20048-05-9; **2h**, 120634-43-7; **2i**, 123206-98-4; **2j**, 123206-99-5; **2k**, 123207-00-1; **2l**, 20048-01-5; **2m**, 123207-02-3; **2n**, 123207-03-4; **5a**, 93-08-3; **5b**, 5156-83-2; **5c**, 42036-59-9; **5d**, 3900-45-6; **5e**, 62759-49-3; **5f**, 33627-00-8; **5g**, 2459-25-8; **5h**, 6162-30-7; **5i**, 101513-13-7; **5j**, 33626-98-1; **5k**, 840-65-3; **5l**, 5043-02-7; **5m**, 33295-54-4; **5n**, 5088-92-6; **5o**, 117745-72-9; **6a**, 123207-04-5; **6b**, 119757-21-0; **6c**, 123207-05-6; **6d**, 123207-06-7; **6e**, 123207-07-8; **6f**, 123207-08-9; **6g**, 123207-09-0; **6h**, 120634-45-9; **6i**, 123207-10-3; **6j**, 123207-11-4; **6k**, 123207-12-5; **6l**, 123207-13-6; **6m**, 123207-14-7; **6n**, 123207-15-8; **7**, 69750-34-1; $HRh(CO)(PPh_3)_3$, 17185-29-4; 4-(methylthio)-benzaldehyde, 3446-89-7.

**Supplementary Material Available:** Tables of spectroscopic data for acetals **6a-n** (Table III) and spectroscopic and analytical data for α-acetylcinnamates **2g-n** (Table II) (3 pages). Ordering information is given on any current masthead page.

# Sequential Wittig-Oxyanion Accelerated Cope Reactions of 2,2,2-Triphenyl-5-vinyl-1,2λ⁵-oxaphospholane

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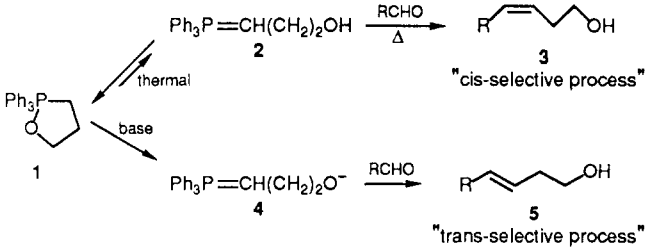
2,2,2-Triphenyl-5-vinyl-1,2λ⁵-oxaphospholane was prepared and condensed with a variety of aldehydes and ketones in a Wittig reaction to produce 3-hydroxy 1,5-dienes. These compounds were next subjected to an oxyanion accelerated Cope rearrangement. In the two-step process, the carbonyl was replaced with a difunctionalized carbon bearing a vinyl moiety and a three-carbon pendant aldehyde.

## Introduction

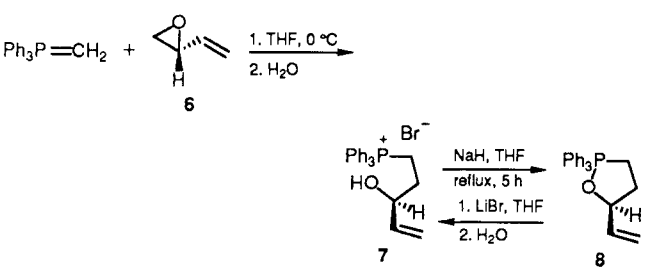
The Cope rearrangement remains one of the most useful tools in the synthetic chemists arsenal.[1] Recent interest in the oxyanion accelerated version[2] of this [3,3]sigmatropic rearrangement in its application to total synthesis[3] and new synthetic methodology[4] easily serve to demonstrate that utility. Our concern with this reaction focuses on the synthetic applications of 2,2,2-triphenyl-5-vinyl-1,2λ⁵-oxaphospholane, a compound which functions as a novel reagent for use in a Wittig-oxyanion accelerated Cope process (vide infra).

In 1967, Hands and Mercer reported the first isolation[5] of a 1,2λ⁵-oxaphospholane when they prepared 2,2,2-triphenyl-1,2λ⁵-oxaphospholane (1) shown in Scheme I. The authors found that this structurally interesting heterocycle reacted more readily with aldehydes than with ketones under thermally mediated conditions (90-120 °C) to afford Wittig products.[6] Although this compound has been the subject of only a few synthetic studies since this report,[7]

**Scheme I**




**Scheme II**




Maryanoff and co-workers[8d] have more recently indicated that reactions of the parent 1,2λ⁵-oxaphospholane can also be promoted by base at much lower reaction temperatures.[8] It has also been demonstrated that the olefin geometry in the homoallyl alcohol products is dependent on the dichotomy of reactivity illustrated in Scheme I. In the presence of base or in the "trans-selective process", the trans product **5** can predominate over the cis in ratios

(1) For recent reviews of the Cope rearrangement, see: (a) Hill, R. K.; Chirality Transfer via Sigmatropic Rearrangements In *Asymmetric Synthesis*, Morrison, J. D., Ed.; Academic Press: Orlando, FL, 1984; Vol. 3, pp 503-563. (b) Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205.

(2) For a review of the oxyanion accelerated Cope rearrangement, see: Swaminathan, S. *J. Ind. Chem. Soc.* **1984**, *61*, 99.

(3) (a) Koreeda, M.; Tanaka, Y. Schwartz, A. *J. Org. Chem.* **1980**, *45*, 1172. (b) Crouse, G. D.; Paquette, L. A. *J. Org. Chem.* **1981**, *46*, 4272. (c) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4186. (d) Paquette, L. A.; DeRussy, D. T.; Cottrell, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 890. (e) Paquette, L. A.; Crouse, G. D.; Sharma, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 4411.

