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N,O-HETEROCYCLICS—14[1]

CONVERSION OF ISOXAZOLIDINES INTO α,β-ENONES

ANGELO LIGUORI, GIOVANNI SINDONA and NICOLA UCCELLA
Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata di Rende (CS), Italy

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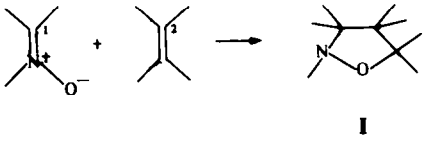
Abstract—Substituted isoxazolidines formed by 1,3-dipolar cycloaddition of nitrones to alkenes undergo ring-opening elimination to α,β-enones when treated with trimethyl phosphate. The reaction involves initial alkylation giving the isoxazolidinium intermediate which collapses to the α,β-enone by a Hofmann-like elimination having an orientation controlled by electronic factors, the first step being rate-determining.

Alternative reaction paths leading to the formation of α, β-unsaturated ketones can be usefully exploited.[2] Although the aldol condensation and related carbonyl processes mantain a fundamental role in the organic synthesis, there are definite restrictions to the widespread application of the classical route to α, β-enones, also through β-hydroxyketonic precursors.[3]

A different way of overcoming some of the limitations of the classical procedure involving carbonyl condensation followed by elimination, has been developed by "directed aldol" reactions[5] and by the application of ketophosphonium derivatives.[6]

Since the α,β-enonic adducts are useful in synthetic organic chemistry,[7] alternatives to the carbonyl condensation have been recently proposed. This leads to aldol derivatives through the exploitation of 1,3-dipolar cycloaddition as the principal step towards the carbon–carbon bond formation.[8,9]

The novel approach, shown in Scheme 1, is here



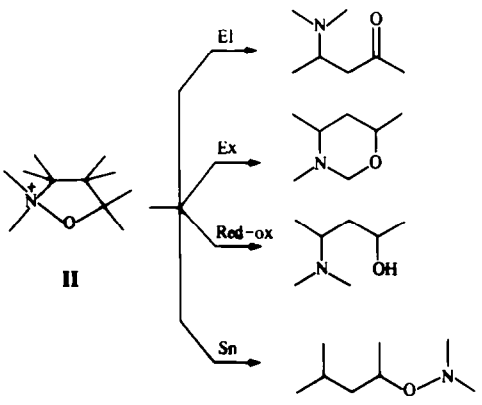
I

Scheme 1.

expanded to the substituted isoxazolidines I obtained by the reaction of nitrones with alkenes.[10,11] The appropriate selection of reactants, whose variety is sufficient large to allow a wide area of applicability, can lead to an ample range of possible carbon skeletons.

Applications of the dipolar adducts I to the field of organic synthesis have only recently developed,[1,11] mainly to production of organic natural products.[12,17] However, the substituted isoxazolidines I should be amenable to subsequent chemical modification which opens up new methods for transforming the N,O-heterocyclic five-membered nucleus into open-chain derivatives.[1,11-17] The chemistry of the isoxazolidine nucleus must, therefore, be thoroughly examined in order to develop the suitable methods for the ring-opening of the cyclic precursors I. Novel reaction paths have been discovered treating the N,O-heterocycles I with m-chloroperbenzoic acid[19] and their methiodides with lithium aluminium hydride (LAH),[1,11] giving N-hydroxy-1,3-tetrahydrooxazines[19] and to N,N,O-trisubstituted hydroxylamines,[1,11] respectively.

The quaternary ammonium cation II, formed by independent procedures,[1,11] can undergo chemical modification which involves overall processes leading to the five-membered ring-opening, as shown in Scheme 2.



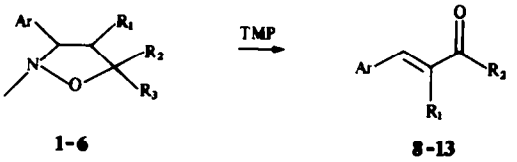
II

Scheme 2.

