EFFICIENT OLEFINATON WITH α-ALKYL CYCLIC PHOSPHONAMIDES *

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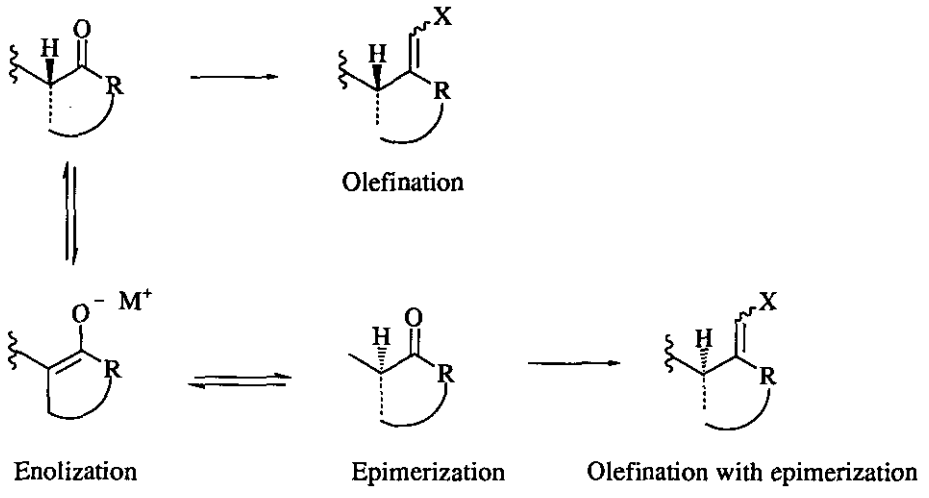
Abstract - A variety of acyclic and cyclic aldehydes and ketones can be converted into the corresponding alkylidene, benzylidene and methoxycarbonyl alkylidene derivatives by treatment with 1,3,2-diazaphospholidine-2-alkyl-1,3-dimethyl 2-oxides (α-alkyl cyclic phosphonamides) under mild conditions. This olefination method is particularly useful in the case of enolizable carbonyl compounds.

The formation of an olefinic linkage from a carbonyl compound *via* the Wittig reaction, the Horner-Wadsworth-Emmons reaction, and their various modifications, constitutes one of the pivotal synthetic methods in organic chemistry.[1] Indeed, with the commercial availability of a large number of phosphorus-based reagents, such reactions have become somewhat of a routine operation in everyday laboratory practice. However, in spite of much extensive use and many improvements, a number of persistent problems continue to plague even the expert user of these reactions. Thus, enolization of, rather than addition to the carbonyl compound, particularly with cycloalkanones, is the major cause of inefficient olefinations. In some cases this may result in epimerization α- to the carbonyl function, which may be followed by olefin formation, thus giving an isomeric product or a mixture of products (Figure 1).

Although the above mentioned problems are the exceptions rather than the norm in Wittig-type olefinations, they occur sufficiently frequently, and at most inopportune stages of critical synthesis sequences so as to warrant attention. As previously pointed out quite succinctly,[2] the problem stems

* Dedicated to Professor E.C. Taylor on the occasion of his 70th birthday, wishing him the best in life and in chemistry.

Figure 1



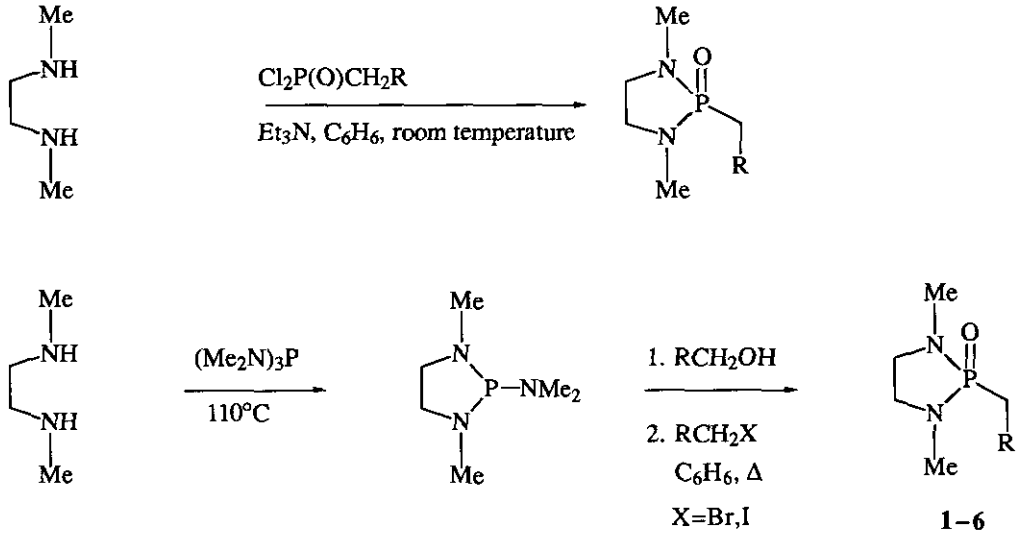
from the classical basicity versus nucleophilicity syndrome in the organophosphorus reagent which is only heightened by the kinetic carbon acidity of the carbonyl compound. Ideally then, a highly nucleophilic phosphorus-based reagent with diminished basicity should alleviate the operational problems encountered in difficult olefinations. An added advantage could come from the design of a reagent which, once bonded to the carbonyl carbon atom, will easily eliminate oxygen and the phosphorus component to yield the desired olefin. In spite of many elegant variations of the original ylid and phosphonate anion based reagents,[1] as well as authoritative mechanistic studies,[3] achieving efficient olefination from carbonyl compounds remains a worthwhile methodological objective and a challenge as well.

