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Dipolar Cycloaddition of a Phosphorylnitrile Oxide to Functionalised Cyclopropenes*

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Abstract: While the reactions of a number of functionalised cyclopropenes with (diisopropoxyphosphoryl)nitrile oxide lead to 2-oxa-3-azabicyclo[3.1.0]hex-3-enes, 1-bromo-3,3-dimethylcyclopropene leads to an isoxazole and 3,3-dimethyl-1,2-dichlorocyclopropene leads to an oxazine

Although there are reports of the formation 2-oxa-3-azabicyclo[3.1.0]hex-2-enes by addition of aliphatic and aromatic nitrile oxides to selected 3,3-disubstituted cyclopropenes,[1] there are few reports of the synthesis of related phosphorus-containing bicyclic compounds.[2,3] Introduction of a phosphorus substituent into such preformed heterocyclic systems causes serious problems, because of the relative lability of cyclopropane and isoxazoline rings. We now report the use of 1,3-dipolar cycloadditions of nitrile oxides for obtaining such bicyclic systems with phosphoryl substituents in the isoxazoline fragment.

When heated or treated with base, oximes of (dialkoxyphosphoryl)carbonylhalides (**1**) lead to highly reactive (dialkoxyphosphoryl)nitrile oxides (**2**),[4,5] valuable reagents for indirect phosphorylation.[4-6] The 1,3-dipolar cycloadditions of compounds (**2**) with terminal alkenes and alkynes lead to polyfunctional 3-phosphoryl substituted isoxazolines and isoxazoles[5-7] which are not obtainable by other routes. The present report describes the cycloaddition reactions of (diisopropoxyphosphoryl)nitrile oxide (**2**) with cyclopropene dipolarophiles, and in particular 1-halocyclopropenes.

As the phosphorylnitrile oxide (**2**) tends to polymerize and dimerize at ambient temperature, forming, eg., bis(diisopropoxyphosphoryl)furoxane,[6-8] the nitrile oxide was generated and introduced into cyclo-addition reactions at 0 – -60 °C. Within range, (**2**) remains stable for a long period, and reacts with many dipolarophiles without forming oligomers. This temperature range is also convenient for studying reactions with labile cyclopropenes. Therefore both thermally stable cyclopropenes (**3 - 10**), which were either preformed and purified (**5 - 10**) or generated in situ (**3, 4**), and rather unstable cyclopropenes (**11, 12**) were

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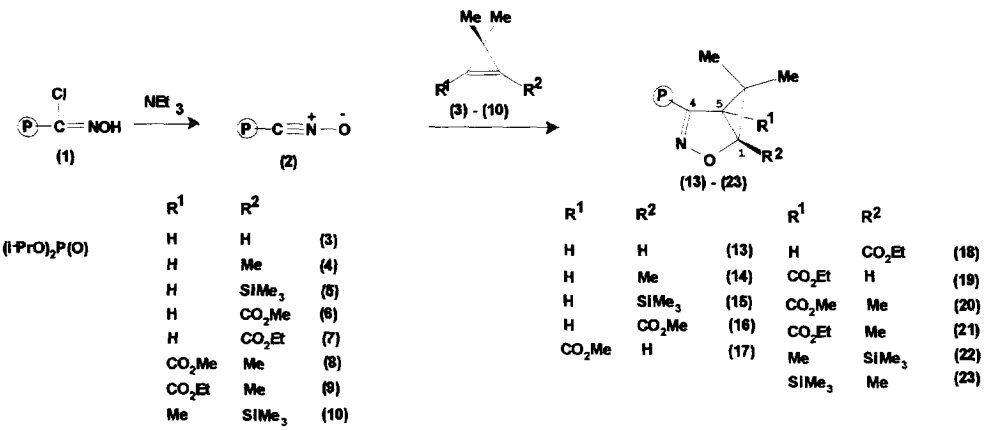
*) Phosphorylnitrile Oxides. IX. This research is supported by the International Foundation INTAS.For part VIII see *Zh.Obshch.Khim.*, 1995, 65 (Pavlov, V.A.; Aristova, N.V.; Gorin , B.I.; Zjablikova, T.A.; Litvinov, I.A.,; Moskva, V.V.)

allowed to react with (**2**) under essentially the same conditions, allowing direct comparison of the results. The reactions of nitrile oxide (**2**) with 3,3-dimethylcyclopropene (**3**) and analogues containing methyl, ester or trimethylsilyl groups in cyclopropene 1- or 2-positions (**4 - 10**), proceeded by typical dipolar cycloadditions and led to the 1:1 adducts (**13 - 23**) with retention of the three-membered ring. The product structures were established by ^{1}H, ^{13}C and ^{31}P NMR and IR-spectroscopy. Thus the ^{1}H NMR spectrum of compound (**13**) included a single-proton doublet at δ_H 4.58 ($^{3}J_{HH}$ 5 Hz) and doublet of doublets at 2.63 ($^{3}J_{HH}$ 5, $^{3}J_{PH}$ 0.6 Hz) in agreement with chemical shifts and coupling constants of analogous non-phosphorylated systems.[1f] The $^{3}J_{PH}$ value of 0.6 Hz confirms that this signal, which is at the higher field, belongs to H-5. Similar chemical shifts were noted for H-1 and H-5 in the spectra of 6-methyl-6-phenyl- and 6-methyl-6-cyano-4-(diisopropoxy-phosphoryl)-2-oxa-3-azabicyclo[3.1.0]hex-3-enes.[2]



Ⓟ = $(i\text{-}PrO)_2P(O)$

R^1	R^2	
H	H	(3)
H	Me	(4)
H	$SiMe_3$	(5)
H	CO_2Me	(6)
H	CO_2Et	(7)
CO_2Me	Me	(8)
CO_2Et	Me	(9)
Me	$SiMe_3$	(10)

R^1	R^2	
H	H	(13)
H	Me	(14)
H	$SiMe_3$	(15)
H	CO_2Me	(16)
CO_2Me	H	(17)

R^1	R^2	
H	CO_2Et	(18)
CO_2Et	H	(19)
CO_2Me	Me	(20)
CO_2Et	Me	(21)
Me	$SiMe_3$	(22)
$SiMe_3$	Me	(23)

