{-1} (s, C=O); nmr ($AsCl_3$) δ 1.1 (d, 3, CH_3, J = 7 Hz), 2.8–3.5 (m, 3, H_ACCH_2P), 7.2–8.0 ppm (m, 25, C_6H_5) (the compound was not sufficiently soluble in any other solvent); ^{31}P nmr ($AsCl_3$) δ −21.3 ppm.

Anal. Calcd for $C_{35}H_{31}O_2P$: C, 81.69; H, 6.07; P, 6.02. Found: C, 81,41; H, 5.98; P, 5.87.

5-Benzoyl-4-methyl-2,2,2,5-tetraphenyloxa-2-phospholane (7b): ir (Nujol) ν 1070 (s, COC), 1100 (m, CP), 1130 (s, POC), 1220 (s, POC), 1655 cm^{-1} (s, C=O); nmr ($CDCl_3$) δ 0.6 (d, 3, CH_3, J = 7 Hz), 2.5–3.9 (m, 3, H_ACCH_2P), 6.7–7.7 ppm (m, 25, C_6H_5).

After the sample was shaken with D_2O and allowed to stand 48 hr, the following spectrum was observed: δ 0.6 (d, 3, CH_3), 3.4 (doublet of quartets, 1, H_ACCP, J_{H_AP} = 34 Hz), 6.7–7.7 ppm (m, 25 C_6H_5).

When **7b** was impure with **7a**, a methyl doublet corresponding to that described for the latter could be seen at high amplitude. ^{31}P nmr ($AsCl_3$) showed δ −21.5 ppm, ($CHCl_3$) δ +56.5 ppm.

Anal. Calcd for $C_{35}H_{31}O_2P$: C, 81.69; H, 6.07; P, 6.02. Found: C, 81.66; H, 6.06; P, 6.05.

From the DMSO reaction filtrate was isolated 5 g of impure 2,3-diphenyl-5-methyl-2,5-dihydrofuran (**14**) which oxidized on work-up, as described in a later experiment, to 1,2-diphenyl-2-pentene-1,4-dione, 4.8 g, corresponding to a 10% yield of the dihydrofuran. When allyltriphenylphosphonium bromide was substituted for **6**, identical results were obtained.

Hydrolysis of 7a and 7b in Aqueous–Ethanolic Sodium Hydroxide.—A sample of **7a**, 1.0 g (0.0002 mol), was allowed to reflux 72 hr in a mixture of 15 ml of ethanol and 15 ml of 20% aqueous sodium hydroxide. The solution was diluted with 100 ml of water and extracted with two 50-ml portions of chloroform which was dried ($MgSO_4$) and concentrated to give benzhydrol, 0.28 g (82%). Acidification of the aqueous solution followed by extraction with chloroform, drying ($MgSO_4$), and concentration afforded 2-carboxypropyldiphenylphosphine oxide (**18**): 0.43 g (77%); mp 135–137°, after recrystallization from acetonitrile–ether (lit.[9] 136°); ir ($CHCl_3$) ν 1120 (s, CP), 1160 (s, P=O), 1720 cm^{-1} (s, C=O); nmr ($CDCl_3$) δ 1.3 (d, 3, CH_3), 2.2–3.2 (m, 3, $CHCH_2$), 7.2–8.0 (m, 10, C_6H_5), 10.5 ppm (s, 1, COOH)

Similar treatment of **7a**, 1.0 g, gave benzhydrol, 0.26 g (77%), and 2-carboxypropyldiphenylphosphine oxide (**18**), 0.41 g (73%).

2-Phenylvinyltriphenylphosphonium Bromide (8).[10–12]—Triphenyl phosphine (**24**), 13.1 g (0.05 mol), and anhydrous aluminum chloride, 6.7 g (0.05 mol), were fused at 150–200° for 2 hr and 2-bromostyrene, 13.8 g (0.075 mol), was added. The mixture was stirred at 180° for 4 hr and then at 120° for 2 days. The remaining aluminum chloride complex was decomposed with water and organic products were extracted with chloroform which was dried ($MgSO_4$), boiled with decolorizing charcoal, filtered, and concentrated. Salt **8** was recovered by precipitation in anhydrous ether and was recrystallized several times from acetone-ether. The yield, after a final recrystallization from chloroform–ether, was 12.1 g (54%), mp 263–265°.[11]