Similar cyclic ammonium cations have shown analogous chemistry in their transformation induced by basic attack.[18] Thus, the most competitive reaction process observed from the five-membered nucleus was the ring-opening substitution (S_N in Scheme 2 for the system here studied) with the corresponding ring-opening olefin-forming elimination (Hofmann-like degradation described El in Scheme 2 for system II) being a minor process.[18]

All the isoxazolidinium ring transformation so far described[1,10-17] have required a two-step sequence of reactions, i.e. alkylation to the quaternary ammonium precursor followed by various reaction procedures leading to the products of Scheme 2, even

when precursor II undergoes ring-opening by basic attack.[19,20] The treatment of substituted isoxazolidines I with trimethylphosphate (TMP)[21] has shown to be a one-flask conversion of isoxazolidines to α,β-enones (Scheme 3) with optimal efficiency.



Scheme 3.

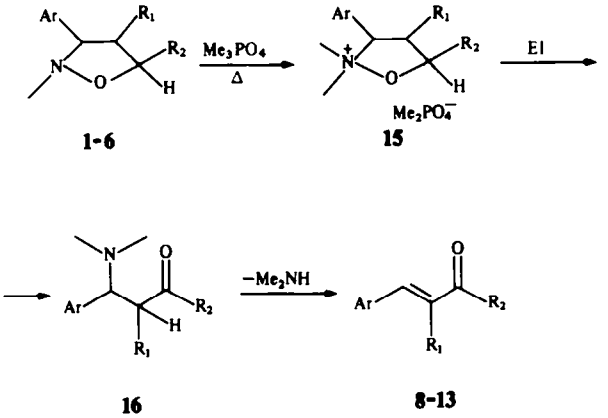
Other reaction products can, however, also be isolated depending on the substituents of the isoxazolidine precursor I (*vide infra*).

RESULTS AND DISCUSSION

The general procedure here adopted uses the substituted isoxazolidines I which can be heated with TMP in the presence or absence of the solvent (diglyme). The reaction products are isolated after the conventional work up and purified by short-column chromatography under slight pressure.[11] The TMP reagent was chosen for its aptitude to be capable of alkylating hindered carboxylic acids,[21] amides[22] and amines.[23] Even if phosphoric esters are known to be scarce alkylating reagent, this is not the case for the methyl and benzyl esters.[23] Tertiary amines undergo alkylation to quaternary ammonium salts of dimethylphosphoric acid, being only one methyl group to be utilizable.[23]

When the substituted isoxazolidines **1–6**, whose structure was ascertained by spectroscopic methods, are treated, as described in the experimental section, the α,β-enonic derivative **8–13**, reported in Scheme 4, can be obtained in sufficiently high yield, as shown in Table 1. The molecular structure of the reaction products **8–13** is well established by chemical and physical evidences.

The reaction of substituted isoxazolidines **1–6** with TMP can develop through a sequence of steps where the ring-opening of the reacting system is envisaged as a Hofmann degradation occurring on the quaternary ammonium intermediate **15** proposed in Scheme 4. The mechanistic path thus proposed should be, in this case, similar to those already verified in different reacting media.[19,20] In addition, the Hofmann-like reactivity of the activated isoxazolidines (**15**), can be also recognized when the N,O-heterocyclic functional group is similarly modified in a non-interacting environment by one electron removal under the mass spectrometric conditions.[24] In fact, according to Scheme 5, the ring-opening reaction of the long-lived cations

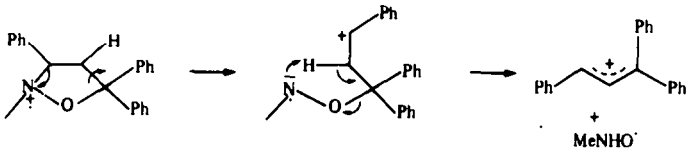


Scheme 4.

