244 (M^+, 8), 199 (5), 175 (10), 174 (86), 167 (3), 121 (48), 93 (21), 92 (10), 53 (100), 52 (68).

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Registry No. 1, 75347-13-6; 2, 75347-14-7; 3, 75347-15-8.

C-Phosphonoketenimines, Characterization and Synthetic Application to Heterocycles

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In recent years, the synthetic applications of multifunctional heteroallenes[1] have been widely investigated. In spite of extensive developments in the chemistry of modified ketenes and isocyanates,[2] little attention has been paid to the uses of ketenimines.[3] From a synthetic point of view it was of interest to synthesize a ketenimine bearing a phosphoryl group[4] as an eliminatable substituent.

Previously we reported[5] a facile preparation of a *C*-phosphonoketenimine[6] which acts as a novel annelation reagent. In this paper we report further investigation of these reactions and their synthetic utility for the preparation of heterocycles.

The ketenimines **2** were successfully synthesized by the dehydration of diethyl (carbamoylalkyl)phosphonates (**1**) prepared from α-halo amides and diethyl phosphite[7] (Scheme I). The dehydration proceeded smoothly with triphenylphosphine, bromine, and triethylamine in dichloromethane at room temperature.[8] For example, *N*-ethylmethyl(diethylphosphono)ketenimine (**2a**), a stable and colorless liquid, was isolated in 82% yield by distillation. The IR spectra of **2a** and **2b** display the characteristic absorptions at 2030 cm^{-1} arising from C=C=N groups. The ^1H NMR spectrum of **2a** showed two splittings at δ 1.69 (d, J_{HP} = 13.6 Hz) and δ 3.51 (dq, J_{HH} = 7.0 Hz, J_{HP} = 4.8 Hz), which were assignable to the allenic methyl and *N*-methylene protons, respectively. The observations of no change in these coupling constants in the 60- and 100-MHz NMR spectra showed that the splittings are not due to the nitrogen atom[9] but to the long-range

Scheme I

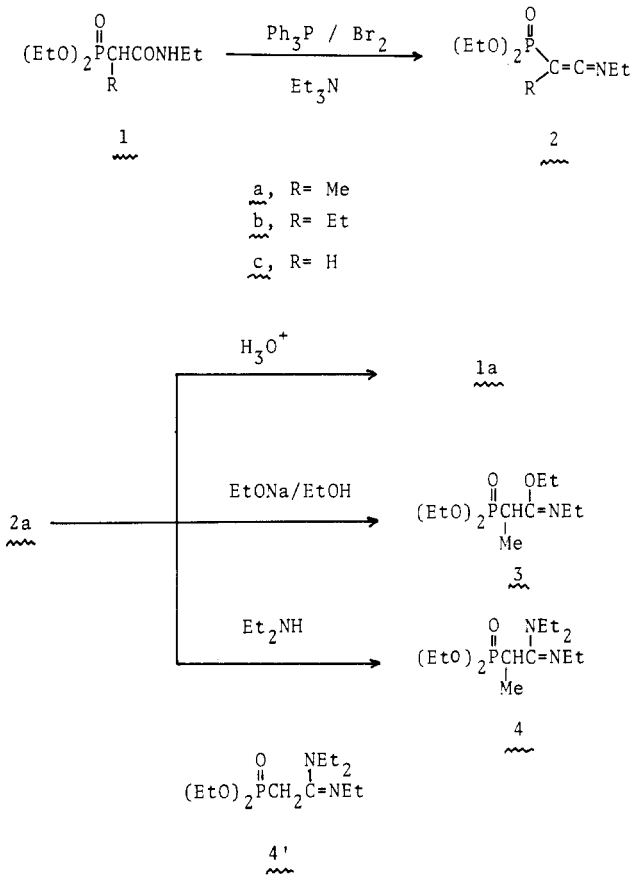
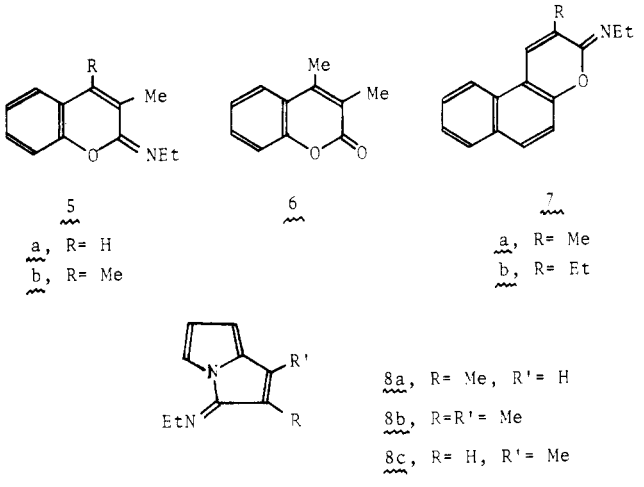


