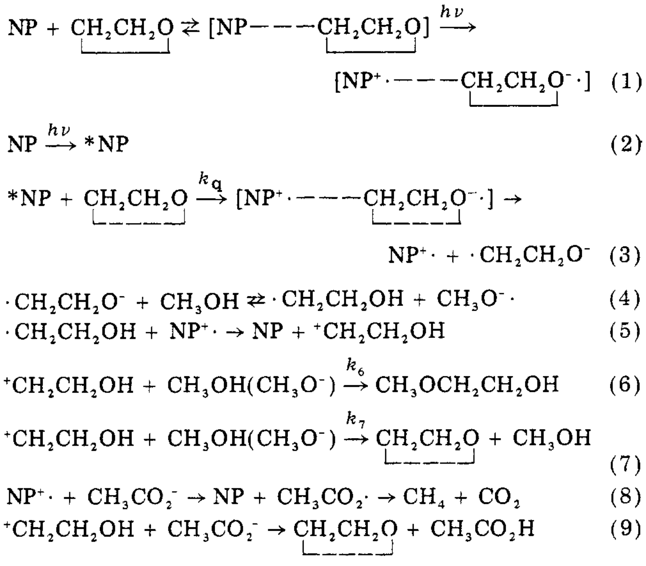
Table I. Naphthalene Derivative Sensitized Photosolvolysis of Oxiranes in Methanol

naphthalenes	$E_{(D/D^+)}$,[a] eV	E_S,[b] eV	τ,[c] ns	cyclohexene oxide Φ[d]	cyclohexene oxide $10^{-9}k_q$, M^{-1} s^{-1}	styrene oxide Φ[d]	styrene oxide $10^{-9}k_q$, M^{-1} s^{-1}
1-OH	0.63	3.84	7.5	0.32	1.1	0.38	1.4
2-OH	1.07	3.76	8.9	0.16	0.38	0.21	0.51
1-OCH_3	1.38	3.86	49	0.33	0.18	0.40	0.23
H	1.54	3.87	96	0.11	0.022	0.21	0.047
1-CN	>2	3.86	26	<0.01	<0.007	<0.01	<0.007

[a] The oxidation potentials are taken from ref 16–18. [b] The lowest singlet-state energies are taken from ref 19 except 1-naphthol, E_S of which was calculated from the 0–0 transition band at 323 nm in methanol. [c] The singlet-state lifetimes are taken from ref 20 and 21. [d] The quantum yields of the epoxide disappearance determined by GC analysis on a SE-30 capillary column: solutions containing 0.058 M of cyclohexene oxide or styrene oxide and ca. 10^3 M of a sensitizer were irradiated with a Pyrex filter for 6 h and 1 h, respectively.

Scheme I



$$NP + \underbracket{CH_2CH_2O} \rightleftarrows [NP{-}{-}{-}\underbracket{CH_2CH_2O}] \xrightarrow{h\nu} [NP^{+}\cdot{-}{-}{-}\underbracket{CH_2CH_2O^{-}}\cdot] \quad (1)$$

$$NP \xrightarrow{h\nu} {}^{*}NP \quad (2)$$

$${}^{*}NP + \underbracket{CH_2CH_2O} \xrightarrow{k_q} [NP^{+}\cdot{-}{-}{-}\underbracket{CH_2CH_2O^{-}}\cdot] \rightarrow NP^{+}\cdot + \cdot CH_2CH_2O^{-} \quad (3)$$

$$\cdot CH_2CH_2O^{-} + CH_3OH \rightleftarrows \cdot CH_2CH_2OH + CH_3O^{-}\cdot \quad (4)$$

$$\cdot CH_2CH_2OH + NP^{+}\cdot \rightarrow NP + {}^{+}CH_2CH_2OH \quad (5)$$

$${}^{+}CH_2CH_2OH + CH_3OH(CH_3O^{-}) \xrightarrow{k_6} CH_3OCH_2CH_2OH \quad (6)$$

