was isolated as a white crystalline solid: mp 173.5–174.5 °C; NMR ($CDCl_3$) 8.65 (br, 2 H), 7.47 (s, 5 H), 7.17 (d, 1 H), 6.90 (d, 1 H), 5.91 (s, 1 H), 5.50 (d, 1 H), 5.42 (d, 1 H), 1.02 (s, 9 H), 0.22 (s, 3 H), 0.10 (s, 3 H). Anal. Calcd for $C_{18}H_{27}N_3OSSi$: C, 59.79; H, 7.53; N, 11.62. Found: C, 59.71; H, 7.29; N, 11.44.

2-(*tert*-Butyldimethylsiloxy)-2-phenylthioacetamide (5b). A mixture of 5.0 g (20 mmol) of 2-(*tert*-butyldimethylsiloxy)-2-phenylacetonitrile (**4b**), 10.4 g (42 mmol) of diphenylphosphinodithioic acid,[3] and 400 mL of isopropyl alcohol was heated at 60 °C for 24 h. The mixture was cooled to room temperature, and the precipitate was removed by filtration, washed with isopropyl alcohol and then ether. The combined filtrate and washings were concentrated and the residue chromatographed over silica gel with 29:1 hexane/ethanol as eluent. After removal of less polar impurities, the product was collected as a solid. Recrystallization from low boiling petroleum ether (4.5 g/7.5 mL of solvent and then cooling in dry ice/acetone) afforded 3.6 g (63%) of **5b** as a white crystalline solid: mp 52–54 °C; NMR ($CDCl_3$) 8.4 (br, 2 H), 7.7–7.2 (m, 5 H), 5.53 (s, 1 H), 0.98 (s, 9 H); 0.17 (s, 3 H), 0.08 (s, 3 H). Anal. Calcd for $C_{14}H_{23}NOSSi$: C, 59.74; H, 8.24; N, 4.98; S, 11.39. Found: C, 59.77; H, 8.10; N, 4.67; S, 11.74.

2-(*tert*-Butyldimethylsiloxy)thioheptanamide (5c). With the same procedure outlined for the synthesis of **5b**, 1-(*tert*-butyldimethylsiloxy)-1-cyanohexane (**4c**) was converted to **5c**, mp 40–41 °C, in 37% yield: NMR ($CDCl_3$) 8.0–7.6 (br, 2 H) 4.59 (t, 1 H), 2.0–1.2 (m, 8 H), 0.96 (s + t, 12 H), 0.13 (s, 3 H), 0.10 (s, 3 H). Anal. Calcd for $C_{13}H_{29}NOSSi$: C, 56.67; H, 10.61; N, 5.08. Found: C, 56.79; H, 10.86; N, 4.79.

2-(*tert*-Butyldimethylsiloxy)-2-(2-pyridyl)thioacetamide (5d). With the same procedure outlined for the synthesis of **5b**, 2-(*tert*-butyldimethylsiloxy)-2-(2-pyridyl)acetonitrile (**4d**) was converted to **5d**, mp 106.5–107.5 °C, in 42% yield: NMR ($CDCl_3$) 8.70 (m, 1 H), 8.60 (br, 2 H), 7.81 (m, 1 H), 7.6–7.4 (m, 2 H), 5.72 (s, 1 H), 0.96 (s, 9 H), 0.20 (s, 3 H), 0.08 (s, 3 H). Anal. Calcd for $C_{13}H_{22}N_2OSSi$: C, 55.28; H, 7.85; N, 9.92. Found: C, 54.90; H, 7.68; N, 9.69.