Chart I



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(7) Diethyl (carbamoylalkyl)phosphonates (**1**) are also prepared in the same yields by the Arbuzov reaction: Speziale, A. J.; Freeman, R. C. *J. Org. Chem.* **1958**, *23*, 1883.
(8) Bestmann, H. J.; Lienert, J.; Mott, L. *Justus Liebigs Ann. Chem.* **1968**, *718*, 24.
(9) Jochims, J. C.; Anet, F. A. L. *J. Am. Chem. Soc.* **1970**, *92*, 5524.

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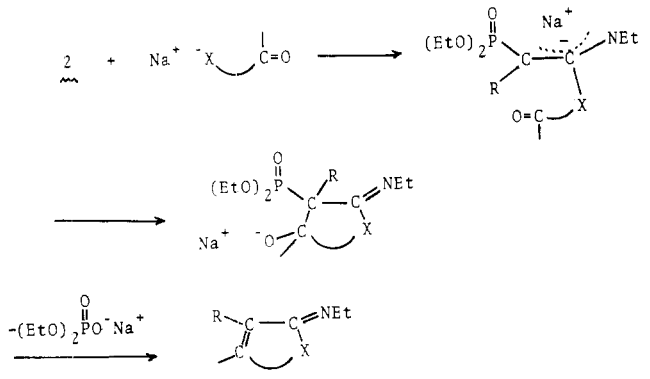
Scheme II



coupling between the protons and phosphorus nuclei of the substituents. The same result was observed for **2b**. Some chemical evidence of **2a** is as follows. Treatment of **2a** with a catalytic amount of hydrochloric acid in aqueous tetrahydrofuran gave the amide **2a**, and the addition of ethanol and diethylamine to **2a** gave the imidate **3** and amidine **4** in good yields, respectively. Although the strong absorption band at 2080 cm^{-1} in the IR spectrum clearly showed the formation of **2c** in the reaction mixture, our attempt to isolate it was unsuccessful. Addition of diethylamine to the above solution of **2c** gave the amidine **4'** in 13% yield.

The reaction of phosphonoketenimine **2a** with the sodium salt of salicylaldehyde and *o*-hydroxyacetophenone in dimethylformamide at 80 °C gave 2-(ethylimino)dihydropyrans **5a** and **5b** (Chart I). Acid hydrolysis of **5b** produced 2,3-dimethylcoumarin (**6**) in a high yield. Similarly 2-(ethylimino)-1-oxa-1,2-dihydrophenanthrenes **7a** and **7b** were obtained when **2a** and **2b** were treated with the sodium salt of 2-hydroxy-1-naphthaldehyde. The structures of these heterocycles were established by spectral data. Furthermore, 3-(ethylimino)pyrrolizines **8a** and **8b** were prepared from **2a** by employing the sodium salts of 2-acylpyrroles, in a process analogous to that of Schweizer and Light with a vinylphosphonium salt.[10] While the ketenimine **2c** was also used without purification for the synthesis of **8c**, the reaction resulted in a poor yield. The stability of the pyrrolizines **8** depends on the substituents. The pyrrolizine **8b** was isolated as a stable crystal, but **8a** and **8b** darkened gradually on being allowed to stand.