$${}^{+}CH_2CH_2OH + CH_3OH(CH_3O^{-}) \xrightarrow{k_7} \underbracket{CH_2CH_2O} + CH_3OH \quad (7)$$

$$NP^{+}\cdot + CH_3CO_2^{-} \rightarrow NP + CH_3CO_2\cdot \rightarrow CH_4 + CO_2 \quad (8)$$

$${}^{+}CH_2CH_2OH + CH_3CO_2^{-} \rightarrow \underbracket{CH_2CH_2O} + CH_3CO_2H \quad (9)$$

relate reasonably linearly with $E_{D/D^+} - E_S$ (Table I); if one uses the recently published reduction potential of styrene oxide ($E^0 = 2.30$ eV) determined by cathodic redox catalysis,[12] electron transfer from the singlet excited naphthalene derivatives to the oxide is thermodynamically feasible, except 1-cyanonaphthalene, according to the Weller's equation.[13] It may be noted that the lowest singlet level energies for the sensitizers are within 3 kcal/mol of one another, supporting the absence of an energy transfer mechanism, in spite of the fact that styrene oxide, having fluorescence[14] at 280–360 nm, should possess a state low enough to participate in energy transfer.

Secondly, sodium acetate at 1×10^{-3} M quenched photosolvolysis sensitized by 1-naphthol or its methyl ether; the gas samples were chromatographically analyzed to show the presence of small amounts of CO_2 and CH_4. These products could be obtained by a competitive electron-transfer reaction as shown in eq 8. Among other possibilities, acetate may also quench the photosolvolysis according to reaction 9. Thus, acetate participates in quenching after the completion of the excited-state interaction as in eq 3. This is supported by the observations that, while the methyl ether sensitized solvolysis of styrene oxide is quenched by the acetate ion, its fluorescence intensity is not affected under the same conditions. The anion radicals of oxiranes proposed in eq 3 have been generated by cathodic reduction mediated by redox catalysis and are shown to open the ring very fast, leading to the solvolysis product.[12,15]

Acknowledgment. We are grateful to the National Sciences and Engineering Research Council of Canada for generous financial support of this project. B.M. thanks the University Council, Universytet im. Adama Mickiewicza, Poznan, for study leave.

Registry No. Cyclohexene oxide, 286-20-4; styrene oxide, 96-09-3; 1-naphthol, 90-15-3; 2-naphthol, 135-19-3; 1-methoxynaphthalene, 2216-69-5; naphthalene, 91-20-3; 1-cyanonaphthalene, 86-53-3.

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Received June 24, 1983

A Novel Catalytic Synthesis of Carbamates by the Oxidative Alkoxycarbonylation of Amines in the Presence of Platinum Group Metal and Alkali Metal Halide or Onium Halide

Summary: Carbamates are prepared in good yields from amines, alcohols, CO, and oxygen in the presence of a novel catalyst system comprising platinum group metal and iodide.

Sir: Carbamates are important as precursors for preparing organic isocyanates without using dangerous phosgene, since they are thermally dissociated to give isocyanates and alcohols in good yields. Thus, the effective catalyst system for preparing them has been desired. We have now found that the catalyst system comprising platinum group metal and alkali metal halide or onium halide is very effective for the oxidative alkoxycarbonylation of amines by CO and oxygen (eq 1).

$$\underset{\mathbf{1}}{RNH_2} + CO + R'OH + {}^{1}/{}_{2}O_2 \rightarrow \underset{\mathbf{2}}{RNHCOOR'} + H_2O \quad (1)$$

