Oxidations of Olefins with Alcoholic Palladium(II) Salts

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Simple olefins, including most monosubstituted and 1,2-disubstituted ethylenes, are readily oxidized by alcoholic solutions of Pd(II) salts to yield the corresponding acetals or ketals. When small amounts of water are present, the free carbonyl compounds are obtained. The oxidations proceed readily with little or no water present, and are retarded by more than small amounts of water. In the presence of molecular oxygen and a reoxidant, these reactions become selective homogeneous catalytic oxidations.

$$R'CH{=}CHR'' + 2ROH + PdX_2 \longrightarrow R'CH_2CR''(OR)_2 + 2HX + Pd(0)$$

In the course of another investigation a solution of acrylonitrile in ethanediol was warmed to 80° in the presence of dissolved palladous and cupric chlorides. Analysis showed the acrylonitrile to have undergone significant conversion into 1,3-dioxolane-2-acetonitrile. This has been found to be an unusually sluggish example of a homogeneous olefin oxidation[2] of great formal similarity to aqueous Wacker oxidations.[3,4]

Ethylene has been shown, by Moiseev[5] and later workers,[6] to be readily oxidized by alcoholic Pd(II) to acetaldehyde derivatives. When ethanediol containing dissolved $PdCl_2$ is stirred at 50° under an ethylene atmosphere a Pd mirror quickly forms and the solution is found to contain 2-methyl-1,3-dioxolane. A similar reaction in ethanol produces acetal. When the reaction is carried out in the presence of cupric chloride and molecular oxygen the reduced Pd metal is continuously reoxidized and the process becomes catalytic.[2,3,7,8] See Scheme I.

SCHEME I

$$CH_2{=}CH_2 + 2ROH + PdCl_2 \longrightarrow CH_3\text{-}CH(OR)_2 + 2HCl + Pd(O)$$

$$Pd(0) + 2CuCl_2 \longrightarrow PdCl_2 + Cu_2Cl_2$$

$$Cu_2Cl_2 + 2HCl + {}^1/_2O_2 \longrightarrow 2CuCl_2 + H_2O$$

Overall,

$$CH_2{=}CH_2 + 2ROH \longrightarrow CH_3CH(OR)_2 + H_2O$$

Terminal olefins are oxidized to the corresponding methyl ketones or ketals. 1-Butene in ethanediol readily forms 2-ethyl-2-methyl-1,3-dioxolane. Higher α olefins are subject to both oxidation and isomerization[9] in the presence of Pd(II) salts. 1-Hexene in 1-propanol readily reacts at 50° to form a mixture of 2- and 3-hexanones, in the approximate ratio of 3:1. 1-Octene reacts similarly to yield mixtures of *n*-octanones. Isomerization may be minimized by carrying out the oxidation at low temperatures. Thus the oxidation of 1-octene yields 2-octanone to the extent of 62% at 90°, 85% at 60°, and more than 97% at 30°.

Styrene oxidizes readily but not always selectively. One reaction in ethanol at 30° yielded nearly equal amounts of phenylacetaldehyde, β-phenyl acetal, acetophenone, and benzaldehyde. Small changes may exert profound effects upon the course of this oxidation. One run with $Cu(NO_3)_2$ replacing $CuCl_2$ afforded an 88% yield of acetophenone. Another run with $CuCl_2$ and with ethanediol as solvent afforded a 90% yield of 2-benzyl-1,3-dioxolane. Acrylonitrile oxidizes in ethanediol, as noted above, to form 1,3-dioxolane-2-acetonitrile; the corresponding oxidation in methanol yields 2,2-dimethoxyacetonitrile. Ethyl acrylate reacts readily in ethanol, but gives no more than traces of the expected diethoxypropionate; the main product (90%) appears on the basis of infrared spectrum to be the dealcoholation product, ethyl *trans*-β-ethoxyacrylate, a compound likely to form readily[10] from the β,β-diethoxypropionate.

1,2-Disubstituted ethylenes oxidize into the corresponding ketones or ketals. In monohydric alcohols containing a few tenths of a per cent water both *cis*- and *trans*-2-butene are readily converted into butanone. Similarly cyclohexene yields cyclohexanone. In anhydrous ethanediol cyclohexene yields 1,4-dioxaspiro[4.5]decane. 2,5-Dihydrofuran in ethanol forms the ketal of 3-oxotetrahydrofuran. Yields of these and other reactions are shown in Table I.

