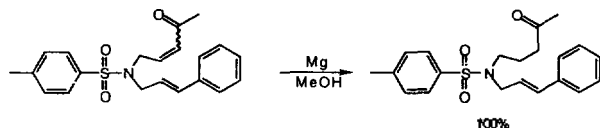


nitrile group tethered to the ketone was cyclized with magnesium metal in absolute methanol, a large amount of saturated product was obtained.<sup>4a</sup> In an attempt to trap a radical intermediate, an  $\alpha,\beta$ -unsaturated ketone tethered to a good radical acceptor as shown below was subjected to the same reaction condition as above, however, we only obtained the simple reduction product in quantitative yield instead of the expected 5-*exo-trig*. cyclized product.



Although the mechanistic explanation of magnesium in methanol had been suggested to proceed through the  $\beta$ -coupling of radical anion intermediate,<sup>6</sup> exact mechanism is needed to be defined further.

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- 1c-cis**: needle-type white crystal; *R<sub>f</sub>* 0.22 (hexane/ethyl acetate, 5/1, v/v); mp 71-72 °C (hexane); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.70-2.87 (m, 2H, H-1 and OH), 2.55 (d, *J*=9.8 Hz, 1H, H-2), 2.33-2.44 (m, 1H, H-5), 2.25 (s, 3H, CH<sub>3</sub>CO), 1.99 (dd, *J*=12.1 and 8.2 Hz, 1H, H-4), 1.52-1.69 (m, 4H, H-8, H-7, and H-6), 1.49 (dd, *J*=12.1 and 11.2 Hz, 1H, H-4'), 1.30-1.43 (m, 2H, H-8' and H-6'), 1.13 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  210.67 (CO), 80.62 (C-3), 68.04 (C-2), 49.55 (C-4), 41.66 (C-1), 37.81 (C-5), 32.94 (C-6), 32.83 (C-8), 31.24 (CH<sub>3</sub>CO), 24.73 (C-7), 23.17 (CH<sub>3</sub>); IR (neat) 3407 (OH), 2957, 1691 (CO), 1456, 1425, 1374, 1291, 1241, 1179, 1140, 1100, 1066, 1037, 978, 940, 823 cm<sup>-1</sup>; MS *m/e* (rel intensity) 184 (M<sup>+</sup>+2, 3.0), 183 (M<sup>+</sup>+1, 9.2), 182 (M<sup>+</sup>, 1.0), 165 (34.0), 125 (18.2), 124 (100), 121 (22.6), 109 (11.4), 97 (13.0), 86 (15.1), 84 (26.6), 81 (17.7), 71 (13.3), 66 (23.0), 43 (71.5). Anal. Calcd for C<sub>11</sub>H<sub>18</sub>

O<sub>2</sub>: C, 72.49; H, 9.95. Found: C, 72.54; H, 9.91.

- 1c-trans**: colorless oil; *R<sub>f</sub>* 0.35 (hexane/ethyl acetate, 5/1, v/v); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.10 (brs, 1H, OH), 2.76-2.85 (m, 1H, H-5), 2.69-2.76 (m, 1H, H-1), 2.35 (d, *J*=9.7 Hz, 1H, H-2), 2.23 (s, 3H, CH<sub>3</sub>CO), 2.00 (dd, *J*=13.2 and 8.1 Hz, 1H, H-4), 1.70-1.79 (m, 1H, H-8), 1.54-1.70 (m, 4H, H-6, H-7, and H-8'), 1.32-1.41 (m, 1H, H-6'), 1.30 (s, 3H, CH<sub>3</sub>), 1.14 (dd, *J*=13.2 and 9.8 Hz, 1H, H-4'); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  214.56 (CO), 82.52 (C-3), 65.97 (C-2), 47.97 (C-4), 47.37 (C-1), 41.74 (C-5), 32.97 (C-8), 32.56 (C-6), 31.95 (CH<sub>3</sub>CO), 25.95 (CH<sub>3</sub>), 25.30 (C-7); IR (neat) 3395 (OH), 2962, 1683 (CO), 1464, 1427, 1384, 1360, 1289, 1257, 1187, 1158, 1136, 1097, 1031, 1006, 957, 852, 639, 582 cm<sup>-1</sup>; MS *m/e* (rel intensity) 163 (M<sup>+</sup>-1-H<sub>2</sub>O), 149 (9.2), 125 (23.2), 124 (71.7), 123 (15.8), 121 (33.2), 111 (9.3), 97 (13.3), 93 (20.2), 86 (18.7), 84 (80.0), 79 (23.9), 71 (16.0), 67 (21.0), 57 (21.0), 43 (100). Anal. Calcd for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>: C, 72.49; H, 9.95. Found: C, 72.57; H, 9.96.
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## A Convenient Method for the Preparation of Nitriles and Carbodiimides Using *N*-Methyl-2-Pyridinecarbamoyl Chloride