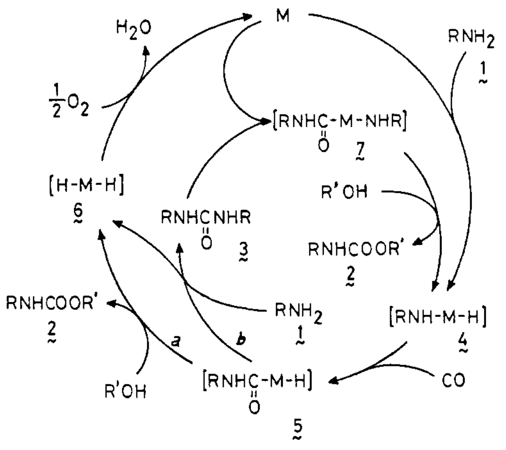
Table I. Platinum Group Metal-Halide-Catalyzed Carbamate Synthesis. Oxidative Ethoxycarbonylation of Aniline by CO and Oxygen[a]

platinum group metal	halide	% yield[b]	
		2a	**3a**
none	KI	1	2
5% Rh/C	none	2	2
Ru black	KI	59 (76)	8 (21)
Ru black	Me_4NI	58 (77)	7 (19)
5% Rh/C	NaI	84 (93)	2 (4)
5% Rh/C	Me_4NI	82 (90)	4 (8)
5% Rh/C	$[Ph_3PMe]I$	72 (85)	5 (12)
RhI_3	CsI	80 (86)	5 (11)
Pd black	KCl	24 (55)	5 (18)
Pd black	KBr	60 (75)	8 (15)
Pd black q	KI	93 (98)	0.5 (1)
2% Pd/SiO_2	Me_4NI	94 (98)	0.5 (1)
$IrCl_3$	Me_4NI	11 (31)	7 (39)
5% Pt/C	CsI	42 (65)	10 (31)
5% Pt/C	Me_4NI	42 (64)	11 (33)

[a] All reactions were carried out under similar conditions as illustrated in the text by using 40 mmol of aniline, 0.5 molar equiv of metal, 1 mmol of halide compound, and 40 mL of EtOH. [b] Based on aniline used. Yields in parentheses were calculated on the basis of the aniline reacted, thus they indicate the selectivities.

Although a few papers concerning the oxidative alkoxycarbonylation of amines using nonnoble transition-metal catalysts have been published,[1] some essential problems have remained. For example, the yields and the selectivities are low,[2] or a large excess of the other reagents are necessary for the reaction to proceed.[3] Of course, it is not known that platinum group metals except Pd have such effective catalytic activity,[4] because these metals cannot catalyze this reaction if they are used alone. The combination of these metals and halide compounds, especially iodide compounds, is very important for this oxidative carbonylation reaction to proceed catalytically. In this communication, we report that such a simple catalyst system is effective for preparing carbamates and urea compounds as intermediates in good yields and with high selectivities.

Scheme I[a]



[a] Other ligands (CO, amine) were omitted.

The reaction is illustrated by the preparation of ethyl phenylcarbamate (**2a**, eq 1, R = Ph, R′ = Et). Into a 200-mL autoclave internally lined with titanium were charged 40 mmol of aniline, 60 mL of EtOH, 0.5 g of Rh/C supported 5 w % of Rh on activated carbon, and 1 mmol of cesium iodide. After the air inside the autoclave had been replaced with CO, CO was pressurized into the autoclave to 80 kg/cm^2 and then oxygen was pressurized, resulting in a total pressure of 86 kg/cm^2. The reaction was carried out at 160–170 °C for 3 h with stirring, and subsequently the reaction mixture was filtered after cooling. GLC and HPLC analyses of the clean pale yellowish filtrate showed that the conversion of aniline was 92%, the yield of **2a** was 86% with a selectivity of 94%, and the yield of *N*,*N*′-diphenylurea (**3a**) which is an intermediate of **2a** was 1.5%.[5] A small amount of 2-methylquinoline was detected.[6]

Results of the other experiments under similar conditions with several catalyst systems are shown in Table I. As shown in Table I, the reaction hardly proceeds catalytically in the absence of either the halide or the platinum group metal. The most effective halogen species is iodine, and the order of the activity is I > Br > Cl. In the platinum group metals, Pd and Rh are the most active species, and the order of the activity is Pd $\gtrsim$ Rh > Ru > Pt > Ir. Thus, the catalyst system comprising Pd or Rh and iodide has the highest activity and high selectivity.

