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REVIEW

Microwave Activation in Organic Synthesis

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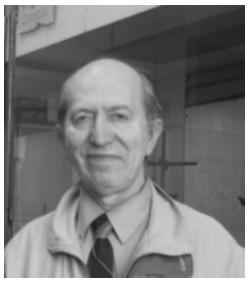
Abstract—Data on the effect of microwave irradiation on organic reactions are reviewed. Possible mechanisms of microwave activation are discussed, and some examples of acceleration of organic reactions and change of their direction and selectivity as compared to traditional thermal activation are described. Specific aspects of the application of microwave activation to various fields of organic synthesis are considered. The review covers mainly the data published over the last 5 years.







From left to right:

Dmitrii Kuznetsov was born in 1967. In 1992, he graduated from the Chemical Faculty, St. Petersburg State University. Assistant professor at the Physical Organic Chemistry Department, St. Petersburg State University, Candidate of chemical sciences, author of 18 publications. Fields of scientific interest: mechanisms of organic reactions and solvation effects.

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1. INTRODUCTION

In the recent years, much attention is given to the development of new energy-saving, economic, and environmentally safe technologies in chemistry. In this respect, search for new ways of activating chemical processes acquires increasing importance. In the last two decades, chemical reactions occurring under microwave irradiation attract continuously increasing interest.

The first studies on microwave (MW) activation in organic synthesis have been published in 1986 [1, 2]. It was found that MW irradiation sharply accelerates Diels–Alder, Claisen, oxidation, and esterification reactions. Since that time, the number of publications in this field strongly increases each year, and the gain has now attained about 1000 papers per annum.

In most cases, MW irradiation leads to a considerable (by up to three orders of magnitude) increase in the rate of a chemical reaction, as compared to traditional thermal process, and the reaction time shortens from several hours or days to a few minutes. Simultaneously, reactions performed under MW activation give as a rule purer products. Microwave activation is also advantageous from the viewpoint of using lesser amounts of solvents; moreover, in many cases, MW-activated reactions can be performed under solvent-free conditions. Some reactions occurring under MW irradiation could not be effected under classical conditions.

Applications of MW irradiation in organic syntheses were reviewed in [3–6]. Probable reasons for acceleration of organic reactions under MW irradiation were considered in [7, 8]. The reviews [9–12] covered MW-activated reactions occurring under solvent-free conditions. Some more specific reviews concerning the application of MW technologies in the synthesis of heterocyclic compounds [13–15], homogeneous [16] and phase-transfer catalysis [17], syntheses of labeled compounds [18], polymers [19, 20], and medicines, and combinatorial chemistry [21–23] were also published. Ways of using MW irradiation in large-scale organic syntheses were discussed in [24, 25]. In 2002, monographs on MW activation of organic reactions have been published [26, 27].

The present review analyzes the relevant data published over the last five years and considers principal mechanisms of interaction between substances and MW irradiation and its effect on the rate and selectivity of organic reactions. Microwave-activated reactions are classified with respect to the type of chemical process, and examples of the application of MW activation in radiochemistry, combinatorial chemistry, and other fields are given.

2. INTERACTION BETWEEN A SUBSTANCE AND MICROWAVE IRRADIATION

Microwave irradiation occupies the electromagnetic spectrum range between infrared and radio waves, i.e., the corresponding wavelengths range from 1 cm to

1 m, and the frequency range is 300 MHz to 30 GHz. This range is also referred to as ultrahigh frequency. The principles of interaction between MW irradiation and substances were given in [28–30]. Among physical effects occurring thereby, the following two lead to heat evolution: orientation polarization of dipoles and ionic conduction.

2.1. Orientation Polarization of Dipoles

The electric constituent of alternating electromagnetic field causes polar molecules to orient in such a way that their dipole moments be antiparallel to the force field lines. Such orientation of molecules in the gas phase is readily achieved, whereas in the liquid phase, owing to its high density, the process is accompanied by absorption of the MW energy and is determined by the field frequency and viscosity of the medium. At low frequencies, molecules undergo in-phase reorientation with field oscillations, and the liquid phase warms up insignificantly. When the field frequency is high, molecules have no sufficient time to change their orientation, they do not move, and the irradiation energy is converted into heat. In the microwave region, e.g., at a frequency of 2.45 GHz, polar molecules begin to rotate under the action of force

Table 1. Physical parameters of solvents used in microwave-assisted syntheses

Solvent	ε [31]	μ, D [31]	bp, °C [31]	tan δ[a] [22]	Heating rate,[b] deg/s [32]	Temperature after heating for 1 min,[b] °C [33]	Boiling point under MW irradiation, °C [32]
Acetone	20.7	2.88	56	0.054	2.23	56	81 (89 [7])
Acetonitrile	36.2	3.92	82	0.062	2.36		107 (120 [7])
1-Butanol	17.1	1.66	117		1.87	109	138 [7]
2-Butanol	15.8	1.7	100				127 [7]
Water	84.2[c]	2.2	100	0.123	1.01	81	104 (105 [7])
Hexane	1.89	0.08	69			25	
Diethylene glycol dimethyl ether			162		2.17		175
Dimethyl sulfoxide	49	3.96	189	0.825			
Dimethylformamide	36.7	3.86	152	0.161	2.18	131	170
1,2-Dimethoxyethane			83		2.54		106
Methylene chloride	8.9	1.60	40	0.042	2.16		55
Diethyl ether	4.34	1.15	35			32	
3-Methyl-1-butanol	14.7	1.82	132		1.92		149
Methanol	32.6	1.7	65	0.659	2.11	65	84
2-Butanone	18.5	2.5	80		2.57		97
Formic acid	58	1.41	101	0.722			
Tetrahydrofuran	7.32	1.63	66	0.047	2.04	81	81
Carbon tetrachloride	2.23	0	77			28	
Trichloroethylene	3.14	0.77	87		1.54		108
Acetic acid	6.19	1.74	118	0.174		110	
Acetic anhydride	21	2.8	140		1.97		155
Chlorobenzene	5.62	1.69	132		2.63		150
Chloroform	4.70	1.87	62	0.091		49	
Ethanol	24.3	1.69	78	0.941	2.06	78	103
Ethyl acetate	6.02	1.78	77	0.059	1.78	73	95 (102 [7])

[a] At a field frequency of 2.45 GHz (25°C).
[b] Volume 150 ml, power 650 W.
[c] At 0°C.

field, but field oscillations and rotation of dipoles occur in different phases; therefore, the MW energy is converted into kinetic energy of molecules, and the solution warms up.

The ability of a material to transform electromagnetic energy into heat is characterized by the slope of the dielectric loss plot, which can be calculated by the following formula:

$$\tan\delta = \varepsilon''/\varepsilon',$$

where ε'' is the dielectric loss coefficient which characterizes the efficiency of the transformation of electromagnetic energy into heat, and ε' is the dielectric constant of the solvent.

Interaction between MW irradiation and various solvents was studied in [32, 33]. It was found that MW irradiation can induce considerable overheat of liquids (above their boiling point). The reason is that, unlike convectional heating, MW irradiation heats the entire volume of a liquid rather than its near-wall layer (where vaporization centers are located). Table 1 contains some physical parameters of commonly used solvents and describes their behavior under MW irradiation.

2.2. Ionic Conduction

Another mechanism of the transformation of MW energy into heat originates from the presence of ionic species in materials. Alternating electric field induces vibrational motion of ions, and resistance of the medium to ion flux leads to heat evolution. The higher the concentration and the mobility of ions, the stronger the heat effect. Therefore, addition of small amounts (10–25 mg/ml) of ionic liquids (e.g., dialkylimidazolium salts) ensures very fast heating of samples in closed vessels to high temperatures [34] (Table 2).

Table 2. Effect of ionic liquids on the rate of heating

Solvent	Heating time, min	T_1,[a] °C	T_2,[b] °C
Hexane	10	46	217
Toluene	150	109	195
Tetrahydrofuran	70	112	268
1,4-Dioxane	90	76	264

[a] Temperature of the pure solvent at an irradiation power of 200 W.
[b] Temperature of the solvent containing *N*-methyl-*N'*-isopropylimidazolium bromide at the same irradiation power.

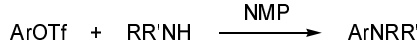
Increase of the polarity of the medium also enhances the effect of MW irradiation. For example, the MW-activated reaction of 2,3-dimethyl-1,3-butadiene with methyl acrylate in the presence of ionic liquids is complete in 5 min (yield 80%), the reaction performed without addition of ionic liquids requires 3 h, while the conventional thermal reaction takes 18–24 h. An analogous effect was observed upon addition of ionic liquids in the cyanation of aryl halides or synthesis of primary alkyl halides from alcohols [35]. The rate of alkylation of secondary amines under microwave irradiation increases as the ionic strength of the medium rises [36].