The reactions with cyclopropenes (**4, 5**) occured regioselectively with formation of adducts in which the methyl or trimethylsilyl substituents are in the 1-position of the bicycle, (**14** and **15**). Thus in the ^{1}H NMR spectra of each, single-proton signals were observed at δ_H 2.22 or 2.65, rather than at lower field as would be expected for the regio-isomers. The coupling constant $^{3}J_{PH}$ was not, however, observed; probably, due to its low value, it was not detected. Signals were observed for H-5 at a very similar position (δ_H 2.00 and 2.29) for 4-methyl- and 4-phenyl-substituted 1-methyl-2-oxa-3-azabicyclo[3.1.0]hex-3-enes.[1a]

The regioselectivity of the cycloaddition was considerably reduced with 1-methoxycarbonyl- and 1-ethoxycarbonyl-3,3-dimethylcyclopropenes (**6, 7**), when both 1-alkoxycarbonyl- (**16, 18**), and 5-alkoxy-carbonyl-2-oxa-3-azabicyclo[3.1.0]hex-3-enes (**17, 19**) were isolated.[##] From the ^{1}H and ^{31}P NMR spectra the ratio of the isomers (**16**):(**17**) was determined as 81:19 and (**18**):(**19**) as 86:14. Formation of two regioisomers demonstrates the electron-releasing nature of the phosphorylnitrile oxide.[9] The HOMO of the nitrile oxide has a higher electron occupancy on the oxygen atom, and the interaction of this HOMO with the LUMO of the dipolarophile tends to orientate the addends to allow maximum overlap of the interacting

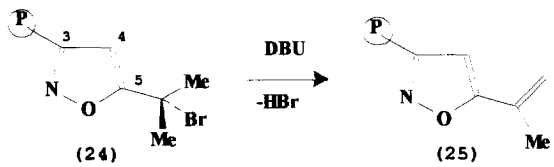
molecular orbitals. Apparently such orbital interactions are similar in magnitude to the steric interactions which occur early in the reaction, and the sterically crowded regioisomers (**17**) and (**19**) are formed together with predominant cycloadducts (**16, 18**). However, the regioselectivity of cycloaddition of 1,2-substituted cyclopropenes to the phosphorylnitrile oxide is probably controlled primarily by steric interactions. Support for this may possibly be seen in the reduction by 5% of the proportion of cycloadduct (**19**) compared with (**17**) due to the greater size of the ethoxycarbonyl rather than the methoxycarbonyl substituent at C-5. Analogous competing steric and electronic interactions may also explain the stereo-chemistry of 1,3-dipolar cycloadditions of non-phosphorylated nitrile oxides to alkenes containing ester or other electron-attracting groups.[10] When the olefins contained alkyl or aryl substituents and a vicinal electron-attracting group (COOR, COR, $CONH_2$, CN, Cl, Br), the reactions led to either a mixture of two isomers or to isoxazolines with the electron-attracting substituent on C-4. This supports the fact that the regioselectivity of 1,3-dipolar cycloadditions of nitrile oxides is controlled mostly by steric interactions early in the reaction. However, the introduction of an electron-attracting substituent on the double bond changes the nature of the LUMO, increasing the influence of electronic interactions and the formation of the sterically unfavourable cycloadduct. Competition between electronic and steric interactions was also observed in the reaction of the nitrile oxide with 1-alkoxycarbonyl-2,3,3-trimethylcyclopropenes (**8**) and (**9**). In these cases only cycloadducts with the methyl group at C-1 were observed.

The reaction with 1-trimethylsilyl-2,3,3-trimethylcyclopropene (**10**) was also controlled by steric factors, the isoxazoline having the bulky trimethylsilyl group at the 1-posititon being the major product (the ratio of (**22**):(**23**) isomers, 82:18). The assignment of these structures is supported by the presence of a coupling constant $^1J_{CSi}$ of 64 Hz for C-1 of (**22**) in the ^{13}C NMR spectrum. An attempt to confirm this structure by substitution of the trimethylsilyl group by hydrogen by reaction with tetra-butylammonium fluoride and water in tetrahydrofuran was unsuccessful, the adduct (**22**) decomposing with the formation of a number of products which were not isolated pure. However, a doublet at δ_P -11.3 with $^1J_{FP}$ of 976.5 Hz in the ^{31}P NMR spectrum of the reaction mixture was assigned to diisopropylfluorinephosphate, suggesting a nucleophilic substitution occurs at phosphorus.[11] A similar P-C bond cleavage was observed on treating the bromineanhydride of (diisopropoxyphosphoryl)formhydroxamic acid with aqueous potassium fluoride, which resulted in the isolation of diisopropylfluorinephosphate.[11]

The signals in the spectra of all adducts were assigned by comparison of ^1H NMR parameters of 4-arylbicyclo[3.1.0]hex-3-enes,[1f] and 4-(diisopropoxyphosphoryl) derivatives,[2] together with data from ^{13}C and ^{31}P NMR spectra, taking into account the effect of the phosphorus on C-4. The shielding effect of the isoxazoline fragment shifts the ^1H NMR signal for the endo-methyl group to higher field than the exo- methyl group,[1f] while the "steric compression" effect, the closeness of the electron pairs on the oxygens of the phosphoryl group to the carbon of the endo-methyl, should lead to its being more shielded than the

exo-methyl in the ^{13}C NMR.[12-14] It should be noted that in ^{1}H NMR spectra of cycloadducts (**14, 20, 23**) containing a methyl group in the 1-position the protons of this appeared as a doublet with $^{5}J_{PH}$ 1.4 - 1.7 Hz.

