$$\underset{1}{RC{\equiv}CH} + \underset{2}{PhIOH{\cdot}OTs} \rightarrow \underset{3}{RC{\equiv}CIPh{\cdot}OTs} + \underset{4}{R(TsO)C{=}CHIPh{\cdot}OTs} \quad (1)$$

procedure suffers from a number of serious shortcomings. Formation of **3** is generally accompanied by the related vinyl species **4** that both decreases the yields of **3** and causes purification problems. Moreover, the original Koser procedure[10] did not give any **3** when the R in **1** (or **3**) was a small primary group such as Me, *n*-Pr, or *n*-Bu. Although our modified procedure[4] afforded these particular compounds, the yields were very poor, with only 19% and 12% respectively for R = CH_3 and *n*-Bu. Finally, no $Me_3SiC{\equiv}CIPh{\cdot}OTs$ could be isolated from the reaction of $Me_3SiC{\equiv}CH$ and **2**.

Hence, we wish to report a simple, much improved procedure for the ready preparation of **3**. This procedure involves the reaction of readily available iodosobenzene (**5**) with 1-(trimethylsilyl)-1-alkynes (**6**) in chloroform in the presence of equimolar amounts of $BF_3{\cdot}OEt_2$ followed by sequential treatment with aqueous $NaOSO_2Ar$ as shown in eq 2. Physical and spectral data for representative

$$\underset{5}{PhIO} + RC{\equiv}CSiMe_3 \xrightarrow[\text{room temp}]{\text{(1) } BF_3{\cdot}OEt_2,\ CHCl_3} \xrightarrow{\text{(2) aq } NaOSO_2Ar} RC{\equiv}CIPh{\cdot}OSO_2C_6H_4X\text{-}p \quad (2)$$

6a, R = Me
6b, R = Et
6c, R = *n*-Pr
6d, R = *n*-Bu
6e, R = Me_3Si

3a, R = Me; X = Me
3b, R = Me; X = NO_2
3c, R = Et; X = Me
3d, R = *n*-Pr; X = Me
3e, R = *n*-Bu; X = Me
3f, R = Me_3Si; X = Me

reactions are summarized in the Experimental Section. The experimental procedure itself is similar to that of Fujita[12] reported for the preparation of the related alkynylphenyliodonium tetrafluoroborates ($RC{\equiv}CIPh{\cdot}BF_4$).

As the data indicate, good to excellent yields of a variety of alkynylphenyliodonium sulfonates (**3**) may be prepared by this procedure. All compounds are stable crystalline solids. Most gratifying is the observation that simple primary alkyl groups such as Me, Et, *n*-Pr, and *n*-Bu work very well. Moreover, $Me_3SiC{\equiv}CSiMe_3$ affords the hitherto unknown silyl-substituted iodonium salt in 70% isolated yield. The products were characterized by spectral means as summarized in the Experimental Section. The spectral data are all in accord with expectations for the individual compounds.

We believe that this improved, more general procedure will further increase the availability and uses of these relatively new and valuable alkynyliodonium species.

