


**Table 1.** Regeneration of Cyclohexanone from Cyclohexanone Oxime

Entry	Dicarbonyl Compound	Conversion Yield <sup>a</sup> (%)
1	CH <sub>3</sub> COCH <sub>2</sub> COCF <sub>3</sub>	100
2	PhCOCH <sub>2</sub> COCF <sub>3</sub>	100
3	CF <sub>3</sub> COCH <sub>2</sub> COCF <sub>3</sub>	100
4	 COCH <sub>2</sub> COCF <sub>3</sub>	82
5	CH <sub>3</sub> COCH <sub>2</sub> COCO <sub>2</sub> CH <sub>3</sub>	100
6	CH <sub>3</sub> COCH <sub>2</sub> COCO <sub>2</sub> Et	100
7	EtCOCH <sub>2</sub> COCO <sub>2</sub> CH <sub>3</sub>	100
8	PhCOCH <sub>2</sub> COCO <sub>2</sub> CH <sub>3</sub>	100
9	CH <sub>3</sub> COCOCH <sub>3</sub>	100
10	PhCOCOCH <sub>3</sub>	100
11	PhCOCOPh	64
12	PhCOCHO	88
13	EtO <sub>2</sub> CCOCO <sub>2</sub> Et	100
14	CH <sub>3</sub> COCH <sub>3</sub>	55
15	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H	40
16	CH <sub>3</sub> COCH <sub>2</sub> COCH <sub>3</sub>	100
17	CH <sub>3</sub> COCO <sub>2</sub> H	100

<sup>a</sup>Determined by GC of the reaction mixture, area percentage.

tone (entry 16) and pyruvic acid (entry 17). However, thioyltrifluoroacetone (entry 4), benzil (entry 11), and phenylglyoxal (entry 12) gave somewhat lower yield due to its poor solubility in aq. EtOH. Acetone (entry 14) and levulinic acid (entry 15) were poorly effective under the present reaction conditions.

In conclusion, we found that certain dicarbonyl compounds such as  $\beta$ -diketones substituted with electron withdrawing group or  $\alpha$ -diketones, can convert effectively cyclohexanone oxime to cyclohexanone. Thereby, these methods could also be applied conveniently to the deoximation reaction of other oxime compounds.

**Acknowledgement.** We wish to thank the Korea Science and Engineering Foundation for financial support of this work.

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## A Convenient Method for Esterification over Perfluorinated Resinsulfonic Acid (Nafion-H)

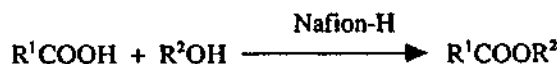
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Nafion-H is perfluorinated resinsulfonic acid having sulfonic acid group in the amount of 0.01 to 5 mequiv/gram resin. The estimated  $H_0$  value for Nafion-H is comparable to or larger than that of 96 to 100% sulfuric acid<sup>1-3</sup>. Nafion-H in contact with solvent system affects only the surface acidity (the solvent phase directly in contact with the catalytic surface). Nafion-H and related perfluoroalkanesulfonic acids are also stable in corrosive environment and at temperatures up to 210°C. These unique properties have led to an extensive development of various acid catalyzed reactions such as alkylation, transalkylation, nitration, polymerization, ether and ester formation, rearrangement, etc<sup>4-7</sup>.

In this paper we wish to report our results of convenient esterification reaction catalyzed by Nafion-H. The esterification experiment was carried out by refluxing a mixture of carboxylic acid (1.0 g), alcohol (5.0 ml), Nafion-H (0.2 g), and 3-nitrotoluene (0.02 g, internal standard for GC analysis) for 8 hours.



Water was removed with small amount of silica gel in a soxhlet thimble suspended just below refluxing condenser. The mixture was analyzed with gas chromatography on a 25 m capillary column of 5% phenylmethylsilicon. The yields are corrected for the molar response of the authentic esters to internal standard. The results are summarized in Table

**Table 1.** Yields<sup>a</sup> of Esterification of Carboxylic acids (R<sup>1</sup>COOH) with Alcohols (R<sup>2</sup>OH) using Nafion-H<sup>b</sup>

R <sup>1</sup>	R <sup>2</sup>	C <sub>2</sub> H <sub>5</sub>	n-C <sub>4</sub> H <sub>9</sub>	n-C <sub>6</sub> H <sub>13</sub>	cy-Hexyl <sup>c</sup>	t-C <sub>4</sub> H <sub>9</sub>
CH <sub>3</sub>		92.9	100	90.0	20.4(47.8)	27.0
C <sub>2</sub> H <sub>5</sub>		92.6	85.4	92.7	33.1(46.3)	18.4
n-C <sub>3</sub> H <sub>7</sub>		100	100	100	40.5(33.5)	8.7
i-C <sub>3</sub> H <sub>7</sub>		97.4	92.1	98.3	46.2(43.2)	14.0
cy-Hexyl		96.0	100	96.5	45.5(61.5)	6.8

<sup>a</sup>Percent yield based on the starting carboxylic acids, <sup>b</sup>Reaction condition, reflux for 8 hours, <sup>c</sup>The number in parenthesis is the yield of cyclohexene based on cyclohexanol.

