Aqueous Sulfolane as Solvent for Rapid Oxidation of Higher α-Olefins to Ketones Using Palladium Chloride

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As the chain length and substitution of olefins are increased, an overall decrease in the rate of their $PdCl_2$-catalyzed oxidation occurs.[1] Long-chain α-olefins are oxidized to methyl ketones only very slowly in entirely aqueous solutions of $PdCl_2$. Clement and Selwitz[2] found that oxidation rates of higher olefins are increased in aqueous *N,N*-dimethylformamide (DMF) solution while double-bond isomerizations are decreased. In a study of α-olefin oxidations with the Clement–Selwitz system, we consistently experienced DMF hydrolysis during oxidations. This resulted in the evolution of CO_2 (from formic acid oxidation[3]) and the formation of $PdCl_2(HNMe_2)_2$. Eventually, the $PdCl_2$ catalyst becomes completely poisoned.

As illustrated by the results given in Table I for the oxidation of 3,3-dimethylbut-1-ene, rapid oxidation can be achieved in aqueous 3-methylsulfolane (3-methyltetramethylenesulfone). Of the four solvent combinations listed in Table I, the aqueous 3-methylsulfolane system is clearly superior with respect to reaction rate and product yield. Sulfolanes are chemically very stable, and their low volatility allows easy product recovery. Sulfolane and 3-methylsulfolane can be used interchangeably, but sulfolane is less expensive and more readily available. Aqueous *N*-methylpyrrolidone (NMP) is an improved solvent compared to the corresponding DMF system, but its performance is less satisfactory than sulfolane's. The oxidation is very much slower in entirely aqueous media.

Table I
Solvent Dependence on 3,3-Dimethylbut-1-ene Oxidation[a]

Solvent (50 ml)	H_2O, ml	Reaction time, hr	Alkene conversion, %[b]	3,3-Dimethylbutan-2-one yield, %[c]
3-Methylsulfolane	7	1.4	~100	91
NMP	7	7.5	~100	79
DMF	7	8.0	~70	33
DMF	0	8.0	~70	58

[a] All solutions contained 200 mmol of 3,3-dimethylbut-1-ene, 20 mmol of $PdCl_2$, and 20 mmol of $CuCl_2 \cdot 2H_2O$. Reactions were conducted at 70–80° under 40–99 psig O_2. [b] Estimated by glpc as $wt_{ketone}/(wt_{alkene} + wt_{ketone}) \times 100\%$. [c] Distilled yield based on 200 mmol of 3,3-dimethylbut-1-ene.

At high alkene to $PdCl_2$ mole ratios, high selectivities to the ketone are obtained only at moderate olefin conversions (*e.g.*, entry 1 in Table II). In oxidations with similar turnover numbers of Pd, the highest selectivity to the ketone occurs at the highest alkene to $PdCl_2$ ratio (Table II).

Table II
Selectivity to Ketone at High Alkene to $PdCl_2$ Ratios

Mole ratio of 3,3-dimethylbut-1-ene to $PdCl_2$	Alkene conversion, %	Number of Pd turnovers	Selectivity to 3,3-dimethylbutan-2-one, %
421	24	101	96
211	59	123	81
100	100	100	77

When low selectivities are observed, they are a result of further reactions of the ketone. Two by-products which have been isolated are 1-chloro-3,3-dimethylbutan-2-one and 2,2-dimethylpropanoic acid.

Experimental Section

3,3-Dimethylbut-1-ene and the sulfolanes were Phillips Petroleum Co. products and were used without purification. Palladium chloride was purchased from Engelhard Industries. Other reagents were obtained commercially in high purity.

Small-Scale 3,3-Dimethylbut-1-ene Oxidations. Solvent studies were performed in a 6-oz (177 ml) aerosol compatibility bottle equipped with a stainless steel cap and sealed by a neoprene rubber ring. The cap was fitted with a pressure gauge and a valve connected to an oxygen source. After the bottle was charged with the desired reactants, as described in Table I, the bottle was pressured to 30–45 psig with O_2 and was then immersed in an oil bath held at 70–80°. The mixture was magnetically stirred, and whenever the pressure dropped to 40 psig, oxygen was added to increase the pressure to *ca.* 80 psig. After completion of the reaction, the reaction mixture was distilled, and all the material distilling up to 106° was collected. The organic portion of the distillate was redistilled, and 3,3-dimethylbutan-2-one was collected at 100–106°. This fraction and its immediate forerun were analyzed by glpc on a 6 ft × 0.125 in. column packed with 10% SP-1200–1% H_3PO_4 on 80/100 Chromosorb W AW temperature programmed from 80 to 140°. Each yield shown in Table I is the sum of the ketone product contained in these two fractions. The 100–106° fraction was 96–99% 3,3-dimethylbutan-2-one.