Other amines (e.g., cyclohexylamine, *n*-butylamine) also reacted with CO, oxygen, and alcohols (EtOH, MeOH) to give the corresponding carbamates and ureas in similar yields with similar selectivities (the total selectivities of them were almost over 90% in the case with iodide as a promoter).

The catalytic cycles for the formation of carbamate are explained by the following simplified mechanism (Scheme I). The oxidative addition of amine 1 to the platinum group metal M affords the amino–metal species 4, which undergoes the insertion of the coordinated CO to produce the carbamoyl–metal species 5.[7] The carbamate 2 is

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(1) The catalyst system comprising $PdCl_2$ and Lewis acid, which must contain metal components capable of undergoing redox reactions such as $CuCl_2$, $FeCl_3$, and FeOCl, has been proposed. In this case, the reaction seems to proceed by the Wacker-type redox reaction, because the catalysts have been present at several oxidation or reduction states, e.g., Pd^0, Pd^{2+}, Fe^0, and Fe^{3+}, in the reaction mixture during and after the reaction. (a) Scholl, H-J.; Zenner, A. Ger. Offen. 2 908 250, 1980. (b) Merger, F.; Platz, R.; Towae, F. Ger. Offen. 2 910 132, 1980. In our catalyst system, however, these metal components are not necessary, and the catalyst components (e.g., Rh/C and CsI) are completely recovered in the same state as the initial one from the mixture during or after the reaction. Thus, a quite different type mechanism would be presumed. Another catalyst system (Se–base) is also known. (c) Kondo, K.; Sonoda, N.; Tsutsumi, S. *Chem. Lett.* **1972**, 373.

(2) Saegusa, T.; Tsuda, T.; Isayama, K. *Tetrahedron Lett.* **1967**, 4123. The reaction of $Th(OAc)_3$ with CO, piperizine, and methanol has been reported.

(3) (a) Moy, D. U.S. Pat. 4 242 520, 1980. In addition to the Mo catalyst, an excess of COS or S and an excess of disulfide are necessary as a reagent and as an oxidizing reagent, respectively. (b) Kesling, H. S., Jr. U.S. Pat. 4 251 667, 1981. In addition to copper salt catalyst, an excess of dehydrating reagent (e.g., trimethyl orthoformate) is necessary.

(4) It is well-known that these metals with the aid of Lewis acids catalyze the reductive alkoxycarbonylation of aromatic nitro compounds to give carbamates. For example, see: (a) Mountfield, B. A. U.S. Pat. 3 338 956, 1967. (b) Gamlen, G. A.; Ibbotson, A. U.S. Pat. 3 448 140, 1969. (c) Licke, G. C. U.S. Pat. 4 052 420, 1977. (d) Hirai, Y.; Miyata, K.; Aiga, M. U.S. Pat. 4 186 269, 1980. (e) Watanabe, Y.; Tsuji, Y.; Suzuki, N. *Chem. Lett.* **1982**, 105. There has been only one example in which aniline reacts with nitrobenzene, CO, and alcohol to give a carbamate in the presence of $RhCl_3$ and FeOCl (without using oxygen). (f) Becker, R.; Grolig, J.; Rasp, C. U.S. Pat. 4 297 501, 1981.

(5) *N*,*N*′-Diphenylurea was confirmed to be an intermediate by the following fact: the compound was converted to ethyl *N*-phenylcarbamate almost quantitatively under similar conditions when it was used as a starting material instead of aniline.

