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

Michel Roussel and Hubert Mimoun*

Laboratoire d'Oxydation, Institut Français du Pétrole, 92506 Rueil-Malmaison, France

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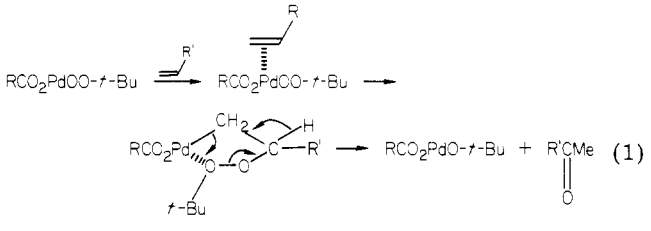
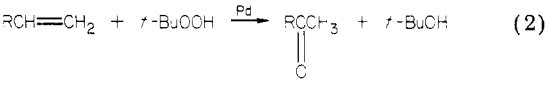
The use of the Wacker $PdCl_2$–$CuCl_2$ system for the oxidation of higher terminal olefins to methyl ketones presents major drawbacks, i.e., formation of chlorinated, aldehydic, and internal ketones as byproducts, precipitation of metallic palladium, and corrosion.[1,2] Some improvements have been achieved 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

(1) Smidt, J.; Happer, W.; Jira, R.; Sieber, R.; Sedlmeier, J.; Sabl, A. *Angew. Chem., Int. Ed. Engl.*, **1962**, 1, 80.
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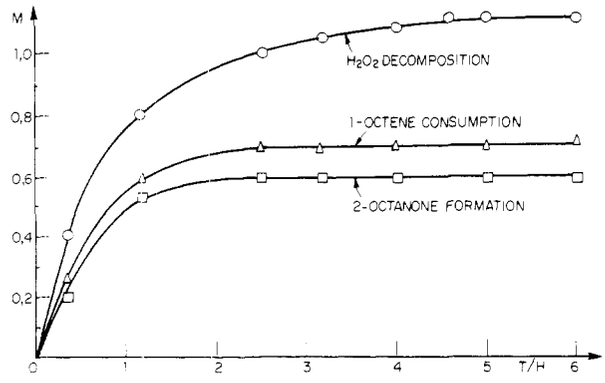


Figure 1. Pd-catalyzed oxidation of 1-octene: (●) H_2O_2 decomposition; (▲) 1-octene consumption; (■) 2-octanone formation. Reaction conditions: 0.5×10^{-3} M $Pd(AcO)_2$; 0.75 M 1-octene; 3.75 M H_2O_2; solvent AcOH; temp 80 °C.

hydrogen peroxide using a palladium catalyst and operating in the absence of halogens and co-metals. Although H_2O_2 has been used as a reoxidant in the Wacker system for the transformation of ethylene to acetaldehyde,[10] no systematic investigation of this type of reaction has been previously reported.

Results

Addition of 30% hydrogen peroxide to a solution of palladium(II) acetate in acetic acid or *tert*-butyl alcohol at room temperature resulted in an immediate decomposition with evolution of molecular oxygen. When this addition was carried out in the presence of 1-octene (1-octene–Pd = 20), no apparent decomposition occurred and a change in color from yellow-orange to deep orange resulted. GLC analysis showed the formation of 2-octanone as the major product, according to the reaction (eq. 3).

$$RCH{=}CH_2 + H_2O_2 \xrightarrow{Pd} RCCH_3 + H_2O \quad (3)$$
(O)

This reaction may be carried out either in biphasic medium, using solvents such as ethyl acetate or dichloroethane, or in homogeneous solution, using *tert*-butyl alcohol or acetic acid. Basic solvents, e.g., DMF, DMA, HMPA, were found to be strong inhibitors for the reaction. Figure 1 shows a typical plot of 1-octene comsumption, 2-octanone formation, and H_2O_2 decomposition vs. time at 80 °C, using $Pd(OAc)_2$ catalyst (1-octene–Pd = 1500), AcOH solution, and 30% H_2O_2 as oxidant (H_2O_2–1-octene = 5). A high selectivity in 2-octanone formation was observed throughout the reaction, and a quite complete conversion of 1-octene (90–95%) was obtained after ca. 3 h of reaction time. 3- and 4-octanone were the major byproducts detected in the reaction, while no octanal was identified. *Under these conditions, 1 mol of palladium was found to transform ca. 400 mol of 1-octene into 2-octanone per hour.*

Decomposition of hydrogen peroxide occurred, as shown from oxygen evolution during the reaction. This decomposition was in part due to a thermal effect (ca. 15%), but the major part was attributed to a palladium-catalyzed reaction. Taking into account this H_2O_2 decomposition, ca. 2–3 mol of H_2O_2 were consumed per 1 mol of 1-octene transformed.