(4) (a) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. (b) Corey, E. J.; Shulman, J. I. *J. Am. Chem. Soc.* **1970**, *92*, 5522. (c) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *J. Am. Chem. Soc.* **1978**, *100*, 2242. (d) Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 774. (e) Miller, S. A.; Gadwood, R. C. *J. Org. Chem.* **1988**, *53*, 2214. (f) Paquette, L. A.; Learn, K. S.; Romine, J. L.; Lin, H.-S. *J. Am. Chem. Soc.* **1988**, *110*, 879. (g) Paquette, L. A.; Pierre, F.; Cottrell, C. E. *J. Am. Chem. Soc.* **1987**, *109*, 5731. (h) Sworin, M.; Lin, K.-C. *J. Org. Chem.* **1987**, *52*, 5640.

(5) Hands, A. R.; Mercer, A. J. H. *J. Chem. Soc. C* **1967**, 1099.

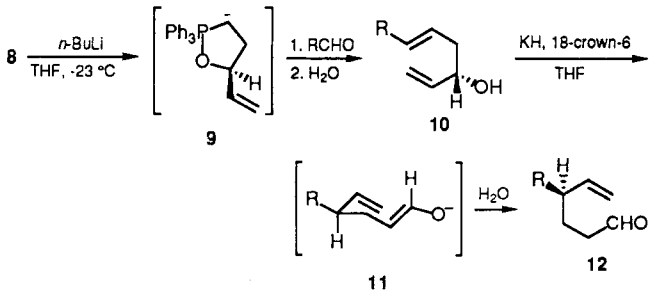
(6) Hands, A. R.; Mercer, A. J. H. *J. Chem. Soc. C* **1968**, 2448.

(7) (a) Leppard, D. G.; Raynolds, P. W.; Chapleo, C. B.; Dreiding, A. S. *Helv. Chim. Acta* **1976**, *59*, 695. (b) LeCorre, M.; Hercourt, A. *Tetrahedron* **1981**, *37*, 2855.

(8) (a) Maryanoff, B. E.; Duhl-Emswiler, B. A. *Tetrahedron Lett.* **1981**, 4185. (b) Maryanoff, B. E.; Reitz, A. B.; Duhl-Emswiler, B. A. *Tetrahedron Lett.* **1983**, 2477. (c) Maryanoff, B. E.; Duhl-Emswiler, B. A.; Reitz, A. B. *Phosphorus Sulfur* **1983**, *18*, 187. (d) Maryanoff, B. E.; Reitz, A. B.; Duhl-Emswiler, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 217. (e) Reitz, A. B.; Maryanoff, B. E. *J. Chem. Soc., Chem. Commun.* **1984**, 1548.

0022-3263/90/1955-0324$02.50/0 

**Scheme III**



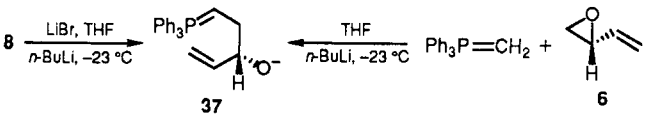

exceeding 25:1.[8] This observation is particularly intriguing because high *E* selectivity for unstabilized triphenylphosphonium ylides is rarely observed.[9] In direct contrast, the thermally mediated "cis-selective process" (without base) can produce ratios of ca. 1:4 favoring the cis product **3**.[8]

## Results and Discussion

Because the synthetic utility of this reagent in the formation and control of the olefin geometry in homoallylic alcohols appeared promising, it was surprising to find that very few substituted derivatives of **1** had been prepared.[7b,10] We have now isolated 2,2,2-triphenyl-5-vinyl-1,2λ⁵-oxaphospholane (**8**) in 89% overall yield as a hygroscopic plates (mp 126–127 °C) from the reaction of methylene triphenylphosphorane with butadiene monoepoxide at 0 °C, followed by treatment with sodium hydride, as shown in Scheme II. Our initial expectations were that the 1,2λ⁵-oxaphospholane would form directly without the need to isolate the protonated phosphonium salt **7**; however, the desired product could only be obtained in low yields. After extensive variation of experimental conditions, the two-step procedure was found to be the most expedient and convenient route. When **8** was treated with 1 equiv of anhydrous lithium bromide at ambient temperature, the lithium alkoxide of phosphonium salt **7** was formed in less than 10 min at ambient temperature. Thus, in the presence of lithium bromide, which is formed during the preparation of **7**, the acyclic bis-salt form appears to be favored over the 1,2λ⁵-oxaphospholane. Unfortunately, various lithium-free bases were unsuccessful. Normal aqueous workup techniques were also unsuccessful in the isolation of **8** because the compound underwent partial hydrolysis; so direct filtration under inert atmosphere was employed. Interestingly, $S_N2'$ opening of the epoxide did not play a significant role in this reaction, and products from this mode of attack were not observed. Finally, compound **8** was also subjected to single-crystal X-ray analysis, which confirmed the unusual 1,2λ⁵-oxaphospholane structure.

With compound **8** in hand, we were now able to examine the sequential Wittig–oxyanion accelerated Cope reactions. Ultimately, both "cis- and trans-selective processes" shown in Scheme I should each be potentially accessible with this sequence and each synthetically useful. Thus, examining the "trans-selective process" shown in Scheme III, deprotonation of **8** with *n*-BuLi, would produce **9**, which appears to not spontaneously eliminate to an acyclic alkoxide (vide infra). A subsequent condensation with an aldehyde (or a ketone) would then provide **10**, a 3-hydroxy-1,5-hexadiene. In addition to being precursors for pericyclic reactions it should be noted that the 3-hydroxy 1,5-diene functionality is a synthetically useful subunit which is found in several natural products such as leukotriene B and prostaglandin $F_3$.[11]

**Scheme IV**




In the second step of our sequence, we hoped to subject the dienols to an oxyanion accelerated Cope rearrangement, which proceeds through a chair transition state,[1] to produce compounds such as **12**. Note that in the overall sequence, an aldehyde or ketone carbonyl is replaced by a new difunctionalized carbon bearing a vinyl functionality and a three-carbon pendant aldehyde.