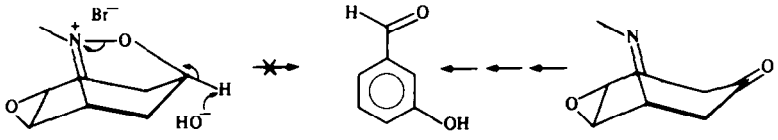
Table 1. The reaction of some isoxazolidines with Me_3PO_4

Compound*	Ar	R_1	R_2	R_3	Product*	Yield (%)
1	Ph	H	n-C_4H_9	H	8	92
2	Ph	H	n-C_5H_{11}	H	9	95
3	p-MeOC_6H_4	H	n-C_5H_{11}	H	10	97
4	Ph	- $CH_2(CH_2)_6CH_2$ -		H	11	90
5	Ph	H	Ph	H	12	95
6	p-MeC_6H_4	H	Ph	H	13	92
7	Ph	H	Ph	Ph	14	84

*Analytical and physico-chemical data for compounds 1-6 and 8-13 were consistent with those reported in the literature



Scheme 5.



17 18 19

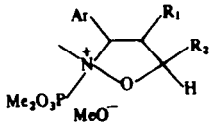
Scheme 6.

leading to the alkene fragment and to the hydroxylamine radical can be visualized as an intramolecular Hofmann-like degradation where the hydrogen atom on C-4 is attacked by the nitrogen atom of the opened intermediate.[24]

The mechanism of the ring-opening reaction, which can lead to α,β-enones in the condensed phase (Scheme 4), can be similar to that in the gas-phase[24] and in solution,[19,20] being also a Hofmann degradation activated by a base removal of the hydrogen atom at C-5, as described in Scheme 4. A similar reaction path has also been suggested for the transformation of scopinium bromide (**17**) into the m-hydroxybenzaldehyde (**18**) by base,[25] again quoted in the recent literature.[11,20] This proposed modification of the isoxazolidinium salt **17** reported in Scheme 6 was, however, found to be unsuccessful by two independent experiments,[26] since reaction of scopolamine with hydrogen peroxide gave scopolamine-N-oxide and not scopinium bromide, while scopinone (**19**) gave **18** (Scheme 6).

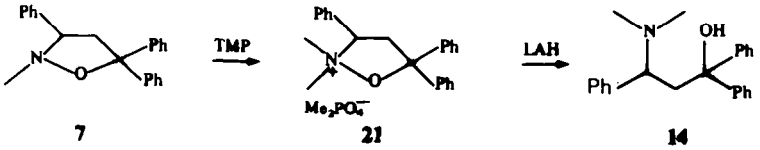
Therefore, according to the sequence proposed in Scheme 4, the ring-opening transformation of the N,O-heterocyclic nucleus with a five-membered structure, being the presursor of several α,β-enones, can be comprised into the chemistry of the isoxazolidinium system.[1,11,19,20]

If the proposed mechanism of Scheme 4 is actually involved in the substituted isoxazolidine transformation, so far observed under the TMP experimental conditions, some evidence of the quaternary ammonium cation (**15**) as intermediate during the sequence of steps outlined should be found, since this would greatly affect the nature of the free base which operates the Hofmann-like elimination of the now assumed precursor **15**. In fact, similar cationic intermediate could be suggested; the corresponding phosphamide (**20**) would be responsible for the ring- opening elimination of the isoxazolidinium reactant. Simple isoxazolidines have already shown to react with methylphosphonate to give the corresponding phosphonamide.[27]



20

The reaction of substituted isoxazolidines **7**, lacking hydrogen atoms at C-5, under the identical experimental conditions as those applied for **1–6** with TMP, should demonstrate the capability of the alkylating reagent to exert the same action found for other functional groups,[21,23] i.e. amines and amides. TMP treatment of **7** actually involve the quaternary ammonium salt, as is also demonstrated by the successive reaction with LAH reported in Scheme 7. When TMP is made to react with **7**, the isoxazolidinium salt can be analyzed by NMR. The ^{1}H spectrum shown signals which



7 21 14

Scheme 7.

were assigned to the protons of the isoxazolidinium salt examined (see Experimental).

In addition, reaction of **7** with TMP followed by the LAH reduction gives ring-opening of the substituted isoxazolidine **7** through the isoxazolidinium phosphate **21** undergoing the red-ox cleavage of the N–O bond yielding the 1,3-amino-alkanols **14**. This chemical behaviour has above been recognized to be one of the fundamental ring-opening reaction of the isoxazolidinium system II, as shown in Scheme 2. This experiment clearly indicates that the TMP reagent is able to alkylate the cyclic hydroxylamine derivative.