The proposed mechanism for the formation of heterocycles is shown in Scheme II; the anionic species would attack the center carbon atom of the ketenimines that might be activated by the phosphoryl group, and the subsequent intramolecular Horner–Emmons reaction[11] would proceed smoothly because the negative charge is stabilized in the intermediate by the imino group.[12]

In conclusion, *N*-ethylmethyl- and -ethyl(diethylphosphono)ketenimines are easily prepared and relatively stable, and they behave as good acceptors in the reactions with nucleophiles, such as alcohols and amines, to give the adducts bearing phosphoryl groups. Furthermore, it is a more significant matter that the *C*-phosphonoketenimines can be used as precursors to heterocycles, owing to the character of the substituents, the eliminatable phosphoryl groups.

(10) Schweizer, E. E.; Light, K. K. *J. Org. Chem.* **1966**, *31*, 870.
(11) Annelations with vinylphosphonates based on the intramolecular Horner–Emmons reaction are described in the following papers: (a) Kleshick, W. A.; Heathcock, C. H. *J. Org. Chem.* **1978**, *43*, 1256; (b) Minami, T.; Suganuma, H.; Agawa, T. *Chem. Lett.* **1978**, 285.
(12) Nagata, W.; Hayase, Y. *J. Chem. Soc. C* **1969**, 460.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a JASCO IR-E or JASCO IRA-1 spectrometer. ^1H NMR (internal Me_4Si) spectra were taken in $CDCl_3$, unless otherwise stated, on JEOL JMN-C-60HL, JNM-PMX-60, and JMN-PS-100 spectrometers. Mass spectra were obtained from a Hitachi RMU-6E or JEOL JMS-01SG-2 spectrometer on line to a JEOL JEC-6 spectrum computer. Gas chromatographic–mass spectral data were obtained from a JMS-D300 mass spectrometer attached to JGC-20KD gas chromatograph.

Diethyl (Carbamoylalkyl)phosphonates (1a–c). To a suspension of sodium hydride (19.2 g, 0.4 mol, 50% in oil) in tetrahydrofuran (100 mL) was added dropwise diethyl phosphite (55.2 g, 0.4 mol) under a nitrogen stream. After the evolution of hydrogen was ceased, *N*-ethyl-α-chloropropionamide (48.6 g, 0.4 mol) dissolved in tetrahydrofuran (50 mL) was added dropwise, and the solution was heated under reflux for 1 h. Then the solvent was removed, and the residue was acidified with hydrochloric acid. The resulting aqueous solution was extracted with chloroform, and the organic layer was dried (Na_2SO_4). Concentration and distillation at 120–122 °C (1 mm) gave diethyl [α-(ethylcarbamoyl)ethyl]phosphonate (**1a**) in 77% (73.4 g) yield. In a similar manner, diethyl [(ethylcarbamoyl)methyl]phosphonate (**1c**) was obtained in 73% yield; bp 127 °C (1 mm).

Diethyl [α-(ethylcarbamoyl)-*n*-propyl]phosphonate (**1b**) was prepared by ethylation of **1c** with ethyl iodide in the presence of sodium hydride in 68% yield; bp 130–131 °C (1 mm).

Synthesis of *N*-Ethylmethyl- and -ethyl(diethylphosphono)ketenimines 2a and 2b. To a solution of triphenylphosphine (65.5 g, 0.25 mol) in dichloromethane (300 mL) were added bromine (40 g, 0.25 mol), triethylamine (150 mL), and amide **1a** (47.4 g, 0.2 mol). The solution was stirred for 6 h under a nitrogen stream and allowed to stand overnight at room temperature. After removal of the solvent, the residue was treated with petroleum ether and filtered. Concentration and distillation of the residual liquid at 86–90 °C (1 mm) gave **2a**: 82% yield (35.9 g); IR 2030 cm^{-1}; NMR δ 1.32 (t, 9, CH_3CH_2), 1.69 (d, 3, CH_3C=, J_{HP} = 13.6 Hz), 3.51 (dq, 2, CH_3CH_2N, J_{HH} = 7.0 Hz, J_{HP} = 4.8 Hz), 4.07 (dq, 4, CH_3CH_2, $J_{HH} = J_{HP}$ = 7.0 Hz); mass spectrum, *m/e* 219 (M^+). Anal. Calcd for $C_9H_{18}NO_3P$: C, 49.31; H, 8.27; N, 6.39. Found: C, 48.91; H, 8.45; N, 6.31.