Some monosubstituted ethylenes undergo solvolytic rather than oxidative reactions. In ethanol containing palladous and cupric chlorides ethyl vinyl ether yields principally acetal; vinyl acetate yields equimolar quantities of ethyl acetate and acetal; vinyl chloride yields principally acetal along with a little chloro acetal. Under these mild reaction conditions some 1,2-disubstituted ethylenes are unreactive (*e.g.*, *cis*-stilbene, *cis*-1,2-dichloroethylene). 1,1-Disubstituted ethylenes are generally unreactive. Thus isobutylene and 2-methyl-1-pentene are inert under conditions permitting the facile oxidations of 1- and 2-butenes and 3-methyl-1-pentene.

Methanol and ethanol are excellent reaction media. Runs with styrene at 30° and with cyclohexene at 50° show conversion rates to fall off with increasing chain length of primary monohydric alcohols through 1-octanol. Among the butanols 2-methyl-2-propanol

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TABLE I

OXIDATIONS OF SOME OLEFINS WITH ALCOHOLIC Pd(II) SALTS

Olefin	Alcohol	Catalyst	Conditions	Products	Yield,[a] %
Ethylene	Ethanediol	*b*	*c*	2-Methyl-1,3-dioxolane	91
				Acetaldehyde	9
Ethylene	1,3-Propanediol	*b*	*c*	2-Methyl-1,3-dioxane	High
1-Butene	Ethanediol (wet)	*d*	*c*	2-Ethyl-2-methyl-1,3-dioxolane	68
				2-Butanone	30
1-Hexene	1-Propanol	*e*	*f*	2-Hexanone	75
				3-Hexanone	25
1-Octene	1-Propanol	*e*	*g*	Octanones	89[h]
				2-Octanone	87
				3-Octanone	1.5
				4-Octanone	Trace
1-Octene	1-Propanol	*e*	*i*	Octanones	80[h]
				2-Octanone	68
				3-Octanone	9
				4-Octanone	3
1-Octene	1-Propanol	*e*	*j*	Octanones	73[h]
				2-Octanone	45
				3-Octanone	18
				4-Octanone	10
Cyclohexene	Ethanol	*k*	*j*	Cyclohexanone	95
Cyclohexene	Ethanediol	*k*	*f*	1,4-Dioxospiro[4.5]decane	High
trans-3-Hexene	1-Propanol	*l*	*f*	3-Hexanone	84
				2-Hexanone	14
cis-2-Butene	Methanol	*d*	*m*	Butanone	99+
trans-2-Butene	Methanol	*d*	*m*	Butanone	99+
2,5-Dihydrofuran	Ethanol	*l*	*f*	3,3-Diethoxytetrahydrofuran	94
2,5-Dihydrofuran	Ethanol	*n*	*f*	3,3-Diethoxytetrahydrofuran	86
Acrylonitrile	Ethanediol	*e*	*o*	1,3-Dioxolane-2-acetonitrile	High
Acrylonitrile	Methanol	*e*	*p*	2,2-Dimethoxypropionitrile	High
1-Hexene	Glycerol	*e*	*q*	2-*n*-Butyl-2-methyl-1,3-dioxolane-4-methanol	70
				Hexanone	26

[a] Based upon integrated areas of gas chromatograms.
[b] 0.028 *M* $PdCl_2$, 0.586 *M* $CuCl_2 \cdot 2H_2O$.
[c] 40 min at 50° in autoclave under initially 100 psi oxygen.
[d] 0.028 *M* $PdCl_2$, 0.141 *M* $CuCl_2 \cdot 2H_2O$.
[e] 0.020 *M* $PdCl_2$, 0.100 *M* $CuCl_2 \cdot 2H_2O$.
[f] 120 min at 50° and 3 atm oxygen.
[g] 120 min at 30° and 3 atm oxygen.
[h] Using technical grade 1-octene.
[i] 120 min at 60° and 3 atm oxygen.
[j] 120 min at 90° and 3 atm oxygen.
[k] 0.028 *M* $PdCl_2$, 0.117 *M* $CuCl_2 \cdot 2H_2O$.
[l] 0.020 *M* $PdCl_2$, 0.100 *M* $CuCl_2$.
[m] 45 min at 50° under initially 100 psi oxygen.
[n] 0.020 *M* $PdCl_2$ 0.100 *M* $Cu(NO_3)_2$.
[o] 180 min at 80° under 3 atm oxygen.
[p] 180 min at 75–85° under 3 atm oxygen.
[q] Combined with an equal volume of methanol to make system completely homogeneous, then allowed to react for 120 min at 50° and 3 atm oxygen.