2.3. Possible Reasons for Acceleration of Reactions

There are two concepts concerning the reasons for acceleration of organic reactions in the microwave field. The first of these [37] implies that acceleration results exclusively from thermal effect, i.e., change of the temperature profile during the process, local overheating in the so-called "hot spots," and heating of the solvent above its boiling point. The other concept [8] involves a "specific" (nonthermal) microwave effect leading, e.g., to change of the activation energy of a reaction under MW irradiation. Both these concepts were analyzed in [38].

Most reactions successfully occurring under classical conditions proceed at a higher rate and with a greater yield under MW activation. Some reactions occur under MW irradiation but not on heating. For example, MW-activated arylation of secondary amines with nonactivated aryl trifluoromethanesulfonates [39] in 1-methyl-2-pyridinone (NMP) in the absence of a catalyst takes 45–60 min. Heating of the same reagents at the same temperature even for 2 days gives no expected anilines (Scheme 1).

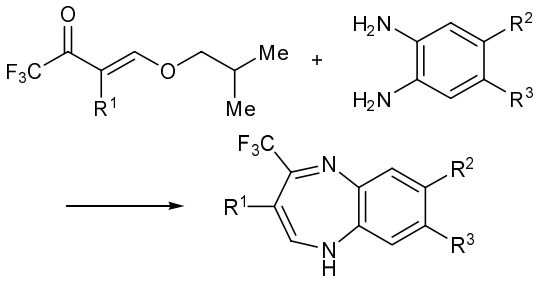
Scheme 1.



Likewise, condensations of substituted *o*-phenylenediamines with enol ethers derived from 1,3-diketones give the corresponding diazepines in 10–20 min [40] (Scheme 2), while no reaction occurs under conditions of convectional heating.

The main problem encountered while studying MW-activated reactions is that it is difficult to measure the temperature of the medium with a sufficient accuracy. Brykov *et al.* [41–43] measured the kinetic

Scheme 2.

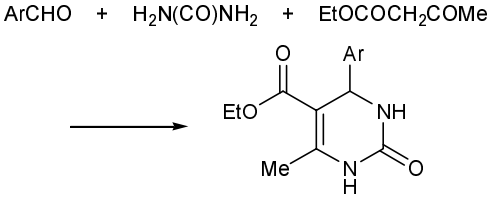


parameters of solid-phase isomerization of sodium 4-hydroxynaphthalene-1-sulfonate into sodium 1-hydroxynaphthalene-2-sulfonate. The authors proposed a mathematical model for estimation of distribution of the heat energy evolved due to interaction of MW irradiation with the substrate, and comparison of the theoretical and experimental data led them to conclude that no specific microwave effect is involved therein.

The Arrhenius equation parameters for esterification of 2,4,6-trimethylbenzoic acid with 1-propanol under conventional conditions and MW irradiation turned out to be similar [44]. Likewise, the mode of heating had no effect on the rate of esterification of acetic acid with isopentyl alcohol under conditions of heterogeneous acid catalysis [45].

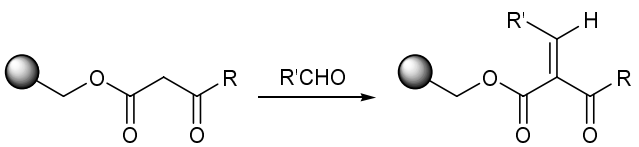
Studies of the Biginelli reaction [46, 47] (Scheme 3) performed at the same temperature under MW irradiation and without it showed that the rate of the MW-activated reaction is higher only in the absence of a solvent (Δ: reaction time 2–3 h, yield 24–79%; MW: 3–4 min, 78–96%); this may be due to increase in the reactant concentration.

Scheme 3.



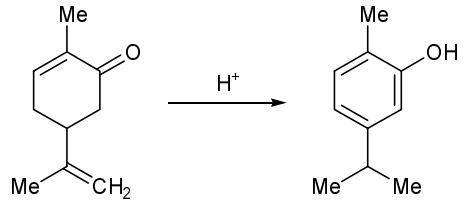
Strohmeier and Kappe [48] studied the kinetics of the reaction of benzaldehydes with polymer-supported β-keto esters (Scheme 4) under temperature-controlled conditions and revealed no difference between the

Scheme 4.



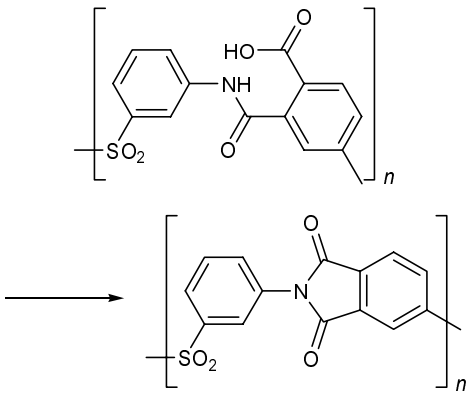
parameters of the MW-activated and thermal processes (Δ: DMF or benzene, 70°C, 16–48 h; MW: 1,2-dichlorobenzene, 170°C, 1–10 min). The activation parameters of the Diels–Alder reaction of anthracene with diethyl maleate and aromatization of carvone to substituted phenol [49] (Scheme 5) were also found to be independent on the activation mode.

Scheme 5.



On the other hand, different Arrhenius parameters were obtained in [50] (Table 3) for the cyclization of poly(amidophthalic acid) under conditions of convectional heating and MW activation (Scheme 6).

Scheme 6.



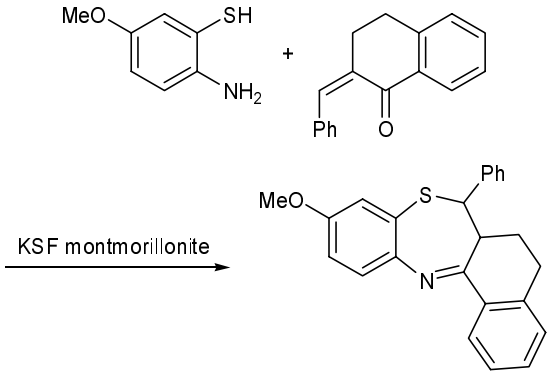
Development of devices capable of controlling temperature in MW-activated reactions made it possible to reveal specific effect of MW irradiation; however, its nature remains so far unclear. For example, the yields of tetracyclic dihydro-1,4-benzothiazepines [51] (Scheme 7) in the thermal and MW-activated reactions performed at the same temperature were 12%

Table 3. Activation parameters of some reactions[a]

Reaction	$E^{\neq}_{MW}$, kJ/mol	$\ln A_{MW}$	$E^{\neq}_{\Delta}$, kJ/mol	$\ln A_{\Delta}$
Aromatization	83±5	19.7±1.6	89±3	21.5±0.8
Diels–Alder reaction	88±8	13.9±2.0	94±10	15.6±2.3
Cyclization	57±5	13±1	105±14	24±4

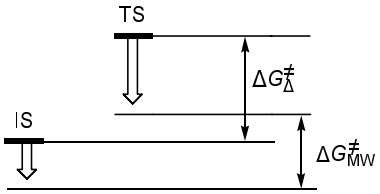
[a] Hereinafter, parameters indexed with Δ refer to classical heating, and those indexed with MW, to microwave heating.

Scheme 7.

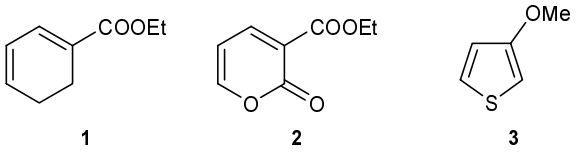


(17 min) or 36% (2 h) and 77% (17 min), respectively. The authors presumed that polar activated complex warms up at a higher rate than the initial weakly polar molecules and that the relation $\Delta G_{\Delta}^{\neq} < \Delta G_{MW}^{\neq}$ is valid (Scheme 8).

Scheme 8.



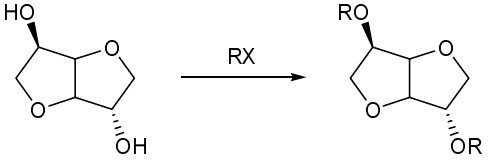
In the Diels–Alder reactions of dienes **1**–**3** with acetylenes, an appreciable specific microwave effect was observed only for compounds **2** and **3** which were presumed to give more polar transition states [52].



1 **2** **3**

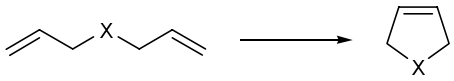
Specific microwave effect was revealed in the alkylation of dianhydrohexitols [53]. The yield of the product from isosorbite and octyl bromide in the presence of KOH and phase-transfer catalyst (tetrabutylammonium bromide) under MW irradiation attained 96% in 5 min against 10% under classical conditions (Scheme 9). It should be noted that in this case only the initial compound absorbed MW irradiation since the reaction was carried out in a weakly polar solvent.