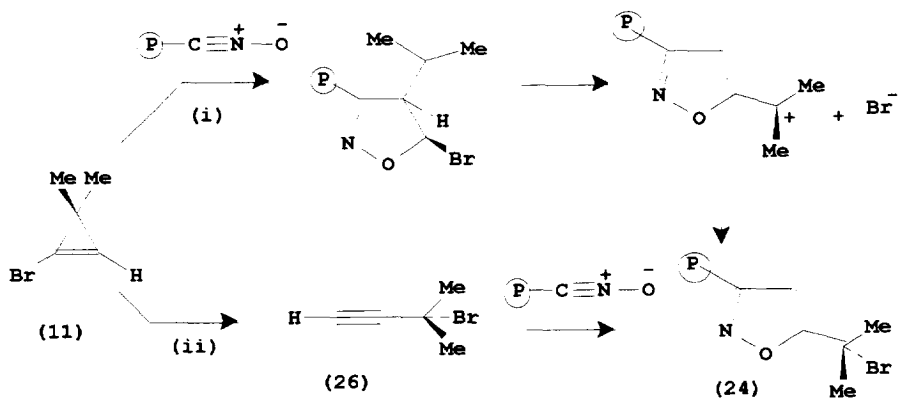
Reaction of 1-bromo-3,3-dimethylcyclopropene (**11**), generated in situ,[15] with the nitrile oxide (**2**), led to a compound for which the ^{1}H NMR spectrum included a six-proton singlet. In addition, a single- proton doublet at δ_H 6.42 ($^{3}J_{PH}$ 0.8 Hz) and signals in the ^{13}C NMR spectrum were very similar to signals in the spectrum of 3-(diisopropoxyphosphoryl)-5-bromomethylisoxazole, obtained by [2+3]-cycloaddition of the nitrile oxide to 3-bromo-1-propyne.[5,6] The product was therefore characterised as isoxazole (**24**).



Minor signals were also observed in the ^{1}H and ^{13}C NMR spectra of the reaction mixture, including broad singlets at δ_H 5.75 and 5.28, assigned to 3-(diisopropoxyphosphoryl)-5-isopropenylisoxazole (**25**); these signals increased on addition of triethylamine, or by elimination of HBr from (**24**) with DBU, which gave (**25**) in quantitative yield. Two mechanisms may be suggested for the formation of adduct (**24**):

(i) interaction of phosphorylnitrile oxide (**2**) with (**11**) to give a bicyclic product, followed by opening of the cyclopropane with bromine migration, and

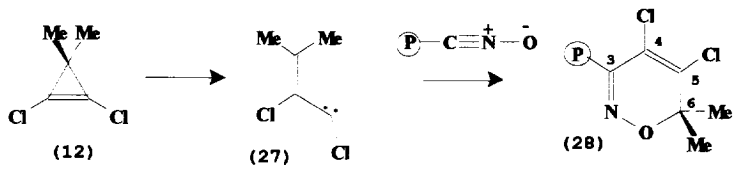
(ii) ring-opening of cyclopropene (**11**) with the formation of 3-bromo-3-methylbutyne-1 (**26**) and cycloaddition of the nitrile oxide to this.



The latter seems more likely,[3] since the bromocyclopropene is known to isomerise to the acetylene under certain conditions.[16-18] However, the first possibility cannot at this point be completely excluded.

Cycloaddition of the phosphorylnitrile oxide to 1,2-dichloro-3,3-dimethylcyclopropene (**12**) also gave a product which was not typical of 1,3-dipolar cycloaddition to the double bond. In the ^{13}C NMR spectrum of

the cycloadduct (**28**) obtained, the shift of the signal for C-6 was 81 ppm; this can be explained by the presence of the neighbouring electronegative oxygen atom. Similar chemical shifts have been reported for oxazines derived by the reaction of (**12**) with other nitrile oxides, and the structure of one such compound has been established by X-ray crystallography.[19]



It is known that cyclopropenes such as (**12**) undergo a cyclopropene - vinylcarbene rearrangement at ambient temperature and the vinylcarbene (**27**) has been trapped in a range of intermolecular reactions, such as addition to alkenes, alkynes, and phospha-alkynes, or insertion into carbon-hydrogen bonds.[15,17,18,20] Thus, the formation of (**28**) may proceed by an unusual formal [3+3]-cycloaddition between the nitrile oxide and vinylcarbene (**27**), which is derived by ring-opening of the cyclopropene; it is not clear whether the 1,2-oxazine (**28**) is actually formed by a concerted cycloaddition or by a stepwise process.

Experimental Section

Reagents were obtained from commercial suppliers and used without further purification unless stated. Dichloromethane was distilled over calcium hydride. Diethyl ether was distilled over sodium wire. Petroleum ether was either of b.p. 40 - 60 °C or 60 - 80 °C., and was purified by distillation. Reactions requiring anhydrous conditions were performed using oven dried glassware (250 °C) cooled under a stream of dry nitrogen or argon; the experiments were conducted under a positive atmosphere of one of these gases. The term "dried" refers to the storage of a solution of the compound over anhydrous magnesium sulphate for a few minutes. The term evaporated refers to solvent removal at 14 mm Hg at 30 - 50 °C or at ca. 1 mm Hg at 25 °C for higher boiling solvents. Yields quoted are for purified compounds unless stated. New compounds were homogeneous by tlc or by glc. Glc was conducted using a Perkin-Elmer Model F17 F.I.D. on a capillary column (30 m x 0.32 mm id Phase). The carrier gas was hydrogen. Tlc was performed using Aldrich silica plates coated with silica gel 60 (F254). Compounds were visualised by examination under an ultraviolet source, exposure to iodine vapour or by contact with dodecanmolybdophosphoric acid solution (5% in 95:5 ethanol water) followed by heating to 180 °C. Column chromatography was conducted with Merck 7736 silica gel under medium pressure. IR spectra were obtained as liquid films on a Perkin-Elmer 1600 FTIR. Mass spectra were obtained using a Finnigan Mat 1020 spectrometer. Microanalyses were performed with a Carlo-Erba Model 1106 CHN analyser. NMR spectra were obtained on a Brucker AC250 at 250 MHz for ^{1}H, at 62.5 MHz for ^{13}C, and at 101.26 MHz for ^{31}P. ^{1}H and ^{13}C chemical shifts were referenced to tetramethylsilane (TMS) and ^{31}P to 85% H_3PO. The assignment of signals in ^{13}C

NMR spectra was done on the basis of correlation of broad band decoupled data and data obtained in D.E.P.T. experiments. NMR spectra were run in deuteriochloroform unless otherwise stated.