5-Benzoyl-2,2,2,4,5-pentaphenyloxa-2-phospholane (9).—To a prereacted mixture of NaH, 0.9 g (0.02 mol), and 50 ml of dry DMSO was added **1**, 6.4 g (0.03 mol). After this stirred for 15 min at ambient temperature, a solution of salt **8**, 9.0 g (0.02 mol, freshly dried at 100° for 24 hr), in 50 ml of DMSO was added slowly and the reaction mixture allowed to stir 24 hr. No precipitate formed but the green color of the sodium salt of benzoin faded slowly leaving a clear, tan solution which was diluted with 300 ml of water and extracted with two 150-ml portions of chloroform. These were combined, dried over molecular sieves, filtered, concentrated to approximately 75 ml, and dropped slowly into ether (anhydrous). The resulting precipi-

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[7] Unpublished results, W. S. Creasy.

[8] E. E. Schweizer and J. G. Liehr, *J. Org. Chem.*, **33**, 583 (1968).

[9] H. Hoffman, *Chem. Ber.*, **94**, 1331 (1961).

[10] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1192 (1940).

[11] D. W. Allen and J. C. Tebby, *Tetrahedron*, **23**, 2795 (1967).

[12] S. Trippett and B. J. Walker, *J. Chem. Soc. C*, 887 (1966).

tate was collected by filtration yielding **20**, 1.6 g (12%), mp 176–179°, identified by ir and nmr (described elsewhere). Concentration of the ether filtrate, dilution with an equal volume of methanol, and cooling at 0° produced very slow crystallization of oxaphospholane **9** which was dissolved in chloroform and recrystallized by the addition of hexane and cooling. The yield of **9** was 2.7 g (24%), mp 158–159°. This appeared to be one isomer only: ir ($CHCl_3$) ν 1070 (s), 1085 (s, CO), 1110 (s, CP), 1150 (m), 1180 (m, POC), 1240 (s), 1675 cm^{-1} (s, C═O); nmr ($CDCl_3$) δ 3.1–3.9 (m, 2, CH_2P), 4.2–4.9 (m, 1, CH), 6.6–7.8 ppm (m, 30, C_6H_5).

When this sample was shaken with D_2O and allowed to stand 48 hr, the following spectrum was observed: δ 4.6 (d, 1, HCCP, J_{HP} = 11 Hz), 6.6–7.8 ppm (m, 30, C_6H_5). ^{31}P nmr ($CHCl_3$) showed δ +58.1 ppm.

Anal. Calcd for $C_{40}H_{33}O_2P$: C, 83.41; H, 5.77; P, 5.37. Found: C, 83.19; H, 5.59; P, 5.74.

The remaining solution was concentrated and the resulting oil dissolved in a small amount of chloroform, diluted with hexane until turbid, and allowed to stand. White crystals of 1,2-diphenylethyldiphenylphosphine oxide were deposited, mp 228–230° (lit.[12] 232–233°), 3.9 g (51%). This probably arises from basic hydrolysis of **8**.

Concentration of the remaining solution gave an oil which proved to be benzil (**23**) (probably *via* autoxidation of benzoin in alkaline solution) contaminated with trace amounts of benzaldehyde, styrene, and triphenylphosphine oxide, identified by nmr, vpc, and tlc. The oil weighed 2.9 g, corresponding to approximately 44% of the benzoin used.

Total recovery of phosphorus was 87%. No evidence for the other oxaphospholane isomer was observed and, if present at all, this must be formed in very small amounts.

1-Methylvinyltriphenylphosphonium Bromide (10).[13,14]—Anhydrous nickel bromide, 10.9 g (0.05 mol), and triphenylphosphine, 13.1 g (0.05 mol), were fused at 200° for 1 hr in a three-necked round-bottomed flask. Benzonitrile (100 ml) was added and water was removed by means of a Dean-Stark trap (about $^1/_3$ of the solvent was removed), and the temperature reduced to 50°, at which time 2-bromopropene, 9.0 g (0.075 mol), was introduced. The mixture was allowed to stir 24 hr at 50° and then 72 hr at 200° (mantle temperature) and filtered to remove lumps of black intractible material. Benzonitrile was removed by steam distillation and the salt extracted with chloroform. Concentration followed by several precipitations in ether and several recrystallizations from ethyl acetate-ether gave **10**, 13.4 g (70%), mp 195-197° (lit.[14] 196.5-197.5°). This is a modification of a previously reported method which failed to give the desired product.[14]

5-Benzoyl-3-methyl-2,2,2,5-tetraphenyloxa-2-phospholanes (11a and 11b).—To a prereacted mixture of NaH, 0.65 g (0.015 mol), and 50 ml of dry DMSO was added **1**, 3.2 g (0.015 mol), and then (slowly) **10**, 5.8 g (0.015 mol), as a solution in 50 ml of DMSO. A light green precipitate formed slowly and was collected by filtration after 4 hr. The residue was washed with DMSO, water, and ether. Fractional crystallization of this product from a chloroform-hexane mixture afforded two similar oxaphospholanes, **11a** and **11b**, the bulk of the latter being recovered by concentration of the clear solution after addition of hexane failed to bring about further precipitation.