The first reaction of the two-step sequence was reduced to practice with **8** and a variety of very simple aldehyde and ketone substrates. These results have been tabulated and are shown in Table I (method A). Overall, we have found the reaction to be quite successful. In this series of reactions, attention was paid to the olefinic trans:cis ratios in the products in the crude mixture. Examining the series of 3-hydroxy 1,5-dienes (**21–28**) produced in the first step of the two-step sequence, it is clear that the benzaldehyde in entry 2 provides the highest trans:cis ratios. The phenyl-substituted dienol **22** possessed the most synthetically useful (90:10) trans:cis ratio, the highest we were able to obtain from 2,2,2-triphenyl-5-vinyl-1,2λ⁵-oxaphospholane. Aliphatic examples generally produced ratios not favoring either geometric isomer, and a 1:1 ratio was observed in every case. Dienol **27** was obtained as a 1:1 mixture of diastereomers where the existing chiral center in citronellal (**19**) did not induce asymmetric control in the formation of ϵ-hydroxyl stereocenter in the Wittig reaction, probably because of their lack of proximity. In nearly all cases except for the sterically encumbered entry 8, the yields were generally good.

The same series of 3-hydroxy 1,5-dienes can also be prepared by treatment of oxaphospholane **8** with lithium bromide prior to deprotonation with *n*-BuLi to produce ylide **37**, shown pictorially in Scheme IV. The ylide can be obtained in a more direct manner via *n*-BuLi deprotonation of the acyclic adduct formed from methylenetriphenylphosphorane and butadiene monoepoxide. This ylide produced different cis:trans ratios for the 3-hydroxy 1,5-dienes (method B) illustrated in Table I, in contrast to method A. In this series, the trans compounds were formed somewhat more selectively albeit at generally lower yields when compared to the products obtained by direct deprotonation of 2,2,2-triphenyl-5-vinyl-1,2λ⁵-oxaphospholane.

The two aromatic examples **14** and **17**, as before, gave the highest ratios favoring the trans olefin in **22** and **25**, respectively. It also appears that branching at the α- or

(9) (a) Schlosser, M. *Top. Stereochem.* **1970**, *5*, 1. (b) Cadogan, J. I. G. *Organophosphorus Reagents in Organic Synthesis*; Academic Press: New York, 1979; pp 17–153. (c) Bestmann, H. J.; Stransky, W.; Vostrowski, O. *Chem. Ber.* **1976**, *109*, 1694. (d) Sreekumar, C.; Darst, K. P.; Still, W. C. *J. Org. Chem.* **1980**, *45*, 4260.

(10) (a) Turcant, A.; LeCorre, M. *Tetrahedron Lett.* **1977**, 789. (b) Turcant, A.; LeCorre, M. *Tetrahedron Lett.* **1976**, 1277. (c) Schweitzer, E. E.; Creasy, W. S. *J. Org. Chem.* **1971**, *36*, 2244. (d) Bestman, H. J.; Denzel, T.; Kunstman, R.; Lengyel, J. *Tetrahedron Lett.* **1968**, 4262.

(11) For examples of 3-hydroxy-1,5-hexadienes in synthesis and natural products containing this subunit, see: (a) Bindra, J. S. The Synthesis of Prostaglandins In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley Interscience: New York, 1981; Vol. 4, pp 353–390. (b) Corey, E. J.; Shirahama, H.; Yamamoto, H.; Terashima, S.; Venkateswarlu, A.; Schaaf, T. K. *J. Am. Chem. Soc.* **1971**, *93*, 1490. (c) Johnson, F.; Paul, K. G.; Favarda, D.; Ciabatti, R.; Guzzi, U. *J. Am. Chem. Soc.* **1982**, *104*, 2190. (d) Corey, E. J.; Marfat, A.; Hoover, D. J. *Tetrahedron Lett.* **1981**, 1587. (e) Corey, E. J.; Niwa, H.; Knolle, J. *J. Am. Chem. Soc.* **1978**, *100*, 1942.

Table I. "Trans-Selective" Wittig Reactions

| entry | substrate | dienol | method[a] | yield,[b] % | ratio[c] trans:cis |
|---|---|---|---|---|---|
| 1. | $CH_3(CH_2)_5CHO$ 13 | $CH_3(CH_2)_5$, OH, H 21 | A | 56 | 54:46 |
| | | | B | 49 | 69:31 |
| 2. | CHO 14 | OH, H 22 | A | 83 | 90:10 |
| | | | B | 70 | 97:3 |
| 3. | CHO 15 | OH, H 23 | A | 89 | 55:45 |
| | | | B | 75 | 84:16 |
| 4. | O 16 | OH, H 24 | A | 66 | |
| | | | B | 56 | |
| 5. | O, CHO 17 | O, OH, H 25 | A | 76 | 68:32 |
| | | | B | 55 | 95:5 |
| 6. | Ph, CHO 18 | Ph, OH, H 26 | A | 76 | 53:47 |
| | | | B | 40 | 56:44 |
| 7. | CHO 19 | H, OH 27 | A | 81 | 48:52 |
| | | | B | 79 | 73:27 |
| 8. | O, Ph, Ph 20 | Ph, Ph, OH, H 28 | A | 35 | |
| | | | B | 87 | |

[a] Method A: 2,2,2-triphenyl-5-vinyl-1,2λ⁵-oxaphospholane, THF, *n*-BuLi, −23 °C. Method B: methylenetriphenylphosphorane, butadiene monoepoxide, THF, 0 °C. [b] All yields are for chromatographically homogeneous material and are unoptimized. [c] As determined by capillary VPC analysis using a 30-m J&W DP-1701 column; all compounds shown are racemic with one enantiomer shown for clarity.

even the β-carbon of the starting aldehyde increased the *trans*-dienol somewhat as compounds **23** and **27** clearly demonstrate. A decrease in the temperature of the reaction did not appear to greatly increase the amount of *trans*-dienol when **23** was prepared at different temperatures (−78, −61, and −23 °C) with trans:cis ratios of 86:14, 86:14, and 84:16 obtained, respectively. The Wittig reaction was generally complete in less than 30 min for all entries except for the case of benzophenone (entry 8), which required 6 h.