Table I shows that the use of a large excess of H_2O_2 (H_2O_2–1-octene > 2:1) is necessary to achieve a complete

Table I[a]

H_2O_2:1-octene	1-octene consumption, mol %[b]	2-octanone formation, mol %[b]	H_2O_2 decomposition,[b] %
1	22	21	70
2	50	45	50
5	95	90	100
7	97	92	

[a] Reaction conditions: temp = 80 °C; H_2O_2 (30%):1-octene = 5; 1-octene:Pd = 1500; reaction time = 6 h. [b] HFAcac = hexafluoroacetylacetone.

Table II.[a] Dependence of the Anion Borne on Pd on the Catalytic Activity

catalyst	solvent	1-octene conversion, %	2-octanone selectivity, %
$Pd(OAc)_2$	*t*-BuOH	89	82
	AcOH	96	95
$Pd(CF_3CO_2)_2$	*t*-BuOH	85	82
$[CF_3CO_2PdOO$-*t*-Bu$]_4$	*t*-BuOH	97	75
$[CH_3CO_2PdOO$-*t*-Bu$]_4$	*t*-BuOH	96	73
$Pd(acac)_2$	*t*-BuOH	0	
	AcOH	92	85
$Pd(HFacac)_2$[b]	*t*-BuOH	0	
	AcOH	94	85
Na_2PdCl_4	*t*-BuOH	82	57

[a] Reaction conditions: temp = 80 °C; H_2O_2 (30%):1-octene = 5; 1-octene:Pd = 1500; reaction time = 6 h. [b] HFAcac = hexafluoroacetylacetone.

conversion of 1-octene. At lower ratios, a precipitation of metallic palladium was observed and the decomposition of H_2O_2 occurred at the expense of 2-octanone formation. If the temperature was lowered to 60 °C, no significant reduction of H_2O_2 decomposition on behalf of 2-octanone formation was observed.

At H_2O_2–1-octene = 5 and under the conditions of Figure 1, a linear dependence of initial rates on the concentration of $Pd(OAc)_2$ was observed.

The influence of the nature of the palladium catalysts on the oxidation of 1-octene by H_2O_2 is shown in Table II. In acetic acid solvent, no major differences were observed between the different catalysts, probably due to the exchange of the anion bonded to palladium by AcOH. However, a larger influence of the anion resulted when the reaction was carried out in *tert*-butyl alcohol. Palladium complexes bearing strongly coordinating anions such as acetylacetonate or hexafluoroacetylacetonate were found to be inactive for the transformation of 1-octene to 2-octanone, suggesting the occurrence of a necessary exchange of at least one anion on palladium by H_2O_2 (vide infra). The use of Na_2PdCl_4 as catalyst resulted in a lower selectivity in the formation of 2-octanone, with extensive double bond migration and production of internal ketones.

Several modifications of the reaction medium have been tried, using *tert*-butyl alcohol as a solvent in order to improve the understanding of the general features of this catalytic system. The $Pd(OAc)_2$-catalyzed oxidation of 1-octene by H_2O_2 (H_2O_2–olefin = 5; olefin–Pd = 1500) was not influenced by the addition of a radical inhibitor such as di-*tert*-butylparacresol (DTPC–Pd = 10) either in the 2-octanone formation or in H_2O_2 decomposition. The presence of water in the medium also had no effect on the reaction and H_2O_2 solutions can be used at any dilution. The oxidation is best carried out in neutral (*t*-BuOH) or

(10) British Patent 941951 (to ICI Ltd), 1964; *Chem. Abstr.* **1964**, *60*, 4011.