Although the melting points and mixture melting point of these compounds are identical, 179–181°, the nmr spectra show that they are different. Yields were 2.6 g of **11b** (34%) and 2.8 g of **11a** (36%). Integration of the nmr spectrum of the original product mixture (methyl peaks) gave relative percentages of 48 (**11b**) and 52 (**11a**).

5-Benzoyl-3-methyl-2,2,2,5-tetraphenyloxa-2-phospholanes (11b): ir ($CHCl_3$) ν 1065 (s, CO), 1100 (s, CP), 1200 (m), 1230 (m), 1250 (m), 1650 cm^{-1} (s, C═O); nmr ($CDCl_3$) δ 1.2 (d d, 3, CH_3), 1.6–2.5 (m, 1, H_B, CCP), 2.9–3.8 (m, 2, H_A, CCHP), 6.9–8.0 ppm (m, 25, C_6H_5).

When the above sample was shaken with D_2O and allowed to stand 10 min, the following spectrum was observed: δ 1.2 (d, 3, CH_3, J_{H_3CCP} = 21 Hz), 2.0 (d d, 1, $H_{B'}$ CCP, $J_{H_{B'}P}$ = 27, $J_{H_{A'}H_{B'}}$ = 13 Hz), 3.3 (d d, 1 $H_{A'}$CCP, $J_{H_{A'}P}$ = 20 Hz), 6.9–8.0 ppm (m, 25, C_6H_5). This spectrum was unchanged after 24 hr. ^{31}P nmr showed δ +48.5 ppm.

Anal. Calcd for $C_{35}H_{31}O_2P$: C, 81.67; H, 6.07; P, 6.02. Found: C, 81.74; H, 5.91; P, 6.20.

5-Benzoyl-3-methyl-2,2,5-tetraphenyloxa-2-phospholanes (11a): ir ($CHCl_3$) was identical with that reported for **11b**; nmr ($CDCl_3$) δ 1.4 (d d, 4, CH_3), 2.1–2.6 (m, 1, H_BCCP), 2.7–3.9 (m, 2, H_ACCHP), 6.9–8.0 ppm (m, 25, C_6H_5).

When the above sample was shaken with D_2O and allowed to stand 10 min, the following spectrum was observed: δ 1.4 (d, 3, CH_3, J_{H_3CCP} = 21 Hz), 2.3 (d d, 1, H_BCCP, J_{H_BP} = 9 Hz), 3.4 (d d, 1, H_ACCP, J_{H_AP} = 35 Hz), 6.9–8.0 ppm (m, 25, C_6H_5).

After 24 hr the sample had isomerized to a 50:50 mixture of **11a** and **11b**, as determined by the nmr integration. After 10 days the sample was essentially pure **11b**. Solubility was not sufficient for determination of a ^{31}P nmr spectrum.

Anal. Calcd for $C_{35}H_{31}O_2P$: C, 81.69; H, 6.07; P, 6.02. Found: C, 81.72; H, 5.98; P, 5.88.

5-Benzoyl-2,2,2,3,5-pentaphenyloxa-2-phospholane (13).—To a prereacted mixture of NaH, 0.9 g (0.02 mol), and 50 ml of dry DMSO was added benzoin (**1**), 4.5 g (0.2 mol), and then (slowly) a solution of **12**,[15] 9.0 g (0.02 mol), in 50 ml of DMSO. A light green precipitate formed slowly and was collected by filtration after 4 hr. The residue was washed with small amounts of DMSO, water, acetonitrile, and ether and fractionally crystallized from a chloroform–hexane mixture. All of these recovered fractions, as well as the material recovered from washings of the initial residue, proved to be the same compound, **13**: combined yield 8.0 g (70%); mp 169–171°; ir ($CHCl_3$) ν 1070 (s, CO), 1100 (m, CP), 1120 (m), 1170 (m, COP), 1230 (s), 1660 cm^{-1} (s, C═O); nmr ($CDCl_3$) δ 2.2–2.8 (m, 1, H_BCCP), 3.5–4.6 (m, 2, H_ACCHP), 6.8–8.0 ppm (m, 30, C_6H_5).