(6) This compound was confirmed to be formed by oxidative dehydrocondensation of two molecules of ethanol and one molecule of aniline by the another experiment without using CO. But it was also confirmed that this compound was not formed until the content of aniline became very low.

considered to be formed through two paths, a and b. In path a, **5** reacts with alcohol to give **2** directly and the metal hydride species **6**. On the other hand, **5** reacts also with **1** to give N,N'-disubstituted urea **3** and **6** in path b. Furthermore, **3** adds oxidatively to M to give the (amino)(carbamoyl)metal species **7**, which reacts with alcohol to produce **2** and regenerates **4**. Finally, oxidation of **6** by oxygen produces water and regenerates M. In the intermediate species **4**–**7** illustrated, of course, some other ligands such CO or amine must coordinate to the metal. The alkali metal halide or onium halide seems to promote the partial redox reactions of the metal by lowering the oxidation–reduction potential or to serve as an activator of oxygen or CO, although it is not clear now that the halide compound has influence on what steps of the reaction.

Further studies are in progress to clarify the detailed mechanism and the role of the halide compound.

Acknowledgment. We are especially grateful to Dr. Maomi Seko for his stimulating discussion and helpful advice, to Kohsaku Washio for his excellent technical assistance, and to Tomonari Watanabe and Toshiya Aoki for their helpful suggestions.

Registry No. 1 (R = Ph), 62-53-3; 1 (R = cyclohexyl), 108-91-8; 1 (R = *n*-Bu), 109-73-9; 2 (R = Ph, R' = Et), 101-99-5; 2 (R = cyclohexyl, R' = Et), 1541-19-1; 2 (R = cyclohexyl, R' = Me), 5817-68-5; 2 (R = *n*-Bu, R' = Et), 591-62-8; 2 (R = *n*-Bu, R' = Me), 2594-21-0; 3 R = Ph, 102-07-8; EtOH, 64-17-5; MeOH, 67-56-1; Rh, 7440-16-6; Ru, 7440-18-8; RhI_3, 15492-38-3; Pd, 7440-05-3; $IrCl_3$, 10025-83-9; Pt, 7440-06-4; KI, 7681-11-0; Me_4NI, 75-58-1; NaI, 7681-82-5; $[Ph_3PMe]I$, 2065-66-9; CsI, 7789-17-5; KCl, 7447-40-7; KBr, 7758-02-3.

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[7] The carbamoyl metal species have been thought to play important roles in the carbonylation of amines. For example, an intermediate carbamoyl cobalt complex, $R_2NCO{-}Co(CO)_3PPh_3$, has been isolated. (a) Palágyi, J.; Markó, L. *J. Organomet. Chem.* **1969**, *17*, 453. And we have also reported another type of carbamoyl nickel complex, $Li[(CH_3)_2NCO{-}Ni(CO)_3]$, which is available for a nucleophilic carbamoylation reagent. (b) Fukuoka, S.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1968**, *33*, 2973; **1971**, *36*, 2721.

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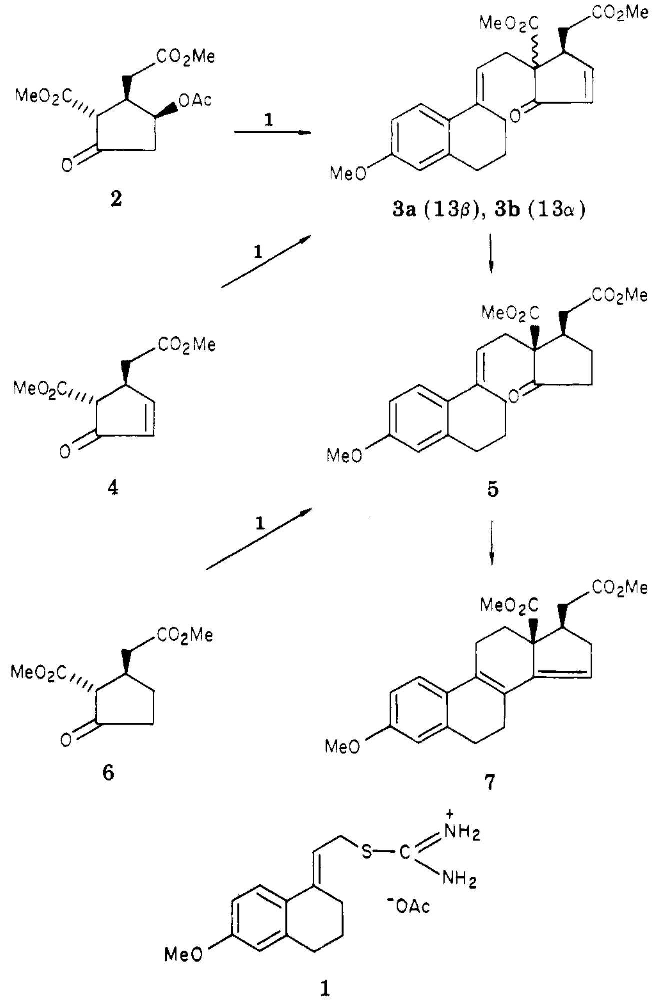
Received May 4, 1983