2-Hydroxy-2-phenylthioacetamide (8b). A mixture of 1.65 g (5.9 mmol) of 2-(*tert*-butyldimethylsiloxy)-2-phenylthioacetamide (**5b**) and 65 mL of dry THF was stirred at 0 °C, and 3.72 g (11.8 mmol) of tetra-*n*-butylammonium fluoride was added in one portion. The mixture was allowed to stir at room temperature for 1 h, and then the mixture was concentrated. The oil residue was partitioned between 100 mL of water and 100 mL of ether. The ether portion was separated and the aqueous solution extracted twice more with 50-mL portions of ether. The combined ether extracts were dried (Na_2SO_4), filtered, and evaporated leaving a solid. Recrystallization from toluene afforded 965 mg (98%) of **8b** as a white crystalline solid: mp 113.5–116 °C; NMR (Me_2SO-d_6, D_2O) 7.6–7.2 (m, 5 H), 5.33 (s, 1 H). Anal. Calcd for C_8H_9NOS: C, 57.46; H, 5.42; N, 8.38; O, 9.57; S, 19.18. Found: C, 57.62; H, 5.59; N, 7.95; O, 9.30; S, 18.65.

2-Hydroxythioheptanamide (8c). With the same procedure outlined for the synthesis of **8b**, 2-(*tert*-butyldimethylsiloxy)-thioheptanamide was converted into **8c**. This product was initially isolated as an oil but was crystallized by trituration with 2:1 hexane/toluene and scratching with a glass rod. Recrystallization from 2:1 hexane/toluene afforded the product as a white crystalline solid, mp 68–70 °C, in 54% yield: NMR (Me_2SO-d_6): 9.78 (br, 1 H), 9.06 (br, 1 H), 5.67 (d, 1 H), 4.17 (br 1 H), 1.91–1.1 (m, 8 H), 0.90 (t, 3 H). Anal. Calcd for $C_7H_{15}NOS$: C, 52.14; H, 9.38; N, 8.69. Found: C, 52.31; H, 9.21; N, 8.78.

2-[(1-Benzyl-2-imidazolyl)hydroxymethyl]-4-(2-methyl-4-imidazolyl)thiazole (7). A mixture of 17.8 g (87.5 mmol) of 1-(2-methyl-4-imidazolyl)-2-bromoethanone (**2**),[5] 31.6 g (87.5 mmol) of 2-(*tert*-butyldimethylsiloxy)-2-(1-benzyl-2-imidazolyl)thioacetamide (**5a**), and 2 L of acetone was stirred at room temperature. After 15 min, the mixture became homogeneous, and, after another 15 min, a precipitate began to form. After the mixture was stirred at room temperature for 48 h, the precipitate was collected, washed with acetone, and dried in vacuo, giving adduct **6** as its hydrobromide, mp 179–180 °C. This was converted to its free base by partitioning between 500 mL of ethyl acetate and 300 mL of saturated sodium bicarbonate solution. The organic portion was separated, and the aqueous solution was extracted twice more with 150-mL portions of ethyl acetate. The combined ethyl acetate layers were dried (Na_2SO_4), filtered, and evaporated, leaving 34.6 g (85%) of **6** as a yellow solid. This was generally deprotected directly.

A mixture of 9.74 g (21 mmol) of **6** in 250 mL of dry THF was stirred at −10 °C under nitrogen and 15.8 g (50 mmol) of tetra-*n*-butylammonium fluoride was added directly. The mixture was stirred at −10 °C for 1 h and then at room temperature for 30 min. The mixture was concentrated, and the residue was repeatedly triturated with water and decanted, all the while being sure to break up the yellow solid into tiny particles. The yellow solid was collected, washed with water, and dried in vacuo to afford 4.0 (54%) of pure **7**: mp 230–232.5 °C; NMR (Me_2SO-d_6) 7.37 (s, 1 H), 7.3–7.1 (m, 5 H), 7.0 (s, 1 H), 6.90 (d, 1 H), 6.68 (d, 1 H), 5.96 (s, 1 H), 5.09 (s, 2 H), 2.12 (s, 3 H). Anal. Calcd for $C_{18}H_{17}N_5SO$: C, 61.52; H, 4.88; N, 19.93; S, 9.12. Found: C, 61.81; H, 5.16; N, 19.45; S, 8.87.