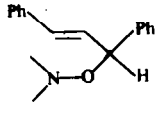
Direct evidence of the intermediate ammonium cation **15** has been sought in the model ring-opening of precursor **5**. TMP treatment of **5** was carried out as described in the experimental section with the top of the condenser connected with the gas inlet system vessel of a mass spectrometer. The gas was then analyzed with the aid of the MIKE method also. In fact, the mass spectrum of the gaseous mixture derived from the reaction of **5** with TMP showed several signals from *m/z* 59 towards lower masses. Those of interest were at *m/z* 45 (92%) and at *m/z* 44 (100%). Since the $C_2H_6N^+$ (*m/z* 44) cations are well investigated,[28] the metastable ion spectrum of *m/z* 44 from the gaseous mixture studied has been performed. The MIKE spectrum of the *m/z* 44 revealed three peaks which were assigned to the metastable transitions leading to the fragment ion *m/z* 43 (8%), *m/z* 42 (12%) and *m/z* 18 (80%) from the precursor ion $C_2H_6N^+$ (*m/z* 44) corresponding to the elimination of hydrogen radical, hydrogen molecule and acetylene. The metastable transitions originated from $C_2H_6N^+$ and their relative intensity are consistent with the dimethylamine precursor being present into the gaseous mixture thus analyzed after the ejection from the reaction where the isoxazolidine **5** was heated with TMP.

The experimental results clearly demonstrate that the dimethylaminoketone **16** of Scheme 4 is indeed an intermediate in the ring transformation of the substituted isoxazolidines here investigated. This intermediate, carefully sought as described in the experimental section, but never isolated, can be derived from basic attack, for instance, of the dimethyl phosphate anion onto the hydrogen atom at C-5, thus giving rise to the ring-opening step of the overall process. This assumption requires that, as already shown for the isoxazolidinic precursor **7**, the TMP, actually exerting the alkylating activity on the N,O-heterocycles **1–6**, should then be able to give rise to the Hofman-like elimination. Therefore, an independent chemical evidence could be found by an additional mechanistic check. The isoxazolidinium intermediate **15** with Ar=R_2=Ph and R_1=H can be alternatively obtained[1,11] with the counterion being the iodide one. This precursor was reacted with NaH_2PO_4 and $Na(Me)_2PO_4$, both bases being comparable in pK with the conjugate acid is concerned, i.e. 2.1 and 1.3[29] respectively, while the methoxide anion eventually acting on the intermediate **20** would be a much stronger base (pKa = 16 for the conjugate acid) than the phosphate. The reaction of the model isoxazolidinium iodide with both the sodium phosphate quoted above in dioxane gave the expected α,β-enone **12** in high yield (80%). The concomitant action of the iodide as base attacking the hydrogen atom on the C-5 of the N,O-heterocyclic ammonium derivative can be excluded, since the molecule was not capable of undergoing any ring-opening reaction of the same type as precursor II, as shown by the same experiment carried out with the model isoxazolidinium iodide itself without additional reagent in the identical medium. In fact, the starting isoxazolidinium iodide was recovered essentially unaltered also after treatment in diglyme.

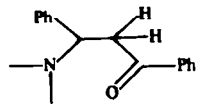
The latter experimental data on the reactivity of the isoxazolidinium precursor **15** with the phosphate anions in the chosen solvent demonstrate, also, that the rate-determining step for the general ring-opening transformation of the substituted isoxazolidines **1–6** to the α,β-enones **8–13** is the formation of the quaternary ammonium cation **15**. In fact, similar reaction has been attempted with the same reagents, i.e. **5** and TMP, and tested with the reaction mixture in different solvents (THF, dioxane, or toluene in sealed vial at 120°C), recovering starting material.

This novel method of production of α,β-enones from substituted isoxazolidines directly with TMP, involving a one-flask synthesis leading to almost quantitative yield, is, therefore, characterized by a complex mechanism (Scheme 4), where the first step of the process is kinetically controlled with the last step driven to completion because of the evolution of the dimethylamine gas. That the intermediate step similar to the Hofmann degradation should develop as already experimentally ascertained is clearly indicated by kinetic and thermodynamic considerations too.