Table III. Reactivity of Olefins[a]

olefin	solvent	products[b]	% conversion[c]	% selectivity[c]
1-octene	*t*-BuOH	2-octanone	89	82
	AcOH	2-octanone	96	95
1-decene	*t*-BuOH	2-decanone	90	80
	AcOH	2-decanone	95	92
1-dodecene	*t*-BuOH	2-dodecanone	89	75
		2-dodecanone	92	90
allyl acetate	*t*-BuOH	3-acetoxy-2-propanone	8	83
	AcOH	3-acetoxy-2-propanone	100	85
allyl alcohol	none	HCO_2H (30%) $MeCO_2H$ (33%) $EtCO_2H$ (35%)	96	
ethyl acrylate	*t*-BuOH	none		
cyclohexene	*t*-BuOH	none		

[a] Reaction conditions: temp = 80 °C; H_2O_2 (30%):olefin = 5; olefin:$Pd(OAc)_2$ = 1500; reaction time = 6 h. [b] Identification by GLC-MS coupling and ^1H NMR spectra. [c] GLC determination using *o*-dichlorobenzene as internal standard.

slightly acidic (AcOH) solutions. The addition of a base such as potassium *tert*-butoxide (*t*-BuOK–Pd = 1) inhibited the oxidation and resulted in a complete decomposition of H_2O_2. The addition of a noncoordinating strong acid such as $MeSO_3H$ ($MeSO_3H$–Pd = 1) resulted in lower conversion and selectivity.

The reactivity of several different olefins towards H_2O_2 in the presence of $Pd(OAc)_2$ is illustrated in Table III. Only terminal olefins are transformed to methyl ketones by this catalytic system in both AcOH and *t*-BuOH solution. However, AcOH was found to be more efficient in the oxidation of allyl acetate to 3-acetoxy-2-propanone. Allyl alcohol was transformed into a mixture of formic, acetic, and propionic acid, presumably via the formation of pyruvic compounds. Internal and cycloolefins such as cyclohexene were unreactive, as previously observed with the peroxidic $[RCO_2PdOO\text{-}t\text{-}Bu]_4$ complexes.[8]

Discussion

These results are consistent with the suggested mechanism depicted in Scheme I. Palladium hydroperoxidic species (**1**) probably obtained by the addition of H_2O_2 to palladium compounds appear to be the most likely active intermediates in this catalytic oxidation. Because of extensive H_2O_2 decomposition, our attempts to isolate such species failed. However, several pieces of evidence favor the involvement of peroxidic palladium compounds in this reaction.

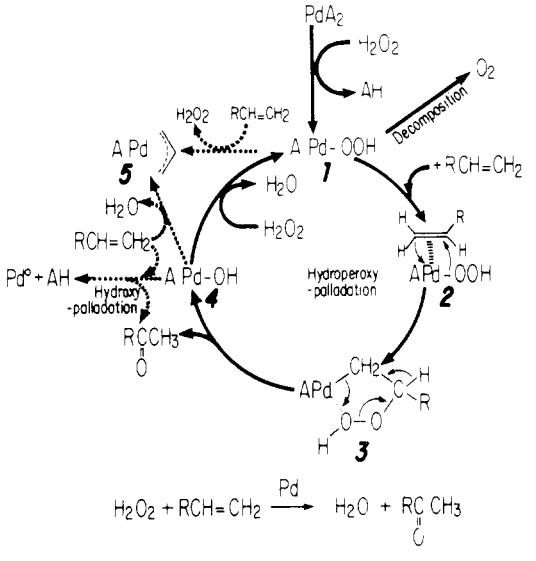
PdOOH species, generated from a noncoordinating acid hydrolysis of $(Ph_3P)_2PdO_2$ have been recently shown by us to be active in the selective transformation of terminal olefins to methyl ketones. PdOOH species undergo an oxygen transfer to olefin through a pseudocyclic hydroperoxypalladation mechanism (such as **2**–**3**) of the coordinated olefin.[11] The involvement of such pseudocyclic peroxidic intermediates (**3**) is further supported by the exchange reaction between Na_2PdCl_4 and $CF_3CO_2HgCH_2CH(Ph)OOH$ affording acetophenone[8,11]

The reactivity of olefins toward H_2O_2 in the presence of palladium is very close to that previously observed with $[CF_3CO_2PdOO\text{-}t\text{-}Bu]_4$ (PPT). Only terminal olefins can be oxidized to methyl ketones. The coordination of the olefin to the metal prior to its peroxypalladation is strongly inhibited by competing ligands or σ donor solvents.