(Diisopropoxyphosphoryl)nitrile oxide (2)

Triethylamine (0.41 g, 1.0 mol.equiv.) in dry ether (10 ml) was added over 2 min at 0 – -78 °C to a stirred solution of (diisopropoxyphosphoryl)hydroximoyl chloride (1.0 g, 1.0 mol.equiv.) in dry ether (20 ml). Unless stated, the precipitated triethylamine hydrochloride was quickly filtered off after cooling, giving a quantitative yield of (diisopropoxyphosphoryl)nitrile oxide[3] in ether which showed δ_P -15.94 (acetone-d_6); -16.9 (CCl_4); δ_C 75.96 (OCH-iPr d, $^2J_{POC}$ 6.0 Hz), 23.94, 23.88, 23.65, 23.57 (CH_3); ν_{max} 2990, 2950, 2890, 2290, 1640, 1475, 1460, 1395, 1385, 1290, 1185, 1150, 1110, 1020, 925, 895, 855, 785 cm^{-1}.

4-(Diisopropoxyphosphoryl)-6,6-dimethyl- 2-oxa-3-azabicyclo[3.1.0]hex-3-ene (13)

Methyl lithium (30.67 ml, 1.5 M, 2.4 mol.equiv.) was added at -78 °C under argon to a stirred solution of 1,1-dibromo-3-chloro-2,2-dimethylcyclopropane (5 g) in dry ether (20 ml).[21] The products were allowed to reach 20 °C, stirred for 30 m, and then cooled to -78 °C and treated with water (5 ml). Ether (30 ml) was added and the organic layer was dried and filtered at -20 °C and the filtrate was added at -78 °C to (diisopropoxyphosphoryl)nitrile oxide (1.27 g, 0.32 mol.equiv.) in dry ether (20 ml). The mixture was stirred for 2 h at -78 °C and then allowed to reach room temperature. After 16 h, the solvent was evaporated; chromatography over silica gel gave a single product as a pale yellow oil, characterised as *4-(diisopropoxyphosphoryl)-6,6-dimethyl-2-oxa-3-aza-bicyclo[3.1.0]hex-3-ene* (0.8 g, 47.3 %) which showed : δ_H 4.75 (2H, m, OCH-iPr), 4.58 (1H, d, $^3J_{HH}$ 5 Hz, H-1), 2.63 (1 H, dd, $^3J_{HH}$ 5 Hz, $^3J_{PH}$ 0.6 Hz, H-5), 1.37 - 1.22 (12H, m, CH_3iPr), 1.05 (3H, s, CH_3 exo), 0.78 (3H, s, CH_3 endo); δ_P: 2.59 s; δ_C 153.56 (d, $^1J_{PC}$ 214.4 Hz, C-4), 74.70 (d, $^3J_{PC}$ 3.9 Hz, C-1), 72.35 (d, $^2J_{POC}$ 7.0 Hz, OCH-iPr), 41.79 (d, $^2J_{PC}$ 24.1 Hz, C-5), 23.79, 23.74, 23.54, 23.47 (CH_3-iPr), 21.78 (CH_3-exo), 12.39 (C-6), 11.98 (CH_3 endo); ν_{max} 3488, 2982, 2934, 1738, 1649, 1540, 1468, 1454, 1386.5, 1261, 1104.5, 1005, 842, 768 cm^{-1}.

1,6,6-Trimethyl-4-(diisopropoxyphosphoryl)-2-oxa-3-azabicyclo[3.1.0]hex-3-ene (14)

Methyl lithium (10.4 ml, 1.5 M, 2.5 mol.equiv.) was added at -78 °C under argon to a stirred solution of 1,1,3-tribromo-2,2,3-trimethylcyclopropane[21] (2 g) in dry ether (20 ml). The products were allowed to reach 20 °C, stirred for 30 min., cooled to -30 °C, treated with water (1.5 ml), dried and filtered at -20 °C. The filtrate was added at -80 °C to a solution of (diisopropoxyphosphoryl)nitrile oxide (0.85 g, 0.65 mol.equiv.) in dry ether (40 ml) and stirred for 30 m at 20 °C. After 16 h, the solvent was evaporated to give an oil;

chromatography over silica gel gave a single product as a pale yellow oil, characterised as *1,6,6-trimethyl-4-(diisopropoxyphosphoryl)-2-oxa-3-azabicyclo[3.1.0]hex-3-ene* (0.8 g, 67.3 %) (Found: C, 53.86; N, 4.69; H, 8.67. Calculated for $C_{13}H_{24}NO_4P$: C, 53.97; N, 4.84; H, 8.30) which showed: δ_H 4.70 (2 H, m, OCH-iPr), 2.22 (1H, s, H-5), 1.53 (3H, d, $^5J_{PH}$ 1.37 Hz), 1.38 - 1.18 (12H, m, CH_3-iPr), 1.10 (3H, s, CH_3-exo), 0.71 (3H, s, CH_3-endo); δ_P 3.04 s; δ_C 153.86 (d, $^1J_{PC}$ 214.8 Hz, C-4), 80.95 (d, $^3J_{PC}$ 5.2 Hz, C-1), 72.28 (d, $^2J_{POC}$ 6.0 Hz, OCH-iPr), 72.07 (d, $^2J_{POC}$ 6.2 Hz, OCH-iPr), 43.67 (d, $^2J_{PC}$ 23.3 Hz, C-5), 23.70, 23.54, 23.51, 23.48 (CH_3-iPr), 20.94 (CH_3-exo), 15.56 (C-6), 13.50 (CH_3), 13.23 (CH_3-endo); ν_{max} 3488, 2990, 2934, 1734, 1540, 1466, 1387, 1260, 1180, 1141, 1105, 993, 901, 772, 634 cm^{-1}.