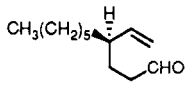
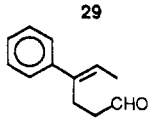
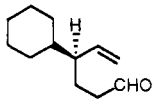
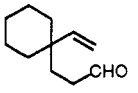
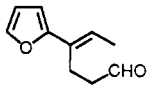
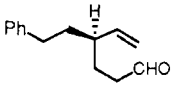
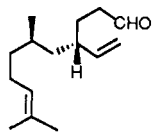
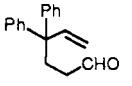
Mechanistically, it would appear that the alkoxide moiety in γ-oxido ylide **37** is exerting an effect on the oxaphosphetane in its formation or decomposition. These same interactions are not present in the initial condensation of anion **9** with a carbonyl compound, as is demonstrated in the different product ratios for methods A and B. The preference for the trans product differs markedly from the expected cis olefin geometry which is normally obtained from unstabilized ylides. Such results may be attributed to a "Schlosser-type"[12] mechanism in which a favorable distance exists between the oxygen and phosphorus atoms in the intermediate γ-oxido ylide. A base-induced equilibration involving proton transfer between the γ-oxygen and β-carbon atoms in the ylide results in the formation of the trans olefin.[13] Recent studies, however, have indicated that the source of the trans geometry is more likely due to a reversible dissociation of the oxaphosphetane to ylide and carbonyl starting substrate induced by the γ-anionic oxygen on the carbon chain.[8d,e] In either case, these processes introduce a measure of thermodynamic control in the reaction in accord with the predominant obtention of the trans olefin.

When we focused attention on the second step of our process, we found very few examples of the oxyanion accelerated Cope which utilize structurally simple 3-hydroxy 1,5-dienes similar to the one shown in Table II.[1,2] Every example which was attempted was complete in less than 2 h, and the yields for most entries ranged from low (35%) to good (76%). The reaction successfully produced the desired vinyl aldehydes in all cases except **30** and **33**. In these examples, the hyperbasic conditions employed in the oxyanion accelerated Cope reaction led to the formation

(12) In this context, the term "Schlosser type" mechanism refers to an internal base induced "trans-selective Wittig", which was first described by Schlosser.[9a] The term has also been extended to the trans selectivity seen in γ-oxido ylides.[8b]

(13) (a) Salmond, W. G.; Barta, M. A.; Havens, J. L. *J. Org. Chem.* **1978**, *43*, 790. (b) Kozikowski, A. P.; Ishida, H.; Chen, Y.-Y. *J. Org. Chem.* **1980**, *45*, 3350.

**Table II. Oxyanion Accelerated Cope Reactions**

| entry | dienol | aldehyde | yield,[b] % |
|---|---|---|---|
| 1. | 21 |  29 | 66 |
| 2. | 22 |  30 | 43[c] |
| 3. | 23 |  31 | 64 |
| 4. | 24 |  32 | 76 |
| 5. | 25 |  33 | 55 |
| 6. | 26 |  34 | 51 |
| 7. | 27 |  35 | 70 |
| 8. | 28 |  36 | 35 |

[a] Procedure: KH, 18-crown-6, THF (0.10 M), reflux. [b] All yields are for chromatographically homogeneous material and are unoptimized. [c] Sole *E* geometry as confirmed by NOE experiments; the olefin geometry for **33** is assumed the same by analogy. All compounds shown are racemic with one enantiomer shown for clarity.

of the conjugated olefin product in which the double bond has migrated. This occurred presumably after successfully undergoing the [3,3]sigmatropic rearrangement. The potential for transfer of chirality has already been demonstrated in the oxyanion accelerated Cope rearrangement,[1] and this reaction sequence lends itself easily to this studies through the control of both the dependent variables: the olefin geometry in the Wittig reaction and the single asymmetric vinyl center in the 1,2λ⁵-oxaphospholane **8**.[14]

In summary, the sequential Wittig–oxyanion accelerated Cope process delineated above should find considerable value in synthesis of both 3-hydroxy 1,5-dienes and hexenal substrates. The two-step bifunctionalization sequence results in the net introduction of two carbon appendages at a carbonyl carbon, which can be easily further elaborated. Conventional methodology which accomplishes the same transformations as the sequence demonstrated above would generally require a longer series of steps and would lack the direct simplicity of using an easily prepared λ⁵-oxaphospholane reagent. We are currently extending the scope of this reaction to a thermal (cis) version of the reaction.

(14) We have recently prepared **8** in optically active form from *d*-glyceraldehyde acetonide and studies on transfer of chirality through this sequence will be reported in due course.

## Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer and are reported in wavenumbers ($cm^{-1}$). Nuclear magnetic resonance (NMR) spectra were recorded at 300 MHz on a Varian VXR-300 (300 MHz) spectrometer. $^{13}C$ NMR spectra were recorded at 75 MHz on a Varian VXR-300 spectrometer. Chemical shifts are reported in ppm ($\delta$) downfield relative to tetramethylsilane ($CH_4Si$) as an internal standard in $CDCl_3$. Exact mass measurements were performed on an AEI M530 mass spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA 30091.

All reactions were run under an inert atmosphere of $N_2$ or Ar using a flame-dried apparatus. All yields reported refer to isolated material judged to be homogeneous by thin-layer chromatography and NMR spectroscopy. Temperatures below ambient temperature refer to bath temperatures unless otherwise stated. Solvents and anhydrous reagents were dried according to established procedures[15] by distillation under $N_2$ from an appropriate drying agent: ether and THF from benzophenone ketyl; chloroform and ethyl acetate from $CaH_2$.