2-(1-Benzyl-2-keto-2-imidazolyl)-4-(2-methyl-4-imidazolyl)thiazole (1). A mixture of 315 mg (0.9 mmol) of 2-[(1-benzyl-2-imidazolyl)hydroxymethyl]-4-(2-methyl-4-imidazolyl)thiazole (**7**), 3 g of MnO_2, and 20 mL of dry THF was stirred 0 °C for 2 h. The mixture was filtered through Celite and the filtrate concentrated. The resulting yellow solid was triturated with ether, finely powdered with a glass rod, and then stirred in ether for 30 min. The solid was collected, washed with ether, and dried in vacuo to afford 228 mg (73%) of pure **1**: mp 198.5–199.5 °C; NMR (Me_2SO-d_6) 8.06 (s, 1 H), 7.90 (s, 1 H), 7.5–7.2 (m, 7 H), 5.74 (s, 2 H), 2.32 (s, 3 H). Anal. Calcd for $C_{18}H_{15}N_5OS$: C, 61.87; H, 4.33; N, 20.04. Found: C, 61.53; H, 4.54; N, 19.89.

Registry No. **1**, 99808-97-6; **2**, 92049-88-2; **3**, 10045-65-5; **4a**, 99808-98-7; **4b**, 99808-99-8; **4c**, 99809-00-4; **4d**, 99809-01-5; **5a**, 99809-02-6; **5b**, 99809-03-7; **5c**, 99809-04-8; **5d**, 99809-05-9; **6**, 99809-10-6; **6**·HBr, 99809-09-3; **7**, 99809-08-2; **8b**, 99809-06-0; **8c**, 99809-07-1; diphenylphosphinodithioic acid, 1015-38-9; *tert*-butyldimethylsilyl cyanide, 56522-24-8; benzaldehyde, 100-52-7; hexanal, 66-25-1; pyridine-2-carboxaldehyde, 1121-60-4; tetra-*n*-butylammonium fluoride, 311-28-4.

(5) LaMattina, J. L.; Lipinski, C. A. U.S. Patent 4 374 843, Feb 22, 1983.

Palladium-Catalyzed Double Carbonylation of Aryl Halides Affording α-Keto Amides. Applications to Synthesis of Isatin and Quinoline Derivatives

Fumiyuki Ozawa, Hisayoshi Yanagihara, and Akio Yamamoto*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Received August 6, 1985

Recently developed palladium-catalyzed double carbonylation reactions provide convenient synthetic means for introducing two reactive carbonyl groups into organic moieties. Various organic halides can be readily converted into corresponding α-keto acid derivatives in these reactions.[1-3] Since α-keto acid derivatives are known to be potentially useful starting materials of various organic

(1) (a) Ozawa, F.; Soyama, H.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1982**, *23*, 3383. (b) Ozawa, F.; Soyama, H.; Yanagihara, H.; Aoyama, I.; Takino, H.; Izawa, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1985**, *107*, 3235. (c) Ozawa, F.; Kawasaki, N.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1985**, 567.

(2) (a) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem.* **1982**, *233*, C64. (b) Tanaka, M.; Kobayashi, T.; Sakakura, T. *J. Chem. Soc., Chem. Commun.* **1985**, 837.

(3) Itatani, H.; Dan-no, H.; Zushi, K. Jpn. Kokai Tokkyo Koho JP60-19750, 1985. Tanaka, M.; Kobayashi, T.; Sakakura, T.; Itatani, H.; Danno, S.; Zushi, K. *J. Mol. Catal.* **1985**, *32*, 115.

0022-3263/86/1951-0415$01.50/0

Table I. Double Carbonylation of o-Haloacetanilide in the Presence of Et_2NH[a]

run	halide	catalyst[b]	reacn temp, °C	CO, atm	reacn time, h	yield,[c] % α-keto amide 2	yield,[c] % amide 3	conversion of halide, %
1	1a	A	60	56	17	47 (37)	48 (38)	100
2	1a	A	40	52	40	82 (63)	18 (15)	100
3	1a	A	30	56	72	67	26	87
4	1a	A	40	46	48	77 (53)	17 (13)	100
5	1a	A	40	42	40	64 (55)	34 (34)	100
6	1a	B	40	52	40	30	70	100
7	1b	A	100	25	70	49	51	100
8	1b	A	100	45	70	62	14	77