In a similar manner, **2b** was obtained in 40% yield: bp 114–119 °C (2 mm); IR 2030 cm^{-1}; NMR δ 0.9–1.45 (m, 12, CH_3CH_2), 2.03 (dq, 2, CH_3CH_2C=, J_{HH} = 7.5 Hz, J_{HP} = 4.35 Hz), 4.04 (dq, 4, CH_3CH_2O, $J_{HH} = J_{HP}$ = 7.5 Hz); mass spectrum calcd for $C_{10}H_{20}NO_3P$ *m/e* 233.1181, found *m/e* 233.1193.

Hydrolysis of 2a. A solution of **2a** (2.19 g, 10 mL) in tetrahydrofuran (10 mL) and water (10 mL) containing 1 drop of concentrated hydrochloric acid was stirred for 1 h at room temperature. After evaporation of the solvent, the aqueous solution was extracted with chloroform, and the organic layer was dried (Na_2SO_4). Removal of the solvent gave amide **1a** in 87% (2.07 g) yield.

Reaction of 2a with Ethanol. A solution of **2a** (2.19 g, 10 mmol) in ethanol (10 mL) containing a catalytic amount of sodium ethoxide was heated under reflux for 2 h. After removal of the excess ethanol the residual liquid was distilled to give **ethyl *N*-ethyl-α-(diethylphosphono)propionimidate (3)**: 64% yield (1.70 g); bp 104–107 °C (2 mm); IR 1665 cm^{-1}; NMR δ 0.98–1.60 (m, 15, CH_3CH_2), 2.93–3.45 (m, 3, CH_3CH_2N, CH_3CHP), 3.83–4.33 (m, 6, CH_3CH_2O); mass spectrum calcd for $C_{11}H_{24}NO_4P$ *m/e* 265.1443, found *m/e* 265.1443.

Reaction of 2a with Diethylamine. A mixture of **2a** (4.57 g, 21 mmol) and diethylamine (1.53 g, 21 mmol) was stirred without solvent for 30 min at ambient temperature. Distillation gave ***N,N*-diethyl-*N'*-ethyl-α-(diethylphosphono)propionamidine (4)**: 93% yield (5.70 g); bp 109–115 °C (1 mm); IR 1605 cm^{-1}; NMR δ 0.93–1.75 (m, 18, CH_3CH_2), 2.70–3.68 (m, 7, CH_3CH_2N, CH_3CHP), 3.69–4.39 (m, 4, CH_3CH_2O); mass spectrum, calcd for *m/e* 292.1914, found *m/e* 292.1899.

Reaction of 2c with Diethylamine. To a solution of *N*-ethyl(diethylphosphono)ketenimine (**2c**), generated from **1c** (14 g, 63 mmol), triphenylphosphine (19.7 g, 75 mmol), bromine (3.85 mL, 75 mmol), and triethylamine (81 mL) in 200 mL of dichloromethane, was added diethylamine (6.2 mL, 63 mmol) at

room temperature. After a workup similar to that described before, ***N,N*-diethyl-*N'*-ethyl-α-(diethylphosphono)acetamidine (4')** was obtained: 13.2% yield (2.2 g); bp 114–116 °C (2 mm); IR 1610 cm^{-1}; NMR δ 0.98–1.55 (m, 15, CH_3CH_2), 3.0 (d, 2, CH_2P, J_{HP} = 21.8 Hz), 3.43 (q, 6, CH_3CH_2N), 4.13 (dq, 4, CH_3CH_2O); mass spectrum calcd for $C_{12}H_{27}N_2O_3P$ *m/e* 278.1759, found *m/e* 278.1774.

Synthesis of Heterocyles 5, 7, and 8. Typical Procedure. An equimolar amount of ketenimine **2** and the sodium salt of the aromatic carbonyl compound in dry dimethylformamide was heated for 3–5 h at 80–100 °C. The reaction mixture was poured into ice–water and extracted with chloroform. The organic layer was washed with water and brine before being dried (Na_2SO_4). After removal of the solvent the residue was distilled or recrystallized to give pure products.