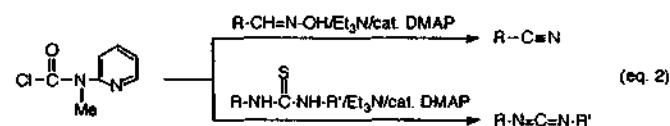
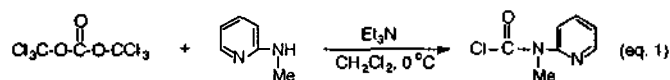
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In connection with our study on the synthetic utility of active carbamoyl chloride, we have reported that *N*-methyl-2-pyridinecarbamoyl chloride is an efficient coupling reagent of carboxylic acids.<sup>1</sup> We now wish to report that nitriles can be prepared from aldoximes in high yields and thioureas are cleanly converted into the corresponding carbodiimides using *N*-methyl-2-pyridinecarbamoyl chloride.

*N*-Methyl-2-pyridinecarbamoyl chloride was new conveniently prepared by addition of an equimolar solution of 2-(methylamino)pyridine and triethylamine in methylene chloride to a solution of one-third equivalent of bis(trichloromethyl)carbonate ("triphosgene"),<sup>2</sup> a crystalline, stable solid, in methylene chloride at 0 °C (eq. 1).



**Table 1.** Preparation of Nitriles and Carbodiimides Using *N*-Methyl-2-pyridinecarbamoyl Chloride<sup>a</sup>

Compound	Reaction time, h	Product	Isolated yield, % <sup>b</sup>
C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> CH=NOH	0.3	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> CN	86
<i>c</i> -C <sub>6</sub> H <sub>11</sub> CH=NOH	0.2	<i>c</i> -C <sub>6</sub> H <sub>11</sub> CN	78
C <sub>6</sub> H <sub>5</sub> CH=NOH	0.2	C <sub>6</sub> H <sub>5</sub> CN	90
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=NOH	0.3	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CN	89
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CH=NOH	0.3	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CN	86
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=NOH	0.2	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CN	80
( <i>c</i> -C <sub>6</sub> H <sub>11</sub> NH) <sub>2</sub> C=S	7	<i>c</i> -C <sub>6</sub> H <sub>11</sub> N=C=N- <i>c</i> -C <sub>6</sub> H <sub>11</sub>	84
[(CH <sub>3</sub> ) <sub>3</sub> CNH] <sub>2</sub> C=S	5	(CH <sub>3</sub> ) <sub>3</sub> CN=C=NC(CH <sub>3</sub> ) <sub>3</sub>	92
(C <sub>6</sub> H <sub>5</sub> NH) <sub>2</sub> C=S	1	C <sub>6</sub> H <sub>5</sub> N=C=NC <sub>6</sub> H <sub>5</sub>	88
( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH) <sub>2</sub> C=S	1.5	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> N=C=N- <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	82
( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NH) <sub>2</sub> C=S	0.5	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> N=C=N- <i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	85
C <sub>6</sub> H <sub>5</sub> NHCSNH- <i>c</i> -C <sub>6</sub> H <sub>11</sub>	3	C <sub>6</sub> H <sub>5</sub> N=C=N- <i>c</i> -C <sub>6</sub> H <sub>11</sub>	89
C <sub>6</sub> H <sub>5</sub> NHCSNH(CH <sub>3</sub> ) <sub>3</sub>	2	C <sub>6</sub> H <sub>5</sub> N=C=NC(CH <sub>3</sub> ) <sub>3</sub>	95

<sup>a</sup>The dehydration of aldoximes was carried out in methylene chloride and the dehydrosulfurization of *N,N'*-disubstituted thioureas was carried out in tetrahydrofuran at room temperature. <sup>b</sup>All products were purified by Kugelrohr vacuum distillation or short pathway column chromatography and gave satisfactory spectral data.

The reagent was separated by dissolving mixture in dry *n*-hexane after evaporation of methylene chloride, followed by filtering off triethylamine hydrochloride. The purification of the crude filtrate by Kugelrohr vacuum distillation gave *N*-methyl-2-pyridinecarbamoyl chloride as a colorless oil in 85% yield.<sup>3</sup> It is worth noting that bis(trichloromethyl)carbonate not only is convenient in handling but also is used only one-third equivalent for the preparation of *N*-methyl-2-pyridinecarbamoyl chloride.

