Graphite-Supported Ketodecarboxylation of Carboxylic Diacids

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Received 30 January 2001

Abstract: Thermal decarboxylative cyclization of several carboxylic diacids supported on graphite gave the corresponding five- and six-membered cycloalkanones in high yields. The process took advantage of the retention of diacid on graphite, even for high temperature experiments (450 °C), which avoid its vaporization. Moreover, the addition of catalyst is useless, the iron-containing inclusions present on graphite play this function. The reactions were also realized under microwave irradiation.

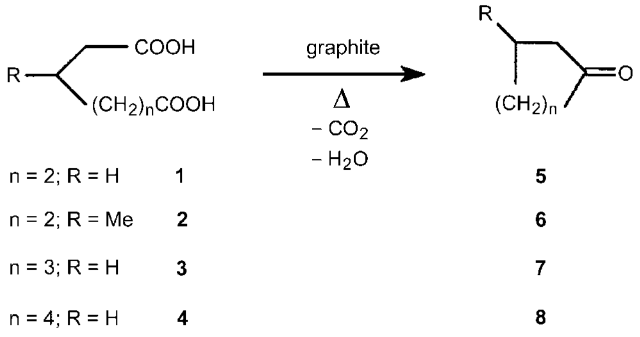
Key words: cycloalkanones, decarboxylation, diacids, graphite, microwaves

Thermal bimolecular decomposition of carboxylates yields symmetrical ketones.[1,2] This reaction can be carried out using a carboxylic acid in the presence of several catalysts,[2] such as thorium[3] or manganous[4] oxides. Various mechanisms, which seem to depend on the acid, on the metal and on the experimental conditions, have been proposed.[2a,5] The catalytic way allows a lowering of the reaction temperature, but, whatever the catalyst, a high temperature is needed (250-350 °C). Nevertheless, this ketodecarboxylation is an important route, especially for preparing cyclic ketones from carboxylic diacids.[2,6] For cyclopentanone, a typical procedure using barium hydroxide has been described,[7] but various catalysts exist, such as metal oxides,[2a] carbonates,[8] and potassium fluoride.[5a] This ketone is an important industrial compound used in fragrances, as an intermediate in organic synthesis, and also as a solvent.[9] Several recent patents deal with its industrial preparation, indicating that the subject is of current interest.[10,11] Among them, the Rhodia process presents the novelty of performing the decarboxylation-dehydration of carboxylic diacids in liquid phase at about 250 °C.[10] The catalyst is a metal (Al, Ga, In, Sn, Sb, Bi.), a metallic oxide, or a salt (phosphate, carbonate, borate). High-boiling organic compounds such as hydrocarbons or aromatic ethers are used as solvents.

One of the most important objectives now is to adapt classical processes so that pollution effects are kept to a minimum, with both a reduction in energy and consumption of raw materials. In this respect, dry-media reactions are promising, and a new approach has been undertaken using graphite-supported chemistry. The exceptional ability of graphite to adsorb organic molecules is well known.[12] Consequently, the vaporization (boiling or sublimation) of adsorbed molecules is delayed, and reactions involving low boiling (or subliming) reagents can be performed at relatively high temperature in an open reactor. Diels-Alder and ene reactions,[13a-g] Friedel-Crafts acylations,[13a-c] decarboxylations,[13a,b,h] decomplexations[14] and rearrangements[13a,b,15] were effected using such conditions. Moreover, a catalytic activity of graphite was found,[13a-c,h,16,17] and our investigations concerning the Friedel-Crafts acylation have shown the catalytic effect of the graphite impurities (mainly Fe_3O_4).[13c,17]

The main problem with the catalytic decarboxylative cyclization of diacids results from the necessity of having a high reaction rate and a reaction temperature low enough (two contradictory factors) in order to avoid or to limit the vaporization of the diacid. For adipic acid the limiting reaction temperature is about 290-295 °C; higher temperatures lead to rapid vaporization of adipic acid from the mixture together with the cyclopentanone produced.[6] Graphite could be used to retain the diacid allowing higher reaction temperatures and, as it has been shown that Fe_3O_4 is also a catalyst for the decarboxylation of acids,[18] no added catalyst would be necessary.