Scheme 9.



Specific microwave effect was also observed in the synthesis of amides from esters and amines under phase-transfer catalysis [54] and from amines and carboxylic acids [55]. Specific microwave effect is stronger when a reaction is performed in a weakly polar solvent. For example, the reaction of 2,3-dimethyl-1,3-butadiene with methyl vinyl ketone in nonpolar xylene is accelerated to a greater extent than in polar dibutyl ether [56]. Considerable increase in the yield with the use of a solvent which does not absorb in the MW region (e.g., methylene chloride) was found for cyclizations of diallyl ethers, diallylamines, etc., catalyzed by rhodium [57] and ruthenium complexes [58, 59] (Scheme 10, Δ: 5 h, 75%; MW: 5 min, 97%). The rate of the MW-activated reaction was much higher in spite of the lower temperature.

Scheme 10.



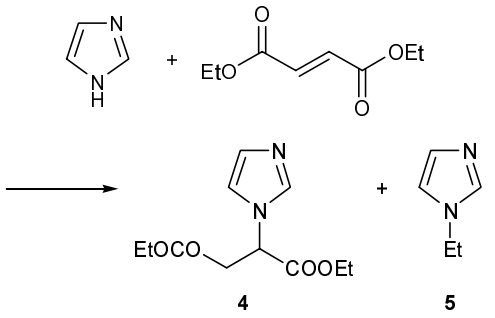
X = O, NTs, $C(CO_2Et)_2$, CHOH.

While studying the kinetics of Pd/C-catalyzed hydrogenation of unsaturated carboxylic acids, Leskovgek *et al*. [60] concluded that the observed acceleration cannot be attributed solely to the thermal effect. Nonthermal microwave effect was also revealed in some enzymatic reactions [61].

2.4. Effect of Microwave Irradiation on Reaction Selectivity

Microwave irradiation can change not only the rate but also selectivity of organic reactions. For instance, the selectivity in the sulfonation of naphthalene [62] depends on the irradiation power: high power favors formation of 1-naphthalenesulfonic acid, while a mixture of 1- and 2-naphthalenesulfonic acids is formed at a lower power. Microwave irradiation sometimes promotes a more profound reaction, as compared to convectional heating. Heating of a mixture of imidazole with diethyl maleate or diethyl fumarate gives 2-(1-imidazolyl)succinate **4** (25 h, 94%). The corresponding MW-activated reaction leads to a mixture of ester **4** and 1-ethylimidazole (**5**), and the product ratio depends on the irradiation power and time [63] (Scheme 11). At a power of 200 W, the ratio **4**:**5** is 59:6 in 2 min, 64:4 in 3 min, 50:14 in 4 min, and

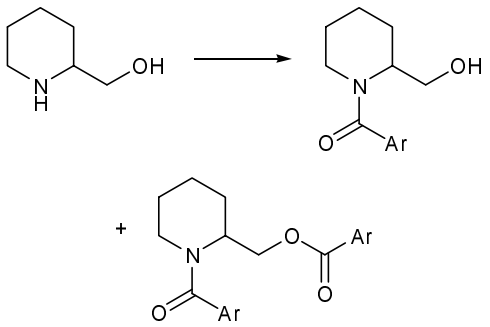
Scheme 11.



35:24 in 5 min. At an irradiation power of 400 W, compound **5** is formed as the only product in 2 min.

The selectivity in the acylation of 2-hydroxymethylpiperidine catalyzed by dibutyltin oxide [64] also depends on the irradiation power: the higher the power, the greater the yield of the *N*,*O*-diacyl derivatives (Scheme 12).

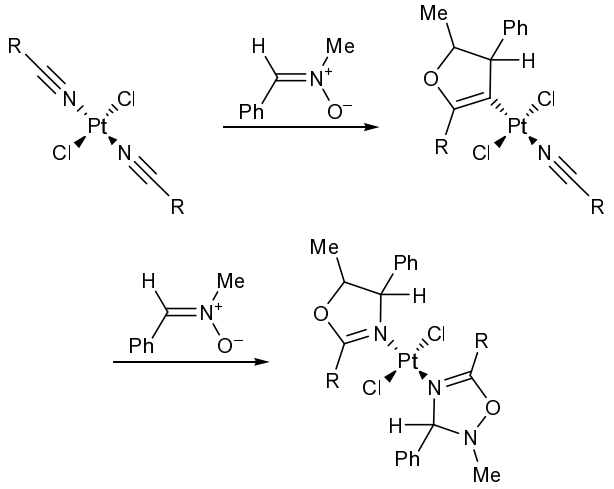
Scheme 12.



The reduction of nitroarenes with bismuth in the presence of potassium hydroxide at room temperature and on heating gives azoxy compounds, whereas MW-activated process leads to azo derivatives [65]. The reaction in boiling nitrobenzene afforded 60% of azoxybenzene in 45 min. When the reaction time was prolonged to 8 h, a mixture of azobenzene and azoxybenzene was formed (75 and 10%, respectively). The same process under conditions of MW activation resulted in formation of azobenzene as the only product in 85% yield (8 min).

Sometimes, MW-activated reactions give rise to products which cannot be obtained by classical procedures. The MW-activated reaction of *N*-benzylidenemethylamine oxide with (*E*)-3-phenylacrylonitrile coordinated to platinum or palladium [66] in 20 min gives only the corresponding monoadduct even in the presence of excess nitrone. The product of addition of two nitrone molecules is formed only in 2 h (Scheme 13). Analogous thermal reaction is complete in 2 days, and it always results in formation of a mixture of the mono- and bis-adducts. Enhanced selectivity was also observed in analogous reaction of *N*-benzylidenemethylamine oxide with coordinated benzonitrile [67].

Scheme 13.



R = Ph, (*E*)-PhCH=CH–.

Alkylation of 1,2,4-triazole with 2,4-dichlorophenacyl chloride gives compounds **6–8** (Scheme 14). In nonpolar solvents, as well as in the absence of a solvent, MW irradiation increases the selectivity of the process [8, 68] so that quaternary salt **8** is not formed. On the other hand, in polar solvents the selectivity remains unchanged, regardless of the activation mode (Table 4).

Scheme 14.

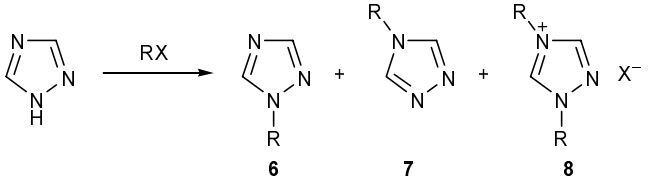
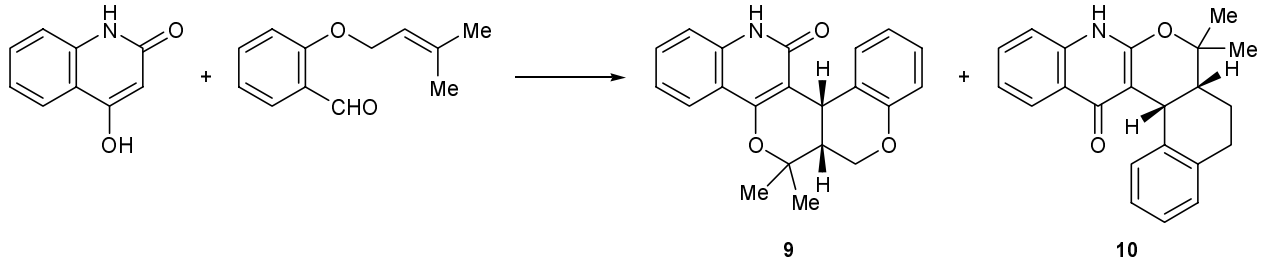


Table 4. Solvent effect on the alkylation of 1,2,4-triazole with 2,4-dichlorophenacyl chloride under conditions of microwave activation

Solvent	Conversion of 1,2,4-triazole, %		Product ratio **6**:**7**:**8**	
	MW	Δ	MW	Δ
1-Pentanol, DMF	90	90	95:5:0	95:5:0
o-Xylene	82	95	100:0:0	32:28:40
No solvent	92	100	100:0:0	36:27:37

Scheme 15.



By contrast, the selectivity in the cycloaddition of azomethine ylides to C_{70} fullerene in nonpolar solvents does not depend on the way of heating, while MW irradiation considerably changes the ratio of isomeric products when the reaction is carried out in polar media [69]. In this case, molecules of the substrate (fullerene) are nonpolar, and the temperature increases due to interaction between microwave irradiation and the solvent.