Stabilized Wittig-type reagents and their phosphonate anion functional counterparts (ex. $Ph_3P{=}CHCO_2R$ and $(EtO)_2P(O)CH_2CO_2R$) are normally not known for adverse reactions due to their basicity. In general, anions derived from alkylphosphonic acid derivatives, (ex. $(RO)_2P(O)CH_2Li$) where a stabilizing electron withdrawing group is not present in the alkyl portion are not used for olefination. In 1969, Corey and Kwiatkowsky[4] demonstrated that anions of α-alkylphosphonic acid diamides and the corresponding phosphinothioates add to aldehydes and ketones to give diastereomeric β-hydroxyphosphonamides, which could be separated and individually transformed into *cis* and *trans* olefins by refluxing in toluene in the presence of silica. In the case of the sulfur-based reagents, elimination was triggered by alkylation and the fragmentation of the resulting sulfonium salts. Reactions occurred smoothly with a number of aldehydes and ketones, although some unreacted starting ketone was recovered in the case of acetophenone, possibly due to enolization. In subsequent work Corey and Cane[5] extended the utility of the olefination reaction to

the synthesis of dienes by using α-allyl cyclic phosphonamides such as 1,3,2-diazaphospholidine-2-allyl-1,3-dimethyl 2-oxide. In an interesting variation of the Corey reagents, [4,5] ohnson and Elliot[6] have shown the utility of α-lithioalkyl-α-phosphinothioic amides *in alkylidenations* of aldehydes and ketones by an addition-fragmentation protocol. Patois and Savignac[7] have recently reported a synthesis of α,β-unsaturated esters from monocyclic phosphonamides. Olefin synthesis with phophonamides has also been studied with aromatic aldehydes.[8]

As an introductory study to our work on asymmetric olefinations of cyclohexanone derivatives with topologically unique bicyclic phosphonamides derived from (*R,R*)- and (*S,S*)-1,2-*N, N'*-dimethylamino-cyclohexanes,[9] we investigated the reactivity of monocyclic analogues in the olefination of aldehydes and ketones.[10,11] We had chosen 1,3,2-diazaphospholidine-2-alkyl-1,3-dimethyl 2-oxides as cyclic versions of Corey's acyclic alkylphosphonic acid bis(dimethylamides),[4] primarily to promote a more facile decomposition of the corresponding β-hydroxyphosphonamide product. A variety of cyclic phosphonamides were easily prepared from the reaction of *N, N'*-dimethyl-1,2-ethylenediamine and the

Scheme 1



1–6

1, R= H; **2**, R= Me; **3**, R= $CH_2CH{=}CH_2$; **4**, R= $CH_2CH{=}CHMe$; **5**, R= Ph; **6**, R= CO_2Me

appropriate alkylphosphonyl dichlorides[12] as shown in Scheme 1. An alternative method consists of the treatment of *N,N'*-dimethyl-(2-dimethylamino)-1,3,2-diazaphospholidine with an alcohol followed by the alkyl halide in an Arbuzov-type reaction[13] to give the same cyclic phosphonamide.

Treatment of the phosphonamides with 1.1 equivalents of n-butylithium at –78 °C, followed by addition of an aldehyde or a ketone at the same temperature, and quenching with glacial acetic acid at –78 °C, led to the formation of the corresponding olefin directly and in high yield, without the necessity to isolate the intermediate β-hydroxyphosphonamide adducts (Scheme 2).

Scheme 2

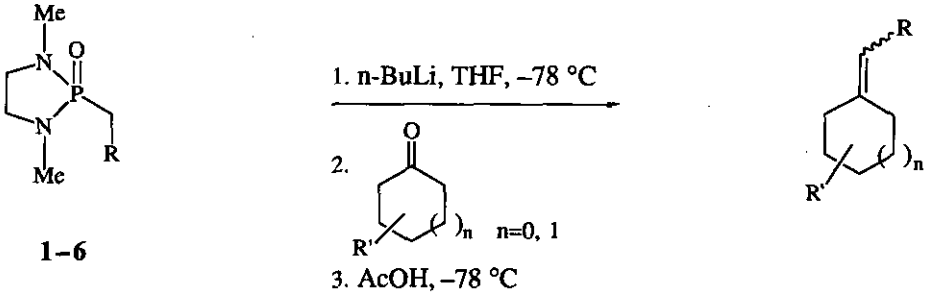
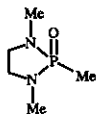
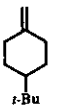
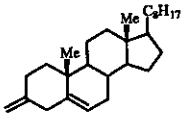
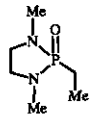
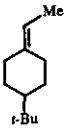
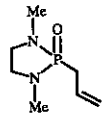
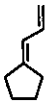
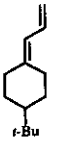
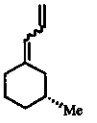
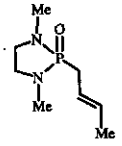
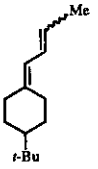
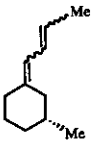
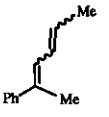
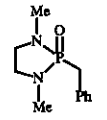
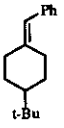
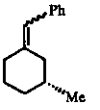
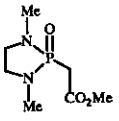
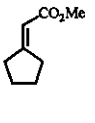
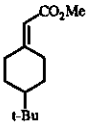
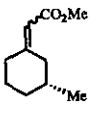
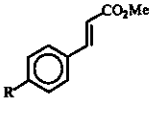
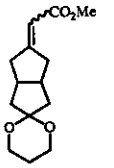