PdOOH species appear to be less stable than PdOO-*t*-Bu species previously prepared and are probably responsible for the H_2O_2 decomposition. The presence of a large excess of H_2O_2 is necessary not only to compensate its unavoidable Pd-catalyzed decomposition but also to regenerate PdOOH species from PdOH (**4**). At low H_2O_2 concentrations, PdOH species may undergo a hydroxypalladation of the olefin, affording the ketone and metallic palladium precipitation. This metallic palladium does not dissolve again in the solution when excess H_2O_2 is added. Furthermore, the presence of excess H_2O_2 is necessary to avoid the formation of π–allylic complexes (**5**) and regenerate the initial PdOOH species.

This palladium-catalyzed synthesis of methyl ketones from terminal olefins and H_2O_2 appears to be most useful in synthetic applications. It provides very high selectivity in methyl ketones at quite complete conversions of the olefins and only needs very low amounts of palladium (20–40 ppm) in the medium.

Scheme I



Experimental Section

Materials. Reagent-grade *tert*-butyl alcohol (Prolabo) and glacial acetic acid (Merck) were used without further purification. Olefins such as 1-octene (Merck), 1-decene, 1-dodecene (Ethyl Corp.), and cyclohexene (Prolabo) were passed through a column containing active alumina to remove peroxidic impurities and distilled before use. Other olefinic compounds, i.e., allyl acetate, allyl alcohol, and ethyl acrylate (Aldrich), were used without purification. 30% H_2O_2 (Merck) or 70% (Air Liquide) was used as such. Palladium catalysts were purchased from Ventron ($Pd(OAc)_2$), Cie des Métaux Précieux ($Pd(acac)_2$, $Pd(Hfacac)_2$), and Prolabo ($Pd(NO_3)_2$, Na_2PdCl_4). Palladium trifluoroacetate was synthesized according to Wilkinson.[14] $[RCO_2PdOOtBu]_4$ complexes were prepared according to ref 8.

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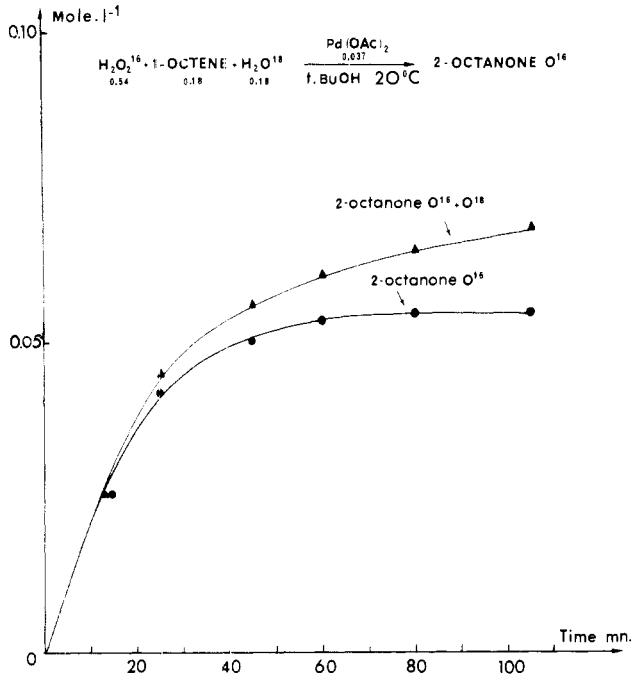

Figure 2.

Apparatus. The olefins were oxidized in a three-necked 1-L thermostated glass reactor equipped with a magnetic stirrer, a condenser, and a 100-mL glass funnel (for introduction of H_2O_2) and connected through a gas counter (for the evaluation of O_2 evolution) to the atmosphere. H_2O_2 solution was introduced dropwise into the mixture of olefin, solvent, and catalyst during 30 min at the reaction temperature. When the reaction was complete, the mixture was cooled and water was added. The yellow upper layer containing the catalyst was separated and passed through a column of alumina in order to eliminate the catalyst and distilled under reduced pressure.

Analysis. The reaction was followed by GLC analysis; the oxygenated products were identified on a Girdel flame-ionization model gas chromatograph using a 2-m column of DEGS 10% on Chromosorb WHP 80–100 with *o*-dichlorobenzene as internal standard. NMR spectra were recorded on a Varian CFT 20. Mass spectra were obtained by an AEI Model MS12 mass spectrometer. Identification of products was achieved by GLC–MS coupling and comparison of the mass spectra with those of authentic samples.

