

tion on the starting material, dihydrooxazine **1d** has been reported to be converted to pyrrole **2d** in 93% yield under the same reaction condition.⁸ It is quite understandable that dihydrooxazine **1c** does not afford the desired pyrrole. Unlike **1d**, the proton at the 6-position (H_a in Scheme 3) of dihydrooxazine **1c** is much more weakly acidic than that of **1d** thus would prevent the formation of carbonyl group to be attacked by the N-phenylamino group in the intermediate for cyclization (Scheme 3).⁹

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- Synthetic and structure determination methods will be described in full paper. The NMR (¹³C and ¹H), IR, and mass spectra of the compounds reported here were all consistent with the assigned structures. All products were recrystallized and reported yields are purified yields.
- Irradiations were carried out in the Rayonet Photochemical Reactor. Standard photochemical experimental procedures were employed for this study.
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An Efficient Electrophile-Assisted Homoconjugate Addition of Triphenylphosphine to Cyclopropyl Ketone

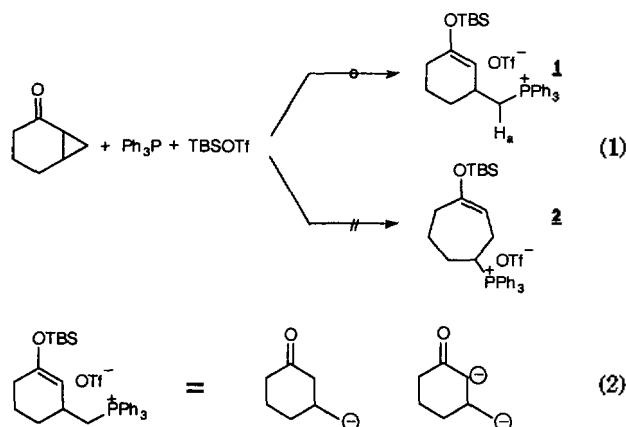
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Recent advances in the formation of three-membered rings have led to the steadily increasing usage of cyclopropyl derivatives as reagents for organic synthesis.¹ In this respect, cyclopropyl ring opening reactions by nucleophiles or electrophiles have received considerable attention over the past

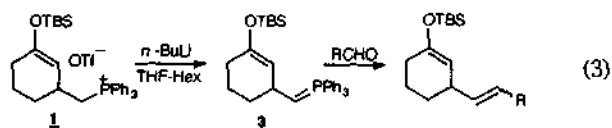
years.² In contrast to double bonds, which are susceptible to the Michael reaction in the presence of one activating group, comparable homoconjugate additions to monoactivated cyclopropane derivatives are few and normally restricted to highly strained systems, powerful nucleophiles or electrophile-assisted nucleophilic reactions. In connection with our recent of research for the functionalization of α,β -unsaturated carbonyl compounds *via* phosphoniosilylation,³ we have had an occasion to study ring opening reaction of cyclopropyl ketone and it has been found that TBSOTf assisted homoconjugate addition of triphenylphosphine to the fused bicyclic cyclopropyl ketone occurred cleanly to provide 1,5-addition product **1** in which ketone group is protected as silyl enol ether (Eq. 1). Moreover, the silyl enol ether phosphonium salt **1** has a wide potential since further functionalization can be possible at α or γ -position (Eq. 2). As far as we are aware, this is the first example in which trivalent phosphorus compound opened monoactivated cyclopropane.



Among the solvent tested in this study, dichloromethane gave the best result, although tetrahydrofuran, diethyl ether and toluene were effective to some extent. Notably, triphenylphosphine by virtue of TBSOTf unlike TMSOTf and $BF_3 \cdot OEt_2$ opened regioselectively the cyclopropane ring to give **1**. This result suggested that geometry-dependant orbital interaction (stereoelectronic effect) appears to control the direction of the cyclopropane ring opening and the bond that cleaves is the one which has the greater overlap with the carbonyl π -system. The structure of **1** was determined by coupling constant for H_a (δ 5.40(ddd, $J=18.52, 12.92, 5.60$ Hz, 1 Ha)). In case of cyclopropyl phenyl ketone, ring opening reaction was not effective under the present condition.

As shown in Eq. (3), silyl enol ether of ketone containing alkenyl group at β -position was prepared in one pot procedure from cyclopropyl ketone without any isolation of the intermediate. While such β -alkenyl ketones are generally derivable from the parent enones by copper conjugate addition procedures followed by enolate trapping, the yields which attend such process in case of containing electrophile in transfer ligand are some times low and the requisite organocuprates are difficult to procure.⁴ Also, *n*-BuLi in hexane does effect deprotonation of enol phosphonium salt without competing desilylation.