Experimental Section

General Procedure. To a suspension of iodosobenzene (**5**) (PhIO, 5.0 mmol) and the appropriate 1-(trimethylsilyl)-1-alkyne (**6**) (5.0 mmol, prepared from 1-alkyne and Me_3SiCl in nearly quantitative yield or a commercial sample) in 10 mL of $CHCl_3$ was slowly added 5.0 mmol of $BF_3{\cdot}OEt_2$ at 0 °C. After addition was complete the mixture was stirred at room temperature for 3–4 h. After the resulting yellow homogeneous solution was recooled to 0 °C, a solution of the appropriate sodium arylsulfonate (20 mmol) in water (20 mL) was added and the resulting mixture was vigorously stirred for a few minutes. The organic phase was separated and the aqueous phase extracted with additional $CHCl_3$. The combined organic phase was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residual oil solidified upon addition of ether. The solid was filtered, washed with ether, and air-dried. In no case was any **4** observed in these reactions. The respective yields and physical and spectral data are as follows. **3a**: yield 62%; mp 123–125 °C dec (lit.[4a] mp 123–127 °C); ^1H NMR ($CDCl_3$) δ 2.07 (s, Me), 2.30 (s, Me), 7.02–7.63 (m, ArH), 7.95–8.08 (m, ArH); IR (Nujol) 2185 (m, C≡C), 1220 (s), 1150 (vs), 1115 (s), 1025 (m), 993 (s), 982 (m), 820 (m), 735 (s), 680 (s) cm^{-1}; FABMS *m/e* 243 ($MeC{\equiv}CIPh^+$). **3b**: yield 69%; mp 135–138 °C dec; ^1H NMR ($CDCl_3$–DMSO-d_6) δ 2.17 (s, Me), 7.33–7.72 (m, ArH), 7.88–8.20 (m, ArH); IR (Nujol) 2185 (m, C≡C), 1522 (s), 1345 (s), 1235 (s), 1180 (s), 1160 (s), 1115 (s), 1020 (s), 998 (s), 983 (w), 850 (s), 734 (s), 628 (s) cm^{-1}; FABMS *m/e* 243 ($MeC{\equiv}CIPh^+$). **3c**: yield 81%; mp 108–110 °C dec; ^1H NMR ($CDCl_3$) δ 1.10 (t, *J* = 7.5 Hz, Me), 2.30 (s, Me), 2.40 (q, *J* = 7.5 Hz, CH_2), 7.00–7.60 (m, ArH), 7.93–8.04 (m, ArH); IR (Nujol) 2180 (m, C≡C), 1220 (s), 1160 (s), 1110 (m), 1024 (m), 1000 (s), 985 (w, sh), 810 (w), 738 (m), 675 (s) cm^{-1}; FABMS *m/e* 257 ($EtC{\equiv}CIPh^+$). **3d**: yield 89%; mp 93–95 °C dec; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.5 Hz, Me), 1.50 (sext, *J* = 7.5 Hz, CH_2), 2.30 (s, Me), 2.40 (t, *J* = 7.5 Hz, CH_2), 6.98–7.62 (m, ArH), 7.93–8.05 (m, ArH); IR (Nujol) 2185 (m, C≡C), 1229 (s), 1140 (s), 1110 (m), 1025 (w), 995 (s), 807 (w), 743 (m), 675 (s); FABMS *m/e* 271 (*n*-$PrC{\equiv}CIPh^+$). **3e**: yield 76%; mp 76–78 °C dec (lit.[4a] mp 81–83 °C); ^1H NMR ($CDCl_3$) δ 0.73–0.92 (m, Me), 1.12–1.58 (m, CH_2CH_2), 2.30 (s, Me), 2.30–2.50 (m, CH_2), 6.98–7.60 (m, ArH), 7.92–8.05 (m, ArH); IR (Nujol) 2185 (m, C≡C), 1225 (s), 1175 (m), 1145 (vs), 1115 (m), 1025 (m), 1000 (s), 985 (m, sh), 807 (m), 730 (m), 675 (s) cm^{-1}; FABMS *m/e* 285 (*n*-$BuC{\equiv}CIPh^+$). **3f**: yield 70%; mp 107–109 °C dec; ^1H NMR ($CDCl_3$) δ 0.15 (s, Me), 2.30 (s, Me), 7.00–7.61 (m, ArH), 7.97–8.07 (m, ArH); IR (Nujol) 1222 (s), 1145 (vs), 1112 (m), 1023 (m), 998 (s), 985 (w, sh), 850 (s), 835 (m, sh), 810 (w), 742 (w), 700 (m), 674 (s) cm^{-1}; FABMS *m/e* 301 ($Me_3SiC{\equiv}CIPh^+$). Acceptable combustion analytical data for C and H (±0.4%) were obtained for **3a**, **3c**, **3d**, and **3f**; compounds **3a** and **3b** are known compounds.[4a]

Acknowledgment. This research was supported by the NCI of NIH, Grant CA 16903-11.

Registry No. **3a**, 94957-41-2; **3b**, 114820-32-5; **3c**, 114820-34-7; **3d**, 114820-36-9; **3e**, 94957-42-3; **3f**, 114820-38-1; **5**, 536-80-1; **6a**, 6224-91-5; **6b**, 62108-37-6; **6c**, 18270-17-2; **6d**, 3844-94-8; **6e**, 14630-40-1; $NaOSO_2C_6H_4Me$-*p*, 657-84-1; $NaOSO_2C_6H_4NO_2$-*p*, 5134-88-3.