Microwave activation enhances the selectivity in benzoylation of 1,*n*-diols with benzoyl chloride in the presence of triethylamine. Under classical conditions, 5–9% of the corresponding *O*,*O*-diacyl derivative is always formed, whereas only the primary hydroxy group undergoes benzoylation under MW irradiation [70]. The use of microwave activation made it possible to avoid reactions at the vinyl and ester groups of the substrate in the synthesis of α-aminophosphonates from protoporphyrin dimethyl ester [71].

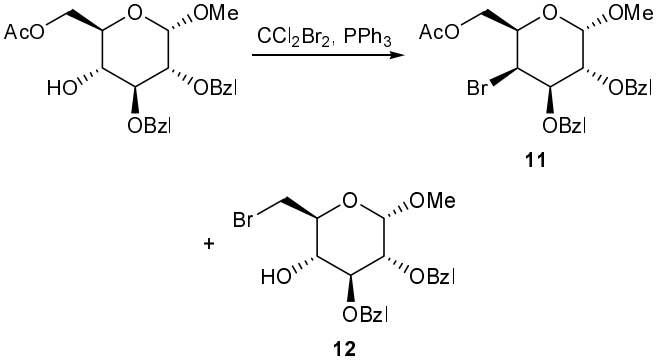
Enhanced selectivity was observed in the MW-activated domino Knoevenagel/hetero-Diels–Alder reactions [72]. Heating of 4-hydroxy-1,2-dihydroquinolin-2-one with 2-(3-methyl-2-butenyloxy)benzaldehyde for 14 h in boiling ethanol in the presence of piperidine leads to formation of polycyclic compounds **9** and **10** at a ratio of 55:45 (overall yield 67%; Scheme 15); in the same process under MW irradiation, the product ratio is 88:12 in 3 min (overall yield 79%). Analogous increase in selectivity was reported for reactions of 4-hydroxycoumarins and their benzo-fused derivatives with various aldehydes [73].

Table 5. Effect of microwave irradiation on enzymatic reactions

Enzyme	R	R'	ee_{Δ}	ee_{MW}	"E_{Δ}"	"E_{MW}"
LP/LSC	Bu	Et	32	47	3	8
LP/LSC	Me	$H_2C{=}CCH_3$	50	79	16	42
SP435	C_7H_{15}	Et	62	75	50	>100
SP435	C_7H_{15}	H	62	93	10	44

The reaction of methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside with dibromodichloromethane in the presence of triphenylphosphine under MW irradiation gave compound **11** as the major product (yield 50%) and 13% of **12** [74]. Convectional heating afforded the reverse product ratio: 12% of **11** and 29% of **12** (Scheme 16).

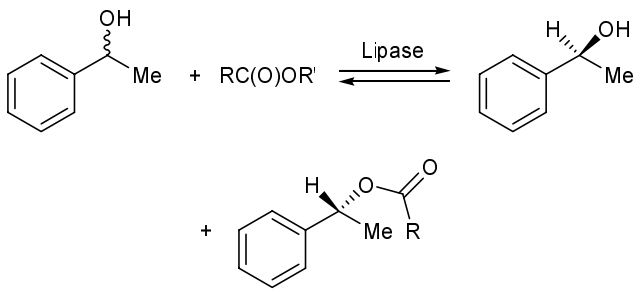
Scheme 16.



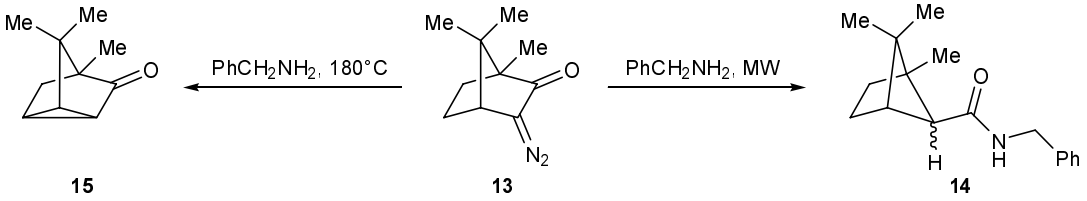
Enzymatic separation of racemic 1-phenylethanol via both transesterification of methyl methacrylate and esterification of fatty acids under MW irradiation considerably improves the enantioselectivity (Scheme 17, Table 5) [75]. According to the authors, MW irradiation facilitates removal of water and lower alcohols from the system and changes the energy of activation due to polarization of dipoles.

Microwave activation could also change the direction of a reaction. For example, MW-activated reaction

Scheme 17.



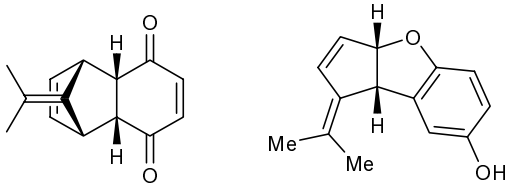
Scheme 18.



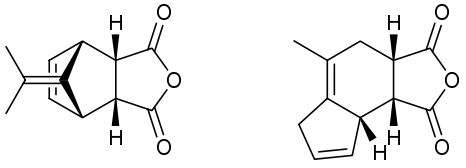
15 **13** **14**

of diazocamphor **13** with benzylamine leads to formation of the Wolff rearrangement product (compound **14**), while traditional heating yields intramolecular carbene insertion product **15** [76] (Scheme 18).

Heating of fulvenes with various dienophiles [77] gave the corresponding Diels–Alder adducts at the endocyclic double bonds. Under conditions of MW activation, unusual products were obtained. In the reaction of 6,6-dimethylfulvene with benzoquinone (benzene, 80°C, 2 h), compound **16** was formed in 70% yield, while MW irradiation (DMSO, 120°C, 10 min) afforded [2+3]-cycloaddition product **17** in 60% yield. The reaction of the same fulvene with maleic anhydride under classical conditions (48 h) yielded adduct **18**, and under MW irradiation (30 min) compound **19** was formed via addition of maleic anhydride to 1-isopropenyl-1,3-cyclopentadiene which is isomeric to 6,6-dimethylfulvene.



16 **17**



18 **19**

Effect of the mode of activation on the product composition was also observed in the Stille [78] and Suzuki reactions [79] and Claisen rearrangement [80].

3. EXPERIMENTAL CONDITIONS OF MICROWAVE-ACTIVATED SYNTHESES

3.1. Equipment for Microwave-Activated Syntheses

At present, there are many types of microwave cavities designed specially for laboratory use. However, until recently, most MW syntheses were performed in domestic microwave furnaces which are considerably less expensive than special equipment but are not free from some principal disadvantages and limitations.

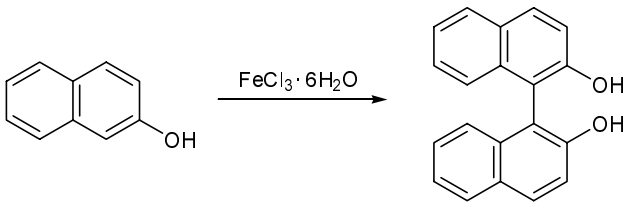
With respect to the mode of irradiation distribution over the working compartment (cavity, resonator, etc.), MW setups are grouped into multimode and single-mode (often referred to as monomode). The source of MW irradiation (magnetron) in multimode cavities is mounted directly in the cavity or is linked thereto through a short waveguide. The size and shape of the cavity allow reactions to be carried out with large amounts of reactants. On the other hand, reflection of microwaves from the walls of the cavity generates standing waves (modes), so that the field strength inside the cavity is heterogeneous: there are both "hot" and "cold" zones. Therefore, the heating pattern may be essentially variable, especially if a sample has a small size. To achieve reproducible results, large reaction vessels must be used and reaction mixtures should be effectively stirred or the reaction vessel should be rotated inside the cavity.

An example of a multimode cavity is a domestic microwave furnace. Variation of the irradiation power in household MW furnaces is achieved by periodical switching off of the source which is characterized by a fixed power. This also favors uneven distribution of electromagnetic energy, only a part of which is absorbed by the sample, while the remaining part is dissipated as heat into the environment or turned back to the magnetron.

In single-mode cavities, microwave irradiation is passed to the cavity through a long waveguide. Standing wave thus appearing has the maximal amplitude just in the place occupied by reaction vessel. However, the size of the cavity (and hence the size of reaction vessel) is limited by the microwave length, which makes enlarged syntheses impossible. A coupling device is installed in the waveguide before the cavity. This device measures the absorption of MW irradiation by the sample and reduces reflected wave. As a result, energy losses are minimized, and syntheses can be effected at a much lower power of MW irradiation.

Advantages of single-mode cavities with respect to domestic MW furnaces were repeatedly noted [12]. An example is iron(III) chloride-catalyzed coupling of β-naphthol (Scheme 19), which is characterized by a 96% yield in 30 s in a single-mode cavity at a power of 40 W, while the same reaction in a domestic MW furnace gives 66% of 1,1'-binaphthalene-2,2'-diol at 280 W, the reaction time being the same [81].