1. Primary alcohols reacted readily with carboxylic acids to afford the corresponding esters in excellent yields. The yields are much higher than 40-60% obtained by Olah under comparable condition without using the drying agent but similar to those observed in the gas phase reaction<sup>6</sup>. The yields were lower with secondary and tertiary alcohol presumably because of the steric effect and the competing dehydration reactions. Thus in reactions of cyclohexanol with carboxylic acids and the ester was produced only 20-46% but cyclohexene was obtained in 30-60% yields under the same condition. When tertiary alcohol was used only poor results were obtained; formation of gaseous isobutylene was visibly noticeable. This esterification procedure is, however, very efficient also for sterically hindered carboxylic acids.

The present procedure provides an efficient method for esterification of aliphatic carboxylic acids and primary alcohols. In this procedure, only a catalytic amount of the acidic resin is needed, and the heterogeneous catalyst provides for a very simple work up. Application of Nafion-H on other acid catalyzed reactions are in progress in our laboratory.

**Acknowledgment.** This investigation was supported by grants from the Basic Science Institute Program, Korea Ministry of Education (1989) and the Organic Chemistry Research Center sponsored by the Korea Science and Engineering Foundation.

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### Indirect Determination of Rare Earths by Amperometric Detection for Flow Injection Analysis

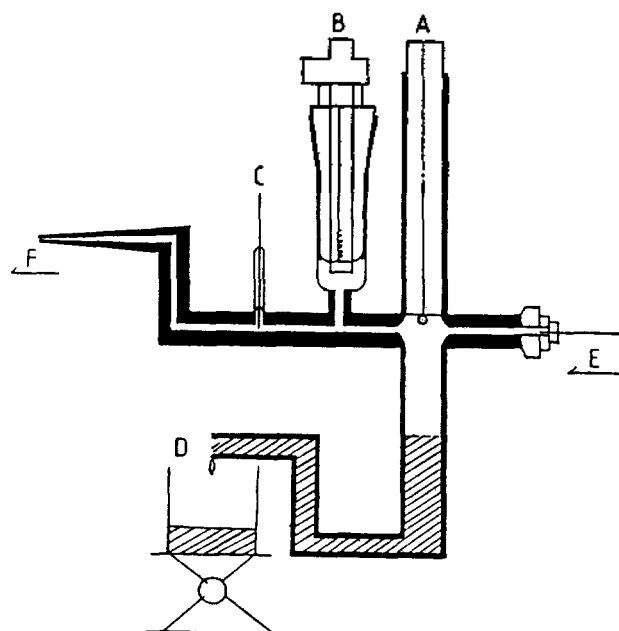
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Received October 27, 1990

The rare earths are usually determined by optical emission



**Figure 1.** Electrochemical cell for flow injection analysis. A: working electrode, B: reference electrode (SCE), C: counter electrode (Pt wire), D: reservoir for mercury droplet, E: inlet F: outlet (to waste).

spectrometry<sup>1,2</sup>, mass spectrometry coupled with inductively coupled plasma<sup>3</sup>, neutron activation analysis<sup>4</sup> and electrochemical methods<sup>5-7</sup>. One of the problems with electrochemical methods is that most rare earth ions, except Sm, Eu, and Yb, are hardly reduced to their divalent state at the mercury electrode in aqueous solution<sup>8</sup>. The standard reduction potential of most rare earth ions is more negative than that of hydrogen ion in acidic media and so the reduction is interfered by hydrogen evolution. This is a reason why the polarographic analysis of rare earth ions is not usually employed. The detection of rare earth ions with electrochemical techniques after separation by high performance liquid chromatography (HPLC) has been reported earlier by Boissonneau *et al.*<sup>9</sup>. These researchers mixed ethylenediaminetetraacetic acid (EDTA) in the flow stream of rare earths at the exit of the HPLC column. The concentration of the element was then determined indirectly by measuring the concentration of free EDTA. Here, we chose diethylenetriaminepentaacetic acid (DTPA) as a ligand to determine rare earth ions by flow injection analysis. The choice of DTPA as a complexing agent has two advantages: the larger value of formation constant of DTPA with rare earth ions leads to almost all ions complexed in the flow stream, guaranteeing more quantitative determination. Oxidation potential of DTPA at a mercury electrode is less positive than that of mercury itself. Hence, anodic current for the oxidation of DTPA is not interfered with by oxidation of mercury electrode. In this work, we have demonstrated quantitative determination of the rare earth ions indirectly by amperometric techniques in flow injection analysis.

The principle of detection for flow injection analysis is as follows: A ligand such as diethylenetriaminepentaacetic acid (DTPA) is injected with a constant flow rate into a flow stream containing the rare earth ions to be determined. The