2-(Ethylimino)-3-methyl-2*H*-benzopyran (5a): yield 52%; bp 78–81 °C (1 mm); IR 1650 cm^{-1}; NMR δ 1.20 (t, 3, CH_3CH_2), 2.07 (s, 3, CH_3), 3.56 (q, 2, CH_3CH_2), 6.76 (s, 1, HC=), 6.83–7.23 (m, 4, Ar); mass spectrum, *m/e* 187 (M^+). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.67; H, 6.97; N, 7.37.

2-(Ethylimino)-3,4-dimethyl-2*H*-benzopyran (5b): yield 73%; bp 120–121 °C (1 mm); mp 31–32 °C; IR 1645 cm^{-1}; NMR δ 1.25 (t, 3, CH_3CH_2), 2.08 (s, 6, CH_3C=), 3.50 (q, 2, CH_3CH_2), 6.8–7.5 (m, 4, Ar); mass spectrum, calcd for $C_{13}H_{15}NO$ *m/e* 201.1155, found *m/e* 201.1154.

2-(Ethylimino)-3-methyl-1-oxa-1,2-dihydrophenanthrene (7a): yield 54%; mp 105–108 °C; IR 1650 cm^{-1}; NMR δ 1.26 (t, 3, CH_3CH_2), 2.14 (d, 3, CH_3C=), 3.54 (q, 2, CH_3CH_2), 7.1–8.2 (m, 7, Ar); mass spectrum, calcd for $C_{16}H_{15}NO$ *m/e* 237.1155, found *m/e* 237.1143.

2-(Ethylimino)-3-ethyl-1-oxa-1,2-dihydrophenanthrene (7b): yield 42%; mp 75–77 °C; IR 1645 cm^{-1}; NMR δ 1.36 (t, 6, CH_3CH_2), 2.58 (q, 2, CH_3CH_2C=), 3.53 (q, 2, CH_3CH_2N), 7.12–8.25 (m, 7, Ar); mass spectrum, calcd for $C_{17}H_{17}NO$ *m/e* 251.1311, found *m/e* 251.1290.

2-Methyl-3-(ethylimino)pyrrolizine (8a): yield 51%; bp 85–90 °C (3 mm); IR 1650 cm^{-1}; NMR δ 1.41 (t, 3, CH_3CH_2), 1.96 (s, 3, CH_3C=), 3.57 (q, 2, CH_3CH_2), 5.76 (d, 1, H-7, J_{HH} = 3.6 Hz), 6.05 (dd, 1, H-6, J_{HH} = 3.6, 3.0 Hz), 6.46 (m, 1, H-1), 6.90 (d, 1, H-5, J_{HH} = 3.0 Hz); mass spectrum, *m/e* 160 (M^+). Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55; N, 17.49. Found: C, 75.23; H, 7.63; N, 17.37.

1,2-Dimethyl-3-(ethylimino)pyrrolizine (8b): yield 60%; bp 110–111 °C (5 mm); mp 41–42 °C; IR 1660 cm^{-1}; NMR δ 1.33 (t, 3, CH_3CH_2), 1.85 (s, 3, 2-CH_3), 1.95 (s, 3, 1-CH_3), 3.58 (q, 2, CH_3CH_2), 5.79 (d, 1, H-7, J_{HH} = 3.15 Hz), 6.06 (dd, 1, H-6, J_{HH} = 3.15, 2.85 Hz), 6.79 (d, 1, H-5, J_{HH} = 2.85 Hz); mass spectrum, calcd for $C_{11}H_{14}N_2$ *m/e* 174.1157, found *m/e* 174.1138.

1-Methyl-3-(ethylimino)pyrrolizine (8c). To a solution of the sodium salt of 2-acetylpyrrole (1 g, 8 mmol) in dimethylformamide (10 mL) was added the crude **2c** (1.63 g), which was prepared from **1c** (10 g, 45 mmol) after removal of byproducts (triphenylphosphine oxide, etc.) and solvent. The mixture was heated at 80 °C for 3 h. Treatment similar to that described above gave **8c**: 0.24 g (19% yield, based on the sodium salt); bp 70–75 °C (2 mm); IR 1660 cm^{-1}; NMR (CCl_4) δ 1.25 (t, 3, CH_3CH_2), 2.0 (d, 3, CH_3C=), 3.50 (q, 2, CH_3CH_2), 5.54–6.10 (m, 3, H-2, H-6, H-7), 7.0 (d, 1, H-5); mass spectrum, calcd for $C_{10}H_{12}N_2$ *m/e* 160.0998, found *m/e* 160.0997.