Scheme 19.



Up to now, flow [82–84] and batch MW reactors [85] have been developed. Several articles are devoted to scaling of chemical syntheses under MW irradiation [86, 87]. Many special devices for MW syntheses are equipped by systems for monitoring of irradiation power and reaction temperature.

Several manufacturers of microwave cavities for organic syntheses are known worldwide. CEM Corp. (USA) produces both types of MW reactors: single-mode and multimode. Single-mode CEM Discover can be equipped by various accessories, e.g., automatic system for syntheses of combinatorial libraries, automatic sampler, etc. An automatic flow system placed inside the cavity makes it possible to scale MW syntheses, thus overcoming the known limitation for single-mode cavities.

Milestone Inc. (Italy) produces multimode cavities with a tilting plate mounted in the site of coupling of the waveguide and the cavity, which eliminates the main disadvantage of multimode systems, uneven distribution of the microwaves over the cavity.

Personal Chemistry AB (Sweden) produces single-mode cavities both designed for single operation and equipped with automatic samplers for supply of liquid and solid samples in serial syntheses.

Multimode cavities manufactured by Prolabo (France) utilize open vessels, so that common organic laboratory glassware kits can be used therein. The instruments are equipped by systems protecting magnetron from overheating and providing variation of irradiation power.

3.2. Procedures for Microwave-Enhanced Syntheses

The most frequently used procedures for MW syntheses can be divided into three groups: (1) syntheses in solvents, (2) syntheses with no solvent (only reactants), and (3) supported syntheses. Syntheses in flow reactors should also be set apart. The application of one or another procedure depends on the particular conditions (properties of solvent and/or reactants, necessity of increased or reduced pressure, etc.). Optimization of synthetic parameters is especially important in MW-enhanced reactions, for even small variation of one or another parameter could essentially change the result of the process.

3.2.1. Syntheses in solvents. First experiments on microwave activation of organic reactions were carried out under the same conditions as conventional syntheses in a solvent. Insofar as domestic microwave furnaces were used as irradiation source, some adapters were built therein to avoid irradiation loss through aperture for attachment of reflux condenser to the reaction vessel [1]. These procedures were advantageous due to minimal modification of classical methods [88–91], and the only but important limitation was strong dependence of the efficiency on the polarity of solvents and reactants [76]. Polar solvents were used with weakly polar reactants [92, 93] or strongly polar substances (such as ionic liquids) were added to a nonpolar solvent [57].

Microwave-activated syntheses can be performed in high-pressure glass and polymeric vessels which are transparent for microwaves. The solvents, reactants, and reactant ratios are the same as in classical syntheses [94]. However, the lack of temperature and pressure control could result in explosion [95]. To avoid explosion, high-boiling solvents may be used, and reactions may be carried out in an open vessel; however, in this case, removal of the solvent from the reaction mixture may be difficult [96].

Some solvents give rise to homogeneous mixtures on heating, while after cooling the mixture divides into two liquid phases or liquid and solid phases. For example, polyfluorinated hydrocarbons are immiscible with water and organic solvents at room temperature, but they readily dissolve organic substances at elevated temperature. Poly(ethylene glycol) (PEG) with an average molecular weight of 3000–6000 a.m.u. is an excellent polar solvent which is liquid at elevated temperature and solid at room temperature; moreover, it can also be used as phase-transfer catalyst. When the

reaction is complete, PEG is separated by filtration and washed by a low-boiling solvent, and the latter can readily be removed. Apart from PEG, crown ethers and ammonium salts are used as catalysts [97].

Syntheses with the use of phase-transfer catalysts should be considered separately. Such reactions are carried out in a solvent or without it. When one of the reactants (usually inorganic compound) is insoluble and/or immiscible with the other components, classical heterogeneous reactions are slower than homogeneous. Microwave enhancement considerably reduces the difference in the reaction time between homogeneous and heterogeneous processes.

3.2.2. Solvent-free syntheses. Reactions under solvent-free conditions on heating usually involve homogenization of the system: liquid reactant mixtures become homogeneous, and solid components melt and/or dissolve in liquid components. The absence of solvent simplifies subsequent treatment of reaction mixtures [98] and makes syntheses less expensive [99]. If the initial reactants and products are not volatile, the reactions may be carried out in open vessels [100, 101]. Solvent-free reactions may be ineffective when reactants poorly absorb MW irradiation. In this case, the product yield can sometimes be raised by adding a few drops of water. In the reactions of dry sodium chloromethanesulfonate with phenols, the product yields are poor; addition of several drops of water increases the yield up to 85–96% in 30–40 s [102] (cf. Δ: 200–220°C, 4 h, 25–83%).

3.2.3. Syntheses on solid supports. Syntheses on solid supports have long been used in combinatorial chemistry and peptide syntheses. One reactant is adsorbed [103, 104] or immobilized (grafted) [105] on the surface of a solid support, and the resulting system is treated with the other reactant. The reaction takes several days against a few hours in solution. Microwave-activated reaction on a solid support is complete in several minutes with a high yield [106].

3.2.4. The use of flow reactors as a way of scaling syntheses. It is convenient to perform MW reactions in a flow system when large amounts of product are necessary but appropriate large cavity is unavailable. In this case, the reaction vessel is a tube made of any material which is transparent for microwaves, e.g., quartz, Teflon, or glass). The tube is placed inside the cavity, and the irradiation time is controlled by the flow rate of the reaction mixture through the tube. Some parts of the tube are placed outside the cavity and cooled to avoid overheating. Such systems are suitable for both syntheses involving solutions of reactants in appropriate solvents and reactions without a solvent [84, 107, 108]. A suspension containing solid reactants and/or catalysts may be passed through the reactor [107] or reaction mixture may be passed through the tube charged with a catalyst on a solid support [45, 108].

4. CREATION AND MODIFICATION OF FUNCTIONAL GROUPS

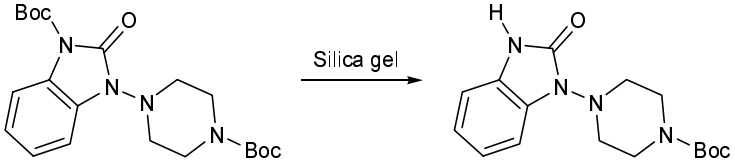
Sections 4 and 5 describe some examples of using microwave activation in organic synthesis, numerous MW-activated reactions are systematized, and Tables 6–11 compare the reaction times and product yields in the reactions performed under classical conditions and MW irradiation. All reactions are grouped according to the up-to-date classification of chemical transformations: creation of a functional group without change in the oxidation number of atoms, oxidation and reduction processes, formation of one or two bonds, heterocyclizations, and rearrangements.

4.1. Isohypsic Reactions

Table 6 contains the data on 26 isohypsic reactions (i.e., those involving substitution without change of the carbon oxidation state). Microwave irradiation shortens the time of halogen exchange by the action of nickel halides from 4 h to 5 min [95]. Microwave activation increases the rate of nucleophilic replacement of halogen atoms both in the aliphatic series in reactions with primary amines (Δ: 20 h; MW: 15 min) [109] and in the aromatic series by the action of cyclic amines [110–112] (Δ: 3–10 h, 60–75%; MW: 3–5 min, 73–90%), anilines [98] (Δ: 160–180°C, 12–48 h; MW: 2–20 min, 60–93%), amides [113–115], and sulfonamides [116] (Δ: 20 h, low yield; MW: 2–4 min, 54–90%), as well as in reactions with phenols and benzenethiols in the presence of cesium fluoride [117] (Δ: 110°C, 12–20 h, 62–73%; MW: 3–6 min, 75–94%). Likewise, halogen replacement by boronate group (Table 6, reaction no. 1) and formation of phosphonium salts (reaction no. 2), ethers, esters, and sulfides (reaction nos. 3–7) are also accelerated by MW irradiation.

Microwave activation is widely used for both protection and deprotection of functional groups. Aldehydes and ketones are readily converted into the corresponding oximes and hydrazones [118–120] (Δ: 2–25 h, 40–94%; MW: 1–30 min, 75–96%) and

Scheme 20.



acetals in aqueous medium [121] (Δ: 1–5 h; MW: 1–2 min, 20–90%) or without a solvent on silica gel in the presence of sodium hydrogen sulfate [103] (Δ: 110°C, 8–12 h, 20–30%; MW: 2–6 min, 71–98%). Microwave activation allows synthesis of acylals from aldehydes and acetic anhydride to be performed in 6–20 min with 75–98% yield [122], while classical procedures require a lot of time (up to 120 h) or give a poor yield (4% in 24 h from 4-nitrobenzaldehyde). Phthalimide protection of amino groups is achieved in 2 min (yield 86%) against 2 h under conventional heating (yield ≤12%). Removal of *tert*-butoxycarbonyl protection from amino groups over silica gel under MW irradiation takes 1 to 3 min with high selectivity [88] (Δ: 100–110°C, 12–30 h, 98%). Irradiation of 3-*tert*-butoxycarbonyl-1-(4-*tert*-butoxycarbonyl-1-piperazinyl)-2,3-dihydrobenzimidazol-2-one for 1 min leads to deprotection of only the N^3–H group, and further irradiation for (3 min) results in complete removal of both protecting groups (Scheme 20).