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Synthesis of Dihydrophosphorins by the Thermal Transformation of Phosphole–Dichlorocarbene Adducts

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Ring enlargement of unsaturated cyclic compounds through dichlorocarbene adducts is a useful synthetic method.[1-3] The addition of dichlorocarbene to the double

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0022-3263/88/1953-4106$01.50/0

Scheme I

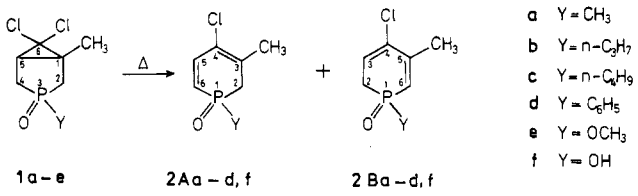


Table I. Thermally Induced Phosphole–Dichlorocarbene Adduct (1) → Dihydrophosphorin (2) Transformations[a]

	decomp temp[b] of 1, °C	product ratio,[c] % 2A	2B	yield[d] of 2, %	ΔH,[e] kJ mol^{-1}
a	117 (97–135)	74	26	98	−8.0
b	122 (112–134)	74	26	79	−8.1
c	124 (103–136)	71	29	88	−9.6
d	126 (122–141)	72	28	93	−25.3
e, f[f]	130 (109–145)	72	28	44[g]	−11.5

[a] Reactions were carried out at 135 °C for 3 min. [b] The value for the maximum of the DSC curve; the range is given in parentheses. [c] Determined by ^{1}H NMR spectroscopy. [d] After flash chromatography. [e] From two or three parallel DSC measurements. [f] Product **2f** is formed from adduct **1f**. [g] 6-min reaction time.

bond and the transformation of the resulting adduct generally involve simple procedures with variable yields. Thermal transformation is the simplest way to convert adducts into ring-expanded products.[1] Some adducts are unstable and are immediately transformed into ring-expanded products,[2] while others are resistant to thermally induced rearrangement.[1a,3]

Recently we reported on the reaction of 2,5-dihydro-1*H*-phosphole 1-oxides with dichlorocarbene, which gave the primary adducts along with the ring-expanded products dihydrophosphorin and phosphacycloheptatriene.[4] The conversion of stable phosphole–dichlorocarbene adducts into dihydrophosphorins through hydroxy-1,2,3,6-tetrahydrophosphorin 1-oxides has also been described.[5] In this paper we discuss the direct transformation of phosphole–dichlorocarbene adducts into dihydrophosphorins in light of the thermal stability of the adducts.

Results and Discussion

Adducts **1a–e** of 2,5-dihydro-3-methyl-1*H*-phosphole with dichlorocarbene decompose at elevated temperatures, as indicated by their GC behavior and unsuccessful attempts at distillation. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) of **1a–e** revealed an exothermic transformation in the range 100–140 °C. The products obtained by heating **1a–d** proved to be mixtures of the regioisomers of 1,2-dihydrophosphorin 1-oxides **2Aa–d** and **2Ba–d** (Scheme I), resulting from rearrangement and elimination of a molecule of hydrogen chloride.[6] The formation of a less-strained ring system may be the driving force for the loss of hydrogen chloride. In contrast, adducts of dihalocarbene to cyclopentene rearrange on heating without loss of hydrogen halide.[1a,b]

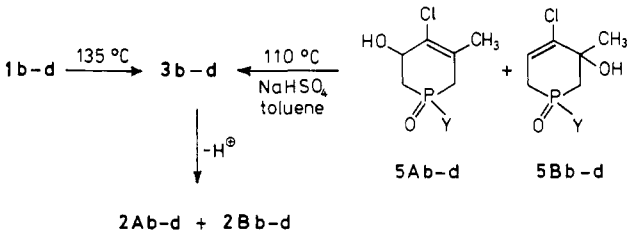
The transformation of methyl ester **1e** on heating gives phosphinic acids **2Af** and **2Bf** (Scheme I) and a polymer[7] instead of the expected esters **2Ae** and **2Be**. Phosphinic acids **2Af** and **2Bf** are obviously produced by reaction of the methyl ester with the chloride ion formed in the cyclopropane ring-opening reaction.[8]

Table II. Ratio of Regioisomers 2 Obtained from 1 and from the Indicated Mixture of 5

	2A/2B obtained from 1	from 5	5A/5B[a]
b	74/26	73/27	86/14
c	71/29	75/25	82/18
d	72/28	74/26	52/48

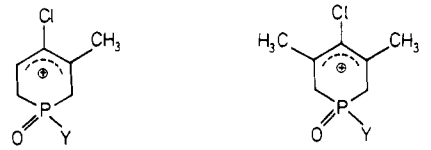
[a] From ref 5.