Table 1 lists the products obtained from such a procedure which include acyclic and cyclic ketones as well as some aldehydes. With the exception of Δ-5-cholestenone, all other olefinations proceeded in yields exceeding 70%. The direct olefination of Δ-5-cholestenone to the corresponding unconjugated diene has been problematic, as shown in a careful study by McMurry and von Beroldingen.[2] For example, treatment with methylenetriphenylphosphorane in DMSO gave a 61% yield of the *conjugated* diene as a result of a fast enolization, proton exchange, double bond isomerization, followed by olefination of the resulting conjugated ketone. It was found however, that with Corey's reagent,[4] α-lithio-methylphophonic acid bis-(dimethylamide), the desired unconjugated diene could be obtained in 20% yield after isolating the initially formed β-hydroxyphosphonamide, then refluxing in a suspension of benzene containing silica gel.[2] In the present study, the anion from the monocyclic phosphonamide (**1**; R=H), gave a 31% yield of the expected unconjugated diene (Table 1). Interestingly, the bulk of the recovered ketone was the starting Δ-5-cholestenone and not the conjugated isomer. Partial enolization of ketones under the conditions of olefination with the Corey reagent was remarked in the case of acetophenone[4] as well as with Δ-5-cholestenone[2] along with the formation of the expected β-hydroxyphosphonamide. The tendency of cycloalkanones and bicycloalkanones to enolization under the conditions of the Wittig reaction is well

Table 1

Reagents	Olefination Products [a]			
	 75% [c]	 74%	 31% [b]	 85%
	 75% [c]	 75%	 88%	 80% (3:2 Trans / Cis)
	 95% [c]	 76%	 74% (2:1 Trans:Cis)	 77% (6:1 Trans:Cis)
	 76% (4:1 Trans:Cis)	 76% (4:1 Trans:Cis)	 78% (5:1 Trans:Cis)	
	 73%	 80%	 78% (2:1 Trans:Cis)	
	 77%	 82%	 83% (2:1 Trans:Cis)	 R=H, 93% R=OMe, 85% R=Cl, 88%, (96:4 Trans:Cis)	 88% [d]

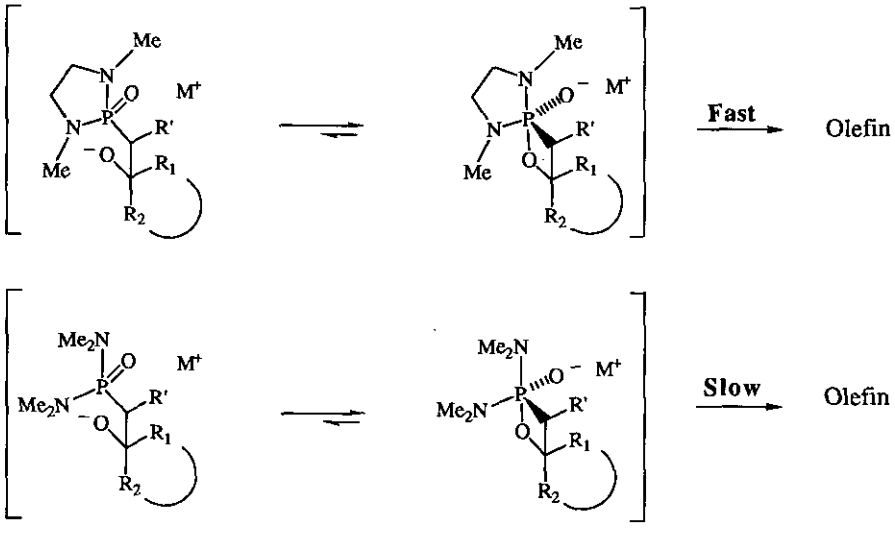
a. Isolated yields, the ratios were determined by ^{1}H nmr. b. Starting Δ^5-cholestenone recovered in 61% c. Gc yields, the isolated yields in these series were low due to volatility of the olefins. d. Yield of isolated olefin after 5 h at 0 °C; see also, H. Rehwinkel, J. Skupsch, and H. Vorbrüggen, *Tetrahedron Lett.*, 1988, **29**, 1775. We thank Dr. Vorbrüggen for a sample of the ketone.

documented, and constitutes a source of inefficient olefination.[2] For example, alkylidenation cyclopentanone and cyclohexanone derivatives takes place in moderate yields under standard

conditions.[1b, 14] Alternative methods such as the use of the Tebbe reagent,[14] sulfur ylids,[16] organozinc reagents,[17] as well as the use of organosilicon-based reagents[18] for methylenation and alkylidenation of aldehydes and ketones have proved to be very useful. In some instances alkylidenation of aldehydes has been inefficient except when the resulting olefin is conjugated.

