

DIELS-ALDER AND RETRO-DIELS-ALDER REACTIONS SUPPORTED ON GRAPHITE UNDER MICROWAVES

S. Dahmani¹, Y. Kandri Rodi¹, K. Misbahi¹,
E.M. Essassi², Bernard Garrigues^{3*}

¹*Université Sidi Mohamed Ben Abdallah, Faculté des Sciences et
Techniques, Laboratoire de Chimie Organique Appliquée, Fès, Maroc*

²*Université Mohammed V – Agdal, Faculté des Sciences, Laboratoire de
Chimie Organique Hétérocyclique, Avenue Ibn-Batouta, Rabat, Maroc*

³*Université Paul Sabatier, Laboratoire d'Hétérochimie Fondamentale et
Appliquée, Toulouse, France*

*Corresponding author: garriguesbernard@hotmail.com

Received: 29/01/2009

Accepted after revision: 26/02/2009

Abstract: The coupling of graphite (as a support) with microwaves (as an energy source), a new type of « dry reaction », was studied for some Diels-Alder and Hetero-Diels-Alder reactions. It was also possible to achieve in a few minutes, at atmospheric pressure and without solvent, retro-Diels-Alder reactions. All these synthesis have been realized in very short times, without any thermal decomposition products and even in presence of volatile reagents.

Keywords: *microwaves, graphite, Diels-Alder*

INTRODUCTION

« Dry » organic reactions by means of microwaves introduce an interesting novelty for this type of heating [1]. Many studies using clays, inorganic oxides (alumina, silica) or

zeolithe as supports have been described recently. We thought that *graphite*, when strongly coupled with microwaves by a conduction process, might be a chemically inert support able to transmit high thermal energy to the supported reactants [2]. This property of graphite under the effect of microwave has been used previously in a different context, that is, for the processing of a gas flow on a carbon bed. The recent result of Shushan and al. [3] who described the microwave-assisted reaction of 1,4-diphenyl-1,3-butadiene with maleic anhydride without solvent, prompted us to report on our results relating to the graphite-supported Diels-Alder reactions under microwave activation (2.45 GHz).

EXPERIMENTAL

The microwave-assisted organic reactions were performed in a monomode apparatus (Maxidigest 350, Prolabo) at 2.45 GHz. During the irradiation time, the reactor was stirred by alternative rotations. After switching off the microwave radiation, the temperature was measured by means of a thermocouple located inside the graphite powder, and at the surface of the reactor with an IR thermometer (Horiba IT 340). The graphite used as support was a graphite powder, purchased either from Aldrich (ref. 28-286-3) or Fluka (ref. 50870). In both cases the results were the same.

Typical Procedure

A mixture of 0.144g (1 mmol) of diethyl fumarate and 0.178 g (1 mmol) of anthracene was dissolved into 50 mL of chloroform. After addition of 4 g of graphite, the mixture was stirred for 5 min and the solvent was evaporated under reduced pressure. The resulting powder was placed in an open microwave reactor under nitrogen and was irradiated three times with a 30 W-IP for 1 min (intermediate time of non-irradiation: 3 min). After cooling, the products were desorbed from the graphite with dichloromethane (50 mL) in an ultrasonic bath. The graphite was separated by filtration through Celite and washed with dichloromethane. The combined filtrates were dried (sodium sulfate) and concentrated. The product obtained analytically pure (mass: 0.296 g; 92% yield) was identified by a comparison with an authentic sample.

RESULTS AND DISCUSSION

At first we describe some [4+2]cycloaddition reactions by using the dienic substrates anthracene, metacrolein dimethylhydrazone and 3,6-diphenyl-1,2,4,5-tetrazine, all known as weakly reactive and to require long reaction times under classical heating conditions. In all reactions, reagents were deposited on graphite powder in chloroform solution, and products were desorbed by treatment with dichloromethane by using ultrasound [4, 5].

Retro-Diels-Alder reactions carried out from adducts containing a rest of anthracene have been studied. In classical conditions the authors use flash thermolysis at temperatures higher than 550 °C [6] or by heating at 230 °C/20 mmHg [7], to avoid decomposition of adducts. The effect of substituents in cycloadducts of anthracene, on retro-Diels-Alder speed has been approached in solution at 200 °C in diethyl ether [8].

In our study, we suggest a new methodology, which consists in carrying out retro-Diels-Alder reactions by using microwave heating, with graphite as support.

Concerning the Diels-Alder reactions, we report the use of anthracene as a dienic substrate and maleic anhydride, ethyl fumarate, dimethyl or diethyl acetylene dicarboxylate, benzoquinone as dienophiles [4]. After some sequential irradiations at low power (around 30 W) the corresponding adducts are obtained with excellent yields (75-97 %, Table 1). Otherwise, we observed that these adducts, upon more powerful irradiation, were decomposed by retro-Diels-Alder reaction. The temperature gradient was so high that it was necessary to precisely monitor the microwave irradiation conditions.