6,6-Dimethyl-1-trimethylsilyl-4-(diisopropoxyphosphoryl)-2-oxa-3-azabicyclo[3.1.0]hex-3-ene (15)

3,3-Dimethyl-1-trimethylsilylcyclopropene (0.96 g, 1.7 mol.equiv.) in dry ether (20 ml) was added at -78 ^oC with stirring to (diisopropoxyphosphoryl)nitrile oxide (0.81 g, 1.0 mol.equiv.) in dry ether (30 ml), allowed to reach room temperature and stirred for 16 h. The solution was filtered through a small amount of silica gel and the solvent evaporated to give *6,6-dimethyl-1-trimethylsilyl-4-(diisopropoxyphosphoryl)-2-oxa-3-azabicyclo[3.1.0]hex-3-ene* (0.92 g, 68 %) as a pale yellow oil (Found: C, 51.99; N, 4.25; H 8.51. Calculated for $C_{15}H_{30}NO_4PSi$: C, 51.87; N, 4.03; H, 8.64) which showed: δ_H 4.70 (2H, m, OCH-iPr), 2.65 (1H, s, H-1), 1.6 - 1.4 (12H, m, CH_3-iPr), 1.28 (3H, s, CH_3-exo), 0.95 (3H, s, CH_3-endo), 0.29 (9H, s, $SiCH_3$); δ_P 3.16 s; δ_C 152.10 (d, $^1J_{PC}$ 213.6 Hz, C-4), 78.13 (d, $^3J_{PC}$ 4.2 Hz, C-1), 71.88 (d, $^2J_{POC}$ 6.2 Hz, OCH-iPr), 71.72 (d, $^2J_{POC}$ 6.0 Hz, OCH-iPr), 46.16 (d, $^2J_{PC}$ 24.6 Hz, C-5), 23.56, 23.48, 23.27, 23.20 (CH_3-iPr), 21.82 (CH_3-exo), 15.55 (C-6), 13.80 (CH_3-endo), -1.84 (s, $SiCH_3$ with satellites for $^1J_{CSi}$ at 50.3 Hz); ν_{max} 2980, 1544, 1466, 1378, 1253, 1179, 1143, 1105, 1003, 928, 869, 843, 751, 629 cm^{-1}.

1-Methoxycarbonyl- and 5-methoxycarbonyl-4-(diisopropoxyphosphoryl)-6,6-dimethyl-2-oxa-3-aza-bicyclo[3.1.0]hex-3-enes (16) and (17)

A solution of methyl 3,3-dimethylcyclopropene carboxylate[21] (0.58 g, 1.0 mol. equiv.) in dry ether (15 ml) was added over 2 min at -78 ^oC to a stirred solution of (diisopropoxyphosphoryl)nitrile oxide (0.57 g, 0.6 mol. equiv.) containing triethylamine hydrochloride in dry ether (40 ml). The mixture was stirred for 1 h at -78 ^oC and then allowed to reach room temperature. After 16 h, the mixture was filtered and the solvent was evaporated to give a pale yellow oil, a mixture of 4-(diisopropoxyphosphoryl)-6,6-dimethyl-1-methoxycarbonyl-2-oxa-3-aza-bicyclo[3.1.0]hex-3-ene and 4-(diisopropoxyphosphoryl)-6,6-dimethyl-5-methylcarbonyl-2-oxa-3-azabicyclo[3.1.0]hex-3-ene in ratio 4.3: 1 (Found: C, 51.27; H, 7.42; N, 4.31. Required for $C_{14}H_{24}NO_6P$: C, 50.45; H, 7.21; N, 4.20). Chromatography gave a single major product (0.7 g, 76 %) and a minor product (0.2 g, 21 %). The major product showed δ_H 4.70 (2H, m, OCH-iPr), 3.71 (3H, $COOCH_3$), 3.06 (1H, s, H-5), 1.18

(3H, d, $^4J_{HH}$ 0.5 Hz, CH_3-exo), 1.32 - 1.22 (12H, m, CH_3-iPr), 0.81 (3H, d, $^4J_{HH}$ 0.5 Hz, CH_3-endo); δ_P 0.99 s; δ_C 166.56 (C=O), 153.33 (d, $^1J_{PC}$ 214.1 Hz, C-4), 77.68 (d, $^3J_{PC}$ 3.8 Hz, C-1), 72.79 (d, $^2J_{POC}$ 8.9 Hz, OCH-iPr), 72.66 (d, $^2J_{POC}$ 8.5 Hz, OCH-iPr), 52.25 (CH_3O), 48.54 (d, $^2J_{PC}$ 24.2 Hz, C-5), 23.83, 23.67, 23.44, 23.27 (CH_3-iPr), 21.29 (C-6), 19.43 (CH_3-exo), 13.91 (CH_3-endo). The minor product showed δ_H 4.78 (1H, s, H-1), 4.70 (2H, m, OCH-iPr), 3.66 (3H, $COOCH_3$), 1.32 - 1.22 (15H, m, CH_3-exo, CH_3-iPr), 0.83 (3H, d, $^4J_{HH}$ 0.5 Hz, CH_3-endo); δ_P 0.99 s; δ_C 165.16 (C=O), 152.33 (d, $^1J_{PC}$ 216.0 Hz, C-4), 80.12 (d, $^3J_{PC}$ 3.8 Hz, C-1), 72.50 (d, $^2J_{POC}$ 6.5 Hz, OCH-iPr), 72.27 (d, $^2J_{POC}$ 6.3 Hz, OCH-iPr), 53.20 (d, $^2J_{PC}$ 22.0 Hz, C-5), 51.94 (CH_3O), 23.78, 23.62, 23.37, 23.17 (CH_3-iPr), 20.32 (C 6), 18.25 (CH_3-exo), 13.91 (CH_3-endo); ν_{max} (mixture) 3478, 2982, 2936, 1740, 1546, 1439, 1387, 1304, 1267, 1235, 1180, 1136, 1105, 1000, 897, 861, 770, 690 cm^{-1}.