Steroids. 3. A New Synthetic Approach to Optically Active Steroids. Total Synthesis of (+)-18-Hydroxyestrone

Summary: A stereospecific synthesis of (+)-18-hydroxyestrone has been accomplished from (*S*)-malic acid via a chiral β-keto ester intermediate previously used for the synthesis of (+)-$PGF_{2\alpha}$. The key step involves the coupling of this intermediate with a modified Torgov steroid precursor. The latter reaction is mediated by cupric acetate in aqueous ethanol. Elaboration of the coupled product to the finished steroid follows established methods.

Sir: In a recent paper[1] we describe a method for the alkylation of various β-keto esters as their Cu(II) chelates in aqueous solution with the modified[2] Torgov[3] steroid precursor **1**. This allowed us to synthesize certain tetracyclic pentaenes whose conversion to a series of C-18-functionalized steroids already has been partially described.[4]

Scheme I



We have now exploited this methodology for the synthesis of optically active steroids by employing the (−)-β-keto ester **2** easily derived[5a] from (*S*)-malic acid. The intermediate **2** has considerable versatility as evidenced by its previous use for the synthesis[5b] of (+)-$PGF_{2\alpha}$.

Thus, the isothiouronium acetate **1** is coupled (Scheme I) with **2** in 50% aqueous ethanol in the presence of Cu(II) acetate (1 equiv) and sodium acetate (0.1 M) to keep the pH within the range for maximum yield, as discussed[1] previously. This leads to a 54% yield of an 8:1 chromatographically (column) separable mixture of the 8,14-secosteroids[6] **3a** and **3b**, in which the acetoxy group of **2** has been eliminated. One recrystallization gives **3a** in 95% optical purity and 40% overall yield from **1**. When **1** is omitted from this reaction, **4** is produced, and this, when alkylated under the same conditions, gives an identical

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[1] Magriotis, P. A.; Murray, W. V.; Johnson, F. *Tetrahedron Lett.* **1982**, *23*, 1993.

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[4] Pillai, K. M. R.; Murray, W. V.; Shooshani, I.; Williams, D. L.; Gordon, D.; Tseng, C. K. H.; Wang, S. Y.; Johnson, F. *J. Med. Chem.*, in press.

[5] (a) Paul, K. G.; Johnson, F.; Favara, D. *J. Am. Chem. Soc.* **1976**, *98*, 1285. (b) Johnson, F.; Paul, K. G.; Favara, D.; Ciabatti, R.; Guzzi, U. *J. Am. Chem. Soc.* **1982**, *104*, 2190.

[6] ^1H and ^{13}C NMR evidence indicates that **3a** and **3b** are isomeric only at C-13 (steroid numbering). Proof of the structure of **3a** lies self-consistently in its stereospecific conversion to (+)-18-hydroxyestrone.

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