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Reaction of Urea with Ethylene in the Presence of Oxygen and a Nitrile-Sodium Tetrachloropalladate-Cupric Chloride Catalyst System

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The reactions of amines and amides with olefins in the presence of palladium chloride are generally complicated because of the fact that both the nucleophiles and the products form complexes with palladium chloride.[1–3] By hydrogenation of the resulting complexes Stern and Spector demonstrated the addition of nitrogen functions to olefins.[1] Hirai and Sawai reported the formation of *N*-vinylamides along with their complexes with palladium chloride by the reaction of ethylene-palladium(II) chloride complex with some cyclic amides in tetrahydrofuran.[3]

We found that urea in an acidic aqueous solution reacts with ethylene at room temperature to yield acetylurea in the presence of oxygen and a nitrile-sodium tetrachloropalladate-cupric chloride catalyst system. Sodium tetrachloropalladate was stirred in acetonitrile or benzonitrile for 1 to 3 hr. Most of the palladate dissolved to form a reddish-orange solution of the nitrile-palladium(II) chloride complex[4] leaving precipitates of sodium chloride. Toluene and an aqueous hydrochloric acid solution of urea and cupric chloride were added, and the mixture was stirred while ethylene and oxygen were bubbled through.[5] Crystals of crude acetylurea separated. The results are summarized in Table 1. In the absence of nitrile, Pd(II) readily combined with urea to form precipitates of bis(urea)dichloropalladium(II), which could not catalyze the reaction.

When the reaction temperature was above 30°C, formation of 6-methyl-2-oxo-4-hexahydropyrimidinylurea became predominant. There is hardly any doubt that this compound results from the condensation of urea with acetaldehyde formed by the oxidation of ethylene with Pd(II), since it is known that the

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[1] E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, **1961**, 370.

[2] H. Hirai, H. Sawai, and S. Makishima, This Bulletin, **43**, 1148 (1970).

[3] H. Hirai and H. Sawai, *ibid.*, **43**, 2208 (1970).

[4] R. A. Walton, *Spectrochim. Acta*, **21**, 1795 (1965).

[5] Cupric chloride and oxygen obviously function to regenerate Pd(II) by the redox cycle [J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Ruttinger, and H. Kojer, *Angew. Chem.*, **71**, 176 (1959)].

Table 1. Reaction of urea with ethylene in the presence of oxygen and a nitrile–sodium tetrachloropalladate–cupric chloride catalyst system[a)]

Expt. No.	Nitrile, m*l*	Na_2PdCl_4 g	$PhCH_3$ m*l*	H_2O m*l*	$CuCl_2$ g	Urea g	pH	Time hr	Yield of acetylurea[b)] %
1	CH_3CN, 50	1.34	50	100	2.5	15	0.9[c)]	18	1810
2	CH_3CN, 50	1.34	50	200	2.5	15	1.4[c)]	18	3150
3[e)]	CH_3CN, 50	3.4	—	50	5.5	15	1.5[d)]	13	f)
4	PhCN, 50	1.34	50	100	2.5	15	0.9[c)]	7	860
5	PhCN, 50	1.34	50	100	2.5	15	1.3[c)]	13	1510
6	PhCN, 50	1.34	50	100	2.5	15	3.2[c)]	13	770
7[e,g)]	PhCN, 50	1.34	50	50	2.5	7.5	1.4[c)]	14	340

a) Reactions were carried out at room temperature and at flow rates of ethylene and oxygen, 0.25 and 0.5 mol/hr, respectively, unless otherwise stated.

b) The yields are given based on Pd(II), assuming the stoichiometry of 1 mole of acetylurea per 2 moles of Pd(II).

c) The value indicates the pH of the aqueous phase containing $CuCl_2$ and urea.

d) The value indicates the pH of aqueous hydrochloric acid, in which $CuCl_2$ and urea were dissolved.

e) Flow rate was 0.3 mol/hr for both ethylene and oxygen.

f) 10.7 g of a mixture of acetylurea and 6-methyl-2-oxo-4-hexahydropyrimidinylurea was obtained.

g) Reaction was carried out at 0—5°C.

condesnation leads to the cyclic product in an acidic aqueous solution and at an elevated temperature.[6)]

N-vinylation (Eq. 1) rather than ethylolation of urea (Eq. 2) might be involved in acetylurea formation:[3)] Acetaldehyde in place of ethylene gives no acetylurea under otherwise similar reaction conditions.

$$\begin{aligned} &CH_2{=}CH_2 + H_2NCONH_2 \xrightarrow{Pd^{++}} \\ &\qquad [CH_2{=}CHNHCONH_2] + 2H^+ + Pd^0 \\ &\qquad \Big\downarrow {\scriptstyle H_2O \,\mid\, Pd^{++}} \\ &\qquad CH_3CONHCONH_2 + 2H^+ + Pd^0 \qquad (1) \end{aligned}$$

$$\begin{aligned} &CH_3CHO + H_2NCONH_2 \longrightarrow \\ &\qquad [CH_3CH(OH)NHCONH_2] \\ &\qquad \Big\downarrow {\scriptstyle Pd^{++} \,\mid\, \text{or } Pd^0} \\ &\qquad CH_3CONHCONH_2 \qquad (2) \end{aligned}$$

Experimental

Melting points are uncorrected. The infrared spectra were obtained with a Nihon Bunko Model IR-S spectrophotometer using KBr disks.