1-Ethoxycarbonyl- and 5-ethoxycarbonyl-4-(diisopropoxyphosphoryl)-6,6-dimethyl-2-oxa-3-aza-bicyclo[3.1.0]hex-3-enes (18) and (19)

A solution of ethyl 3,3-dimethylcyclopropenecarboxylate[21] (0.2 g, 1.0 mol.equiv.) in dry ether (20 ml) was added over 2 min at -78 °C with stirring to (diisopropoxyphosphoryl)nitrile oxide (0.25 g, 0.85 mol equiv.) containing triethylamine hydrochloride in dry ether (40 ml). The mixture was stirred for 1 h at -78 °C and then allowed to reach room temperature. After 16 h the triethylamine hydrochloride was filtered off. The solvent was evaporated to give a mixture of two isomers in ratio 86:14 (0.3 g, 74 %) (Found: C, 51.41; H, 7.75; N, 3.97. Required for $C_{15}H_{28}NO_6P$: C, 51.87; H, 7.49; N, 4.03). Chromatography gave a mixture characterised as *4-(diisopropoxyphosphoryl)-1-ethoxycarbonyl-6,6-dimethyl-2-oxa-3-azabicyclo[3.1.0]hex-3-ene* (major) and *4-(diisopropoxyphosphoryl)-5-ethoxycarbonyl-6,6-dimethyl-2-oxa-3-azabicyclo[3.1.0]hex-3-ene* (minor) as a pale yellow oil which showed: (major) δ_H 4.72 (2H, m, OCH-iPr), 4.19 (2H, q, CH_2O), 3.07 (1H, s, H-5), 1.34 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3-Et), 1.32 - 1.25 (15H, m, CH_3-iPr, CH_3-exo), 0.83 (3H, s, CH_3-endo); δ_P 1.14 s; δ_C 166.28 (s, C=O), 153.43 (d, $^1J_{PC}$ 214.5 Hz, C-4), 80.37 (d, $^3J_{PC}$ 3.9 Hz, C-1), 72.94 (d, $^2J_{POC}$ 6.2 Hz, OCH-iPr), 72.77 (d, $^2J_{POC}$ 6.2 Hz, OCH-iPr), 61.70 (CH_2O), 48.44 (d, $^2J_{PC}$ 24.3 Hz, C-5), 23.82, 23.77, 23.59, 23.53 (CH_3-iPr), 21.27 (C-6), 19.59 (CH_3-exo), 14.09 (CH_3-Et), 13.94 (CH_3-endo); (minor) δ_H 4.80 (1H, s, H-1), 4.72 (2H, m, OCH-iPr), 4.02 (2H, q, $^3J_{HH}$ 7.1 Hz, CH_2O), 1.32-1.25 (18H, m, CH_3-iPr, CH_3-exo, CH_3-Et), 0.86 (3H, s, CH_3-endo); δ_P 0.87 s; δ_C 164.85 (s, C=O), 152.55 (d, $^1J_{PC}$ 207.5 Hz, C-4), 77.70 (d, $^3J_{PC}$ 3.9 Hz, C-1), 72.35 (d, $^2J_{POC}$ 6.2 Hz, OCH-iPr), 61.53 (s, CH_2O), 53.50 (d, $^2J_{PC}$ 25.1 Hz, C-5), 23.82-23.16 (CH_3-Pr), 20.34 (s, C-6), 18.39 (CH_3-exo), 13.94 (CH_3-Et), 13.83 (CH_3-endo); ν_{max} (mixture) 2983, 2937, 2877, 1732, 1692, 1615, 1547, 1468, 1454, 1386, 1303, 1266, 1234, 1204, 1179, 1139, 1104 cm^{-1}.

4-(Diisopropoxyphosphoryl)-5-methoxycarbonyl-1,6,6-trimethyl-2-oxa-3-azabicyclo[3.1.0]hex-3-ene (20)

Methyl 1,3,3-trimethylcyclopropenecarboxylate[21] (0.58 g, 1.0 mol. equiv.) in dry ether (20 ml) was added over 2 min at -78 °C to a stirred solution of (diisopropoxyphosphoryl)nitrile oxide (0.51 g, 0.59 mol. equiv.) with triethylamine hydrochloride in dry ether (40 ml). After 1 h at -78 °C, work-up and chromatography gave a single product as a yellow oil, *4-(diisopropoxyphosphoryl)-5-methoxycarbonyl-1,6,6-trimethyl-2-oxa-3-azabicyclo-[3.1.0]hex-3-ene* (0.7 g, 82.4 %) (Found: C, 52.00; H, 7.78; N, 4.05. Required for $C_{15}H_{26}NO_6P$: C, 51.87; H, 7.49; N, 4.03) which showed: δ_H 4.72 (2H, m, OCH-iPr), 3.68 (3H, s, $COOCH_3$), 1.59 (3H, d, $^5J_{PH}$ 1.5 Hz, CH_3), 1.30 - 1.27 (12H, m, CH_3-iPr), 1.25 (3H, s, CH_3-exo), 0.82 (3H, s, CH_3-endo); δ_P 1.53 s; δ_C 165.88 (s, C=O), 153.77 (d, $^1J_{PC}$ 216.8 Hz, C-4), 84.93 (d, $^3J_{PC}$ 3.8 Hz, C-1), 73.22 (d, $^2J_{POC}$ 6.3 Hz, OCH-iPr), 72.93 (d, $^2J_{POC}$ 6.3 Hz, OCH-iPr), 52.75 (d, $^2J_{PC}$ 22.0 Hz, C-5), 52.58 (CH_3O), 24.68, 24.53, 24.24, 24.16 (CH_3-iPr), 22.99 (CH_3), 17.71 (CH_3-exo), 15.67 (C-6), 12.35 (CH_3-endo); ν_{max} 3478, 2981, 1737, 1535, 1437, 1386, 1305, 1263, 1180, 1141, 1105, 1068, 998, 883, 770 cm^{-1}.