Using the monocyclic phosphonamide anions shown in Scheme 2, efficient olefinations took place with a variety of acyclic and cyclic aldehydes and ketones. Dienes were also easily accessible to give predominantly *trans* isomers. In the case of the α-crotylphosphonamide reagent, the olefins obtained showed some isomerization, even though the reagent was a highly enriched *trans* isomer. Nevertheless, it appears that the utilization of these cyclic variants of the original Corey reagent,[5] has definite advantages in facile and efficient olefin synthesis, particularly since *the intermediate β-hydroxyphosphonamides undergo cleavage under extremely mild conditions*. In the case of the α-methoxycarbonylmethylphosphonamides, reactivity was very pronounced as exemplified by the high yield obtained with cyclopentanone (77% compared to 43% using the triphenylphosphorane analogue).[14b]

Figure 2



The higher reactivity of the β-hydroxyphosphonamides derived from the monocyclic reagents in the elimination step was anticipated in considering such a variant of the original acyclic reagents.[4] (Figure 2). Thus, release of ring strain in an intermediate bicyclic or tricyclic oxaphosphetane was expected to be a strong driving force compared to the acyclic reagent. Elegant studies by Westheimer and co-workers[19]

have demonstrated the enhanced rates of hydrolysis of cyclic phosphates compared to acyclic counterparts. Several theoretical and experimental studies have corroborated these observations in olefination reactions.[20,21] Factors concerned with the attainment of a favored orientation of apicophilic groups around the phosphorus atom (pseudorotation),[1a,22] and the equilibrium between the β-hydroxyphosphonamide and the oxaphosphetane intermediates are also important in such cycloeliminations.[21]

With regard to the nucleophilicity of the *N, N'*-dimethylphosphonamides, it can be argued that as in the case of phosphonate carbanions, reactivity is enhanced by virtue of a diminished net positive charge on phosphorus, as a result of back donation from the nitrogen atoms.[23,24] It is noteworthy however, that unlike anions derived from alkylphosphonates which are generally unreactive unless an electron withdrawing group is present in order to stabilize the carbanion (eg. CO_2Me, etc...)[25] the alkyl mono-[10,11] and bicyclic phosphonamides anions[9] are quite reactive in the absence of such activation leading to preparatively useful yields of olefin (Table 1).

EXPERIMENTAL SECTION

GENERAL. ^1H Nmr spectra were recorded on a Varian 60 MHz, Bruker 90 MHz or Bruker WH-400 MHz instruments using deuteriochloroform as solvent ($CHCl_3$ standard d = 7.265); s, singlet; d, doublet; t, triplet; q, quartet; q5 , quintet; m, multiplet, br, broad). Infrared spectra were recorded with a Perkin-Elmer 781 infrared spectrophotometer. Melting points are not corrected. *N, N'*-Dimethyl 1,2-ethylenediamine, tris-(dimethylamino)phosphine (HMPT) and n-BuLi were purchased from Aldrich Inc. The alkylphosphonic dichlorides were prepared according to reported methods (26). GC was performed on a Varian-3700 coupled to a Varian CDS-111 integrator using chromosob W-HP 80/100 mesh, containing 3% OV-17.

1,3,2-Diazaphospholidine 1,3-dimethyl-2-dimethylamine: In a dry 25 ml flask, equipped with a condenser, were placed 2.00 g (22.7 mmol) of *N, N'* -dimethyl-1,2-ethylenediamine and 2.68 g (23.1 mmol) of tris(dimethylamino)phosphine (HMPT). The mixture was heated at 100 °C under a flow of argon until the evolution of dimethylamine (litmus paper) (14 h) ceased. The mixture was cooled and distilled, 65 °C at 15 mmHg, to give 2.90 g (80% yield) of the desired product; ir (film) 2900 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 2.60 (d, 2 x CH_3, J=8 Hz, 6 H), 2.62 (d, 2 x CH_3, J_{P-H}=12 Hz, 6 H), 2.85-3.45 (m, -CH_2CH_2-, 4H); ms for $C_6H_{16}N_3P$ (161.1681) m/z:162, 87.

General procedure for the synthesis of cyclic phosphonamides by condensation of *N, N'*-1,2-dimethylethylenediamine with alkylphosphonic dichlorides - Method A.