Microwave irradiation efficiently accelerates esterification (reaction nos. 8–12), acidolysis of anisoles (reaction no. 13), amination of alcohols, phenols, and carboxylic acids (reaction nos. 14–18), and alkylation of amines (reaction nos. 19, 20). Tosyl protection of amino and hydroxy groups can be removed under MW irradiation without a solvent (KF/Al_2O_3) in 4–6 min (yield 76–95%) [123, 124]. Carbonyl compounds were obtained from the corresponding oximes and semicarbazones using pyridinium chlorochromate [125] and sodium bismuthate [126, 127] (Δ: 110°C, 18–24 h; MW: 1–8 min, 72–97%), as well as from acylals [128] (Δ: 6 h, 90%; MW: 1 min, 90%) and dithio acetals [129] (Δ: 8.5h, 40–50%; MW: 2 min, 92%). Microwave activation was also applied to the synthesis of thiocarbonyl compounds (reaction no. 21).

Under MW irradiation, the time necessary for opening of epoxy derivatives by the action of amines [130], ammonium hydroxide [131, 132] and acetate [133], and benzenethiols [134] shortens from several

Table 6. Reactions occurring without change in the oxidation state of the carbon atom

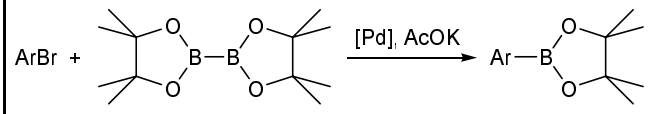
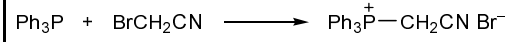
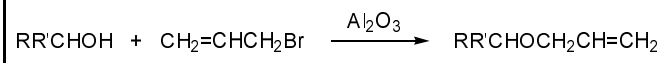
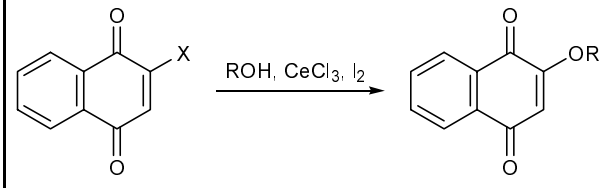
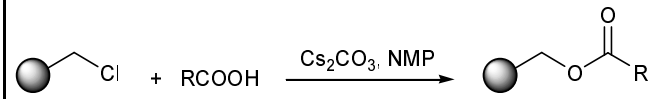
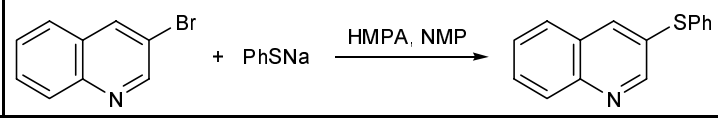
No.	Reaction	Δ	MW	Reference
1		12–48 h, 20–72%	17–27 min, 45–89%	[93, 94]
2		336 h, 99%	3 min, 99%	[135]
3		25°C, 14–240 h, 63%	10–20 min, 52–71%	[136]
4	 X = H, Cl, Br.	60–70°C, 4–8 h, 50–75%	5 min, 57–90%	[137, 138]
5		80°C, 12–48 h	5–15 min	[139]
6		165°C, 7 h, 18%	35 s, 99%	[140]

Table 6. (Contd.)

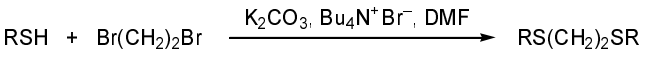
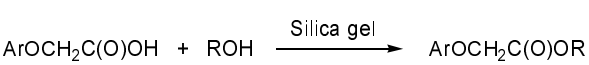
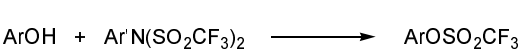
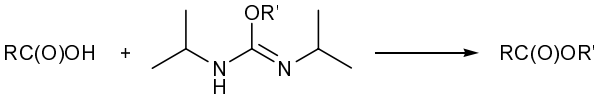
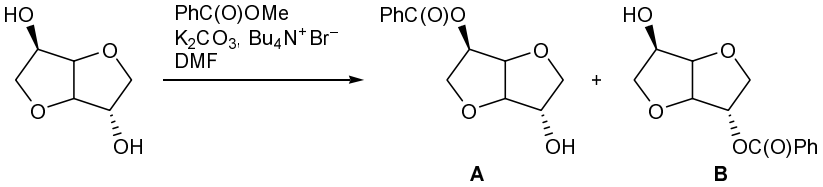
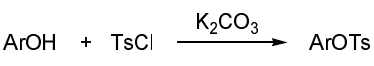
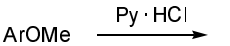
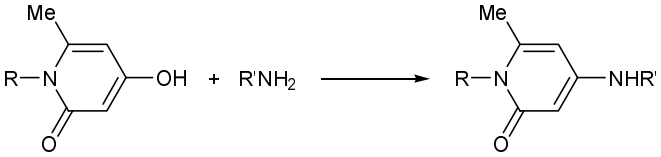
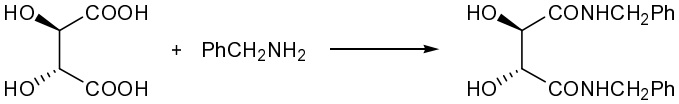
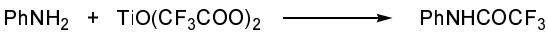
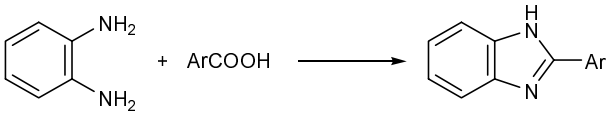
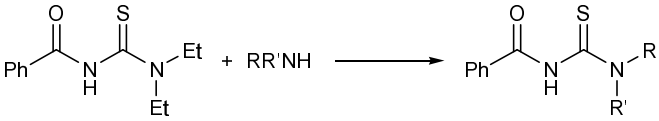
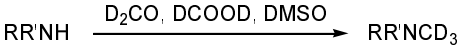
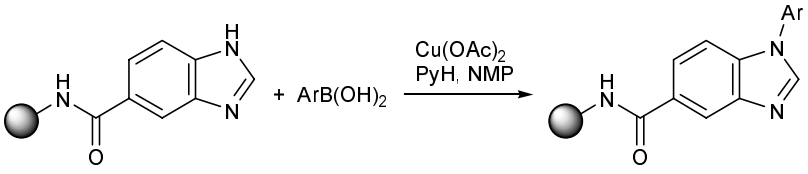
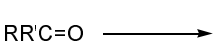
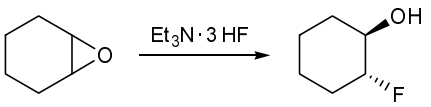
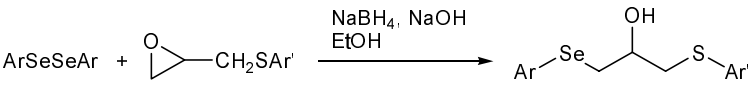
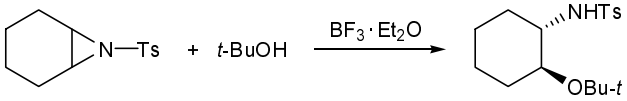
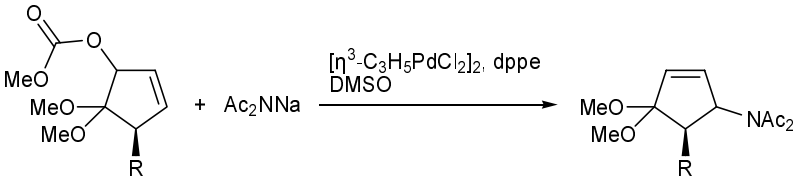
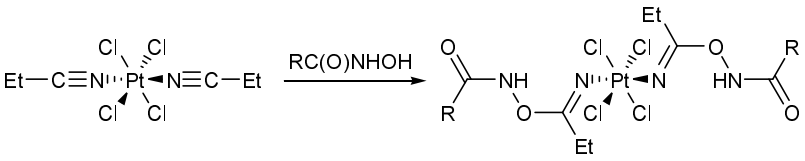
No.	Reaction	Δ	MW	Reference
7		12 h, 90%	15 min, 86%	[141]
8		100–150°C, 2–6 h, 90–94%	3–5 min, 96–99%	[92]
9		3–8 h	6 min, 69–91%	[142]
10		1–72 h	5 min, 75–94%	[143]
11		159°C, 20 h, 14%, **A** : **B** = 9 : 5	15 min, 63%, **A** : **B** = 38 : 25	[144]
12		12–16 h, 75–91%	3–5 min, 92–99%	[145]
13		180–190°C, 3 h	14–16 min, 74–95%	[146]
14		2–72 h	14–20 min, 60–91%	[147]
15		16 h, 68%	12 min, 80%	[148]
16		100°C, 48 h	5 min, 95%	[149]
17		170–200°C, 4–16 h, 60–95%	2.5–4 min, 78–96%	[150, 151]
18		5 h, 4–35%	2–5 min, 69–90%	[152]
19		80°C, 24 h	1–3 min	[153]
20		80°C, 48 h, 30%	30 s, 96%	[105]
21		20–25 h	2–4 min, 76–97%	[100, 154]

Table 6. (Contd.)