Note Added in Proof. In order to determine whether H_2O_2 or H_2O represents the oxygen source for the methyl ketone formation, we have followed a pertinent suggestion of a referee and carried out an $H_2{}^{16}O_2$–$H_2{}^{18}O$ labeling experiment. Thus, 1-octene (0.18 M) was oxidized by 70% $H_2{}^{16}O_2$ (0.54 M) in the presence of $H_2{}^{18}O$ (99% ^{18}O, 0.18 M) and $Pd(OAc)_2$ (0.037 M) in *tert*-butyl alcohol at 20 °C. The reaction was monitored by GLC–MS coupling (AEI Model MS 80) and the ratio of 2-octanone ^{16}O:^{18}O was accurately determined vs. time by measuring the molecular 128:130 peak ratio. Figure 2 shows that no ^{18}O coming from water was incorporated into the 2-octanone for ca. 20 min, after which time an isotopic exchange between the obtained 2-octanone and $H_2{}^{18}O$ occurred.[11,12] Therefore, these results provide strong additional evidence that, contrary to the Wacker process, water is not involved as the oxygen source in this reaction. Under our conditions, the internal pseudocyclic hydroperoxypalladation, i.e., **2** → **3** of the coordinated olefin prevails over external nucleophilic attack by water forming a *trans*-hydroxypalladation adduct.

Registry No. 2-Octanone, 111-13-7; 2-decanone, 693-54-9; 2-dodecanone, 6175-49-1; 3-acetoxy-2-propanone, 592-20-1; formic acid, 64-18-6; acetic acid, 64-19-7; propanoic acid, 79-09-4; 1-octene, 111-66-0; 1-decene, 872-05-9; 1-dodecene, 112-41-4; allyl acetate, 591-87-7; allyl alcohol, 107-18-6; ethyl acrylate, 140-88-5; cyclohexene, 110-83-8.

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Reaction between Azodicarbonamide and Ethyl Diazoacetate. Formation of a Syn Semicarbazone

Martin Pomerantz*† and Shmuel Bittner*[1]

Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019

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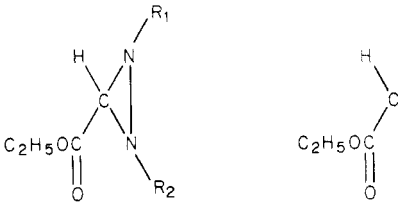
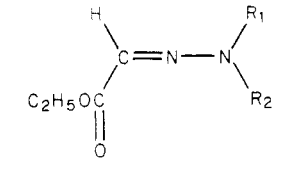
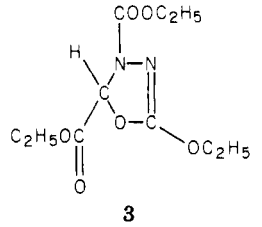
It has long been known that diazo esters react with diethyl azodicarboxylate.[2-5] The originally postulated diaziridine structures for the products (e.g., **1a**) have more recently been shown to be incorrect. The products are actually either diacylhydrazones (e.g., **2a**) or oxadiazolines (e.g., **3**), depending on the starting materials and the reaction conditions.[6-9]



1a, $R_1 = R_2 = COOC_2H_5$
b, $R_1 = R_2 = CONH_2$

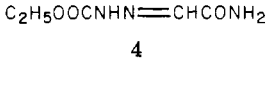


2a, $R_1 = R_2 = COOC_2H_5$
b, $R_1 = H$; $R_2 = CONH_2$

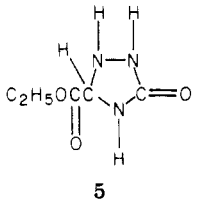


3

It was also shown many years ago by Müller[2] that ethyl diazoacetate reacts with azodicarbonamide in ethanolic solution to produce a colorless crystalline compound, mp 174–175 °C, whose empirical formula is $C_5H_9O_3N_3$.[2] He showed that the compound was neither the known semicarbazone of ethyl glyoxylate, **2b** (mp 212–213 °C), nor the isomeric compound **4**. He could not distinguish between two suggested structures, one containing a three-membered ring, **1b**, and the other containing a five-membered ring, **5**, but the latter was considered a less likely possibility.



4



5

Further, when this compound was heated it isomerized to the semicarbazone of ethyl glyoxylate (**2b**). In a more recent publication,[10] Fahr assumed the three-membered-

† Author to whom correspondence concerning this paper should be addressed.

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