The alternative Hofmann-like elimination onto the isoxazolidinium intermediate obtained by methylation with TMP of isoxazolidines should require the basic attack onto the hydrogen atom of C-4, giving rise to the substituted hydroxylamine **22**. This reaction product would be thermodynamically less favoured than the β-aminoketone **23**, as shown by the calculation below reported.



22



23

To acquire additional insight into the effect controlling the site selectivity of the Hofmann-like step within the overall conversion of the substituted isoxazolidines **1–6** to the α,β-enones 8–13 of Table 1, a model energy diagram has been calculated. The approximate standard heat of formation (ΔH_f^0) for the original isoxazolidine **5**, taken as a model system (+ 53.4 Kcal mol^{-1}), and the TMP (− 258.3 Kcal mol^{-1}) reagent has been derived as previously described.[1] Similar calculations have been performed for the intermediate isoxazolidinium cation **24** with its counteranion dimethylphosphate (− 251.4 Kcal mol^{-1}), the assumed competing reaction product **22** (+ 56.9 Kcal mol^{-1}), having fully substituted hydroxylamine structure, with the resulting dimethylphosphoric acid (− 263.3 Kcal mol^{-1}) and the actually-formed intermediate

β-aminoketone **23** (+ 6.4 Kcal mol^{-1}) with the same phosphoric acid. The resulting ΔH_f^0 data for **5**, **22** **23**, **24** and the phosphoric derivatives have been obtained by the application of the method for estimating heats of formation based on the isodesmic substitution.[31-34]

CONCLUSION

The 1,3-dipolar cycloaddition between nitrones and alkenes has been applied to the synthesis of α,β-enones. The one-step sequence employs the substituted isoxazolidines as precursors of the synthetic equivalent approach of the condensation of aldehydes with ketones, whose enolates must be kinetically controlled. The new "directed" condensation, involving the cycloadducts treated with TMP, provides the kinetically controlled product, having α,β-enonic structure, in the situation where the equivalent unsymmetrical ketone and competition for formation of the isomeric enolates actually experienced.

The overall process of substituted isoxazolidines with TMP developes through a sequence of steps, involving the initial alkylation to an isoxazolidinium intermediate which collapses to the α,β-enone derivative by a Hofmann-like elimination whose orientation is controlled by electronic factors. The experiments carried out allow the definition of the energy profile for the total conversion from isoxazolidines to α,β-enones, where the first reaction step must be rate determining.

The synthesis of the α,β-enones thus involves simple precursors whose C-1 and C-2 substituents appear on the alkene and C-3 on an aldehyde, while the oxygen atom arises from the methylhydroxylamine whose nitrogen atom is lost as dimethylamine.

The 1,3-dipolar cycloaddition method for the synthesis of α,β-enones appears to be a simple and efficient alternative to classical procedures.

EXPERIMENTAL

Melting points were obtained with a Kofler hotstage apparatus and are uncorrected. Elemental analyses were carried out in a Perkin–Elmer 240 Elemental Analyser. IR spectra were recorded on a Perkin–Elmer 377 instrument. ^{1}H NMR spectra were obtained by means of a Varian EM 360 spectrometer for 10% solns in ^{2}H-chloroform with TMS as internal standard. Peak positions are reported in terms of δ(ppm) downfield from TMS. Mass spectra were determined on a Varian MAT CH-5DF mass spectrometer, equipped with a Spectro System SS-100 computer, operating at 70 eV and 3 KV. Samples were introduced via the gas-inlet system for the gas mixture and the direct inlet system for solids and liquids, the sample probe temperature being in the region of the m.p.s of the crystals or kept as low as possible for the more volatile products.

Substituted isoxazolidines were prepared according to previously reported methods.[24]

General procedure for α,β-enone formation from substituted isoxazolidines and trimethylphosphate

(1) The appropriate compound (1.84×10^{-3} mol) in dry diglyme (2 ml) was refluxed for 2 h with trimethylphosphate (2.0×10^{-3} mol). The homogeneous reaction mixture was then diluted with ether (20 ml) and washed several times (normally five) with portions (30 ml) of water. The ether extract was dried (Na_2SO_4) and the solvent removed under vacuum. The product recovered was then purified by column chromatography under slight pressure[11] to give the α,β-enone of Table 1 with almost quantitative yield.