Scheme II



The optimum conditions for the transformation of **1** into **2** involve heating at 135 °C for 3 min. No transformation of **1** was observed on heating at 80 °C for 6 h, whereas products **2** decomposed rapidly above 140 °C or on longer heating at 135 °C. The decomposition temperatures of **1**, the optimum yields and isomer ratios of **2**, and reaction enthalpies are given in Table I. The dihydrophosphorins **2** are obtained in good yields, with isomer **A** predominating over **B** by ~3:1.[9] Compounds **2Ab–d** and **2Bb–d** have been described previously by us,[5] while **2Aa**, **2Af**, **2Ba**, and **2Bf** are new.

Note that while **1a–e** are transformed only above 100 °C, the corresponding 3,4-dimethyl derivatives decompose to dihydrophosphorins at room temperature.[4] This difference in stability can be explained by the mechanism proposed for the opening of a dihalocyclopropane ring. In either thermally induced or electrophilic-catalyzed ring openings, concerted transformation of a cyclopropyl halide into an allylic cation is involved.[10] Thus intermediate **4** is more stable than **3** because of the additional methyl



group and requires less activation energy to achieve the product-like transition state. Other evidence for the proposed mechanism is provided by **5A** and **5B**, which are

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(6) The evolution of hydrogen chloride was observed in each thermal reaction. In one case the quantity of this byproduct was checked and found to be equivalent with that of the dihydrophosphinine after absorption in water and titration.
(7) In the mass spectrum the fragment from the decomposition to the monomer (*m/e* 178) was observed, while in the IR spectrum broad absorption at 1160 cm^{-1} for P=O stretching was present. TG and DTA measurements showed exothermic decomposition without any loss of weight at 303 °C, presumably due to depolymerization.
(8) The result of the TG analysis of **1e** was in accord with the loss of methyl chloride. The calculated and measured loss of weight was 22 and 23%, respectively.
(9) The ratio of the isomers was determined from the ^{1}H NMR spectra on the basis of the methyl signals and certain olefinic protons.
(10) (a) Sandler, S. R. *J. Org. Chem.* **1967**, *32*, 3876. (b) Baird, M. S.; Lindsay, D. G.; Reese, C. B. *J. Chem. Soc. C* **1969**, 1173. (c) Markgraf, J. H.; Finkelstein, M.; Leonard, K. J.; Lusskin, S. I. *J. Chem. Educ.* **1985**, *62*, 265.

formed by reaction of the dichlorocarbene adducts of 3-methyl-2,5-dihydro-1*H*-phosphole 1-oxide with silver nitrate in water[5] and can be regarded as trapped intermediates. Acid-catalyzed dehydration of mixtures of **5Ab–d** and **5Bb–d** produces the regioisomers of **2** in the same ratios as those obtained from thermal transformation of **1b–d** (Table II). This result suggests that the same intermediate, cation **3**, is involved in both reactions (Scheme II).

Experimental Section

TG and DTA curves were determined with an MOM derivatograph, using 50-mg samples in platinum crucibles in static air at a heating rate of 5 °C min^{-1}. DSC measurements were performed on a 990 Du Pont thermoanalyzer at a heating rate of 5 °C min^{-1} in static air with 2-mg samples in aluminum crucibles.

The ^{31}P and ^{13}C NMR spectra were taken on a JEOL FX 100 spectrometer at 40.26 and 25.0 MHz, respectively. ^1H NMR spectra were recorded on a Perkin-Elmer 60-MHz instrument. Deuteriochloroform was the solvent in each case. Chemical shifts are downfield relative to 85% phosphoric acid and to tetramethylsilane, respectively, and have a positive sign. All coupling constants are given in hertz. Infrared spectra were recorded on a SPECORD 75 instrument. Mass spectra were obtained on a JEOL-01SG-2 spectrometer at 75 eV.