[a] Reaction conditions: o-haloacetanilide/Et_2NH/catalyst = 1/10/0.02 (molar ratio). Reactions were carried out without solvent. [b] A: $PdCl_2(PMePh_2)_2$. B: $PdCl_2(Ph_2P(CH_2)_4PPh_2)$. [c] Determined by means of GLC. Isolated yields are in parentheses.

compounds,[4] the present double carbonylation reactions should be useful in organic synthesis. In this paper we describe some of our exploratory studies of utilization of the double carbonylation reaction and demonstrate that it is in fact applicable to the synthesis of isatin[5] and quinoline derivatives.

α-Keto Amidation. Double carbonylation of o-haloacetanilides **1a,b** in the presence of Et_2NH gives corresponding α-keto amide **2** together with amide **3**. Under appropriate conditions **2** is obtained in over 80% yield.

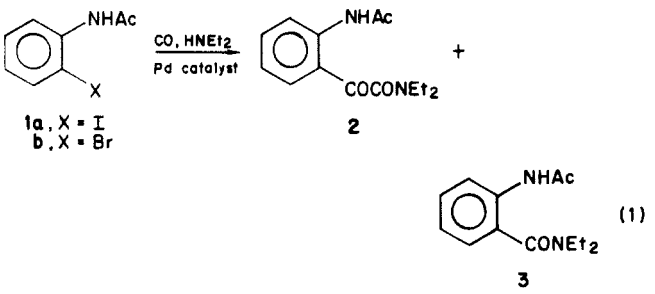
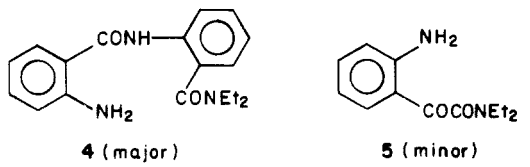
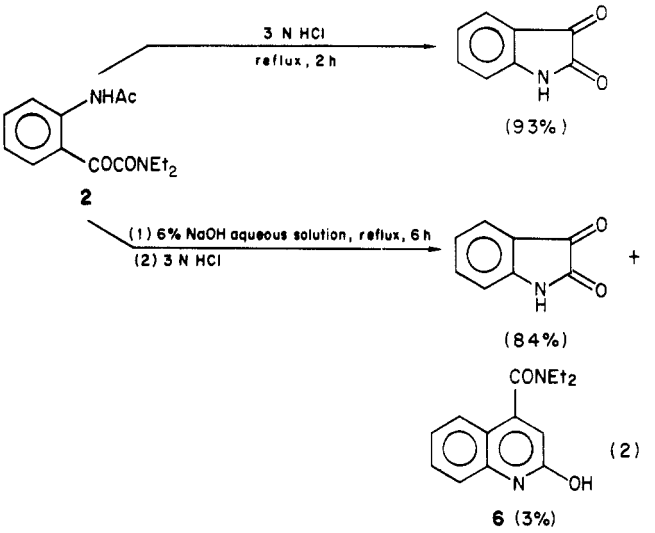


Table I summarizes typical results of the double carbonylation of **1**. Two kinds of palladium complexes, $PdCl_2(PMePh_2)_2$ and $PdCl_2$(dppb) (dppb = 1,4-bis(diphenylphosphino)butane) were examined as catalysts. These complexes were similarly effective catalysts in the double carbonylation of PhBr and PhI in the presence of Et_2NH.[1b] In the present system, however, the $PMePh_2$-coordinated complex gives the α-keto amide in a much higher yield than the dppb-coordinated complex under the same reaction conditions. In the reaction of the iodide **1a**, the selectivity for **2** tends to increase at lower temperature and under higher CO pressure. Reactivity of the bromide is considerably lower than that of the iodide and the reaction of **1b** requires higher reaction temperature and longer reaction time.