When this sample was shaken with D_2O approximately 2 min, the following spectrum was observed: δ 2.5 (d d, 1, H_BCCP, J_{H_BP} = 10, $J_{H_AH_B}$ = 14 Hz), 4.1 (d d, 1, H_ACCP, J_{H_AP} = 38 Hz), 6.8–8.0 ppm (m, 30, C_6H_5). ^{31}P nmr ($CHCl_3$) showed δ +43.4 ppm.

Anal. Calcd for $C_{40}H_{33}O_2P$: C, 83.31; H, 5.77; P, 5.37. Found: C, 83.29; H, 5.66; P, 5.54.

Additional material recovered from washings of the initial residue was shown to be **22a**, 2.8 g (21%), mp 229–230° (described elsewhere), identified by comparison to authentic sample.

Salts of 3- and 4-Substituted Phospholanes.—The salts were made by dissolving or suspending the phospholanes in chloroform, adding excess 6 *M* HBr, and shaking vigorously for about 1 hr. The chloroform solution was then separated, washed with water, dried ($MgSO_4$), concentrated, dropped into a 1:1 ether–hexane mixture, filtered, and recrystallized from a chloroform–hexane mixture. Products and yields are as follows.

Phospholane **7a** gave pure salt **19a**: 98%; mp 246–248°; ir ($CHCl_3$) ν 1110 (s, CP), 1230 (m), 1680 (s, C═O), 3150 cm^{-1} (s, OH); nmr ($CDCl_3$) δ 1.0 (d, 3, CH_3), 2.3–3.2 (m, 2, HCCHP), 4.4–5.1 (m, 1, CHP), 6.2 (s, 1, OH, disappeared on shaking sample with D_2O), 7.2–8.1 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{35}H_{32}O_2PBr$: C, 70.59; H, 5.42; Br, 13.42. Found: C, 70.35; H, 5.31; Br, 13.65.

Phospholane **7b** gave pure salt **19b**: 90%; mp 216–219°; ir ($CHCl_3$) ν 1110 (s, CP), 1235 (m), 1670 (s, C═O), 3100 cm^{-1} (s, OH); nmr ($CDCl_3$) δ 0.6 (d, 3, CH_3), 2.6–3.2 (m, 1, CH), 3.3–4.0 (m, 1), and 4.0–4.8 (m, 1, CH_2P), 5.3 (s, 1, OH, disappeared on shaking sample with D_2O), 7.0–8.1 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{35}H_{32}O_2PBr$: C, 70.59; H, 5.42; Br, 13.42. Found: C, 70.70; H, 5.45; Br, 13.80.

Phospholane **9** gave pure salt **20**: 88%; mp 178–182°; ir ($CHCl_3$) ν 1110 (s, CP), 1230 (s), 1670 (s, C═O), 3100 cm^{-1} (s, OH); nmr ($CDCl_3$) δ 2.0 (s, 1, OH, disappeared on shaking with D_2O), 3.4–4.9 (m, 3-$HCCH_2P$), 6.6–8.2 ppm (m, 30, C_6H_5).

Anal. Calcd for $C_{40}H_{34}O_2PBr$: C, 73.06; H, 5.21; Br, 12.15. Found: C, 72.83; H, 5.28; Br, 12.46.

Phospholane **11a** gave pure salt **21a**: 97%; mp 240–244°; ir ($CHCl_3$) ν 1115 (s, CP), 1240 (s), 1680 (s, C═O), 3150 cm^{-1} (s, OH); nmr ($CDCl_3$) δ 0.8 (d d, 3, CH_3, J_{H_3CCP} = 21 Hz), 1.9–3.5 (m, 3, CH_2 plus OH, broad singlet disappeared and integration dropped to 2 when sample was shaken with D_2O), 5.0–5.7 (m, 1, CHP), 6.9–8.2 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{35}H_{32}O_2PBr$: C, 70.59; H, 5.42; Br, 13.42. Found: C, 70.42; H, 5.30; Br, 13.81.

Phospholane **11b** gave salt **21b**, 92%, containing, however,

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(13) The authors wish to thank R. Cambell for refinement of this procedure.

(14) J. G. Thompson, Doctoral Dissertation, University of Delaware, 1968.