Analytical TLC was performed with E. Merck precoated silica gel plates (0.25 mm) using phosphomolybdic acid in ethanol as an indicator. Column chromatography was performed with E. Merck silica gel 60 (230–400 mesh) by standard flash chromatographic techniques.[16]

**(±)-2,2,2-Triphenyl-5-vinyl-1,2λ⁵-oxaphospholane (8).** Methyl triphenylphosphonium bromide (2.00 g, 5.6 mmol) was magnetically stirred under argon in THF (5.00 mL) at 0 °C. *n*-Butyllithium (2.40 mL, 2.5 M in hexanes) was added, and the reaction mixture was stirred for 15 min and turned yellow. Butadiene monoepoxide (0.50 mL) was added by syringe over 5 min. After warming to 23 °C over 1 h, the reaction was quenched with water and extracted with chloroform (3 × 50 mL). The organic layers were dried over $Na_2SO_4$ and concentrated to produce the crude phosphonium salt **7** as an off-white powder after full pump.

NaH (400 mg, 60% in oil) was washed with pentanes (3 × 5 mL) and diluted with THF (50 mL). The crude phosphonium salt was added, and the suspension was refluxed for 5 h, cooled, and filtered under Ar. The solvent was removed under reduced pressure, and the paste was redissolved in ether (50 mL) and filtered under Ar. Concentration of the mixture gave 1.73 g of crystalline **8** (89%), which can be used without further purification. An analytical sample was obtained as colorless plates by recrystallization from warm ether–hexanes: mp 126–127 °C; 300-MHz $^1H$ NMR ($C_6D_6$) $\delta$ 7.50–6.90 (m, 15 H), 5.85 (m, 1 H), 5.15 (d of t, $J$ = 17.1, 2.0 Hz, 1 H), 4.88 (d, $J$ = 10.4 Hz, 1 H), 3.70 (m, 1 H), 2.63 (m, 1 H), 2.18 (m, 1 H), 1.78 (m, 1 H), 1.42 (m, 1 H); 75-MHz $^{13}C$ NMR ($CDCl_3$) $\delta$ 142.4, 142.3, 131.9, 131.7, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 112.5, 70.2, 70.1 ($P_2$–$C_5$, $J$ = 6.2 Hz), 30.2, 29.9, 28.7 ($P_2$–$C_3$, $J$ = 92.2 Hz); 146.5 MHz $^{31}P$ NMR ($C_6D_6$) $\delta$ 192.9; IR (KBr) 3054, 2960, 1640, 1188, 1007, 882 $cm^{-1}$; mass spectrum (CI) 347 ($MH^+$, 100.0), 269 (92), 193 (22). Anal. Calcd for C, 79.75; H, 6.69. Found: C, 79.58; H, 6.66.

**General Procedure A for the Wittig Reaction and the Synthesis of 3-Hydroxy-1,5-hexadienes.** In a 10-mL flame-dried round-bottom flask was placed (±)-2,2,2-triphenyl-5-vinyl-1,2λ⁵-oxaphospholane (45 mg, 0.13 mmol), THF (0.25 mL), and HMPA (0.10 mL). After the reaction mixture was cooled to −23 °C and *n*-BuLi (60 μL, 2.27 M in hexanes) was added by syringe over 5 min, the reaction was stirred for 0.25 h. An aldehyde or ketone (0.13 mmol) was added neat in one shot, and the reaction mixture was stirred for an additional 2 h. Reaction was then quenched with water (10 mL) and extracted with ethyl acetate (3 × 30 mL), and the organic layers were dried over $Na_2SO_4$. Concentration under reduced pressure and flash chromatography

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rendered the desired 3-hydroxy 1,5-dienes.

**General Procedure B for the Wittig Reaction and the Synthesis of 3-Hydroxy-1,5-hexadienes.** Methyltriphenylphosphonium bromide (1.0 g, 2.8 mmol) was stirred in THF (5.0 mL) at 0 °C. To the slurry was added *n*-BuLi (1.12 mL, 2.8 mmol, 2.5 M in hexanes) over 5 min by syringe, and after 20 min the solution became clear and yellow. To the flask was added butadiene monoepoxide (250 μL), the reaction mixture warmed to 23 °C for 1 h and then recooled to −23 °C, *n*-BuLi (1.12 mL, 2.8 mmol, 2.5 M in hexanes) was added, and after 20 min the solids dissolved and reaction became dark red. An aldehyde or ketone (2.9 mmol) was added in THF (2.0 mL), and the reaction slowly warmed to 23 °C over 6 h and was quenched with water. Extraction with ethyl acetate (3 × 30 mL), drying over $Na_2SO_4$, concentration under reduced pressure, and flash chromatography gave the desired 3-hydroxy-1,5-hexadienes.

**General Procedure for the Oxyanion Accelerated Cope Reaction and the Synthesis of Hexenals.** Potassium hydride (35 wt % in mineral oil, 145 mg) was treated with pentanes (3 × 5 mL) to remove the oil. Tetrahydrofuran (0.20 M in diene, 5.0 mL) was added followed by the 3-hydroxy-1,5-hexadiene substrate (1.0 mmol) and 18-crown-6 (200 mg in THF (2.0 mL)). After the solution stirred at 23 °C or required reflux in some cases, TLC indicated complete consumption of the starting diene, and the reaction was cooled to 0 °C and quenched with cold aqueous saturated $NH_4Cl$ (20 mL) and extracted with ether (3 × 30 mL). The organic layers were dried over $Na_2SO_4$, and solvents were removed under reduced pressure. Subsequent flash chromatography rendered the desired 5-hexenal.