was the poorest solvent for the inorganic salts, and afforded a markedly lower conversion of cyclohexene. Diols are generally good solvent media, often forming the cyclic acetals; thus ethylene with 1,3-propanediol yields 2-methyl-1,3-dioxane. 1-Hexene reacts in a glycerol–methanol mixture to produce principally 2-*n*-butyl-2-methyl-1,3-dioxolane-4-methanol, in accord with expectation that the dioxolane is favored over the 1,3-dioxane.[11]

TABLE II

COMPARISON OF OLEFIN CONVERSIONS IN AQUEOUS AND ALCOHOLIC SYSTEMS[a]

Olefin	Oxidation conditions	Conversion in aqueous systems, %	Conversion in alcoholic systems, % (alcohol)
1-Octene	*b*	2.5	63 (methanol)
1-Octene	*c*	4.5	72 (methanol)
Cyclohexene	*d*	1.7	22 (methanol)
Cyclohexene	*e*	1.0	29 (ethanol)
Acrylonitrile	*f*	Nil[g]	40[h] (methanol)

[a] Oxidations for 120 min under 3 atm oxygen at the temperatures specified.
[b] 0.018 *M* $PdCl_2$, 0.100 *M* $CuCl_2$, 30°, olefin 20 vol. %.
[c] 0.018 *M* $PdCl_2$, 0.100 *M* $CuCl_2$, 60°, olefin 20 vol. %.
[d] 0.200 *M* $PdCl_2$, no Cu salt, 50°, olefin 10 vol. %.
[e] 0.020 *M* $PdCl_2$, 0.100 *M* $CuCl_2$, 50°, olefin 20 vol. %.
[f] 0.040 *M* $PdCl_2$, 0.030 *M* $CuCl_2$, 75–85°, olefin 10 vol. %.
[g] No product detectable by gas chromatograph; no measurable oxygen uptake.
[h] Into the acetal 2,2-dimethoxypropionitrile.

Glacial acetic acid[5,12] and N,N-dimethylformamide[13] have been reported useful for other Pd(II)-catalyzed olefin oxidations. Parallel oxidations of cyclohexene at 50° in various polar organic solvents showed conversions of 30% in ethanol, 1.2% in 1,4-dioxane, and less than 0.5% in dimethylformamide, dimethyl sulfoxide, acetic acid, propylene carbonate, and carbon tetrachloride. The formal similarity between Pd(II)-catalyzed olefin oxidations in alcoholic and aqueous[3,4] systems invites direct comparison. Results of the runs summarized in Tables II and III indicate that even under comparably homogeneous conditions these oxidations proceed more readily in alcoholic media and most readily in media containing little or no water.

There is at present insufficient evidence to provide a detailed mechanistic picture of these oxidations. An adequate mechanism must account for several salient features: the directing effects of electron-releasing and electron-attracting groups attached to the olefinic

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TABLE III

EFFECT OF ETHANOL–WATER COMPOSITION UPON THE CONVERSION OF CYCLOHEXENE[a]

Water content of system: Water added, vol. %	Water content of system: Final water content vol. %[b]	Conversion of cyclohexene, %[c]	Cyclohexanone formed, % (basis, cyclohexene)[c]
Nil	2.5	88	58
10	10.7	48	38
20	22.7	34	27
30[d]	32.8	20	15
60[d]	60	7.2	3.2
90[d]		2.5	0.5

[a] All runs with 0.020 M $PdCl_2$, 0.100 M $CuCl_2 \cdot 2H_2O$, 10.0 vol. % cyclohexene, water charged as indicated, and ethanol qv 100%; all runs for 120 min at 50° under 3 atm oxygen in a glass shaker–reactor. [b] Titrimetric analysis by the Karl Fischer method. [c] Based upon integrated areas of gas chromatograms. [d] Two liquid phases; product assays made on both phases.

double bond (essentially the same as those found in aqueous oxidations[3]), the relatively great ease of oxidation in alcoholic media, perhaps reflecting weaker solvating forces and hence greater reactivity of the alcohol-solvated Pd(II) species,[8] and the well-defined limitations of these reactions, especially the failure of 1,1-disubstituted ethylenes to react significantly under these conditions. We are currently seeking to develop information which will illuminate this problem.