(15) E. E. Schweizer and A. T. Wehman, *J. Chem. Soc.*, 343 (1971).

21% of salt **21a**, mp (of the mixture) 138–145°. These salts were inseparable by column chromatography, tlc, and fractional crystallization and showed no tendency to isomerize to one pure salt under the influence of base. For an 80% pure sample of **21b**, ir ($CHCl_3$) was identical with that described for **21a**; nmr ($CDCl_3$) δ 1.5 ppm (d d, CH_3, J_{H_3CCP} = 20 Hz). Other absorptions cannot be identified with certainty due to contamination with **21a**.

Anal. Calcd for $C_{35}H_{32}O_2PBr$ (mixture of isomers): C, 70.59; H, 5.42; Br, 13.42. Found: C, 70.27; H, 5.45; Br, 13.63.

Phospholane **13** gave a 1:1 mixture of salts **22a** and **22b** 96%. The ratio was determined by nmr integration. Two spots were shown by tlc. When separation of these components was attempted with refluxing benzene in a Soxlet extractor, pure salt **22a** was recovered quantitatively, mp 234–236°. Heating the mixture at 100° in DMSO containing a trace of potassium *tert*-butylate also afforded pure **22a** after 48 hr.

For **22a**: ir (CHCl) ν 1110 (s, CP), 1230 (s), 1670 (s, C=O), 3150 cm^{-1} (s, OH); nmr ($CDCl_3$) δ 2.1 (broad s, 1, OH, disappeared when sample was shaken with D_2O), 2.9–3.5 (m, 3, H_2CCHP), 6.8 (broad s, 5, C_6H_5), 7.0–8.0 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{40}H_{34}O_2PBr$: C, 73.06; H, 5.21; Br, 12.15. Found: C, 72.83; H, 5.28; Br, 12.46.

A 90% pure sample of salt **22b** was obtained by fractional crystallization from chloroform solution in an ether atmosphere, mp 191–193°.

For **22b**: ir ($CHCl_3$) was essentially the same as that described; nmr ($CDCl_3$) δ 2.5 (broad s, 1, OH, disappeared on shaking with D_2O), 2.8–3.5 (m, 1), and 3.6–4.2 (m, 1, CH_2), 5.2–5.8 (m, 1, CHP, appears as broad d d), 6.8–8.0 ppm (m, 33, C_6H_5, including a small peak at 6.8 corresponding to that in the spctrum of **22a**).

Anal. Calcd for $C_{40}H_{34}O_2PBr$ (1:1 mixture of **22a** and **22b**): C, 73.06; H, 5.21; Br, 12.15. Found: C, 72.99; H, 5.04; Br, 12.50.

Conversion of Salts to Phospholanes.—The salts were dissolved in a small amount of methanol and 10 *M* NaOH was added dropwise until the solution became turbid. On standing the phospholanes crystallized and water was added at intervals until no further precipitation occurred. The crystals were recovered by filtration and washed with water and ether. Results are in Table III.

TABLE III

CONVERSION OF OXAPHOSPHOLANE SALTS TO OXAPHOSPHOLANES

Salt	Product	Yield, %
19a	**7a**	95
19b	**7b**	85
20	**9**	90
21a	**11a**	88
21b + **21a** (21%)	**11b** + **11a** (20%)	85
22a	**13**	67
22a + **22b** (50%)	**13**	74

Pyrolysis of 3- and 4-Substituted Oxaphospholanes A.—Samples of oxaphospholanes **7a**, **7b**, **9**, **11a**, **11b**, and **13** were injected into a vpc (column W-98 on Chromosorb, 200°). The only peaks recorded corresponded to benzil (**23**), triphenyl phosphine (**24**), and, in the cases of **9** and **13**, styrene. These products were collected and their identities confirmed by comparison to authentic samples.

B.—Samples of each of the above phospholanes (except **13**) were recovered unchanged from a 4-day reflux in *tert*-butyl alcohol, although very small amounts of benzil, triphenylphosphine, and, triphenylphosphine oxide could also be detected. Compund **13** was recovered in only 32% yield and significant amounts of benzil (**23**, 30%), triphenylphosphine (**24**, 17%), and triphenylphosphine oxide (**4**, 18%) were isolated. Styrene was detected by vpc but no other products were observed.