(2) The alternative procedure devised refers to the conversion of the isoxazolidine in absence of solvent.

The N,O-five membered heterocyclic starting material ($1.25 \cdot 10^{-3}$ mol) was added to TMP (1.43×10^{-3} mol) and the mixture heated at 150°C under stirring for 1.5 h. The reaction mixture was then extracted with benzene (three times). The extracts, after removal of the solvent under vacuum, gave the α,β-enonic products with a slight increase (10% ca) of yield compared to the above quoted procedure.

The organic material left after benzene extraction was treated with $NaHCO_3$ sat. soln. After the abundant CO_2 evolution, the mixture was $CHCl_3$ extracted in order to check the possible presence of any aminoketone freed by the basic treatment. TLC/MS of the organic residue after solvent removal confirmed the absence of any aminoketone.

The same experiment was carried out in different condition, i.e. solvent and temperature. When the isoxazolidine **5** with TMP (1 : 1) was refluxed for 7 h in THF, in dioxane and in toluene (toluene soln at 120° in vials) the starting material was recovered nearly quantitatively.

Reaction of the isoxazolidinium iodide from **5** *at different conditions*

4.0×10^{-4} mol of **5** were refluxed in THF (5 ml) for 7 h. The reaction mixture was solvent removed to give starting material nearly quantitatively. Similar treatment was performed in diglyme (4 ml) for 4 h and worked up as described above with $CHCl_3$ extraction to give, after solvent removal, 89% of starting material only. The same isoxazolidinium iodide (2.1×10^{-3} mol) in dioxane (25 ml) is added of $Na_3PO_4 \cdot 12H_2O$ (2.3×10^{-3} mol) and refluxed for 7 h. After solvent removal under vacuum, the reaction mixture was treated with ether, washed with water and dried over Na_2SO_4 to give the calcone **12** (80% yield). The same experiment was performed with $Na(Me)_2PO_4$ (2.3×10^{-3} mol) to give very similar results.

Reaction of 2*-methyl-*3,5,5*-triphenylisoxazolidine* (**7**) *with TMP*

Compound **7** (1.2×10^{-3} mol) and TMF (1.3×10^{-3} mol) was heated for 1 h at 150°. A portion of the reaction mixture was ^{1}H NMR analyzed to give the following data: δ($CDCl_3$) 7.8–7.2 (15H, m, ArH), 4.9–4.7 (1H, m, H-3), 3.70 [6H, d, $J_{P-C} = 11.0$ Hz, $-O_2P(CH_3)_2$], 3.39 [3H, s, $-\overset{+}{N}(CH_3)_2$], 3.18 [3H, s, $-\overset{+}{N}(CH_3)_2$] and 3.1 – 2.9 (2H, m, $4H_2$).

The remaining portion of the reaction mixture was suspended in dry THF, added of LAH ($1.1 \cdot 10^{-2}$ mol) and refluxed for 7 h. After cooling and cautious addition of NaOH 10% solution, the reaction product was CH_2Cl_2 extracted, dried and the solvent removed under vacuum to give the 3-dimethylamino-1,1,3-triphenylpropanol (**14**) with 80% overall yield. M.p. 140–142°, Found: C, 83.43; H, 7.51; N, 4.17. $C_{23}H_{25}NO$ requires: C, 83.38; H, 7.55; N, 4.23%; ν_{max} 3290(–OH broad), 3060, 3040, 2915, 2860, 1600, 1480, 1450, 1250, 1200, 1100, 1060, 1030, 900, 750 and 700 cm^{-1}; δ($CDCl_3$) 8.0–7.6 (15H, m, ArH), 3.65 (1H, dd, H-3), 2.7–2.3 (2H, m, H-2), 2.02 (6H, s, $-N(CH_3)_2$; *m/z* 331 (M^+, 14%), 270(13), 182(13), 179(20), 148(13), 147(14), 117(16), 103(100, b. peak), 102(25), 77(58).

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