1,3,2-Diazaphospholidine 2-ethyl-1,3-dimethyl 2-oxide: A solution of *N, N'*–dimethyl–1,2-ethylenediamine, 2.0 g (22.7 mmol), 6.55 ml (47 mmol) of Et_3N in 100 ml of dry benzene, was slowly added with a solution of ethyl phosphonic dichloride, 3.05 g (23 mmol) in 20 ml of dry benzene under argon. The mixture was stirred at room temperature for 90 min and filtered on a celite pad. Evaporation of the solvent and bulb to bulb distillation, (91 °C at 0.8 mm Hg) gave 2.74 g of the desired compound, (75% yield). The material solidified upon storage at -5 °C; mp 39-40 °C; ir (melt) 2950, 1280 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 1.00 (dt, CH_3-CH_2-P, J=14 Hz, 3H), 1.95 (dm, CH_3-CH_2-P, J=14 Hz, 2H), 2.70 (d, 2 N-CH_3, J=7 Hz, 6H), 2.85-3.35 (m, -CH_2CH_2-, 4H); ms m/z: 163, 133; HRms calculated for $C_6H_{15}N_2OP$ calcd: 162.09221, found: 162.0939.

General procedure for the synthesis of cyclic phosphonamides through the Arbusoz reaction. - Method B.

1,3,2-Diazaphospholidine-2-methyl-1,3-dimethyl 2-oxide: In a 50 ml flask were placed, 1,3,2-diazaphospholidine-1,3-dimethyl-2-dimethylamine (5.0 g, 31 mmol), 1.37 ml (33 mmol) of dry MeOH, 20 ml of anh. benzene and the mixture was refluxed for 12 h. The solution was then cooled, methyl iodide (1.93 ml, 31 mmol) was added, and the mixture was refluxed for 4 h. Evaporation of the solvent and distillation of the residue (109 °C at 1.5 mmHg) gave 3.20 g of the title phosphonamide (70% yield), (66% yield by method A). The material solidified upon storage at -5 °C; mp 40 °C; bp 109 °C at 1.5 mmHg; ir (melt) 2950, 1280 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 1.45 (d, CH_3-P, J=16 Hz, 3H), 2.66 (d, 2 N-CH_3, J=7 Hz, 6H), 2.85-3.35 (m, -CH_2CH_2-, 4H); ms m/z: 149, 133; HRms for $C_5H_{13}N_2OP$ calcd: 148.0765, found: 148.0762.

1,3,2-Diazaphospholidine-2-allyl-1,3-dimethyl 2-oxide (5): mp 40 °C; bp 150 °C at 11 mmHg (5); ir (melt) 2950, 1630, 1280 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 2.75 (d, 2 x N–CH_3, J=10 Hz, 6H), 2.90-3.50 (m,-CH_2CH_2-, 4H), 3.35 (d, P-CH_2, J=9 Hz, 2H), 5.00-6.00 (m, vinylic H, 3H); ms m/z: 175, 133; HRms for $C_7H_{15}N_2OP$ calcd: 174.0921, found: 174.0882.

1,3,2-Diazaphospholidine-2-crotyl-1,3-dimethyl 2-oxide: mp 40 °C; bp 160 °C at 10 mmHg ; ir (melt) 2950, 1595, 1285 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 1.68 (m, 3H, CH_3), 2.70 (d, 6H, J=9.0 Hz), 2.65-2.90 (m, 4H, ring), 3.20 (m, 2H, CH_2, J=9.8 Hz), 5.35 and 5.44 (mm, 2H CH_2-CH=CH-CH_3); HRms for $C_7H_{17}N_2OP$ calcd: 188.1077, found: 188.1068.

1,3,2-Diazaphospholidine-2-benzyl-1,3-dimethyl 2-oxide: mp 35-36 °C; bp 150 °C at 0.1 mmHg ; ir (melt) 2870, 1600, 1490, 1280 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 2.75 (d, 2 N-CH_3, J=8 Hz, 6H), 2.30-3.30 (m, -CH_2CH_2-, 4H), 3.50 (d, –CH_2Ph, *J=9 Hz, 2H*), 7.3 (m, ArH, *5H*); *ms for* $C_{11}H_{17}N_2OP$ (224.1078); m/z: 225, 133, 91.

1,3,2-Diazaphospholidine-2-methylacetate-1,3-dimethyl 2-oxide: mp 33 °C; bp 240 °C at 0.2 mmHg ; ir (melt) 2950, 1740, 1285 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 2.75 (d, 2 N-CH_3, J=10 Hz, 6H), 2.70-3.50 (m, -CH_2CH_2-, 4H), 3.00 (d, CH_2-P, J= 20 Hz, 2H), 3.80 (s, OCH_3, 3H); HRms for $C_7H_{15}N_2O_4P$ calcd: 206.0820, found: 206.0818; m/z: 207, 133, 90.

General procedure for the olefination using the alkyl monocyclic phosphonamides.

4-*t*-Butylcyclohexane 1-*methylene* (14c): A solution of 106 mg (0.70 mmol) of 1,3,2-diazaphospholidine-2-methyl-1,3-dimethyl 2-oxide was dissolved in 5.0 ml of anhydrous THF and cooled at –78 °C, then slowly treated with 0.75 mmol of a 1.6 M n–BuLi in hexanes solution. After stirring at -78 °C for 45 min, 100 mg (0.65 mmol) of *t*–butylcyclohexanone in 3.0 ml of dry THF was added, and the solution was stirred for an additional 60 min. The mixture was then quenched at -78 °C using 0.5 ml of glacial AcOH and allowed to warm to room temperature. Ether (30 ml) was added, and the organic layer was washed with 2 x 5 ml of $NaHCO_3$ solution, water and dried ($MgSO_4$). Evaporation of the solvent gave a residue which was chromatographed on silica gel using pentane as eluant. Bulb to bulb distillation gave 72 mg (74% yield) of the desired olefin; bp 110 °C at 65 mmHg; ir 2950, 1630, 1490 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 0.95 (s, 9H, $C(CH_3)_3$), 1.15-2.10 (m, ring), 4.62 (s, 2H, $C=CH_2$); ms ($C_{11}H_2O$; 152.1561) m/z: 153, 95.