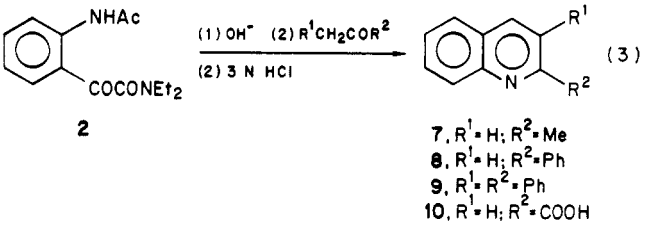
Double carbonylation of o-bromoaniline in the presence of Et_2NH using $PdCl_2(PMePh_2)_2$ as catalyst afforded mainly the substituted benzanilide **4** and little of the desired α-keto amide **5**.



Preparation of Isatin. Compound **2** was readily hydrolyzed in 3 N aqueous HCl under reflux to give almost a quantitative yield of isatin, whereas base-catalyzed hydrolysis of **2** yielded a minor amount (3%) of a quinoline derivative **6** as a byproduct. Compound **6** may have been formed by Camps reaction[6] caused by abstraction of the acetyl proton in **2** by OH^- ion.



Preparation of Quinoline Derivatives. We here show an application to the Pfitzinger reaction affording quinoline derivatives,[7] several of which (**7–10**) were prepared in good yields, with no byproduct, from **2** according to reaction 3. The results are listed in Table II.



Experimental Section

Infrared spectra were recorded on a Hitachi 295 spectrometer. ^1H NMR spectra were measured on a JEOL FX-100 spectrometer. ^1H NMR signals are referred to Me_4Si as an internal standard. Micro analyses (C, H, N, and Cl) were carried out with a Yanagimoto CHN autocorder Type MT-2 and a Yazawa halogen analyzer. Mass spectra were obtained on a Hitachi M-80 spectrometer.

Palladium catalysts were prepared by reactions of $PdCl_2(PhCN)_2$ and corresponding tertiary phosphines. o-Iodo- and o-bromoacetanilides were prepared by acetylation of corresponding

(4) (a) Valentine, D., Jr.; Scott, J. W. *Synthesis* **1978**, 329. (b) Cooper, A. J. L.; Ginos, J. Z.; Meister, A. *Chem. Rev.* **1983**, *83*, 321.
(5) Popp, F. D. *Adv. Hetercycl. Chem.* **1975**, *18*, 1.
(6) Camps, R. *Ber.* **1899**, *32*, 3228.
(7) (a) Pfitzinger, W. *J. Prakt. Chem.* **1886**, *33*, 100. (b) Manske, R. H. *Chem. Rev.* **1942**, *30*, 113.

Table II. Synthesis of Quinoline Carboxylic Acids from α-Keto Amide 2 and $R^1CH_2COR^2$

run	R^1	R^2		reacn conditions	yield, %
1	H	Me	7	8% NaOH (H_2O), 8 h reflux	75[a]
2	H	Ph	8	18% NaOH (H_2O), 18 h reflux	72
3	Ph	Ph	9	33% KOH (EtOH–H_2O), 25 h reflux	81
4	H	COOH	10	33% KOH (H_2O), 16 h at room temperature and 2 h reflux	74

[a] Isolated as immonium salt.

o-holoacetanilides and identified by means of IR spectroscopy and elemental analysis.

Double Carbonylation of *o*-Haloacetanilide. Typical procedure is as follows: *o*-Iodoacetanilide (**1a**, 1.57 g, 6.0 mmol) and Et_2NH (6.0 mL, 58 mmol) were added to a 100-mL stainless steel pressure bottle containing $PdCl_2(PMePh_2)_2$ (0.071 g, 0.12 mmol) under argon. After evacuating the system, 52 atm of CO gas was introduced at room temperature, and the mixture was stirred at 40 °C for 40 h. After purging the CO gas, the mixture was extracted with Et_2O (10 mL × 2). GLC analysis (Silicone OV-1, 2-m column; *o*-terphenyl as internal reference) revealed a mixture of 82% of *N,N*-diethyl-*o*-acetamidophenylglyoxylamide (**2**) and 18% of *N,N*-diethyl-*o*-acetamidobenzamide (**3**).