In the third entry in Table I, a glpc analysis of the gas phase in the bottle after completion of the reaction showed it to be 28% CO_2. The analysis was performed on a 20 ft × 0.25 in. column packed with 20% bis(2-methoxyethoxy)ethyl ether on 35/80 Chromosorb P at 40°. Filtration of this reaction mixture before distillation gave 2.40 g (37%) of gold $PdCl_2(HNMe_2)_2$ contaminated with a small amount of a green solid (a copper complex?). The complex has an ir spectrum identical with that of dimethylamine. Recrystallization of the sample from CH_2Cl_2–pentane afforded yellow crystals, mp 213–215° dec.

Anal. Calcd for $C_4H_{14}Cl_2N_2Pd$: C, 17.96; H, 5.28; Cl, 26.50; N, 10.48; Pd, 39.80. Found: C, 17.85; H, 4.93; Cl, 27.2; N, 10.48; Pd, 40.5.

Large-Scale 3,3-Dimethylbut-1-ene Oxidation. A similar procedure was used for the three reactions, so only a representative example is given. 2,2-Dimethylbutane, bp 49°, was present as an inert internal standard to monitor losses of 3,3-dimethylbut-1-ene, bp 41°, due to evaporation. A 300-ml 316-S.S. stirred autoclave with a glass cup insert was charged with 67.2 g (800 mmol) of 3,3-dimethylbut-1-ene, 0.34 g (1.9 mmol) of $PdCl_2$, 0.66 g (3.9 mmol) of $CuCl_2 \cdot 2H_2O$, 6 ml of 0.4 *N* HCl, 50 ml of sulfolane, and 16.8 g of 2,2-dimethylbutane. The autoclave was pressured to 220 psig with O_2 and was then heated to 120–130°. Heatup required 0.5 hr. The oxidation was allowed to proceed for 2.5 hr, and each time the pressure fell to 250 psig, oxygen was added until the pressure was 310 psig. The reactor was cooled to 25° over 2.5 hr. The product mixture was distilled at 1 mm with a pot temperature of 80°, and the distillate was trapped at −78°. The organic portion of the distillate was redistilled at atmospheric pressure, collecting 3,3-dimethylbut-1-ene and 2,2-dimethylbutane at 40–49° and 3,3-dimethylbutan-2-one at 95–106°. The alkane–alkene fraction was analyzed by glpc on a 20 ft × 0.125 in. column packed with 20% tris-1,2,3-(2-cyanoethoxy)propane on 60/80 Chromosorb P. The alkane recovery was 14.0 g (83.5%), and the alkene recovery was 42.9 g (63.9%). Assuming that the rate of evaporation is the same for both the alkane and the alkene, the actual 3,3-dimethylbut-1-ene conversion is calculated to be 23.5%. The total yield of 3,3-dimethylbutan-2-one was 18.0 g (95.8% selectivity based on 23.5% alkene conversion).

In a separate high-conversion alkene oxidation, two of the more prevalent by-products were isolated by preparative glpc and were identified by their ir, nmr, and mass spectra. 2,2-Dimethylpropanoic acid was confirmed by comparison of its ir spectrum with Sadtler[4] Spectrum No. 6355. The ir and nmr spectra of 1-chloro-3,3-dimethylbutan-2-one compare favorably with published[5] spectral information. Both compounds have the appropriate molecular ions in their mass spectra.

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Registry No. —3,3-Dimethylbut-1-ene, 558-37-2; 3,3-dimethyl-

butan-2-one, 75-97-8; $PdCl_2$, 7647-10-1; $CuCl_2$, 7447-39-4; $PdCl_2(HNMe_2)_2$, 52217-23-9.