The synthetic utility of *N*-methyl-2-pyridinecarbamoyl chloride as a dehydrating agent was studied with the conversion of aldoximes into nitriles<sup>4</sup> (eq. 2). The effect of bases was examined for the dehydration of benzaldoxime with *N*-methyl-2-pyridinecarbamoyl chloride and triethylamine to find out an optimum condition. The reaction using 0.1 equiv of 4-dimethylaminopyridine (DMAP)<sup>5</sup> in methylene chloride gave benzonitrile in 90% yield after 10 min at room temperature, whereas the reaction using no base, 0.5 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 0.5 equiv of tetramethylguanidine (TMG) gave benzonitrile in 53%, 69%, and 73%, respectively, after 24 hrs. Thus, the dehydration of aldoximes using *N*-methyl-2-pyridinecarbamoyl chloride was found to be very effective in the presence of a catalytic amount of DMAP, which is believed to be due, at least in part, to the formation of *N*-acylpyridinium salt between *N*-methyl-2-pyridinecarbamoyl chloride and DMAP.

Several aldoximes were cleanly converted into the corresponding nitriles within 15 min as shown in Table 1. The reaction worked well with both aliphatic and aromatic aldoximes, and furthermore, the presence of electron-donating or electron-withdrawing group in substituted benzaldoximes

didn't affect the efficiency of the reaction under the present reaction conditions.

The synthetic utility of *N*-methyl-2-pyridinecarbamoyl chloride as a dehydrosulfurization agent was also studied with *N,N'*-disubstituted thioureas (eq. 2). Conversion of *N,N'*-disubstituted thioureas into carbodiimides<sup>6</sup> using *N*-methyl-2-pyridinecarbamoyl chloride was carried out in the presence of bases such as DMAP, DBU, and TMG to find out an optimum condition. Reaction of *N,N'*-diphenylthiourea with *N*-methyl-2-pyridinecarbamoyl chloride and 0.1 equiv of DMAP in tetrahydrofuran gave *N,N'*-diphenylcarbodiimide in 88% yield after 1 h at room temperature, whereas the reaction using 0.5 equiv of DBU and 0.1 equiv of TMG gave the product in 54% and 15% yield, respectively, after 24 hrs.

As shown in Table 1, *N,N'*-disubstituted thioureas were cleanly converted into the corresponding carbodiimides in high yields at room temperature. However, the conversion of *N,N'*-dicyclohexylthiourea into the *N,N'*-dicyclohexylcarbodiimide was normally slow and thus was dependent critically on the nature of alkyl groups. Also, the introduction of an electron-withdrawing group promoted the formation of carbodiimide, and thus conversion of *N,N'*-bis(*p*-chlorophenyl)thiourea into *N,N'*-bis(*p*-chlorophenyl)carbodiimide required 0.5 h for the completion of the reaction.

The typical experimental procedure is as follows. **Preparation of *N*-methyl-2-pyridinecarbamoyl chloride;** To a bis(trichloromethyl)carbonate (1.0991 g, 3.70 mmol) in methylene chloride (15 mL) was added a mixture solution of 2-(methylamino)pyridine (1.0814 g, 10.0 mmol) and triethylamine (1.40 mL, 10.0 mmol) in methylene chloride (15 mL) over 20 min at 0 °C. After being stirred for 1 h between 0 °C and room temperature, methylene chloride was evaporated under vacuum. The reaction mixture was dissolved with dry *n*-hexane (50 mL) and filtered off triethylamine hydrochloride. The crude filtrate could be purified by Kugelrohr vacuum distillation (100–110 °C/0.6 mm Hg) to afford *N*-methyl-2-pyridinecarbamoyl chloride as a colorless oil in 85% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.53–8.37 (m, 1H), 7.87–7.20 (m, 3H), 3.52 (s, 3H); IR (film) 3008, 1582 (aromatic), 1740 (C=O) cm<sup>-1</sup>; Mass (m/z) 172 (M+2), 170 (M), 135, 107, 78. **Preparation of nitriles and carbodiimides;** To a solution of a substrate (2.0 mmol) and *N*-methyl-2-pyridinecarbamoyl chloride (341.2 mg, 2.0 mmol) in methylene chloride (6 mL) or tetrahydrofuran (6 mL) was added triethylamine (279 μL, 2.0 mmol), followed by DMAP (24.4 mg, 0.2 mmol) at room temperature. After being stirred until the reaction was complete, the reaction mixture was diluted with methylene chloride (40 mL), washed with 1% HCl (30 mL), sat. NaHCO<sub>3</sub> (30 mL), dried over anhydrous MgSO<sub>4</sub>, and evaporated to dryness. The crude product was purified by Kugelrohr vacuum distillation or short pathway silica gel column chromatography.