The experimental procedure for the synthesis of 3-[(*Z*)-2'-phenylethenyl]-1-cyclohexenyl *tert*-butyldimethyl silyl ether is as follows. To a solution of triphenylphosphine (203.2 mg,



0.77 mmol) in dichloromethane (3 ml) were added bicyclo[4.1.0]-2-heptanone⁵ (80.3 mg, 0.73 mmol) and TBSOTf (192.9 mg, 0.73 mmol) under nitrogen. After being stirred at room temperature for 4 h, dichloromethane was removed under a reduced pressure and tetrahydrofuran (3 ml) was added. The reaction mixture was cooled to -78°C and *n*-butyllithium (0.62 ml, 0.77 mmol) was added dropwise to give a black-colored solution. The reaction mixture was stirred for 1 h at -78°C and benzaldehyde (93.4 mg, 0.88 mmol) was added to the ylide solution. After being stirred at -78°C for 1 h and warmed to room temperature over 30 min, saturated NaHCO_3 solution was added. The extractive work-up and chromatographic separation gave silyl enol ether⁶ (130.4 mg, 57%). Aliphatic (1° and 2°) as well as aromatic aldehydes can be used successfully in the Wittig condensation step. The reaction of ylide 3 with 6-bromohexanal⁷ and cyclohexanecarboxaldehyde gave the corresponding compounds in 54% and 51% yield, respectively. In case of bicyclo[3.1.0]-2-hexanone,⁸ 3-(2'-phenylethenyl)-1-cyclopentanone was produced in 23% yield after treatment of hydrogen fluoride.

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- R_f 0.70 (EtOAc/Hexane=1/20). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.35-7.19 (m, 5H), 6.39 (d, $J=11.48$ Hz, 0.37H), 6.36 (d, $J=11.50$ Hz, 0.63H), 5.56 (dd, $J=11.55, 10.23$ Hz, 0.37H), 5.49 (dd, $J=11.32, 10.48$ Hz, 0.63H), 4.88 (br s, 0.37H), 4.77 (br s, 0.63H), 3.41-3.39 (m, 0.63H), 2.88-2.98 (m, 0.37H), 2.09-1.24 (m, 6H), 0.91 (s, 9H), 0.13 (s, 3.8H), 0.12 (s, 2.2H).
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Solvent Effect on the α -Effect in Nucleophilic Substitution Reaction of 4-Nitrophenyl Acetate in MeCN- H_2O Mixtures

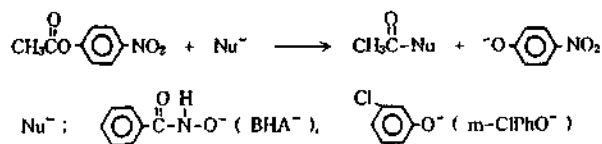
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Abnormally enhanced nucleophilicity has often been observed in reactions of nucleophiles containing an atom with one or more nonbonding electron pairs adjacent to the reaction center (the α -position). Thus, the term α -effect was given to the enhanced nucleophilicity shown by this type of nucleophiles.¹ Since then, numerous studies have been performed to investigate the cause of the α -effect.²⁻⁵ However, the origin of the α -effect has not been clearly understood. Particularly, the theory concerning solvent effect has been the subject controversy.⁶⁻⁸

In a recent study, we have demonstrated that the solvent effect on the α -effect is important for the nucleophilic substitution reaction of *p*-nitrophenyl acetate (PNPA) with butane-2,3-dione monoximate (Ox^-) and *p*-chlorophenoxide (*p*-Cl- PhO^-) in MeCN- H_2O mixtures of varying compositions.⁹ We have now chosen a different set of nucleophiles: benzohydroxamate (BHA^- , $pK_a=8.88$) and *m*-chlorophenoxide (*m*-Cl- PhO^- , $pK_a=9.02$) as an α -nucleophile and the corresponding normal one, respectively. Such a change in the nucleophile would allow us to examine whether the previous result was only a limited phenomenon in the Ox^- system.



The rate constants were measured spectrophotometrically by monitoring the appearance of *p*-nitrophenoxide ion at 400 nm. All the reactions obeyed pseudo-first-order kinetics up to over 90% of the total reaction. In Figure 1 are plotted the kinetic results, in which the logarithmic second-order rate constant for the *m*-Cl PhO^- system decreases upon the initial addition of the MeCN into H_2O and is followed by a gradual increase of the rate constant upon further addition of MeCN, resulting in a rate minimum near 40 mole% MeCN. Such a rate minimum was also observed previously in the reac-