4-(Diisopropoxyphosphoryl)-5-ethoxycarbonyl-1,6,6-trimethyl-2-oxa-3-azabicyclo-[3.1.0]hex-3-ene (21)

A solution of ethyl 1,3,3-trimethylcyclopropenecarboxylate[21] (0.57 g, 1.0 mol. equiv.) in dry ether (20 ml) was added over 2 min at -78 °C to a stirred solution of (diisopropoxyphosphoryl)nitrile oxide (0.67 g, 0.87 mol. equiv.) with triethylamine hydrochloride in dry ether (40 ml). The mixture was stirred for 30 m at -78 °C and then allowed to reach 20 °C. After 16 h, the mixture was filtered and the solvent was evaporated to give a yellow oil; chromatography gave a single product characterised as 4-(diisopropoxyphosphoryl)-5-ethoxycarbonyl-1,6,6-trimethyl-2-oxa-3-azabicyclo[3.1.0]hex-3-ene (0.6 g, 51.3 %) which showed: δ_H 4.79 (2H, m, OCH-iPr), 4.18 (2H, q, CH_2-Et), 1.64 (3H, t, $^3J_{HH}$ 1.4 Hz, CH_3-Et), 1.35 - 1.29 (18H, m, CH_3, CH_3-iPr, CH_3-exo), 0.87 (3H, d, $^4J_{HH}$ 1.4 Hz, CH_3-endo); δ_P 1.47 s; δ_C 164.55 (C=O), 153.08 (d, $^1J_{PC}$ 216.3 Hz, C-4), 83.90 (d, $^3J_{PC}$ 4.3 Hz, C-1), 72.44 (d, $^2J_{POC}$ 6.1 Hz, OCH-iPr), 72.06 (d, $^2J_{POC}$ 6.0 Hz, OCH-iPr), 61.15 (CH_2O), 51.98 (d, $^2J_{PC}$ 21.6 Hz, C-5), 23.86, 23.81, 23.41, 23.33 (CH_3-iPr), 21.85 (CH_3), 16.95 (CH_3-exo), 14.87 (C-6), 13.79 (CH_3-Et), 11.54 (CH_3-endo); ν_{max} 2981, 2936, 2876, 1734, 1535, 1467, 1386, 1375, 1303, 1264, 1223, 1180, 1142, 1105, 1066, 998, 994, 902, 883, 830, 771 cm^{-1}.

5,6,6-Trimethyl-1-trimethylsilyl- and 1,6,6-trimethyl-5-trimethylsilyl-4-(diisopropoxyphosphoryl)-2-oxa-3-azabicyclo[3.1.0]-hex-3-enes (22) and (23)

A solution of 2,3,3-trimethyl-1-trimethylsilylcyclopropene[21] (0.4 g, 1.0 mol.equiv.) in dry ether (15 ml) was added over 2 min at -78 °C to a stirred solution of (diisopropoxyphosphoryl)nitrile oxide (0.53 g, 0.85

mol.equiv.) in dry ether (40 ml). The mixture was stirred for 1 h at -78 °C and then allowed to reach room temperature. After 16 h, the solvent was evaporated to give a pale yellow oil (0.83 g, 90 %) (Found: C, 52.98; H, 8.72; N, 3.77. Required for $C_{16}H_{32}NO_4PSi$: C, 53.18; H, 8.86; N, 3.87) characterised as a mixture of 4-(diisopropoxyphosphoryl)-5,6,6-trimethyl-1-trimethylsilyl-2-oxa-3-azabicyclo[3.1.0]hex-3-ene and 4-(diisopropoxyphosphoryl)-1,6,6-trimethyl-5-trimethylsilyl-2-oxa-3-azabicyclo[3.1.0]hex-3-ene (ratio 4.5:1), which showed: δ_H (major) 4.72 (2H, m, OCH-iPr), 1.42 (3H, s, CH_3), 1.33 - 1.28 (12H, m, CH_3-iPr), 1.14 (3H, s, CH_3-exo), 0.78 (3H, s, CH_3-endo), 0.12 (9H, s, Si CH_3 with satellites for $^2J_{HSi}$ at 6.8 Hz); δ_P 3.34 s; δ_C 155.77 (d, $^1J_{PC}$ 209.2 Hz, C-4), 79.59 (d, $^3J_{PC}$ 4.2 Hz, with satellites for $^1J_{CSi}$ at 64.1 Hz, C-1), 72.27 (d, $^2J_{POC}$ 5.8 Hz, OCH-iPr), 72.17 (d, $^2J_{POC}$ 5.7 Hz, OCH-iPr), 49.93 (d, $^2J_{PC}$ 24.2 Hz, C-5), 24.05, 23.87, 23.76, 23.62 (CH_3-iPr), 18.47 (CH_3), 17.95 (CH_3-exo), 15.68 (C-6), 11.08 (CH_3-endo), -1.05 (s, with satellites for $^1J_{CSi}$ at 53 Hz); (minor) δ_H 4.72 (2H, m, OCH-iPr), 1.58 (3H, d, $^5J_{PH}$ 1.7 Hz, CH_3), 1.33 - 1.28 (12H, m, CH_3-iPr), 1.24 (3H, s, CH_3-exo), 0.81 (3H, s, CH_3-endo), 0.22 (9H, s, $SiCH_3$ with satellites for $^2J_{CSi}$ at 6.7 Hz); δ_P 4.67 s; δ_C 158.58 (d, $^1J_{PC}$ 211.9 Hz, C-4), 85.21 (d, $^3J_{PC}$ 5.8 Hz, C-1), 71.65 (d, $^2J_{POC}$ 6.3 Hz, OCH-iPr), 24.00, 23.81, 23.67, 23.53 (CH_3-iPr), 23.53 (CH_3), 19.43 (CH_3-exo), 16.53 (C-6), 13.28 (CH_3-endo), 1.19 (s, with satellites for $^1J_{CSi}$ at 50.0 Hz); ν_{max} (mixture) 2979, 2935, 2876, 2237, 1736, 1547, 1467, 1454, 1386, 1375, 1252, 1179, 1142, 1106, 998, 928, 842, 770, 733, 626, 585 cm^{-1}.