**(±)-3-Hydroxy-1,5-dodecadiene (21).** Physical data for the trans isomer: $R_f$ 0.13 (20% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 5.79 (m, 1 H), 5.55 (m, 1 H), 5.30 (m, 1 H), 5.25 (m, 1 H), 5.12 (m, 1 H), 4.12 (m, 1 H), 2.27 (m, 2 H), 2.00 (m, 3 H), 1.20–1.40 (m, 8 H), 0.90 (t, $J$ = 7 Hz, 3 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 140.4, 135.1, 124.9, 114.5, 72.0, 40.5, 32.6, 31.7, 29.3, 28.8, 22.6, 14.0; IR (neat) 3330 (br), 2900, 2845, 1452, 916 cm$^{-1}$; mass spectrum (EI) (no M$^+$), 126 (33.2), 97 (30.9), 84 (29.8), 83 (39.7), 70 (51.1), 69 (57 (100). Anal. Calcd for C, 79.05; H, 12.17. Found: C, 79.03; H, 12.16.

**(±)-4-Vinyldecanal (29):** $R_f$ 0.48 (20% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 9.79 (m, 1 H), 5.49 (m, 1 H), 5.00 (m, 2 H), 2.92 (m, 2 H), 1.98 (s, br, 1 H), 1.75 (m, 1 H), 1.50 (m, 1 H), 1.20–1.41 (m, 10 H), 0.90 (t, $J$ = 7 Hz, 3 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 202.7, 142.1, 115.3, 43.7, 41.8, 35.0, 31.8, 29.3, 27.0, 27.0, 22.6, 14.0; IR (neat) 2920, 2850, 2720, 1722, 1451, 908 cm$^{-1}$; mass spectrum (EI) 182 (M$^+$, 1.7), 97 (68.8), 70 (32.4), 69 (34.6), 55 (64.27), 41 (100); exact mass calculated for $C_{12}H_{22}O$ 182.1671, found 182.1664.

**(±)-6-Phenyl-3-hydroxy-1,5-hexadiene (22):** $R_f$ 0.20 (35% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 7.30 (m, 5 H), 6.45 (d, $J$ = 15 Hz, 1 H), 6.22 (dt, $J$ = 15, 8 Hz, 1 H), 5.90–6.00 (m, 1 H), 5.29 (dt, $J$ = 15, 2 Hz, 1 H), 5.16 (dt, $J$ = 8, 2 Hz, 1 H), 4.35 (m, 1 H), 2.49 (m, 2 H), 1.62 (s, br, 1 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 140.3, 137.2, 133.2, 128.5, 127.2, 126.1, 125.5, 114.9, 72.2, 40.8; IR (neat) 3430 (s, br), 3010, 2920, 1162, 740, 690 cm$^{-1}$; mass spectrum (EI) 174 (M$^+$, 1.32), 118 (81.2), 117 (100.0), 115 (61.4), 91 (52.4), 57 (86.7). Anal. Calcd: C, 82.72; H, 8.10. Found: C, 82.52; H, 7.99.

**(*E*)-4-Phenyl-4-hexenal (30):** $R_f$ 0.52 (35% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 9.75 (s, 1 H), 7.30 (m, 5 H), 5.79 (q, $J$ = 7 Hz, 1 H), 2.84 (t, $J$ = 7 Hz, 2 H), 2.47 (m, 2 H), 1.82 (d, $J$ = 7 Hz, 3 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 202.0, 142.2, 128.8, 128.4, 126.9, 126.3, 124.1, 42.5, 21.9, 14.1; IR (neat) 3020, 2920, 2720, 1720, 1440 cm$^{-1}$; mass spectrum (EI) 174 (M$^+$, 4.9), 130 (100.0), 129 (32.0), 117 (25.03), 115 (45.7), 91 (19.7); exact mass calculated for $C_{12}H_{14}O$ 174.1045, found 174.1038.

**(±)-6-Cyclohexyl-3-hydroxy-1,5-hexadiene (23).** Physical data for the trans isomer: $R_f$ 0.38 (30% ether hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 5.88 (m, 1 H), 5.52 (dd, $J$ = 15, 7 Hz, 1 H), 5.35 (m, 1 H), 5.24 (dt, $J$ = 17, 2 Hz, 1 H), 5.12 (dt, $J$ = 10, 2 Hz, 1 H), 4.12 (m, 1 H), 2.3 (m, 2 H), 1.98 (m, 1 H), 0.90–1.60 (m, 10 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 141.2, 140.4, 122.3, 114.5, 71.9, 40.8, 40.6, 33.1, 26.1, 26.0; IR (neat) 3340 (br), 2920, 2850, 1446, 965, 915, 730 cm$^{-1}$; mass spectrum (EI) no M$^+$ observed, 149 (2.6), 124 (44.2), 82 (72.2), 81 (98.0), 67 (84.4). Anal. Calcd: C, 79.94; H, 11.18. Found: C, 79.93; H, 11.14.

**(±)-5-Cyclohexyl-6-hexenal (31):** $R_f$ 0.65 (35% THF–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 9.78, (s, 1 H), 5.50 (m, 1 H), 5.04 (dd, $J$ = 10, 2 Hz, 1 H), 4.93 (dd, $J$ = 17, 2 Hz, 1 H), 2.40 (m, 2 H), 1.40–1.92 (m, 8 H), 0.83–1.30 (m, 6 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 202.9, 140.2, 116.2, 49.8, 42.3, 41.8, 31.0, 29.8, 26.6, 26.5, 23.9; IR (neat) 3045, 2920, 2850, 2705, 1722, 1648, 1447, 908 cm$^{-1}$; mass spectrum (EI) 180 (M$^+$, 0.6), 136 (11.0), 98 (11.2), 83 (60.0), 82 (28.4), 80 (49.2); exact mass calculated for $C_{12}H_{20}O$ 180.1501, found 180.1514.

**(±)-5-Cyclohexylidene-3-hydroxy-1-pentene (24):** $R_f$ 0.17 (20% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 5.90 (m, 1 H), 5.25 (m on dt, $J$ = 17, 2 Hz, 2 H), 5.11 (dt, $J$ = 10, 2 Hz, 1 H), 4.10 (m, 1 H), 2.27 (apparent t, $J$ = 7 Hz, 2 H), 2.16 (m, 4 H), 1.71 (m, 1 H), 1.52 (m, 6 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 143.8, 140.6, 115.8, 114.5, 72.6, 37.3, 35.1, 28.9, 28.7, 27.9, 26.8; IR (neat) 3350, 2920, 2850, 1445, 980, 915 cm$^{-1}$; mass spectrum (EI) 166 (M$^+$, 0.7), 110 (44.7), 109 (58.7), 81 (49.5), 67 (100). Anal. Calcd: C, 79.46; H, 10.91. Found: C, 79.32; H, 10.94.