Experimental Section

1,3-Dioxolane-2-acetonitrile.—To 40 ml of 0.020 M $PdCl_2$ and 0.100 M $CuCl_2 \cdot 2H_2O$ in ethanediol was added 10 ml of acrylonitrile and the solution shaken for 3 hr at 80° under 3 atm oxygen in a modified[14] low pressure glass reactor as described previously.[8] The single product, in 18% conversion by gas chromatograph (gc) area, was isolated by preparative chromatography and identified by infrared spectrum in CCl_4 (acetal, nonconjugated nitrile) as 1,3-dioxolane-2-acetonitrile.

Anal. Calcd for $C_5H_7O_2N$: C, 53.1; H, 6.24; N, 12.38. Found: C, 52.8; H, 6.12; N, 12.22.

2-Methyl-1,3-dioxolane.—A 200-ml portion of 0.028 M $PdCl_2$ and 0.586 M $CuCl_2.2H_2O$ in ethanediol was stirred at 50° in a 500-ml stainless steel autoclave under a 2:1 ethylene–oxygen mixture (*Caution:* Explosive mixture) initially at 300 psig. The exothermal reaction required continuous cooling; after 30 min the pressure had fallen to 1 atm. Analysis revealed acetaldehyde (9% yield by gc area) and a colorless liquid (91% yield) identified as 2-methyl-1,3-dioxolane, $n^{25}{}_D$ 1.3960, $d^{25}{}_4$ 0.980 (the product of acetaldehyde–ethanediol condensation at room temperature, $n^{25}{}_D$ 1.3956, $d^{25}{}_4$ 0.980), lit.[15] $n^{20}{}_D$ 1.3972, $d^{20}{}_4$ 0.9795. The molar refraction (MR) calcd for 2-methyl-1,3-dioxolane was 21.76, found 21.60.

2-Ethyl-2-methyl-1,3-dioxolane.—To 200 ml of 0.028 M $PdCl_2$ and 0.141 M $CuCl_2$ in 95:5 ethanediol–water in a 500-ml autoclave was added 4.0 g of 1-butene and the mixture stirred at 50° under an initial partial pressure of 100 psig oxygen. Analysis after 40 min showed the products to be 2-butanone (30% by gc area), a minor product of residence time matching that of 2-*n*-propyl 1,3-dioxolane (2%), and a major product (68%) identified as 2-ethyl-2-methyl-1,3-dioxolane. Residence times and infrared spectrum in CCl_4 matched those of the butanone–ethanediol condensation product, $n^{25}{}_D$ 1.4061, lit.[16] $n^{20}{}_D$ 1.4097.

2- and 3-Hexanone.—A 50-ml portion of 0.665 M 1-hexene, 0.020 M $PdCl_2$ and 0.100 M $CuCl_2 \cdot 2H_2O$ in 1-propanol was shaken for 120 min at 50° under 3 atm oxygen. The reaction mixture contained 2.0% water from all sources (salt hydration, impurity in the alcohol and water of oxidation). Of the hexene charged, 13% (by gc area) remained unreacted and 86% was converted into hexanone and 1.0% into side products. Resolution of the hexanone peak showed 75–76% 2-hexanone and 24–25% 3-hexanone, both identified by means of residence times and infrared spectra in comparison with authentic samples.

2-Benzyl-1,3-dioxolane.—To 5 ml of 0.030 M $PdCl_2$, 0.50 M $CuCl_2$, and 0.50 M $Cu(BF_4)_2$ in ethanediol at 70° was added 0.200 ml of styrene, and samples were then withdrawn periodically for analysis. After 15 min gc areas showed 11% unreacted styrene, 8.5% acetophenone, 1.5% phenylacetaldehyde, and 79% major product. This product was separated by preparative chromatography; residence times and infrared spectra in CCl_4 and in CS_2 conformed with those of authentic 2-benzyl-1,3-dioxolane prepared by the condensation of phenylacetaldehyde and ethanediol.[17]