The dichlorocarbene adducts were prepared as described earlier.[4]

6,6-Dichloro-1,3-dimethyl-3-phosphabicyclo[3.1.0]hexane 3-Oxide (1a). Yield 32%; mp 90–92 °C; ^{31}P NMR δ +84.7; ^{13}C NMR δ 15.4 ($^1J_{PC}$ = 61.5, P-CH_3), 21.3 ($^3J_{PC}$ = 6.6, C-CH_3), 30.9 ($^1J_{PC}$ = 66.0, C_4), 37.0 ($^1J_{PC}$ = 66.7, C_2), 36.1 ($^2J_{PC}$ = 7.4, C_1), 36.9 ($^2J_{PC}$ = 5.8, C_5), 71.9 ($^3J_{PC}$ = 8.7, C_6), ^1H NMR δ 1.66 (s, 3 H, C-CH_3), 1.69 (d, 3 H, P-CH_3, $^2J_{PH}$ = 13), 1.90–2.74 (m, 5 H, CH_2, CH); MS *m/e* (relative intensity 212 (M^+, 13), 177 (100), 115 (21); IR (KBr disk) 1405, 1300, 1180, 820 cm^{-1}. Anal. Calcd for $C_7H_{11}Cl_2OP$: C, 39.46; H, 5.21. Found: C, 39.11; H, 51.30.

1,3- and 1,5-Dimethyl-4-chloro-1,2-dihydrophosphorin 1-Oxide (2Aa and 2Ba). **1a** (0.4 g, 1.9 mmol) was heated at 135 °C for 3 min. The crude product was purified by flash chromatography on silica gel using 97:3 chloroform–methanol as eluant to give a mixture (0.33 g, 98%) containing 74% of **2Aa** and 26% of **2Ba**: ^1H NMR δ 1.63 (d, 3 H, P-CH_3, $^2J_{PH}$ = 13), 2.07 (s, 2.22 H, C-CH_3(A)), 2.14 (d, 0.78 H, C-CH_3(B), $^4J_{PH} \sim 2$), 2.32–3.19 (m, 2 H), 6.15 (t, P-CH=(A), $^2J_{PH} = {}^3J_{HH}$ = 12), overlapping the signals of the olefinic protons in B, total intensity 1.26 H, 6.70 (dd, 0.74 H, P-CH=C*H*, $^3J_{PH}$ = 34, $^3J_{HH}$ = 13); MS *m/e* (relative intensity) 176 (M^+, 86), 161 (15), 141 (11), 79 (100); IR (neat) 2880, 1600, 1545, 1410, 1360, 1140, 740 cm^{-1}. Anal. Calcd for $C_7H_{10}ClOP$: C, 47.60; H, 5.72. Found: C, 47.36; H, 5.51.

2Aa: ^{31}P NMR δ +20.7; ^{13}C NMR δ 15.4 ($^1J_{PC}$ = 75.5, P-CH_3), 22.2 ($^3J_{PC}$ = 8.8, C-CH_3), 34.4 ($^1J_{PC}$ = 70.4, C_2), 119.8 ($^1J_{PC}$ = 90.8, C_6), 122.7 ($^2J_{PC}$ = 16.1, C_3), 130.1 ($^3J_{PC}$ = 9.5, C_4), 141.2 (C_5).

2Ab: ^{31}P NMR δ +20.0; ^{13}C NMR δ 15.0 ($^1J_{PC}$ = 75.5, P-CH_3), 23.2 ($^3J_{PC}$ = 12.5, C-CH_3), 28.5 ($^1J_{PC}$ = 69.6, C_2), 119.3 ($^1J_{PC}$ = 95.3, C_6), 122.1 ($^2J_{PC}$ = 7.3, C_3), 130.6 ($^3J_{PC}$ = 20.6, C_4), 146.7 (C_5).

3- and 5-Methyl-4-chloro-1-hydroxy-1,2-dihydrophosphorin 1-Oxide (2Af and 2Bf). **1e** (0.46 g, 2.04 mmol) was heated at 135 °C for 6 min. The chloroform extract of the mixture was purified by column chromatography as described above to give a mixture (0.16 g, 44%) consisting of 72% of **2Af** and 28% of **2Bf**: ^1H NMR δ 2.02 (s, 2.16 H, C-CH_3(A)), 2.12 (s, 0.84 H, C-CH_3(B)), 2.79 (d, CH_2(A), $^2J_{PH}$ = 20), overlapping the signal of CH_2(B), total intensity 2 H, 6.11 (t, P-CH=(A), $^2J_{PH} = {}^3J_{HH}$ = 11), overlapping the signal of the olefinic protons in B, total intensity 1.28 H, 6.71 (dd, 0.72 H, P-CH=C*H*, $^3J_{PH}$ = 40, $^3J_{HH}$ = 12), 12.3 (s, 1 H, OH); MS *m/e* (relative intensity) 178 (M^+, 91), 143 (9), 79 (100); M^+_{found} = 177.9975, $C_6H_8ClO_2P$ requires 177.9950.