General procedure for the olefination using phosphonamide 6.

Cyclopentanemethylene methyl ester:[14b] A solution of 267 mg (1.30 mmol) of 1,3,2-diazaphospholidine-2-methyl acetate 1,3-dimethyl 2-oxide in 3.0 ml of anhydrous THF was cooled at 0 °C and added to a suspension of NaH (1.35 mmol) in 2.0 ml of THF under argon atmosphere. After stirring for 30 min at 0 °C, 100 mg of cyclopentanone dissolved in 2 ml of THF and added to the mixture. Stirring was continued for 60 min at 0 °C. The reaction was then quenched using 0.5 ml of a satd. NH_4Cl solution and warmed to room temperature. Ether (45 ml) was added, and the organic layer washed with 3 x 5 ml of a satd. $NaHCO_3$ solution, dried ($MgSO_4$) and evaporated. Silica gel flash chromatography of the residue (hexanes: EtOAc, 9 : 1), gave 77% of the desired olefin; ir 2950, 1745, 1650, 1490 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 0.70-2.90 (*m, 4H, ring*), 3.70 (*s, 3H, OCH_3*), 5.80 (m, 1H, $C=CHCO_2CH_3$); ^{13}C NMR ($CDCl_3$)

22.59, 26.47, 32.60, 36.00 (4C, ring), 50.7 (OCH_3), 111.3 ($C=CHCO_2CH_3$), 167.2 ($C=CHCO_2CH_3$), 169.3 (C=O); ms ($C_8H_{12}O_2$; 140.0837) m/z 109 (M- OCH_3), 81.

Cyclopentane methylene (27): Yield 22% (76% GC), bp 76 °C; ir 2900, 1620, 1490 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 0.67-3.00 (m, 8H, ring), 4.80 (s, 2H, $C=CH_2$).

1,1-Diphenylethylidene (28): Yield 88%; ir 3100, 2850, 1620, 1590, 1500, 1450, 1030, 900, 780, 700 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 5.45 (s, 2H, $C=CH_2$), 7.20 (s, 10 H, ArH).

1-Methylene Δ–5-cholestene (2, 29): Yield 31%; mp 107 °C; ir 3100-2850, 1670, 1470 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 0.69 (s, 3H, CH_3), 0.90 (d, 6H, $CH(CH_3)_2$, J= 6.1 Hz) 0.92 (d, 3H, CH_3-CH-C, J= 10.5 Hz), 1.15 (s, 3H, C-CH_3), 1.25-2.65 (m, -CH_2-, aliph.), 4.57 (s, 2H, $C=CH_2$), 5.28 (s, 1H, C-CH); ms ($C_{28}H_{44}$; 380.344) m/z: 383 (10%), 381 (M+1), 367, 95.

Cyclopentane ethylidene: Yield 22% (76% GC); bp 79 °C; ir 2900, 1630, 1485 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 0.85-2.90 (m, 8H, ring), 1.60 (d, 3H, J=9 Hz), 5.20 (s, 2H, $C=CH_2$).

4-*t*-Butylcyclohexane 1-ethylidene: Yield 75%, bp 105 °C at 30 mmHg; ir 2900, 1635, 1490 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 0.80 (s, 9H, $C(CH_3)_3$), 0.90-2.80 (m, 9H, ring), 1.70 (d, 3H, J=7.5 Hz), 5.10 (m, 1H, CH-CH_3).

1,1-Diphenyl 2-propene : Yield 88%; ir 2900, 1630, 1610, 1490, 1450, 1030, 900, 770, 700 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 1.75 (d, 3H, J=8 Hz), 6.10 (q, 1H, J=6.7 Hz), 7.35 (m, 10H, ArH).

2-Butene 1-phenyl: Yield 80%; ir 2950, 1630, 1590,1495, 1450, 1030, 900, 770 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 1.55 (3H, CH_3, J=7 Hz, cis: 40%), 1.76 (3H, CH_3, J=7.5 Hz, trans: 60%), 1.90 (s, 3H, CH_3, cis: 40%), 1.98 (s, 3H, CH_3, trans: 60%), 5.55 (m, 1H, CH-CH_3, cis), 5.75 (m, 1H, CH-CH_3, trans), 7.15 (m, 5H, ArH).

1-Cyclopentane 3-propylidene : Yield 30% (95% GC); ir 3150, 2950, 1620, 1500 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 0.95-2.30 (m, 8H, ring), 4.90 (m, 2H, $CH=CH_2$), 5.65 (m, 1H, CH-$CH=CH_2$), 6.20 (m, 1H, =CH-$CH=CH_2$).

