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Efficient heterogeneous catalytic intramolecular Tishchenko reaction of *o*-phthalaldehyde to phthalide with alkaline earth oxides

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Received (in Cambridge, UK) 10th October 2001, Accepted 30th October 2001
First published as an Advance Article on the web

The heterogeneous catalytic systems realized by alkaline earth oxides are successfully applicable to the highly efficient intramolecular Tishchenko lactonization of *o*-phthalaldehyde to phthalide.

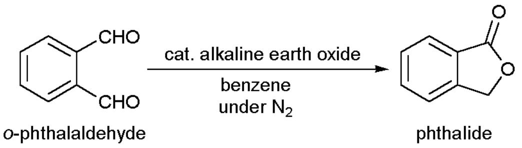
The heterogeneous catalytic Tishchenko reaction using solid bases involves the dimerizarion of aldehydes yielding the corresponding esters initiated by the interactions of polarized carbonyl groups of aldehydes with surface acidic and basic sites of solid bases. The adaptability of solid base catalysts to the Tishchenko reaction has been demonstrated in several investigations.[1] Most of previous development of efficient catalysis for Tishchenko reaction, however, has been confined to homogeneous catalytic systems. Recent articles dealing with homogeneous catalyses have reported considerable improvements in activities for the dimerization of aldehydes in comparison with traditional aluminium alkoxides catalysts.[2,3] Solid base catalysts, unlike these homogeneous catalysts, can be easily separated from the reaction mixture after carrying out the reaction, and are inexpensive and environmentally benign. These excellent properties emphasize the importance of the replacement of homogeneous catalyses with heterogeneous ones both in the laboratory and in industrial processes utilizing Tishchenko esterification.

Although several studies have been conducted on the *intermolecular* Tishchenko reaction over solid base catalysts as mentioned above, there have been no reports of the *intramolecular* Tishchenko reaction which results in cyclization.[2,4] In addition, to our knowledge, in the field of heterogeneous basic catalysis, there has been only one report dealing with intramolecular cyclization (dehydration of monoethanolamine to ethylenimine).[5] Here we report the intramolecular Tishchenko reaction of *o*-phthalaldehyde to phthalide using alkaline earth oxides as powerful and highly selective heterogeneous catalysts. The general reaction equation is shown in Scheme 1.

Experimental procedures are as follows: MgO, CaO, SrO and BaO were prepared from $Mg(OH)_2$, $Ca(OH)_2$, $SrCO_3$ and $BaCO_3$, respectively, by thermal decomposition at elevated temperatures *in vacuo*. The pretreatment temperatures and surface areas of the catalysts examined are listed in Table 1. To a Schlenk tube containing the alkaline earth oxide pretreated (10 or 50 mg) was added a benzene (1 mL) solution of *o*-phthalaldehyde (1 mmol) under N_2 at room temperature. Then the reaction mixture was warmed to 313 K and stirred for a prescribed reaction time. The resulting solution, after alkaline earth oxide was separated, was analyzed by GC equipped with a DB-1 column (total length: 60 m; diameter: 0.25 mm) to determine the yield (%) of phthalide. The product was identified by ^1H NMR and GC–MS analysis.

The catalytic activities of alkaline earth oxides for the intramolecular Tishchenko reaction of *o*-phthalaldehyde to phthalide are given in Table 1. To compare the activities of alkaline earth oxides, *o*-phthalaldehyde was treated with 10 mg of each alkaline earth oxide at 313 K for 60 min (entries 1, 3, 5 and 7). Barium oxide did not furnish the corresponding lactone at all (entry 7). Magnesium oxide and SrO showed almost equal moderate activities (entries 1 and 5). In contrast, however, CaO exhibited an excellent activity (entry 3). It should be emphasized that MgO, CaO and SrO yielded phthalide selectively (intermolecular Tishchenko dimerization products were not observed by GC–MS analysis). In an attempt to attain a synthetically satisfactory level of yield, the amount of MgO, CaO, and SrO was increased without changing the reaction temperature. Thus, when the reaction was carried out at 313 K with 50 mg of CaO, the reaction proceeded instantaneously, and phthalide was obtained quantitatively in a short time of 15 min (entry 4). Under the same conditions, MgO and SrO also furnished pthalide in excellent yields of 91 and 86%, respectively (entries 2 and 6).

In summary we have shown that efficient heterogeneous catalytic lactonization of dialdehydes can be realized by using alkaline earth oxides through the intramolecular Tishchenko reaction of *o*-phthalaldehyde to phthalide.



Scheme 1 Heterogeneous catalytic intramolecular Tishchenko reaction of *o*-phthalaldehyde to phthalide with alkaline earth oxides.

Table 1 Activities of alkaline earth oxides for the intramolecular Tishchenko reaction of *o*-phthalaldehyde to phthalide[a]

Entry	Catalyst	Catalyst weight/mg	Pretreatment temperature/K	Surface area[b]/$m^2\ g^{-1}$	Reaction time/min	Reaction temp./K	Yield[c] (%)
1	MgO	10	873	267	60	313	15
2	MgO	50	873	267	15	313	91
3	CaO	10	873	48	60	313	59
4	CaO	50	873	48	15	313	Quantitative
5	SrO	10	1273	12	60	313	15
6	SrO	50	1273	12	15	313	86
7	BaO	10	1273	2	60	313	0

[a] Reactant: 1 mmol of *o*-phthalaldehyde; solvent, 1 mL of benzene. All reactions were carried out under N_2. [b] Surface areas were determined by the BET method. [c] Yield was determined by the GC analysis of the resulting solution and was calculated by the equation: yield (%) = {(mol% of phthaide)/[(mol% of *o*-phthalaldehyde) + (mol% of phthalide)]} × 100.

DOI: 10.1039/b109249a

This work is supported by a Grant-in aid for Scientific Research of Ministry of Education, Science, Sports, and Culture, Japan.

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