2,2-Dimethoxypropionitrile.—Acrylonitrile was treated with a methanolic solution of $PdCl_2$–$CuCl_2$ under the conditions described for 1,3-dioxolane-2-acetonitrile, and the single product isolated by preparative chromatography as a colorless liquid: $n^{25}{}_{\text{white}}$ 1.4122, $d^{25}{}_4$ 1.001, lit.[13] n^{25} 1.4124 (no reported density); MR calcd 28.32, found 28.35. The mass spectrum showed major peaks at m/e 114, 83, 75, and 47, indicating a *gem*-dimethoxypropionitrile. The bp (capillary) *ca.* 196° (674 mm) was in good agreement with the extrapolated[19] value of 191 ± 2° from Murahashi's measurement of 92.5° (30 mm) for the 2,2-dimethoxy isomer[20] (values of n^{25}, d^{25}, and boiling point reported[21] for the 1,1 isomer are remote from these values). This structural assignment was confirmed by the nmr spectrum which showed a doublet (2 H) at δ 2.67, a singlet (6 H) at 3.38, and a triplet (1 H) at 4.66.

1,4-Dioxaspiro[4.5]decane.—A mixture of cyclohexene and ethanediol (1:4 by volume), containing 0.028 M $PdCl_2$ and 0.117 M $CuCl_2$, was made homogeneous by addition of 5 parts 1,4-dioxane, and this solution was shaken for 2 hr at 50° under 3 atm oxygen to yield a single product, a clear, colorless high-boiling liquid of residence times and infrared spectrum (CCl_4 solution) identical with those of authentic 1,4-dioxaspiro[4.5]-decane prepared by the acid-catalyzed condensation of cyclohexanone with ethanediol.[22]

3,3-Diethoxytetrahydrofuran.—2,5-Dihydrofuran 8.4% by volume in ethanol containing 0.020 M $PdCl_2$ and 0.100 M $Cu(NO_3)_2 \cdot 3H_2O$ was shaken for 2 hr at 50° under 3 atm oxygen. Analysis showed the dihydrofuran to have undergone a 97% conversion, yielding mainly (86% by gc area) a clear, colorless liquid showing only C–H, C–C, and C–O absorptions in the infrared. Ethoxy group assay calcd for $C_4H_6O(OC_2H_5)_2$ was 2.00, found 1.91.

Anal. Calcd for $C_8H_{16}O_3$: C, 60.0; H, 10.07. Found: C, 60.2; H, 10.05.

2-Methyl-1,3-dioxane.—Ethylene was allowed to react under the conditions described for the preparation of 2-methyl-1,3-dioxolane, except for the substitution of 1,3-propanediol for ethanediol. A single product was found: $n^{25}{}_D$ 1.4114, $d^{20}{}_4$ 0.970; lit.[23] for 2-methyl-1,3-dioxane, $n^{25}{}_D$ 1.4119, $d^{20}{}_4$ 0.9701; MR calcd 26.38, found 26.17.

2-*n*-Butyl-2-methyl-1,3-dioxolane-4-methanol.—A mixture of 1-hexene and glycerol (1:2 by volume), containing 0.020 M $PdCl_2$ and 0.100 M $CuCl_2 \cdot 2H_2O$ was made homogeneous by addition of 3 parts methanol and this solution was shaken for 2 hr at 50° under 3 atm oxygen. In addition to hexanone, the major product was a clear, colorless liquid of residence times and infrared spectrum (CCl_4 solution) identical with those of authentic 2-*n*-butyl-2-methyl-1,3-dioxolane-4-methanol, prepared by the acid-catalyzed condensation of 2-hexanone and glycerol.[11]

Solvolyses of Ethyl Vinyl Ether, Vinyl Acetate, and Vinyl Chloride.—When 10% by volume ethyl vinyl ether in ethanol is warmed to 50° for 2 hr only a trace of acetal is formed, but with the addition of 1 drop of concentrated aqueous HCl to 50 ml, *or* 0.10 M $CuCl_2$, *or* 0.020 M $PdCl_2$ the vinyl ether undergoes 98+% conversion into acetal. Vinyl acetate 20% by volume in

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ethanol is stable on standing overnight at 50°, but a parallel solution containing 0.100 *M* $CuCl_2$ undergoes 56% conversion into an equimolar mixture of acetal and ethyl acetate (basis gc areas). Vinyl chloride (approximately 5% by volume) is similarly stable in pure ethanol at 50° but in the presence of 0.10 *M* $CuCl_2$ undergoes substantial conversion into acetal. With 0.020 *M* $PdCl_2$ and 0.100 *M* $CuCl_2$ vinyl chloride yields a mixture of acetal and chloroacetaldehyde diethyl acetal in ratio 10:1

Registry No.—Ethylene, 74-85-1; 1-butene, 106-98-9; 1-hexene, 592-41-6; 1-octene, 111-66-0; cyclohexene, 110-83-8; *trans*-3-hexene, 13269-52-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 2,5-dihydrofuran, 1708-29-8; acrylonitrile, 107-13-1; $PdCl_2$, 7647-10-1.