We applied this graphite-supported synthetic method for the conversion of various carboxylic diacids (**1-4**) into the corresponding ketones (**5-8**) (Scheme 1). For the decarboxylation of adipic acid (**1**) into cyclopentanone (**5**), reactions were conducted at atmospheric pressure at 450 °C for 30 min. Two commercial graphites of similar granular size were used: graphite A and graphite B.[19] As expected, in both reactions, even at 450 °C, no vaporization of adipic acid was observed. While graphite A was a very efficient support for the reaction (90% yield in **5** after 30 min at 450 °C), graphite B gave a low yield under the same conditions (Table 1, entries 1 and 2). The main difference between the two graphites consists in their purity: graphite A is a medium grade graphite (about 99.1%) whereas graphite B is a higher purity one (about 99.9%). In these two graphites, impurities contain mainly iron (0.41% (mass) for A and 0.007% for B), and Fe_3O_4 crystallites in the graphite A have been identified by X-ray diffractometry.[17] From these results, the catalytic effect of the magnetite is obvious. Moreover, the graphite can be reused: three successive reactions on the same sample of graphite A were obtained without significant loss in yield. Two examinations of a graphite A sample before and after a reaction showed the same X-ray diffraction pattern, attesting to the presence of Fe_3O_4. However, these crystallites appeared to be smaller after reaction.



Scheme 1

The method can be applied to the synthesis of other cyclic ketones. At atmospheric pressure, under the same conditions used for adipic acid, 3-methylhexanedioic acid (**2**) gave the corresponding ketone **6** in a lower yield (60%) (Table 1, entry 3). When we investigated the same reaction under a slightly reduced pressure, vaporization of **6** was enhanced and the yield reached 80% (entry 4). This modified method was also suitable for the synthesis of cyclohexanone (**7**) (entry 5). However, for cycloheptanone (**8**), the yield remained low (entry 6).

Table 1 Graphite-Supported Thermal Ketodecarboxylation of Diacids **1-4**[a,b]

Entry	Diacid	Graphite[c]	Pressure (mm Hg)	Ketone Yield (%)[d]
1	**1**	A	760	**5**, 90 (85)[e]
2	**1**	B	760	**5**, 22
3	**2**	A	760	**6**, 60
4	**2**	A	300	**6**, 80 (74)[e]
5	**3**	A	300	**7**, 80 (72)[e]
6	**4**	A	300	**8**, 17

[a]Temperature 450 °C during 30 min, except for entries 5 and 6, 60 min; [b]Diacid : 15 mmol; mass of graphite : 5g; this mass corresponds to an optimized ratio diacid/graphite, an increase of this ratio gave lower yields in ketone; [c]Graphite A : Aldrich, ref. 28,2863; graphite B : Fluka, ref. 50 870; [d]From GC analysis; [e]Isolated yield from 4 experiments.

Some microwave-promoted decarboxylations have been reported in the literature,[20] and even the decarboxylation of Mg, Ca, and Ba salts of alkanoic acids was examined.[20a] For Friedel-Crafts acylations,[17] we have already shown that advantage could be taken both of the use of microwave radiation and of the properties of graphite and magnetite that are also among the solids most efficiently heated by microwaves.[21] The cyclization of **1** was realized also under such conditions,[19] using the MW apparatus recently described, and equipped with an IR-pyrometer for the measurement of temperature.[22] In order to limit the temperature of the reaction mixture to about 450 °C, a sequential mode of MW irradiation was used (Table 2). Under these optimized conditions a 90% yield of **5** was obtained using graphite A, while it was only 33% with graphite B (Table 2, entries 1 and 2). The catalytic effect of the impurities of the support is again evident.

Table 2 Graphite-Supported Ketodecarboxylation of Adipic Acid (**1**) Under Microwave Heating[a,b]

Entry	Graphite (A, B)[c] and Added Catalyst	MW Conditions[d]	Yield (%)[e]
1	A ; none	90 W ; 2 min x 2 + 75 W ; 2 min x 2	90
2	B ; none	90 W ; 2 min x 2 + 75 W ; 2 min x 2	33
3	A ; none	90 W ; 2 min x 2	60
4	B ; none	90 W ; 2 min x 2	19
5	B ; Fe_3O_4 (28 mg)	90 W ; 2 min x 2	51
6	B ; Fe_2O_3 (29 mg)	90 W ; 2 min x 2	51
7	B ; FeO (26 mg)	90 W ; 2 min x 2	35
8	B ; Al_2O_3 (18 mg)	90 W ; 2 min x 2	15
9	B ; Bi_2O_3 (84 mg)	90 W ; 2 min x 2	16
10	B ; KF (21 mg)	90 W ; 2 min x 2	14
11	Fe_3O_4 (3.47 g) without graphite	90 W ; 2 min x 2	10