References and Notes

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A New Synthesis of the Benzothiazole Ring *via* Imidoyl Chlorides and Chloroformamidines

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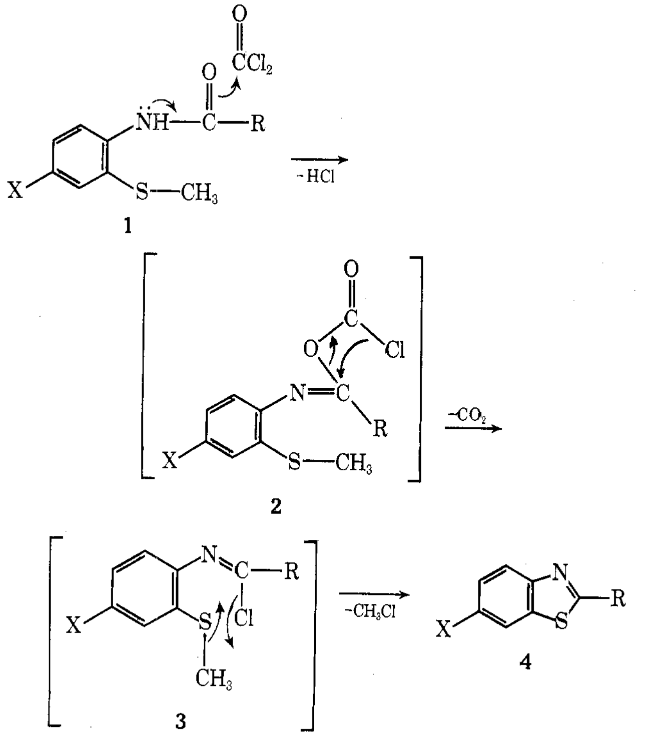
In an attempt to prepare a series of aromatic imidoyl chlorides as intermediates, 2′-(methylthio)acylanilides (**1**) were treated with phosgene in a manner similar to that reported for the preparation of imidoyl chlorides.[1] Although our attempt did not produce the desired imidoyl chlorides, *e.g.*, **3**, we did discover a convenient method of preparing 2-substituted benzothiazoles, **4**.

Results and Discussion

As a model compound, 2′-(methylthio)acetanilide (**1a**) was converted with phosgene into 2-methylbenzothiazole (**4a**) in 86% yield. In a convenient procedure, the reactants were heated (80°) and stirred in *p*-dioxane. After 0.5 to 1 hr, the hydrochloride of 2-methylbenzothiazole was isolated. Prolonged heating (8 hr at 80–98°) brought about evolution of hydrogen chloride to give **4a** as the only detectable reaction product.



a, $R = CH_3$; $X = H$
b, R = ◁; $X = Cl$
c, $R = CF_3$; $X = H$

4′-Chloro-2′-(methylthio)cyclopropanecarboxanilide (**1b**) reacted with phosgene in ethyl acetate at 50–55° (8 hr). Under these conditions, **4b** was obtained in 10% yield. No attempt was made to optimize the yield. The nmr spectrum of **4b** showed the expected proton count, shifts of three aromatic protons at 7–8 ppm, and the five cyclopropyl protons at δ 1.2 (CH_2CH_2) and 2.4 ppm (CH). Consistent with the structure of **4b**, the mass spectrum shows the correct molecular ion at m/e 209, 211 (M^+, base peak), indicating the presence of one chlorine atom in the molecule.

When 2′-(methylthio)trifluoroacetanilide (**1c**) was treated with phosgene under similar conditions, starting material, **1c**, was recovered unchanged after 96 hr at 80°. Attempted reaction with phosgene in refluxing toluene containing catalytic amounts of dimethylformamide was also unsuccessful. It was not possible to obtain 2-(trifluoromethyl)benzothiazole (**4c**) by either procedure.

The formation of benzothiazoles, **4**, from **1** and phosgene suggests that phosgene is attacked by the oxygen rather than the nitrogen of the anilide. O-Acylation of amides has been demonstrated.[2,3] Thus, the O-acylated intermediate, **2**, initially formed from **1** and phosgene apparently loses carbon dioxide and hydrogen chloride with formation of reactive imidoyl chloride,[1] **3**, which is converted into the benzothiazole, **4**, by loss of methyl chloride.

In a similar manner, the reaction of 1,1-dimethyl-3-(2′-(methylthio)phenyl)urea (**5**) with phosgene in *p*-dioxane was found to give the hydrochloride of the known 2-(di-