No.	Reaction	Δ	MW	Reference
22		115°C, 3.5 h, 69%	2–10 min, 61%	[99]
23		9–13 h, 72–86%	15 min, 73–87%	[155]
24		48 h, 72%	15 min, 83%	[156]
25		70°C, 48 h, 3%	2 min, 46%	[157]
26		45°C, 2–3 h	50°C, 15 min, 70–80%	[158]

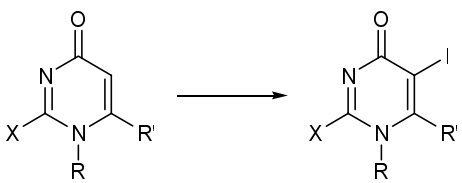
hours to a few minutes, and the yield increases from 10–25 to 75–97% (see also reaction nos. 22, 23). Microwave irradiation accelerates opening of aziridine ring (reaction no. 24) and strongly accelerates addition across multiple bonds (reaction nos. 25, 26).

4.2. Oxidation

This section deals with substitution and addition processes accompanied by increase in the degree of oxidation of carbon atoms (Table 7, reaction nos. 27–34). Microwave irradiation is very effective in halogenation of ketones (reaction no. 27). The iodination of substituted pyrimidinones with *N*-iodosuccinimide in DMF was studied in [96] (Δ: 70°C, 6 h, 5–97%; MW: 3 min, 65–100%; Scheme 21).

Oxidation of methyl groups in quinones and ethylenes is more efficient under MW irradiation

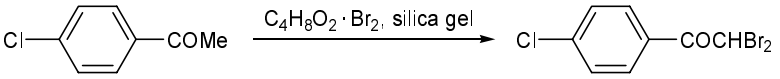
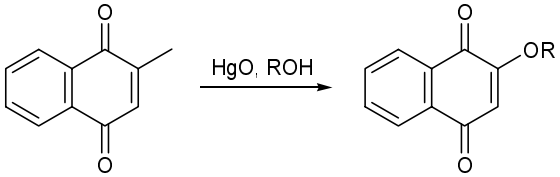
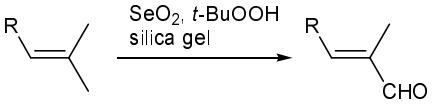
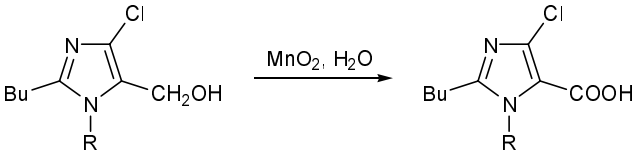
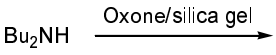
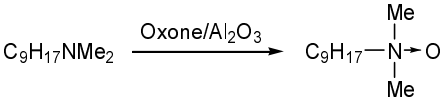
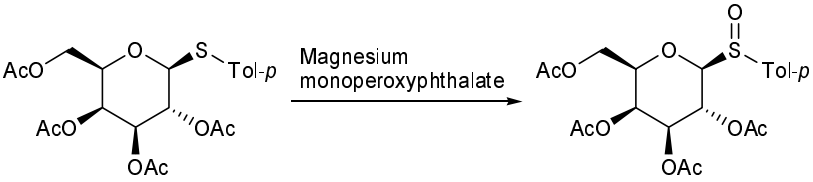
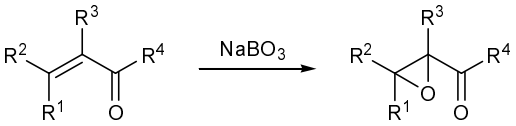
Scheme 21.



(reaction nos. 28, 29). Oxidation of hydroxy groups in alcohols, steroids, and carbohydrates with pyridinium chlorochromate takes 4 h under classical conditions, while the corresponding MW-activated reactions are complete in 2–10 min (yield 70–99%) [159]. Microwave irradiation makes it possible to oxidize alcohols to aldehydes over zeofen under solvent-free conditions [160]. Here, the reaction time shortens from 20–60 min to 10–120 s. Benzoins were oxidized to benzils with copper(II) sulfate over aluminum oxide [161], with nitric acid [162], and over zeolite A [163] (Δ: 1.5 h; MW: 0.5–6 min, 78–96%).

Oxidation of primary alcohols with manganese dioxide leads to carboxylic acids (reaction no. 30). Microwave irradiation shortens the time necessary for oxidation of toluenes to benzoic acids [164] with the urea–hydrogen peroxide complex and increases the yield (Δ: 40 min, 67%; MW: 3 min, 83%). The time of oxidation of fluorene to fluorenone and of diphenylmethane to benzophenone with potassium permanganate over aluminum oxide in the absence of a solvent under MW irradiation is 10 and 30 min, respectively, against 118 and 282 h under classical conditions [165]. Microwave activation is very effective in the oxidation with Oxone of secondary and tertiary amines to hy-

Table 7. Oxidation reactions

No.	Reaction	Δ	MW	Reference
27		2 h, 48%	8 min, 90%	[167]
28		1–4 h, 55–82%	5–8 min, 62–86%	[138]
29		18–24 h, 70–80%	10 min, 68–85%	[168, 169]
30		100 h, 9%	50 min, 64%	[170]
31		80°C, 8 h, 98%	40 s, 97%	[171]
32		80°C, 1 h, 92%	40 s, 94%	[171]
33		3 h, 85%	40 min, 90%	[172]
34		1–48 h, 40–100%	45–180 s, 75–95%	[173, 174]

droxylamines and amine oxides, respectively (reaction nos. 31, 32), and of sulfides to sulfoxides (reaction no. 33). The hydration of *p*-methoxyphenylacetylene under classical conditions in 30 min gives less than 5% of the product, while under MW irradiation the yield increases to 94% [166]. Also, acceleration of epoxidation of unsaturated ketones by MW irradiation was reported (reaction no. 34).

4.3. Reduction

Radical reduction of bromoadamantane was effected in 81% yield with the use of fluorinated trialkylstannanes [175]; no reaction occurred under classical conditions. Benzo- and acetophenone hydrazones were reduced according to Wolff–Kishner in the presence of KOH [118] (Δ: 4–25 h, 40–91%; MW: 25–30 min, 75–95%), as well as with moist sodium tetrahydridoborate over K10 montmorillonite [176] (Δ: 65°C, 5 h; MW: 0.5–5 min, 78–97%). Benzaldehydes are reduced to benzyl alcohols with formaldehyde in the presence of alkali in 20–25 s (yield 90%) [177]; for comparison, heating of benzaldehyde in boiling methanol for 12 h gives only 50% of the product.

The reduction of α-methylcinnamic acid with *N*,*N*,*N*′,*N*′-tetramethylethylenediammonium diformate takes 5 min under MW irradiation against 2 h at 50°C

or 30 min at 100°C [178]. Substituted cinnamic acids were reduced with sodium formate in the presence of $PdCl_2$ [179] (Δ: 14 h, 76%; MW: 3 min, 83%).

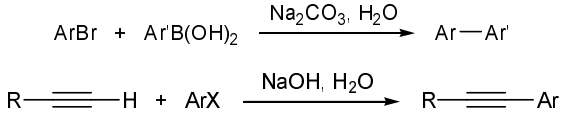
5. BUILDING UP OF MOLECULAR SKELETONS

Reactions leading to formation of a new carbon skeleton are very important in organic chemistry. These reactions may involve formation of one (Table 8) and two C–C bonds, the latter including cycloaddition processes (Table 9). Rearrangements constitute a specific class of such reactions.