[a]Microwave irradiation using the 2.45 GHz monomode MW oven (Synthewave 402 from Prolabo) previously described,[22] equipped with an IR-pyrometer and driven by a computer; [b]Mass of **1:** 2.19 g (15 mmol); mass of graphite : 5 g; [c]See table 1; [d]Sequential MW irradiation controlled to a maximum temperature of 450 °C; applied incident power (W) and irradiation time (t); period between two irradiations : 2 min; [e]Yield into ketone **5** from GC analysis using **6** as internal standard.

Activities of various catalysts were then compared. The reaction was at first observed under conditions giving moderate yields with graphite A (Table 2, entry 3). As in the previous example, the use of graphite B alone resulted in a lower yield (entry 4). Doping this one with a quantity of a metal compound corresponding to the molar quantity of iron present in graphite A, was explored. With iron oxides the yield increased (entries 5-7) but remained lower than with graphite A alone. This can be due to the particular size, properties and distribution of the oxide particles incorporated in the graphite during the graphitization process, inevitably different from those of the added oxides. Aluminum oxide, bismuth oxide and potassium fluoride were inactive under such conditions (entries 8-10). A last but significant experiment (entry 11) shows that even when the most efficient catalyst, Fe_3O_4, was used in the absence of the graphite, the yield in **5** decreased dramatically. Adipic acid, not retained under these conditions, was vaporized and condensed on the walls of the reactor and on the cold finger.

The mechanism of thermal decarboxylation of diacids in the presence of metallic oxides has been already discussed.[23] Concerning the reactions described here, since iron(II) and iron(III) oxides are catalysts (Table 2, entries 6 and 7), the Fe_3O_4 catalysis could involve these two oxidation states of iron. After the transient formation of iron(II) and iron(III) carboxylates from the diacid and Fe_3O_4, the decarboxylative thermolysis of these two salts could give the cyclic ketone with regeneration of the catalyst.

In conclusion, the graphite-supported thermal decomposition of carboxylic diacids produces five- and six-membered cycloalkanones very efficiently. Under such ”dry“, solvent-free conditions, and even at high temperature the diacid is confined on the support and the ketone is obtained on distillation as the only organic compound. A medium grade commercial powdered graphite appeared the most suitable, as among its impurities the magnetite (Fe_3O_4) is a very efficient catalyst for the reaction.

In order to save energy, the method can also take advantage of MW heating. Thus, the diacid was brought to elevated temperature through the medium of graphite support which heats strongly and quickly under MW irradiation, while avoiding the vaporization of the diacid.

Acknowledgement

Support of this work by the *Centre National de la Recherche Scientifique* and *Rhodia Organique Fine* are gratefully acknowledged. We thank Professor M. Onyszchuk (McGill University) for his assistance in the preparation of the manuscript.

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(19) **Typical Procedure for the Synthesis of Cyclopentanone** (**5**). ***Conventional Heating*** (Table 1, entry 1). To a 2.19 g (15 mmol) sample of adipic acid (**1**), 5 g of graphite A were added, and the mixture was ground in a mortar prior to being placed in the reactor. The flask, surmounted by a Dean-Stark condenser equipped with an ice-cold finger, was immersed in a preheated tubular electric furnace and heated at 450 °C for 30 min. The ketone **5** condensed mainly in the cold trap, and the remainder was extracted from graphite powder with ether. A 90% overall yield in **5** was determined by GC analysis (internal standard: cyclohexanone). To obtain a larger sample of product, four successive runs were performed, and the combined organic phases were distilled to obtain 4.29 g (85% yield) of pure **5** (bp. 130-131 °C). ***Microwave Heating*** (Table 2, entry 1.) The same mixture as before was introduced in the quartz reactor of the MW apparatus, surmounted by the same Dean-Stark condenser. MW irradiation was programmed using the computer for a sequential process in which the sample was exposed for periods of 2 min separated by periods

of 2 min. This sequence was repeated 6 times with an incident power of 90 W for the first two irradiations and of 75 W for the others. After the mixture cooled, the same treatment as before gave a 90% yield in **5**.

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Article Identifier:
1437-2096,E;2001,0,04,0493,0496,ftx,en;G02101ST.pdf