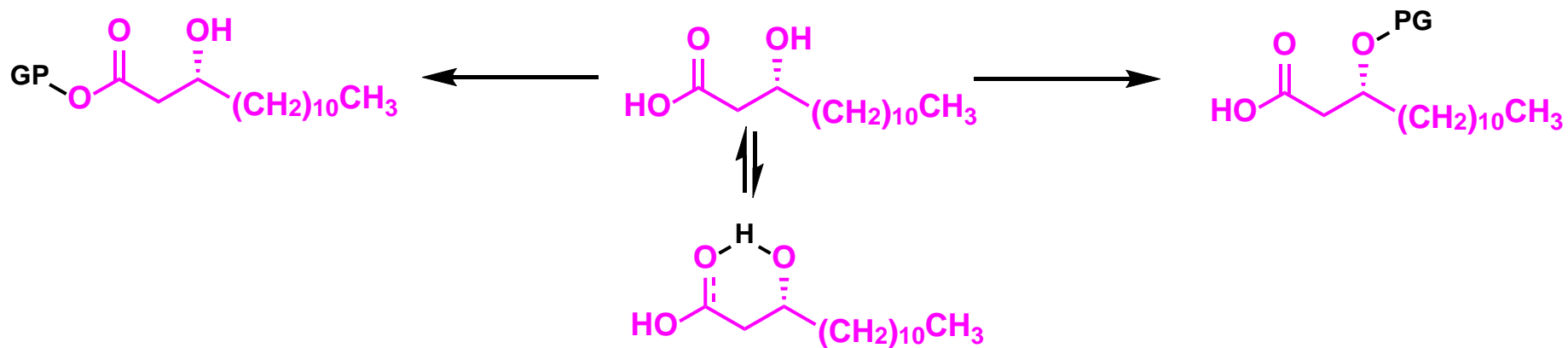


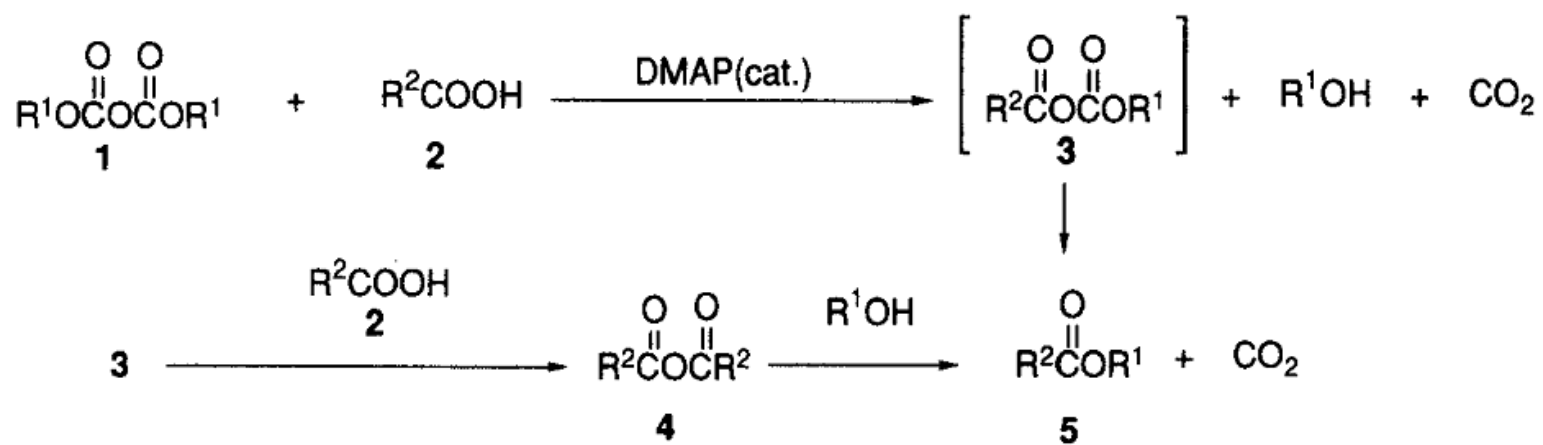
# Dicarbonates: Convenient 4-Dimethylaminopyridine Catalyzed Esterification Reagent

Synthesis, 1994.10

wzq

# PROBLEM





**a** R<sup>1</sup> = Me, **b** R<sup>1</sup> = Et, **c** R<sup>1</sup> = *t*-Bu, **d** R<sup>1</sup> = Allyl, **e** R<sup>1</sup> = Benzyl

**Table 1.** Effect of Solvent, Catalyst and Time on the Reaction of Dicarbonate **1** and Z-Pro (**2**)<sup>a</sup>

Run	Dicarbonate <b>1</b> R <sup>1</sup> (equiv) <sup>b</sup>	Solvent	Base or Catalyst <sup>b</sup>	Time	Products (ratio) <sup>c</sup>	Yield (%) <sup>b</sup>
1	Me (1.4)	MeOH	NEt <sub>3</sub> (1.0 equiv)	46 h	<b>6</b>	81
2	Me (1.4)	THF	NEt <sub>3</sub> (1.0 equiv)	19 h	<b>6</b>	80
3	Me (1.8)	MeOH	DMAP (10 mol%)	92 h	<b>6</b>	7
4	Me (1.4)	THF	DMAP (10 mol%)	5 min	<b>6</b>	96 <sup>d</sup>
5	Me (1.4)	<i>t</i> -BuOH	DMAP (10 mol%)	46 min	<b>6/7</b> (96 : 4)	76
6	<i>t</i> -Bu (2.0)	<i>t</i> -BuOH	NEt <sub>3</sub> (1.0 equiv)	44 h	<b>7</b>	15
7	<i>t</i> -Bu (2.0)	THF	NEt <sub>3</sub> (1.0 equiv)	44 h	<b>7</b>	trace
8	<i>t</i> -Bu (2.0)	<i>t</i> -BuOH	DMAP (30 mol%)	55 min	<b>7</b>	100 <sup>e</sup>
9	<i>t</i> -Bu (2.0)	THF	DMAP (30 mol%)	3.3 h	<b>7</b>	99
10	<i>t</i> -Bu (2.0)	MeOH	DMAP (30 mol%)	27 h	<b>7/6</b> (17 : 83)	6

<sup>a</sup> Reaction was carried out at room temperature.

<sup>b</sup> Based on acid.

<sup>c</sup> The ratio of Z-Pro-OMe (**6**) and Z-Pro-OBu-*t* (**7**) was estimated on the basis of integration in the NMR spectrum.

<sup>d</sup> Oil,  $[\alpha]_D^{26} - 54.8^\circ$  ( $c = 0.46$ , MeOH). {Lit.,<sup>8</sup> oil,  $[\alpha]_D - 57.3^\circ$  ( $c = 1.0$ , MeOH)}.

<sup>e</sup> Mp. 43–48 °C,  $[\alpha]_D^{27} - 54.3^\circ$  ( $c = 1.0$ , EtOH) {Lit.,<sup>9</sup> mp 44–45 °C,  $[\alpha]_D - 54.2^\circ$  ( $c = 2.0$ , EtOH)}.

- THANK YOU