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Metalation Reactions. III. Metalation of Octadecynols and Octadecynyl Methyl Ethers

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Octadecynyl alcohols and methyl ethers were metalated with butyllithium in ether and yielded on carbonation mono- and diacids. The two carboxyls in the diacids were situated on the same carbon atom. The alcohols were metalated faster than the ethers. The composition of the products was determined. The proton abstraction from both propargylic positions proceeded to a similar extent. Carbonation was more pronounced at the initially sp-hybridized atoms. The distance from the functional group was of little influence on the protonation and carbonation reactions, except for the case when the triple bond was very near the functional group.

The transformation of unsaturated fatty acids into new products by addition to double bonds[1] has been studied for many years. Allylic oxidations and halogenations of these compounds have also been investigated.[1] Some years ago our laboratory embarked on a study of allylic metalation of derivatives of unsaturated acids with a view to the transformation of the metalated adducts into difunctional compounds. We now report our results on the metalation of octadecynols and octadecynyl methyl ethers.

The metalations were at first performed with amylsodium in hexane. Stearolyl alcohol (I) gave precipitates containing the alkoxide, and no metalation was observed. Stearolyl methyl ether (II) did not precipitate under these conditions, and yielded carboxylic acids after carbonation of the reaction mixture with Dry Ice. Since butyllithium did not form precipitates with I, all subsequent metalations were carried out with this reagent in ether solution or in ether–hexane (1:1). The metalated compounds were carbonated with Dry Ice and the products were shown to be a mixture of mono- and diacids. The ratio of these acids was analyzed by glpc, after esterification, etherification, and hydrogenation of the reaction products. The results are recorded in Table I. The metalation of the alcohol is faster than that of the ether, in agreement with the known catalytic influence of alkoxides on the metalation reaction,[2] which is probably due to depolymerization of the organometallic reagent by the catalyst.[3]

TABLE I

METALATION[a] OF STEAROLYL ALCOHOL I AND METHYL ETHER II

Compd	Duration, hr	Yield[b] of monoesters, %	Yield[b] of diester, %	Uv,[c] λ_{max}, mμ (ε)
I	48	45	15	220 (5200)
I	72	32	39	220 (4400)
I[d]	72	44	16	. . .
II	72	45	2	218 (3600)[e]
II	93	44	6	218 (3400)[e]
II	120	24	30	. . .[f]
II[d]	98	43	23	. . .
I[g]	96	34	9	. . .
II[g]	96	29	4	. . .

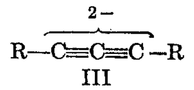
[a] In ether solution at room temperature, with subsequent carbonation and esterification. [b] Determined on the saturated esters. [c] Determined on the mixture of unsaturated esters before their separation. [d] In hexane at room temperature, using TMEDA as a catalyst. [e] ν_{max} 1710, 1740, and 1950 cm^{-1}. [f] ν_{max} 1710, 1740, 1950 (w), and 2750 cm^{-1} (w). [g] In ether–hexane (1:1).

The metalation is faster in ether than in a mixture of ether–hexane (1:1), and proceeds to a very limited extent (5%) in hexane alone, even after long reaction periods. However, the addition of tetramethylethylenediamine (TMEDA) speeds up the reaction in hexane, making it approximately as fast as in ether. The catalytic effect of this substance has been previously observed.[4]

The reaction proceeds largely to the dimetalated derivative after long reaction times. The second proton is abstracted from the same carbon as the first (see below). The formation of such dianions (III), called by us extended acetylenes or sesquiacetylenes,[5] was proved directly for similar propargylic systems.[5] Other metalations on the propargylic posi-

$$CH_3(CH_2)_7C{\equiv}C(CH_2)_8OR$$

I, R = H
II, R = CH_3



$$R{-}\overbrace{C{\equiv}C{\equiv}C}^{2-}{-}R$$

III

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