**(±)-1-(2-Formylethyl)-1-vinylcyclohexane (32):** $R_f$ 0.52 (20% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 9.78 (s, 1 H), 5.58 (dd, $J$ = 17, 10 Hz, 1 H), 5.15 (d, $J$ = 10 Hz, 1 H), 4.95 (d, $J$ = 17 Hz, 1 H), 2.35 (t, $J$ = 7 Hz, 2 H), 1.20–1.70 (m, 12 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 203.1, 135.5, 114.0, 39.10, 38.9, 35.5, 26.4, 22.1, 22.1; IR (neat) 3040, 2922, 2850, 2715, 1725, 1635, 1445, 1000, 910 cm$^{-1}$; mass spectrum (EI) 166 (M$^+$, 0.4), 122 (29), 109 (53.6), 81 (34.8), 79 (29.0), 67 (100.0); exact mass calculated for $C_{11}H_{18}O$ 166.1358, found 166.1358.

**(±)-6-(2-Furanyl)-3-hydroxy-1,5-hexadiene (25).** Physical data for the trans isomer: $R_f$ 0.33 (30% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 7.30 (m, 1 H), 6.32 (m, 2 H), 6.15 (m, 2 H), 5.91 (m, 1 H), 5.27 (dt, $J$ = 17, 1 Hz, 1 H), 5.15 (dt, $J$ = 10, 1 Hz, 1 H), 4.23 (dd, $J$ = 11, 5 Hz, 1 H), 2.45 (m, 2 H), 1.80 (s, br, 1 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 152.7, 141.6, 140.2, 124.4, 121.8, 115.0, 111.1, 106.9, 72.2, 40.7; IR (neat) 3380 (s, br), 2980, 2870, 1641, 1488, 727 cm$^{-1}$; mass spectrum (EI) 164 (M$^+$, 12.3), 108 (49.1), 107 (100.00), 79 (70.0), 77 (57.9); exact mass calculated for $C_{10}H_{12}O_2$ 164.0837, found 164.0859.

**(*E*)-5-(2-Furanyl)-5-hexenal (33):** $R_f$ 0.61 (50% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 9.80 (s, 1 H), 7.32 (s, 1 H), 6.35 (m, 1 H), 6.17 (m, 2 H), 2.70 (m, 2 H), 2.60 (m, 2 H), 1.80 (d, $J$ = 7 Hz, 3 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 202.1, 155.1, 141.7, 129.0, 121.6, 111.4, 104.6, 43.5, 20.4, 13.7; IR (neat) 2920, 2710, 1718, 1008, 729 cm$^{-1}$; mass spectrum (EI) 164 (M$^+$, 31.6), 122 (73.1), 120 (36.7), 107 (42.1), 91 (30.7), 79 (31.9), 77 (28.8); exact mass calculated for $C_{10}H_{12}O$ 164.0837, found 164.0836.

**(±)-8-Phenyl-3-hydroxy-1,5-octadiene (26).** Physical data for the trans isomer: $R_f$ 0.42 (40% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 7.23–7.30 (m, 5 H), 5.80 (m, 1 H), 5.55 (m, 1 H), 5.35 (m, 1 H), 5.18 (m, 1 H), 5.06 (m, 1 H), 4.01 (m, 1 H), 2.67 (dd, 2 H), 2.35 (dd, 2 H), 2.20 (dd, 2 H), 1.82 (s, br, 1 H); IR (neat) 3380 (st, br), 3012, 2920, 980, 918, 695 cm$^{-1}$; mass spectrum (EI) 202 (M$^+$, 0.15), 184 (1.6), 146 (16), 104 (15), 91 (99); exact mass calculated for $C_{14}H_{18}O$ 202.1358, found 202.1368.

**(±)-6-Phenyl-4-vinylhexanal (34):** $R_f$ 0.26 (40% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 9.75 (m, 1 H), 7.25 (m, 5 H), 6.02 (m, 1 H), 5.10 (dd, $J$ = 10, 1 Hz, 1 H), 5.09 (dd, $J$ = 16, 1 Hz, 1 H), 2.65 (m, 1 H), 2.55 (m, 1 H), 2.48 (m, 2 H), 2.02 (m, 1 H), 1.75 (m, 2 H), 1.60 (m, 2 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 202.5, 142.4, 141.6, 128.4, 128.3, 125.7, 116.3, 43.4, 41.8, 36.8, 33.4, 27.0; IR (neat) 3008, 2905, 2702, 1712, 1441, 705, 690 cm$^{-1}$; mass spectrum (EI) 202 (M$^+$, 3.8), 143 (11.5), 129 (19.6), 105 (42.8), 104 (50.1), 97 (26.8), 91 (100.0); exact mass calculated for $C_{14}H_{18}O$ 202.1357, found 202.1352.

**3(*R*,*S*)-Hydroxy-8(*S*)-12-dimethyl-1,5(*E*),11-tridecatriene (27).** Physical data for the trans isomer: $R_f$ 0.16 (20% ether–hexanes); 300-MHz $^1$H NMR ($CDCl_3$) δ 5.88 (m, 1 H), 5.55 (m, 1 H), 5.40 (m, 1 H), 5.22 (m, 1 H), 5.12 (m, 2 H), 4.20 (m, 1 H), 2.28 (m, 2 H), 1.98 (m, 6 H), 1.68 (s, 3 H), 1.60 (s, 3 H), 1.48 (m, 1 H), 1.33 (m, 1 H), 1.15 (m, 1 H), 0.88 (d, $J$ = 7 Hz, 3 H); 75-MHz $^{13}$C NMR ($CDCl_3$) δ 140.4, 133.3, 131.1, 126.3, 124.8, 114.5, 72.1, 40.6, 40.0, 36.6, 32.6, 25.7, 25.3, 19.4, 17.6; IR (neat) 3335 (br), 2905, 1440, 915 cm$^{-1}$; mass spectrum (EI) no M$^+$ observed, 221 (0.5), 149 (1.8), 109 (11.8), 95 (13.9), 81 (15.6). Anal. Calcd: C, 81.04; H, 11.78. Found: C, 80.94; H, 11.75.