2Af: ^{31}P NMR δ +32.7; ^{13}C NMR δ 23.3 ($^3J_{PC}$ = 10.2, C-CH_3), 34.2 ($^1J_{PC}$ = 100.4, C_2), 119.9 ($^1J_{PC}$ = 124.6, C_6), 123.4 ($^2J_{PC}$ = 22.7, C_3), 131.9 ($^3J_{PC}$ = 8.0, C_4), 144.1 (C_5).

2Bf: ^{31}P NMR δ + 32.0; ^{13}C NMR δ 24.6 ($^3J_{PC}$ = 15.4, C-CH_3), 28.6 ($^1J_{PC}$ = 99.7, C_2), 119.1 ($^1J_{PC}$ = 129.6, C_6), 123.3 ($^2J_{PC}$ = 8.8, C_3), 131.4 ($^3J_{PC}$ = 17.6, C_4), 150.0 (C_5). The part of the mixture that was insoluble in chloroform was washed with ethyl acetate to give the polymer of **2f** (0.07 g, 19%): MS *m/e* 178; IR (KBr disk) 1160 cm^{-1}. Anal. Calcd for $(C_6H_8ClO_2P)_n$: C, 40.34; H, 4.48. Found: C, 39.94; H, 4.41.

Acknowledgment. We thank Dr. Ilona Konkoly-Tege for DSC measurements. The advice of Prof. Louis D. Quin, University of Massachusetts, is appreciated.

Registry No. **1a**, 115141-72-5; **1b**, 109011-52-1; **1c**, 109011-53-2; **1d**, 109011-51-0; **1e**, 109011-54-3; **2Aa**, 115141-73-6; **2Ab**, 109891-13-6; **2Ac**, 109891-14-7; **2Ad**, 109891-12-5; **2Af**, 115141-74-7; **2Ba**, 115141-75-8; **2Bb**, 109891-16-9; **2Bc**, 109891-17-0; **2Bd**, 109891-15-8; **2Bf**, 115141-76-9; **5Ab**, 115141-77-0; **5Ac**, 115141-78-1; **5Ad**, 115141-79-2; **5Bb**, 115141-80-5; **5Bc**, 115141-81-6; **5Bd**, 115141-82-7.

[2,3] Wittig Ring Contraction: Synthesis of *p*-Menthane Derivatives

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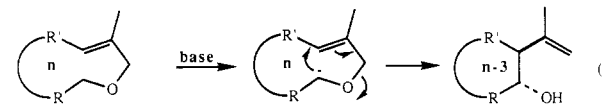
The base-induced [2,3] sigmatropic rearrangement of cyclic diallylic and allylic propargylic ethers ([2,3] Wittig ring contraction) has been shown to constitute a viable strategy for the construction of 10- and 14-membered isoprenoid systems (eq 1).[1-3] In the propargylic cases, the



R = C=C or C≡C
n = 13 or 17

(1)

use of an optically active alkylamide base led to optically active rearranged alcohols of 30–80% ee.[3] The present study was undertaken to determine the applicability of the [2,3] Wittig ring contraction to the synthesis of cyclohexenols.

A suitable substrate for these studies, the nine-membered diallylic ether **5**, was readily prepared from neryl acetate (**1**) by selective allylic oxidation, along the lines reported for geranyl acetate,[4] followed by Collington–Meyers chloride formation,[5] acetate cleavage, and cyclization of the resultant chloro alcohol **4** by treatment with EtMgBr in THF–HMPA[2] (Scheme I). The cyclization proceeded in 65% yield and gave, as a nonvolatile byproduct, the crystalline dimer **11** in 3% yield. Ether **5** underwent facile Cope rearrangement to the tetrahydrofuran **10** upon heating, so solvent removal was best carried out near room temperature. This interesting 3,4-substituted furan is assumed to possess the cis stereochemistry from transition-state considerations.[6]

Ether **5**, upon treatment with lithio-2,2,6,6-tetramethylpiperidide (LTMP), afforded the rearranged alcohol

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