4-*t*-Butylcyclohexane 1-propylidene: Yield 75% ; bp 115 °C at 11 mmHg; ir 3100, 2900, 1650, 1470, 1380 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 0.84 (s, 9H, $C(CH_3)_3$), 1.20-2.90 (m, 9H, ring), 4.91-5.17 (m, 2H, $C=CH_2$), 5.72-5.84 (m, 1H, C=CH- $CH=CH_2$), 6.41-6.83 (m, 1H, C=CH-$CH=CH_2$); ms ($C_{13}H_{22}$; 178.172) m/z:179, 177, 163, 135, 107, 81.

3-(R)-Methylcyclohexane 1-propylidene : Yield 74% ; bp 120 °C at 11 mmHg; ir 3100, 2900, 1650, 1470, 1380 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$) δ 0.91 (d, 3H, J=6.5 Hz, CH_3, trans : 66%), 0.94 (d, 3H, J=6.3

Hz, CH_3, cis: 34%), 1.10-2.65 (m, 9H, ring), 5.00 (m, 2H, $C=CH_2$), 5.80 (m, 1H, $C=CH-CH=CH_2$), 6.60 (m, 1H, $C=CH-CH=CH_2$); ms ($C_{10}H_{16}$; 136.125) m/z: 137, 133, 108, 95, 81.

1,3-Pentadiene 4-phenyl: Yield 77% ; bp 125 °C at 0.6 mmHg; ir 3030, 2900, 2850, 1625, 1600, 1510, 1475, 1380, 990, 910, 780, 695 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ 2.10 (s, 3H, CH_3, cis: 14%), 2.16 (s, 3H, CH_3, trans: 86%), 5.06 (m, 2H, $C=CH_2$, cis), 5.26 (m, 2H, $C=CH_2$, trans), 6.15 (m, 1H, C=CH-CH=CH_2, cis, J=10 Hz), 6.37 (m, 1H, vinylic), 6.44 (m, 1H, J=12 Hz, trans), 6.75 (m, 1H, vinylic), 6.75 (m, 1H, vinylic), 7.30 (m, 5H, ArH); ms ($C_{10}H_{12}$; 132.0939) (EI): 132, 89, 87.

2,4-Hexadiene 2-phenyl: Yield 78% ; bp 130 °C at 0.6 mmHg; ir 3050, 2900, 2850, 1600, 1500, 1475, 990, 910, 780, 760 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ (The vinylic protons are identified as follows: Ph-C(CH_3e)=CHa-CHb=CHc(CH_3d)) 1.68 (d, 3H, J=6.6 Hz, Hd, cis (Hc, Hb): 17:83), 1.83 (d, 3H, J=6.6 Hz, Hd, trans (Hc, Hb): 17:83), 2.07 (s, 3H, He, cis (Ha, He)), 2.14 (s, 3H, He, trans (Ha, He)), 5.65 (dq, 1H, Hc, J_{bc}=10 Hz, J_{cd}=7 Hz, cis (Hc, Hb)), 5.83 (dq, 1H, Hc, J_{bc}=15 Hz, J_{cd}=6.5 Hz, cis (H, Hb)), 6.11 (m, 1H, Ha, cis (Ha, He)), 20:80), 6.45 (m, 1H, Ha, trans (Ha, He), 20:80), 6.48 (1H, Hb, trans (Ha, He)), 6.71 (1H, Hb, cis (Ha, He)), 7.35 (m, ArH); ms ($C_{12}H_{14}$; 158.1095) m/z: 159, 158, 143, 131, 105.

4-*t*-Butylcyclohexane 1-butenylidene: Yield 76% ; bp 130 °C at 0.4 mmHg; ir 3020, 2950, 2850, 1650, 1500, 1380, 960 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ (The vinylic protons are identified as follows: =CHa-CHb=CHc(CH_3d)) 0.82 (s, 9H, $C(CH_3)_3$), 0.90-2.85 (m, 9H, ring), 1.76 (dd, 1H, Hd, Jcd=6.6 Hz, Jbd=1.48 Hz), 5.45 (dq, 1H, Hc, Jbc=10 Hz, Jcd=7.5 Hz, cis), 5.58 (dq, 1H, Hc, Jbc=15 Hz, Jcd=6.5 Hz, trans), 5.72 (d, 1H, Ha, J_{ab}=10.9 Hz, trans), 6.03 (d, 1H, Ha, J_{ab}=11.5 Hz, cis), 6.20 (m, 1H, Hb, cis), 6.30 (m, 1H, Hb, trans), the trans/cis ratio was 80:20; ms ($C_{14}H_{24}$; 192.1877) (EI):192, 135, 109, 93.