Typical Procedure. Acetylurea (Expt. 2): Sodium tetrachloropalladate (1.34 g, 4.55 mmol) was stirred in acetonitrile (50 m*l*) for 1 hr at room temperature. Toluene (50 m*l*) and an aqueous solution (200 ml) containing cupric chloride (anhydrous, 2.5 g) and urea (15 g, 0.25 mol) and adjusted at pH 1.4 with hydrochloric acid were added. The mixture was stirred at room temperature while ethylene and oxygen were bubbled through the mixture. After 18 hr, the crude crystals of acetylurea were filtered, washed successively with cold water, methanol and ether, and dried. The yield was 7.3 g. Recrystallization from ethanol gave needles, mp 215—216°C (lit,[7)] 216—217°C, corrected).

Found: C, 35.32; H, 5.99; N, 27.31%. Calcd for $C_3H_6N_2O_2$: C, 35.29; H, 5.92; N, 27.44%.

The IR spectrum was identical with that of acetylurea reported.[8)] A mixture melting point with the authentic sample showed no depression.

The yield was calculated on the basis of the crude product, which amounted to 29% based on starting urea, corresponding to 3150% based on Pd(II) charged; the crude product was proved to be pure by its IR spectrum.

6-Methyl-2-oxo-4-hexahydropyrimidinylurea: Sodium tetrachloropalladat e(3.4 g, 0.0116 mol) was stirred with benzonitrile (130 m*l*) for 3 hr and ethylene was bubbled for about 30 min. The temperature was raised to 50—60°C and a solution of cupric chloride (5.5 g) and urea (15 g, 0.25 mol) in aqueous hydrochloric acid (25 m*l*; pH, 1.5) was added. The mixture was stirred at 50—60°C, while ethylene and oxygen were bubbled through the mixture each at a flow rate of 0.3 mol/hr. After 6.5 hr, the crude crystals of 6-methyl-2-oxo-4-hexahydropyrimidinylurea were collected, washed with cold water, methanol and ether, and dried (8.4 g). Analytical sample was obtained by recrystallization from water, mp 238°C (lit,[6)] 245°C).

Found: C, 41.86; H, 7.14; N, 32.39%. Calcd for $C_6H_{12}N_4O_2$: C, 41.85; H, 7.03; N, 32.54%.

The IR spectrum was identical with that of the authentic sample prepared from crotonaldehyde and urea.[9)] A mixture melting point determination showed no depression.

The yield of the crude product, the IR spectrum of which was apparently the same as that of the pure one, was 39% based on starting urea, corresponding to 840% based on Pd(II).

Attempted Reaction Using Acetaldehyde in Place of Ethylene. Pd(II) Catalyst: Sodium tetrachloropalladate (1.3 g) was treated with acetonitrile (50 m*l*). Toluene (100 m*l*) and a solution of cupric chloride (2.5 g) and acetaldehyde (5.5 g) in aqueous hydrochloric acid (30 m*l*; pH, 1.3) were added. With the mixture kept at 0—6°C, oxygen was introduced and a solution of urea (7 g) in aqueous hydrochloric acid (20 m*l*; pH, 1.3) was gradually added under stirring. After 13 hr at 0—6°C and additional 2 hr at 15°C, the reaction was stopped. No crystals separated. On standing at room temperature overnight, some crystals deposited from the reaction mixture (1.1 g). The IR spectrum revealed

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6) G. Zigeuner, E. A. Gardziella, and G. Bach, *Monatsh. Chem.*, **92**, 31 (1961).

7) R. W. Stoughton, *J. Org. Chem.*, **2**, 518 (1938).

8) "Sadler Infrared Prism Spectra," No. 36705, Sadler Research Laboratories Inc., Philadelphia, Pa. (1969); T. Uno, K. Machida, K. Hanai, and Y. Saito, This Bulletin, **42**, 619 (1969).

9) A. M. Paquin, *Kunststoffe*, **37**, 165 (1947).

that the product was hexahydro-6-methyl-2-oxo-4-pyrimidinylurea free from acetylurea.

Metallic Palladium Catalyst: Sodium tetrachloropalladate (3.4 g) was treated with benzonitrile (75 m*l*) and ethylene was bubbled through to form ethylene-palladium(II) chloride complex. Metallic palladium was formed when a solution of acetaldehyde (22 g) in aqueous hydrochloric acid (50 m*l*; pH, 1.5) was added and the mixture was stirred for some time. A solution of urea (15 g) in aqueous hydrochloric acid (50 m*l*; pH, 1.5) was gradually added, while oxygen was bubbled through at 0—5°C. The supply of oxygen was continued for 13 hr at 0—5°C under stirring. The precipitate was filtered, which proved to be only metallic palladium.