**4(*R*,*S*)-Vinyl-6(*S*)-10-dimethyl-9-undecenal (35).** Physical data for the 1:1 diastereomeric mixture: $R_f$ 0.52 (20% ether–

hexanes); 300-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 9.78 (s, 1 H), 5.43 (m, 1 H), 5.01 (m, 3 H), 2.42 (m, 2 H), 1.0–2.15 (m, 10 H), 1.68 (s, 3 H), 1.60 (s, 3 H), 0.85 (2 doublets, 3 H); IR (neat) 3040, 2921, 2720, 1732, 1455, 1385, 927 $cm^{-1}$; mass spectrum (EI) 222 ($M^+$, 0.7), 109 (13.5), 69 (46), 55 (20), 41 (34); exact mass calculated for $C_{15}H_{26}O$ 222.1983, found 222.1987.

**(±)-6,6-Diphenyl-3-hydroxy-1,5-hexadiene (28)**: $R_f$ 0.46 (30% ether–hexanes); 300-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 7.35 (m, 10 H), 6.25 (t, $J$ = 7 Hz, 1 H), 5.83 (m, 1 H), 5.40 (d, $J$ = 17 Hz, 1 H), 5.09 (d, $J$ = 7 Hz, 1 H), 4.18 (m, 1 H), 2.39 (t, $J$ = 6 Hz, 2 H), 2.10 (s, br, 1 H); 75-MHz $^{13}C$ NMR ($CDCl_3$) $\delta$ 144.0, 143.9, 142.4, 140.4, 139.8, 129.8, 128.2, 128.0, 127.2, 127.0, 124.6, 114.8, 72.7, 37.2; IR (neat) 3370, 2920, 2808, 758, 696 $cm^{-1}$; mass spectrum (neat) no $M^+$ observed, 194 (17.7), 193 (96.8), 178 (17.6), 115 (100.0); exact mass calculated for $C_{18}H_{18}O_1$ 250.1358, found 250.1379.

**4,4-Diphenyl-5-hexenal (36)**: $R_f$ 0.34 (20% ether–hexanes); 300-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 9.61 (s, 1 H), 7.32 (m, 10 H), 6.38 (dd, $J$ = 17, 11 Hz, 1 H), 5.23 (dd, $J$ = 11, 1 Hz, 1 H), 4.85 (d, $J$ = 17, 1 Hz, 1 H), 2.60 (dd, $J$ = 8.4, 6 Hz, 2 H), 2.30 (m, 2 H); 75-MHz $^{13}C$ NMR ($CDCl_3$) $\delta$ 201.6, 145.9, 143.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.7, 126.2, 114.4, 52.7, 40.1, 30.0; IR (neat) 1715, 695 $cm^{-1}$; mass spectrum (EI) 250 ($M^+$, 8.5), 207 (17.0), 206 (68.5), 193 (88.2), 180 (15.3), 178 (37.4), 115 (100); exact mass calculated for $C_{18}H_{18}O$ 250.1360, found 250.1358.

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# Generation and Reactions of Novel Copper Carbenoids through a Stoichiometric Reaction of Copper Metal with *gem*-Dichlorides in Dimethyl Sulfoxide

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Copper metal and such *gem*-dichlorides as $\alpha,\alpha$-dichloro acid esters, **1a–e**, diphenyldichloromethane, **2**, benzal chloride, **3**, 1,1-dichloroacetone, **4**, 1,1-dichloro-2-butene, **5**, and carbon tetrachloride, **6**, were found to undergo a stoichiometric reaction in dimethyl sulfoxide (DMSO) under a mild condition to produce copper carbenoid intermediates via $\alpha,\alpha$-elimination of dichlorides along with the formation of $CuCl_2(DMSO)_2$. Thus, **1** and **2** gave substituted olefins via a carbenoid coupling reaction. From **5** and **6**, reaction products via the oxygen abstraction from DMSO were produced together with dimethyl sulfide; **3** and **4** were found to cause both types of reactions. The carbenoid intermediates formed from **1** did not cause cyclopropanation reaction with cyclohexene in contrast to the conventional carbalkoxy carbenoid generated by a decomposition reaction of ethyl diazoacetate. Also the carbenoid coupling reaction was completely inhibited by the addition of triphenylphosphine, which was contrastive to the formation of phosphonium ylide with a carbenoid from ethyl diazoacetate.

## Introduction

Copper metal and its salts have been known to promote decomposition reactions of organic halides to generate copper carbenoid or radical intermediates, and these reactions have been utilized for versatile synthetic methods involving a carbon–carbon bond formation.[1] We report here unusual and novel stoichiometric reactions between copper metal and a number of organic halides, in particular *gem*-dichlorides, to form copper carbenoid intermediates under a mild condition. Also we focus on the unique reactivity of carbalkoxy carbenoids generated from $\alpha,\alpha$-dichloro acid esters in the present system by comparing with conventional ones produced through photodecomposition or thermal decomposition of diazoacetic acid esters.

## Results and Discussion

Copper is traditionally known as a coinage metal because of its resistance to corrosion under ordinary atmospheric conditions. However, we found recently[2] that copper metal reacted in dimethyl sulfoxide (DMSO) with some organic halides under an extremely mild condition. For example, copper powder (250 or 40 mesh) was suspended in DMSO

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