Compounds **2** and **3** were isolated as white crystals by column chromatography (silica, hexane–Et_2O). **2**: mp 76–77 °C; IR (KBr) 3270, 1720, 1670, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 and 1.30 (each t, 3 H, J = 7 Hz, NCH_2CH_3), 2.25 (s, 3 H, $COCH_3$), 3.29 and 3.60 (each q, 2 H, J = 7 Hz, NCH_2), 7.13, 7.66, and 8.80 (total 4 H, Ar), 11.32 (s, 1 H, NH); MS, *m/e* 262 (M^+). Anal. Calcd for $C_{14}H_{18}N_2O_3$: C, 64.11; H, 6.92; N, 10.68. Found: C, 64.13; H, 6.99; N, 10.69. **3**: mp 127–128 °C; IR (KBr) 3270, 1700, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (t, 6 H, J = 7 Hz, NCH_2CH_3), 2.12 (s, 3 H, $COCH_3$), 3.44 (q, 4 H, J = 7 Hz, NCH_2), 6.9–7.6 and 8.08 (total 4 H, Ar), 8.71 (s, 1 H, NH); MS, *m/e* 234 (M^+). Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.48; H, 7.78; N, 11.90.

Preparation of Isatin. Compound **2** (390 mg, 1.5 mmol) was hydrolyzed in 3 N HCl aqueous solution (5 mL) under reflux. The initially heterogeneous reaction mixturee turned into a reddish orange homogeneous solution after 30 min. On further reflux, reddish orange crystals of isatin gradually precipitated. After 2 h, the system was cooled to room temperature, and the crystals were collected by filtration, washed with water, and dried in vacuo (170 mg). The filtrate was extracted with ethyl acetate (20 mL × 5) until the aqueous solution became colorless. The extract was evaporated to dryness to give isatin (54 mg) as an orange solid. Sublimation afforded pure isatin (204 mg, 93%), with the mp and IR spectrum identical with those of an authentic sample.

Preparation of 2-Methylquinoline-4-carboxylic Acid Immonium Salt (7). A heterogeneous mixture of **2** (262 mg, 1.0 mmol) and NaOH (250 mg, 6.3 mmol) in water (3 mL) was heated under reflux. After 1 h, the system turned into a yellow homogeneous solution (**2** absent by TLC). Acetone (2 mL) was added to the solution, and the system was refluxed for 8 h. After removal of unreacted acetone by distillation and cooling to 0 °C, the solution was made acidic (pH 2) with 3 N HCl, to yield yellow-brown crystals. Concentration of the solution yielded additional crystals. The crystals were collected by filtration, washed with cold water, EtOH, and $CHCl_3$, and dried in vacuo (176 mg). Sublimation yielded yellow crystals of **7** (167 mg, 89%): mp 257–259 °C dec; IR (KBr) 3400–2600, 1730, 1670, 1260, 1230 cm^{-1}; MS, *m/e* 187 (M^+ – HCl). Anal. Calcd for $C_{11}H_{10}NO_2Cl$: C, 59.36; H, 4.51; N, 6.26; Cl, 15.85. Found: C, 59.36; H, 5.06; N, 5.94; Cl, 15.58.

Compounds **8**, **9**, and **10** were similarly obtained as yellow crystals. The reaction conditions are listed in Table II. **8**: mp 227–228 °C (lit.[8] mp 212–213 °C); IR (KBr) 3400–2450, 1720, 1600, 1550, 1260 cm^{-1}; MS, *m/e* 249 (M^+). Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 76.91; H, 4.37; N, 5.54. **9**: mp 298 °C dec (lit.[9] mp 295 °C); IR (KBr) 3400–2400, 1690, 1650, 1610, 1590, 1280, 1250; MS, *m/e* 325 (M^+). Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30. Found: C, 81.43; H, 4.38; N, 4.41. **10**: mp 257 °C dec (lit.[9] mp 245 °C); IR (KBr) 3500–2300, 1720, 1650, 1620, 1580, 1300, 1260, 1240; MS, *m/e* 217 (M^+). Anal. Calcd for $C_{11}H_7NO_4$: C, 60.84; H, 3.25; N, 6.45. Found: C, 60.26; H, 3.44; N, 6.13.