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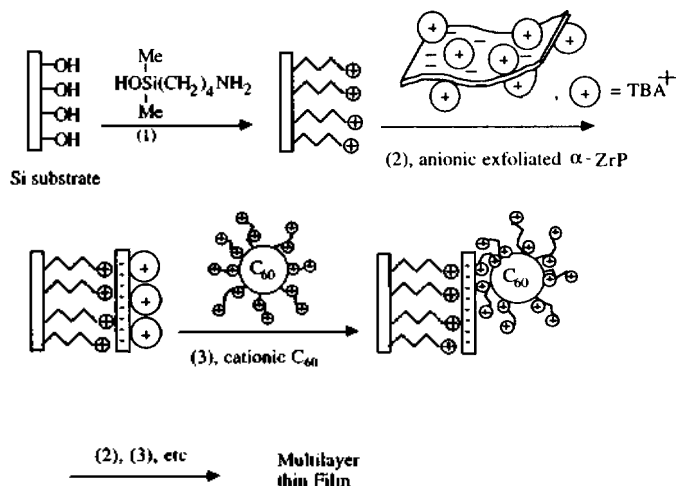
### Multilayer Assembly of Cationic Fullerene with Interleaved Anionic, Two-Dimensional $\alpha$ -Zirconium Phosphate Single Layer

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The construction of ultrathin multilayer assemblies has been received many attentions for the application in many areas such as integrated optics, vectorial electron transfer, nonlinear optics, sensors and molecular electronics.<sup>1,2</sup> Most of these tasks require for the preparation of well-ordered films composed of molecules with appropriate properties and structures. Several preparation methods have been studied to date: the Langmuir-Blodgett (LB) technique,<sup>3</sup> self-assembly monolayer (SAM) technique<sup>1</sup> based on chemisorption and electrostatic interaction.<sup>2</sup> Recently, Decher *et al.*<sup>4</sup> reported a new and simple technique for fabricating multilayer thin films with controlled thicknesses and layer sequences. This method is based on the spontaneous adsorption of monolayers of organic polyelectrolytes with opposite charges by layer-by-layer deposition. In essence, the electrostatic attrac-



**Figure 1.** Sequential adsorption of singly separated, polyanionic  $\alpha$ -ZrP layer prepared by exfoliation of polycrystalline lamellar solid of  $\alpha$ -Zirconium hydrogen phosphate with alternate layer of polycationic C<sub>60</sub>. TBA<sup>+</sup> = tetra(N-butylammonium) ion.

tion between opposite charges is the driving force for the multilayer fabrication. The multilayer film prepared in this method showed considerable layer interpenetration,<sup>5</sup> which results in destruction of highly oriented multilayer. This is mainly due to flexibility and linearity of single-chain polymers used as building block. However, the interpenetration of layer could be solved by use of lamellar inorganic solid such as  $\alpha$ -zirconium hydrogen phosphate. Mallouk and coworkers<sup>6</sup> reported multilayer films composed of semi-infinite anionic sheets interleaved with polymeric cations. This multilayer assemblies were prepared by sequential adsorption from the suspensions of exfoliated inorganic two-dimensional anion  $\alpha$ -Zr(OPO<sub>3</sub>)<sub>2</sub><sup>2-</sup> ( $\alpha$ -ZrP) and solution of polycationic electrolytes.

In this communication, author reports the extension of these last two techniques to fabricate multilayer assembly of fullerene C<sub>60</sub> and  $\alpha$ -ZrP. Fullerene films prepared *via* LB technique,<sup>7</sup> solvent evaporation,<sup>8</sup> resistive evaporation<sup>9</sup> of solid fullerenes and SAM technique<sup>10</sup> have been already reported that they show several interesting mechanical, electrical, superconductive, electrochemical, and optical properties. To my knowledge, this is the first report on the preparation of fullerene multilayer assembly by using electrostatic attraction. The multilayer film prepared in this way would be also expected to show many potential applications based on fullerene properties.

The electron deficient C<sub>60</sub> undergoes nucleophilic addition reaction with primary and secondary aliphatic amines.<sup>11,12</sup> Treating solid C<sub>60</sub> with ethylenediamine easily leads to the formation of fullerene-ethylenediamine adduct. This adduct is quite soluble in water due to its basic amine functionalities. Wudl *et al.*<sup>11</sup> reported that C<sub>60</sub>-ethylenediamine adduct has the average stoichiometry of 6 ethylenediamines per adduct molecule from the titration of aqueous solution of the adduct with HCl. The adduct molecule is positively charged in the acidic solution. Positively charged C<sub>60</sub>-ethylenediamine is alternatively interleaved with anionic zirconium phosphate single layer to make multilayer structure.