3-(R)-Methylcyclohexane 1-butenylidene : Yield 76% ; bp 135 °C at 6 mmHg; ir 3030, 2950, 2850, 1620, 1450 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ (The vinylic protons are identified as follows: =CHa-CHb=CHc(CH_3d)) 0.90 (d, 3H, CH_2-CH-CH_3, J=6.6 Hz, trans), 0.93 (d, 3H, CH_2-CH-CH_3, J=6.2 Hz, cis), 1.00-2.70 (m, 9H, ring), 1.74 (dd, 3H, -CH=CH-CH_3, J_{cd}=6.4 Hz, J_{bd}=1.5 Hz), 5.40 (dq, 1H, Hc, J_{bc}=10 Hz, J_{cd}=7 Hz), 5.58 (dq, 1H, Hc, J_{bc}=14.8 Hz, J_{cd}=6.7 Hz), 5.73 (t, 1H, Ha, J_{ab}=8.4 Hz), 6.04 (t, 1H, Ha, J_{ab}=8.2 Hz), 6.20 (m, 1H, Hb, trans), 6.32 (m, 1H, Hb, cis), the trans/cis ratio was 80:20; ms ($C_{11}H_{18}$; 150.1408) m/z: 151, 138, 95, 81.

4-*t*-Butylcyclohexane 1-benzylidene : Yield 80% ; bp 205 °C at 11 mmHg; mp 36 °C; ir 3060, 3040, 2900, 1650, 1600, 1490, 1450, 1370, 1000, 850 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 0.85 (s, 9H, t-Bu), 1.20-

2.90 (m, 9H, ring), 6.30 (s, 1H, =CH-Ph), 7.30 (m, 5H, ArH); ms ($C_{17}H_{24}$; 228.1877) (EI): 228, 171, 170, 134, 133, 119, 105, 104, 91, 81.

3-(R)-Methylcyclohexane 1-benzylidene : Yield 78% ; bp 155 °C at 8 mmHg; ir 3055, 3020, 2950, 1650, 1600, 1500, 1430 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$) δ 0.89 (d, 3H, CH_3, J=6.6 Hz, trans), 0.94 (d, 3H, CH_3, J=6.3 Hz, cis), 1.00-2.70 (m, 9H, ring), 6.20 (m, 1H, =CH-Ph), 7.35 (m, 5H, Ph), the trans/cis ratio was 2:1; ms ($C_{14}H_{18}$; 186.1408) (EI): 186, 95.

Cyclopentane 1-benzylidene: Yield 73% ; bp 170 °C ; ir 3060, 3040, 2900, 1650, 1600, 1500, 1450, 915, 740, 700 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 1.50-2.00 (m, 8H, ring), 6.40 (m, 1H, =CH-Ph), 7.35 (m, 5H, Ph); ms ($C_{12}H_{14}$; 158.0109); m/z: 159, 64.

3-(R)-Methylcyclohexane 1-methylene methyl ester : Yield 83%; ir 3020, 2950, 1740, 1630, 1500 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$) δ 0.87 (d, 3H, CH_3, J=6.6 Hz, trans), 0.93 (d, 3H, CH_3, J=6.3 Hz, cis), 1.00-2.65 (m, 9H, ring), 3.70 (s, 3H, OCH_3), 5.70 (s, 1H, $CH\text{-}CO_2CH_3$), the trans/cis ratio was 2:1; ms ($C_{10}H_{16}O_2$; 166.1150) m/z: 169, 108.

4-*t*-Butylcyclohexane 1-methylene methyl ester: Yield 82%; mp 69 °C; ir 3020, 2950, 1740, 1630, 1490 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$) δ 0.85 (s, 9H, $C(CH_3)_3$), 1.00-2.38 (m, 9H, ring), 3.67 (s, 3H, OCH_3), 5.60 (s, 1H, $CH\text{-}CO_2CH_3$); ms ($C_{13}H_{22}O_2$; 210.1619) m/z: 211, 153, 122, 91.

Methyl cinnamate: Yield 93%; ir 3090, 3030, 2900, 1725, 1640, 1600,1500, 1450 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$) δ 3.79 (s, 3H, OCH_3), 6.43 (d, 1H, Ha, J=16 Hz), 7.43 (m, 5H, Ph), 7.69 (d, 1H, Hb, J=16 Hz), the product was >98% trans; ms ($C_{10}H_{10}O_2$; 162.0680) m/z: 163,162, 131, 103.

4-Chloromethyl cinnamate: Yield 88%; bp 125 °C at 10 mmHg; ir 3090, 3030, 2900, 1725, 1640, 1600, 1500, 1450 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ 3.78 (s, 3H, OCH_3, 4%), 3.79 (s, 3H, OCH_3, 96%), 5.95 (d, 1H, Ha, J=12.8 Hz, cis, 4%), 6.43 (d, 1H, Ha, J=16.04 Hz, trans, 96%), 6.90 (d, 1H, Hb, J=12.8 Hz, cis, 4%), 7.45 (m, 4H, para sub. ArH), 7.69 (d, 1H, Hb, J=16.0 Hz, trans, 96%); ms ($C_{10}H_9O_2Cl$; 196.0291) m/z: 197, 177, 175, 155, 95, 81, 79.

4-Methoxymethyl cinnamate: Yield 85%; mp 85 °C ; ir 3090, 3030, 2900, 1725, 1640, 1600,1500, 1450 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$) δ 3.77 (s, 3H, OCH_3), 3.80 (s, 3H, $Ph\text{-}OCH_3$), 6.28 (d, 1H, Ha, J=15.8 Hz, trans), 6.80, 7.50 (mm, 4H, para sub. ArH), 7.64 (d, 1H, Hb, J=15.8 Hz, trans); ms m/z: 193, 191, 161. 121, 90.

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