Table 1. *Experimental conditions for Diels-Alder reactions using anthracene as diene*

Dienophile	Conditions : time, power, T_{\max}	Yield (%) (isolated product)	Corresponding cycloadduct
maleic anhydride	3×1 min; 30 W; $T_{\max} = 155\text{ }^{\circ}\text{C}$	75	1
ethyl fumarate	3×1 min; 30 W; $T_{\max} = 147\text{ }^{\circ}\text{C}$	92	2
dimethyl acetylene dicarboxylate	3×1 min; 30 W; $T_{\max} = 130\text{ }^{\circ}\text{C}$	97	3
diethyl acetylene dicarboxylate	3×1 min; 60 W; $T_{\max} = 270\text{ }^{\circ}\text{C}$	86	4
benzoquinone	3×1 min; 30 W; $T_{\max} = 138\text{ }^{\circ}\text{C}$	91	5

So we have carried out retro-Diels-Alder reactions, always without any solvent (« dry-medium »), by using microwave heating with graphite as a support. Adducts have been heated with a 90 or 120 W power, with 3 to 5 microwave irradiation for one minute, after let time the system cool for one minute; following irradiation we were able to notice almost complete reactions. Indeed, the advancement of the reactions is comprised between 79 and 95 % [9 and table 2].

Table 2. *Experimental conditions for retro-Diels-Alder reactions*

Cycloadduct (obtained in table 1)	Conditions : time, power, T_{\max}	Yield (%) in anthracene (isolated product)
1	3×1 min; 90 W; $T_{\max} = 301\text{ }^{\circ}\text{C}$	78
2	3×1 min; 90 W; $T_{\max} = 320\text{ }^{\circ}\text{C}$	80
3	5×1 min; 120 W; $T_{\max} = 421\text{ }^{\circ}\text{C}$	56
4	5×1 min; 90 W; $T_{\max} = 360\text{ }^{\circ}\text{C}$	61
5	3×1 min; 90 W; $T_{\max} = 334\text{ }^{\circ}\text{C}$	75

Next many Diels-Alder cycloadditions, included hetero-Diels-Alder and carbonyl-Diels-Alder reactions, have been lead by using as dienophiles : methyl vinyl ketone, methacrolein, diethyl acetylene dicarboxylate, ethyl glyoxalate, ethyl maleate ; these compounds were introduced in presence of dienic species with low boiling points such as 2,3-dimethyl-1,3-butadiene, isoprene, 2-methyl furane or cyclopentadiene. In all cases, after some sequential irradiations, the corresponding cycloadducts were obtained in significantly reduced reaction times.

This methodology of organic synthesis in dry media on graphite support and under microwave activation lead us to achieve in easy conditions (without solvent, atmospheric pressure) many Diels-Alder cycloadditions. In all cases the cycloadducts were obtained in short reaction times and without the presence of secondary products.

This procedure, allows, for example, the rapid access to heterocycles. These syntheses, which require high energetic levels, have been successful thanks to the instantaneous heating of graphite under microwave irradiation. Moreover, the retention phenomenon of volatile reagents developed by the support presents an original advantage of graphite. Finally, we thought that this technology would allow us to achieve in a « one pot » way, both the dimerisation of the dicyclo-pentadiene dimmer and a cycloaddition reaction [4+2] upon itself. This process fits also with a tandem reaction: retro-Diels-Alder/Diels-Alder. So we have studied the coupling reaction: firstly retro-Diels-Alder leading to cyclopentadiene from its dimmer; then Diels-Alder reaction of cyclopentadiene with methyl maleate. Under conventional heating, the reaction is achieved after four hours of heating at 70 °C in dioxane and by using freshly distilled cyclopentadiene (90% yield). According to our methodology, the final cycloadduct is obtained directly by action of methyl maleate upon dicyclopentadiene. After ten short-lived sequential irradiations (30 sec; P = 60 W), we obtain 100 % conversion with a 61 % yield in isolated product for a mixture containing 65 % (endo/endo) and 35 % (exo/exo). This proportion is the same under classic conditions. The operative conditions are dictated by the monomerisation temperature of dicyclopentadiene. We can notice that the measured temperatures after every scan are included between 200 and 240 °C.

CONCLUSION

The microwave-assisted graphite-supported dry-medium synthesis is an activation process which leads to a shortening of reaction times and which allows us to work at ambient pressure in an open reactor. The high temperatures quickly obtained, which are responsible for this activation, can be easily controlled by the power of the microwave impulse, especially in the case of reversible reactions such as retro-Diels-Alder ones. Moreover, the formation of compounds by a thermal decomposition of reagents or products has not been observed. Furthermore, the control of the evaporation of volatile reagents was possible, probably due to their retention or *confinement* by graphite.

REFERENCES

1. Bram, G., Loupy, A., Villemin, D.: *Review*, Ellis Harwood, London, **1992**, 302-326;
2. Audhuy-Peaudecerf, M., Berlan, J., Dubac, J., Laporterie, A., Laurent, R., Lefevre, S.: *Demande Brevet français*, **1994**, n° 94.09073;
3. Rongshun, Z., Pinjie, H., Shushan, D.: *Synth. Commun.*, **1994**, 24, 2417-2421;
4. Garrigues, B., Laporte, C., Laurent, R., Laporterie, A., Dubac, J.: *Liebigs Annalen*, **1996**, 739-741;
5. Garrigues, B., Laurent, R., Laporte, C., Laporterie, A., Dubac, J.: *Liebigs Annalen*, **1996**, 743-744;
6. Hakiki, A., Ripoll, J.L., Thuillier, A.: *Tetrahedron Lett.*, **1984**, 25, 3459-3460;
7. Kitamura, T., Kawakami, Y., Imagawa, T., Kawanisi, M.: *Tetrahedron*, **1980**, 36, 1183-1189;
8. Chung, Y., Duerr, B.F., Nanjappan, P., Czarnik, A.W.: *J. Org. Chem.*, **1988**, 53, 1334-1336;
9. Garrigues, P., Garrigues, B.: *C.R. Acad. Sci. Paris, t. I, Série II c*, **1998**, 545-550.