Acknowledgment. We are grateful for support of this work by Grants-in-Aid for scientific research from the Ministry of Education, Japan.

Registry No. **1a**, 19591-17-4; **1b**, 614-76-6; **2**, 99686-93-8; **3**, 99686-94-9; **4**, 99686-95-0; **5**, 99686-96-1; **6**, 99686-97-2; **7**, 634-38-8; **8**, 132-60-5; **9**, 99686-98-3; **10**, 5323-57-9; $PdCl_2(PMePh_2)_2$, 52611-08-2; $PdCl_2(Ph_2P(CH_2)_4PPh_2)$, 29964-62-3; $PhCH_2COPh$, 451-40-1; CH_3COCO_2H, 127-17-3; Et_2NH, 109-89-7; CH_3COCH_3, 67-64-1; CH_3COPh, 98-86-2; isatin, 91-56-5.

(8) Boehm, R.; Bournot, K. *Chem. Ber.* **1915**, *48*, 1570.
(9) Pfitzinger, W. *J. Prakt. Chem.* **1877**, *56*, 283.

Reaction of Cycloaliphatic Carbodiimides with Oxalyl Chloride

R. Richter* and E. A. Barsa

Dow Chemical USA, North Haven Laboratories, North Haven, Connecticut 06473

Received September 30, 1985

The addition of oxalyl chloride to the cumulated CN double bonds of carbodiimides has been reported to afford 1,3-disubstituted 2,2-dichloroimidazolidine-4,5-diones in high yields.[1] Similarly, methyloxalyl chloride reacts with *N,N'*-dialkyl- as well as *N,N'*-diarylcarbodiimides across both CN double bonds in a stepwise fashion and with elimination of methyl chloride to ultimately yield 1,3-disubstituted imidazolidine-2,4,5-triones.[2] We recently found that oxalyl chloride adds to isothiocyanates also across both double bonds of the heterocumulene; alkyl and aryl isocyanates, on the other hand, underwent a different type of addition which involved only the CN double bond and afforded 3-substituted 5,5-dichlorooxazolidine-2,4-diones.[2]

In this context it was of interest to study the behavior of aliphatic cyclic carbodiimides[3] toward oxalyl chloride and methyloxalyl chloride and see whether steric restrictions have any influence on the course of the reactions.

1,3-Diazacyclotetradeca-1,2-diene (**1c**) reacts instantaneously with equimolar amounts of oxalyl chloride at room temperature to produce a moisture-sensitive adduct that we believe to have the bicyclic structure **2**. A ^{13}C NMR spectrum of the crude product shows a signal at 103.0 ppm belonging to the orthocarbonic acid carbon bearing two chlorines and two nitrogens while the carbonyl carbons appear at 155.6 ppm downfield from M_4Si. Both chemical shift values compare well with those of other 1,3-disubstituted 2,2-dichloroimidazolidine-4,5-diones. The 1,3-diphenyl derivative has corresponding signals at 102.3 and

(1) Zinner, G.; Vollrath, R. *Chem. Ber.* **1970**, *103*, 766. Gross, H.; Zinner, G. *Chem. Ber.* **1973**, *106*, 2315. Stachel, H. D. *Angew. Chem.* **1959**, *71*, 246. Ulrich, H.; Sayigh, A. A. R. *J. Org. Chem.* **1965**, *30*, 2781.
(2) Richter, R.; Stuber, F. A.; Tucker, B. *J. Org. Chem.* **1984**, *49*, 3675.
(3) All aliphatic cyclic carbodiimides described herein have been synthesized by ring expansion from the corresponding lactam oxime *O*-mesylates in presence of base or by dehydrosulfuration of thioureas as reported: Richter, R.; Tucker, B.; Ulrich, H. *J. Org. Chem.* **1983**, *48*, 1694.

0022-3263/86/1951-0417$01.50/0