5-(2'-Bromoisopropyl)-3-(diisopropoxyphosphoryl)isoxazole (24) and 3-(diisopropoxyphosphoryl)-5-isopropenylisoxazole (25)

Methyl lithium (6.98 ml, 1.5 M, 1.1 mol.equiv.) was added at -78 °C under urgon to a stirred solution of 1,1-dibromo-2-chloro-3,3-dimethylcyclopropane[21] (2.5 g) in dry ether (10 ml). After 30 min, this was treated with water (1.5 ml) and with a solution of (diisopropoxyphosphoryl)nitrile oxide (0.85 g, 0.43 mol.equiv.) containing triethylamine hydrochloride in dry ether (20 ml). The mixture was stirred for 2 h at -78 °C and then allowed to reach room temperature. After 16 h, the triethylamine hydrochloride was filtered off and the solvent was evaporated to give as a pale yellow oil which was purified by chromatography to give a major product characterised as 3-(diisopropoxyphosphoryl)-5-(2'-bromo-isopropyl)isoxazole (0.82 g, 56 %) which showed δ_H 6.42 (1H, d, $^3J_{PH}$ 0.8 Hz, H-4), 4.75 (2H, m, OCH- iPr), 2.07 (6H, s, CH_3), 1.35 - 1.25 (12H, 2 x d, $^3J_{HH}$ 7.0 Hz, CH_3-iPr); δ_P 1.41 s; δ_C 175.92 (d, $^3J_{PC}$ 10.2 Hz, C-5), 156.83 (d, $^1J_{PC}$ 213.9 Hz, C-3), 102.46 (d, $^2J_{PC}$ 20.1 Hz, C-4), 72.69 (d, $^2J_{POC}$ 6.0 Hz, OCH-iPr), 49.85 (s, CBr), 32.75 (CH_3), 23.79, 23.74, 23.59, 23.51 (CH_3-iPr). An excess of 1,5-diaza- bicyclo[5.4.0]undene-5-ene (DBU) was then added. After 2 d, the DBU hydrobromide was filtered off and the solvent removed to give a quantitative yield of 3-(diisopropoxyphosphoryl)-5-isopropenylisoxazole as an oil which showed δ_H 6.39 (1H, s, $^3J_{PH}$ 0.8 Hz, H-

4), 5.75 (1H, s, CH=), 5.28 (1H, s, CH=), 4.75 (2H, m, OCH-iPr), 1.95 (3H, s, CH_3), 1.35 - 1.25 (12H, d.d, $^3J_{HH}$ 7.0 Hz, CH_3-iPr); δ_P 1.89 s; δ_C 170.98 (d, $^3J_{PC}$ 9.4 Hz, C-5), 156.93 (d, $^1J_{PC}$ 213.6 Hz, C-3), 129.95 (CH_2=), 118.00 (C=), 102.65 (d, $^2J_{PC}$ 20.1 Hz, C-4), 72.48 (d, $^2J_{POC}$ 6.0 Hz, OCH-iPr), 23.85, 23.79, 23.63, 23.55 (CH_3-iPr), 19.35 (CH_3).

3-(Diisopropoxyphosphoryl)-4,5-dichloro-6,6-dimethyl-1,2-oxazine-2,4-diene (28)

Methyl lithium (27.06 ml, 1.5 M, 1.4 mol.equiv.) was added at -78 °C under argon to a stirred solution of 1,1,2-trichloro-3,3-dimethylcyclopropane[21] (5.0 g) in dry ether (20 ml), allowed to reach 15 °C and then cooled to -78 °C and treated with water (2 ml). After 30 min the mixture was allowed to reach 20 °C, cooled to -40 °C and treated with (diisopropoxyphosphoryl)nitrile oxide (0.85 g, 0.14 mol.equiv.) in dry ether (40 ml). The mixture was stirred at 20 °C for 16 h, dried and evaporated. Chromatography gave a yellow oil, 3-(diisopropoxyphosphoryl)-4,5-dichloro-6,6-dimethyl-1,2-oxazine-2,4-diene (0.9 g, 64 %) which showed: δ_H 4.79 (2 H, m, OCH-iPr), 1.47 (6 H, s, CH_3), 1.33 (12 H, dd, $^3J_{HH}$ 7.0 Hz, CH_3-iPr); δ_C 149.83 (d, $^1J_{PC}$ 223.2 Hz, C-3), 137.88 (d, $^3J_{PC}$ 10.6 Hz, C-5), 115.94 (d, $^2J_{PC}$ 15.3 Hz, C-4), 80.63 (C-6), 72.75 (d, $^2J_{POC}$ 6.5 Hz, OCH-iPr), 72.63 (d, $^2J_{POC}$ 8.7 Hz, OCH-iPr), 23.70, 23.64 (CH_3-iPr), 23.44 (CH_3), 23.24, 23.14 (CH_3-iPr); δ_P 1.35 s; ν_{max} 3497, 2981, 2936, 1749, 1600, 1509, 1462, 1386, 1262, 1203, 1179.4, 1143, 1104, 1071, 993, 944, 925, 888, 884, 812, 773, 737, 645 cm^{-1}.

Methyl 4-methyl-2-oxo-3-pentenoate (29)

A mixture of 6,6-dimethyl-1-methoxycarbonyl-4-(diisopropoxyphosphoryl)-2-oxa-3-azabicyclo[3.1.0]-hex-3-ene and 6,6-dimethyl-4-(diisopropoxyphosphoryl)-5-methoxycarbonyl-2-azabicyclo[3.1.0]hex-3-ene (ratio 2.5:1; 0.75 g) was heated for 4 h at 100 °C and 10 mmHg. Chromatography gave a major product characterised as methyl 4-methyl-2-oxo-3-pentenoate[22] (0.23 g, 72 %) which showed δ_H 6.77 (1H, q, $^4J_{HH}$ 1.2 Hz, C(O)CH=), 3.85 (3H, s, OCH_3), 2.24 (3H, d, $^4J_{HH}$ 1.2 Hz, CH_3-cis), 2.02 (3H, d, $^4J_{HH}$ 1.2 Hz, CH_3-trans); δ_C 181.54 (C(O)CH=), 165.07 (CH_3OC=O), 162.88 (CH=), 119.04 (C=), 52.80 (CH_3O), 28.46 (CH_3-trans), 21.82 (CH_3-cis); ν_{max}: 1732, 1689 cm^{-1}.

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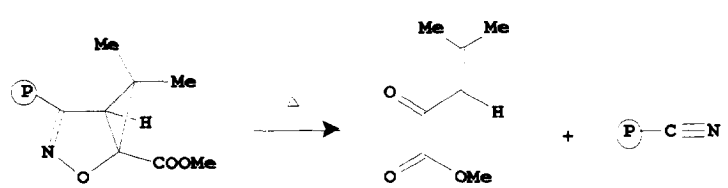
Compound (**16**) decomposed on heating to give methyl 4-methyl-2-oxo-3-pentenoate (**29**):



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