Hydrolysis of 5b. A solution of **5b** (1 g, 5 mmol) in ethanol (5 mL) containing concentrated hydrochloric acid (1 mL) was heated under reflux for 7 h. After evaporation of the solvent, the residue was extracted with chloroform and washed with brine. Drying (Na_2SO_4) and removal of the solvent gave **3,4-dimethylcoumarin (6)**: yield 91% (0.79 g); mp 112–114 °C; IR 1710 cm^{-1}; NMR δ 2.2, 2.39 (s, 6, CH_3), 7.0–7.73 (m, 4, Ar); mass spectrum, calcd for $C_{11}H_{10}O_2$ *m/e* 174.0680, found *m/e* 174.0662.

Acknowledgment. We thank Dr. H. Ishijima and Dr. K. Nojima, JEOL Co., for high-resolution gas chromatographic–mass spectral measurements.

Registry No. **1a**, 73473-50-4; **1b**, 75506-58-0; **1c**, 3699-75-0; **2a**, 73473-51-5; **2b**, 75506-59-1; **3**, 75506-60-4; **4**, 75506-61-5; **4'**, 75506-62-6; **5a**, 73473-52-6; **5b**, 75506-63-7; **6**, 4281-39-4; **7a**, 75506-64-8; **7b**, 75506-65-9; **8a**, 73473-53-7; **8b**, 75506-66-0; **8c**, 75506-67-1; diethyl phosphite, 762-04-9; *N*-ethyl-α-chloropropionamide, 67791-81-5; *N*-ethylchloroacetamide, 105-35-1; ethyl iodide, 75-03-6; ethanol, 64-17-5; diethylamine, 109-89-7; 2-acetylpyrrole sodium salt, 75506-68-2; 2-hydroxybenzaldehyde sodium salt, 3116-83-4; 2-hydroxyacetophenone sodium salt, 49645-89-8; 2-hydroxy-1-naphthaldehyde sodium salt, 41014-30-6; 1*H*-pyrrole-2-carboxaldehyde sodium salt, 66619-36-1.

Palladium-Catalyzed Oxidation of Terminal Olefins to Methyl Ketones by Hydrogen Peroxide

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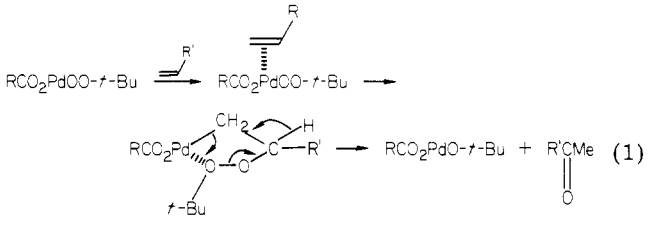
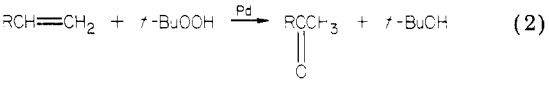
The use of the Wacker $PdCl_2$–$CuCl_2$ system for the oxidation of higher terminal olefins to methyl ketones presents major drawbacks, i.e., formation of chlorinated, aldehydic, and internal ketones as byproducts, precipitation of metallic palladium, and corrosion.[1,2] Some improvements have been achieved by using basic[3] or alcoholic[4] solvents and phase-transfer catalysts,[5] but the disadvantages have not been completely eliminated. We have previously described a highly selective procedure using rhodium catalysts[6] and involving molecular oxygen activation,[7] but a deactivation of the catalyst system was observed. We have also recently synthesized a new class of stable palladium alkyl peroxidic complexes with the formula $[RCO_2PdOO\text{-}t\text{-}Bu]_4$; they undergo an oxygen transfer to terminal olefins through a pseudocyclic peroxypalladation mechanism (eq 1).[8]



(1)

A palladium-catalyzed ketonization of terminal olefins by alkyl hydroperoxides has been displayed from this study (eq. 2).[9]



(2)

This paper describes a very efficient catalytic procedure for the oxidation of terminal olefins to methyl ketones by

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