2,3-Diphenyl-5-methyl-2,5-dihydrofuran (**14**).—To a suspension of sodium hydride (2.1 g, 0.05 mol) in 50 ml of anhydrous ether was added benzoin (**1**), 12.8 g (0.05 mol), and then a solution of salt **6**, 19.2 g (0.05 mol), in 150 ml of dry CH_3CN. After a 48-hr reflux the mixture was filtered and the residue was washed with water and ether and air-dried to give 8.3 g of **7a**, plus a small amount of **7b** (32% total).

Dilution of the filtrate with 500 ml of water followed by extraction with two 100-ml portions of ether, drying ($MgSO_4$), concentration, and dropping into 400 ml of hexane gave a gummy precipitate and a clear yellow solution which was decanted. The gum solidified on stirring and proved to be slightly impure triphenylphosphine oxide (**4**), 7.8 g (56%). Concentration of the decantate and chromatography on silica gel afforded 3.6 g of a light yellow gum which proved to be pure **14** (30%), identified by its ir and nmr spectra. However, after repeated at tempts to crystallize this product, only 1,2-diphenyl-2-pentene-1,4-dione was recovered. Recrystallization from cold CCl_4–hexane gave colorless needles, mp 119–121°, 2.6 g (68%).

2,3-Diphenyl-5-methyl-2,5-dihydrofuran (**14**): ir ($CHCl_3$) ν 1070 cm^{-1} (s, COC); nmr ($CDCl_3$) δ 1.2 (d d, 3, CH_3), 4.8–5.2 (m, 1, CH), 6.2–5.8 (m, 2, ArCH + C=CH), 7.6–6.9 ppm (m, 10, C_6H_5).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.74; H, 6.58.

1,2-Diphenyl-2-pentene-1,4-dione: ir ($CHCl_3$) ν 1680 (s, C=O), 1580 (s, C=C), 1280 (m), 1190 (s), 985 cm^{-1} (m); nmr ($CDCl_3$) δ 2.2 (s, 3, CH_3), 6.8 (s, 1, C=CH), 7.2–7.7 and 7.8–8.0 ppm (m, 8, and m, 2, respectively, C_6H_5).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.36; H, 5.71.

This reaction was repeated using salts **8**, **10**, and **12**.

(A) Reaction of **1** and salt **8** gave compound **9** (8%), **2,3,5-triphenylfuran** [4%, mp 93–94° (lit.[16] 92–93°)], **1,2,4-triphenyl-2-butene-1,4-dione** [6%, mp 129–129.5° (lit.[17] 129°)], and **2,3,5-triphenyl-2,5-dihydrofuran**[18] (**15**) [50%; ir ($CHCl_3$) ν 1030 (m), 1060 (s, COC), 1070 (m), 1600 cm^{-1} (m, C=C); mp 78–80° (lit.[17] 79–80°); nmr ($CDCl_3$) δ 5.8–6.1 (m, 1, C=CH), 6.2–6.4 (m, 2, HCOCH), 6.9–7.16 ppm (m, 15, C_6H_5)].

Anal. Calcd for $C_{22}H_{18}O$ (**15**): C, 88.59; H, 6.00. Found: C, 88.40; H, 5.90.

(B) Reaction of **1** and salt **10** gave compound **11a** containing 36% of **11b** (34% combined) and **2,3-diphenyl-4-methyl-2,5-dihydrofuran** (**16**) [28%; ir ($CHCl_3$) ν 1070 cm^{-1} (s, COC); mp 72–74°; nmr ($CDCl_3$) δ 1.7 (broad doublet, 3, CH_3, *J* = 2 Hz), 4.7 (m, 2, CH_2), 6.0 (m, 1, CH), 6.9–7.7 ppm (m, 10, C_6H_5)].

Anal. Calcd for $C_{17}H_{16}O$ (**16**): C, 86.40; H, 6.83. Found: C, 86.44; H, 6.79.

(C) Reaction of **1** and salt **12** gave compound **13** (76%). There was no discernible evidence for the formation of the dihydrofuran **17** or any products resulting directly from it.

Registry No.—**7a**, 30697-85-9; **7b**, 30697-86-0; **9**, 30745-05-2; **11a**, 30697-87-1; **11b**, 30697-88-2; **13**, 30697-89-3; **14**, 30697-90-6; **15**, 30697-91-7; **16**, 30697-92-8; **18**, 30697-93-9; **19a**, 30697-94-0; **19b**, 30697-95-1; **20**, 30697-96-2; **21a**, 30697-97-3; **21b**, 30697-98-4; **22a**, 30697-99-5; **22b**, 30698-00-1; 1,2-diphenyl-2-pentene-1,4-dione, 24105-46-2.

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