5.1. Formation of One C–C Bond

Table 8 contains examples of MW-activated formation of one ordinary or double carbon–carbon bond. Microwave irradiation facilitates alkylation of aromatic compounds (reaction no. 35), hydroxyalkylation of quinones and acrylates (reaction nos. 36, 37), and aminoalkylation of alkynes (reaction no. 38). Various palladium-catalyzed reactions (reaction nos. 39–44) and those with participation of stannanes (reaction no. 45) occur at a higher rate under conditions of MW irradiation. Microwave activation turned out to be effective in the cyanation of aryl halides with copper(I) cyanide (Δ: 10–18 h; MW: 20–30 min, 56–90%) [180, 181], zinc cyanide in the presence of palladium complexes (Δ: 2–16 h; MW: 2–2.5 min, 78–95%) [182], and nickel cyanide [183]. It was recently found that MW activation of reactions usually catalyzed by metal complexes, e.g., Suzuki [78, 104, 184, 185], Sonogashira, Stille, and Heck reactions, etc. [89, 186–190], allows these reactions to be performed in the absence of a catalyst [191–193] (Scheme 22).

Scheme 22.



Microwave irradiation was used to activate formation of double C=C bond in reactions of aldehydes with compounds possessing an activated methylene group (reaction nos. 46–48) or with the Wittig reagent (reaction no. 49).

Table 8. Formation of one skeletal C–C bond

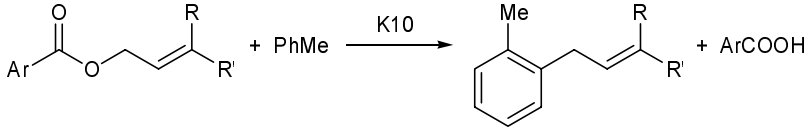
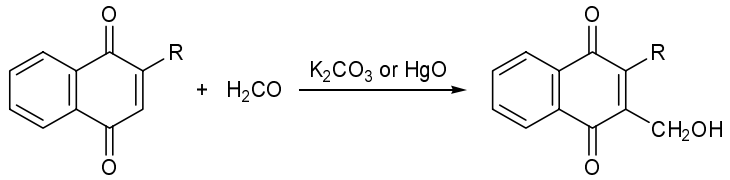
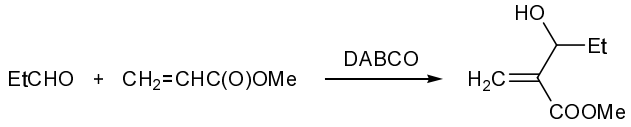
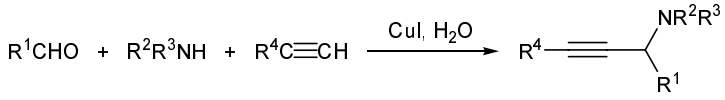
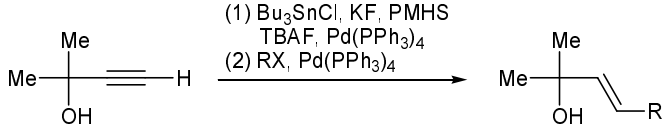
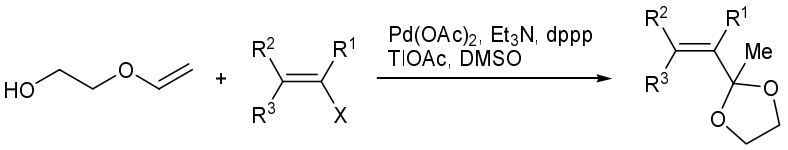
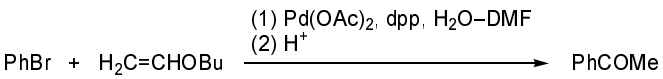
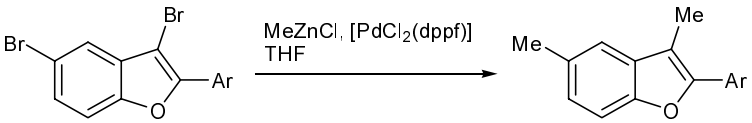
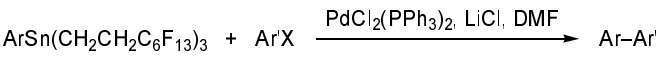
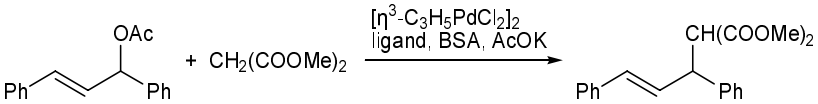
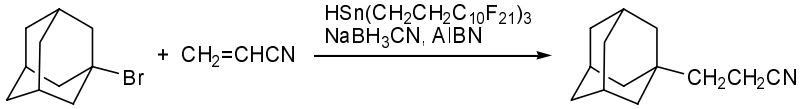
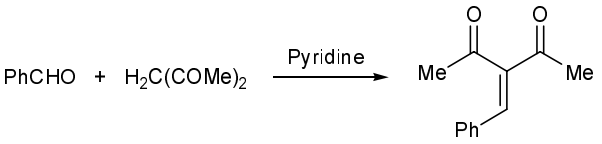
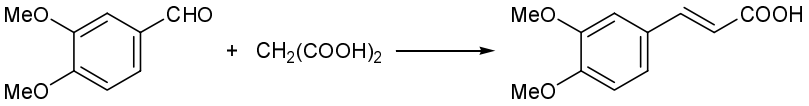
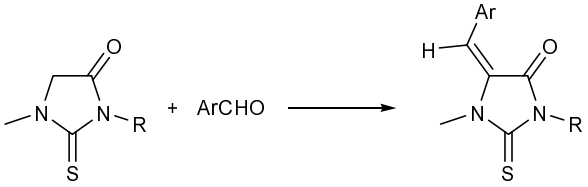
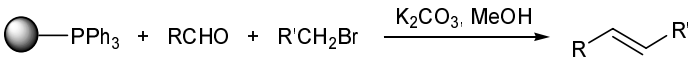
No.	Reaction	Δ	MW	Reference
35		5–20 h, 47–94%	10–20 min, 70–97%	[194]
36		30–90 min, 80–95%	5–6 min, 78–95%	[138]
37		25°C, 4 days, 61%	10 min, 70%	[195]
38		1–5 days	5–30 min, 41–93%	[196]
39		16 h, 60 %	13 min, 90%	[197]

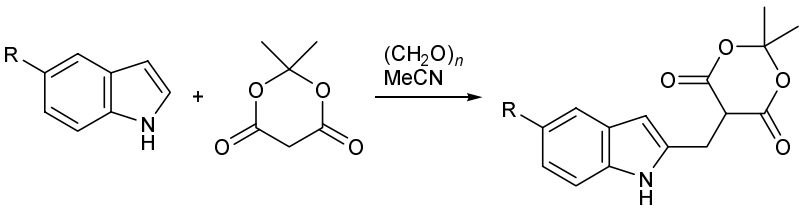
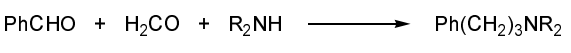
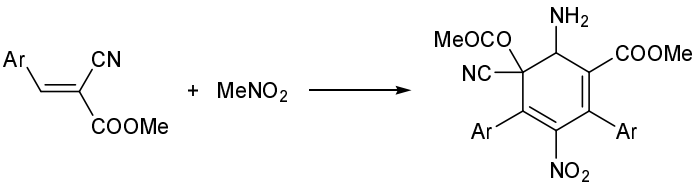
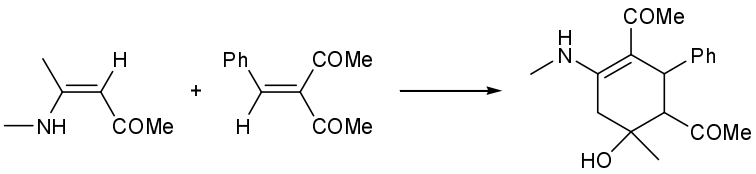
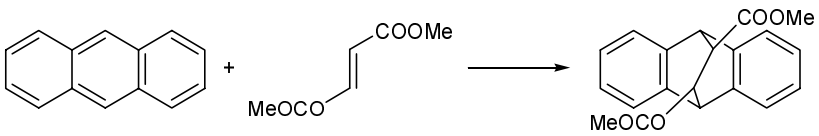
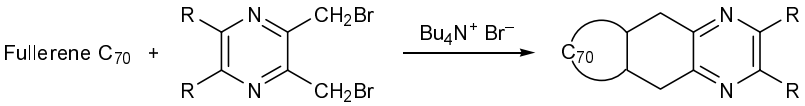
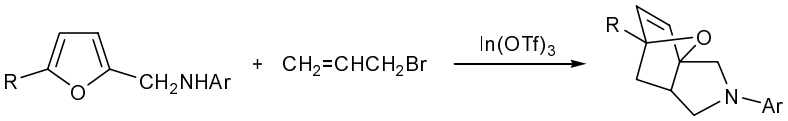
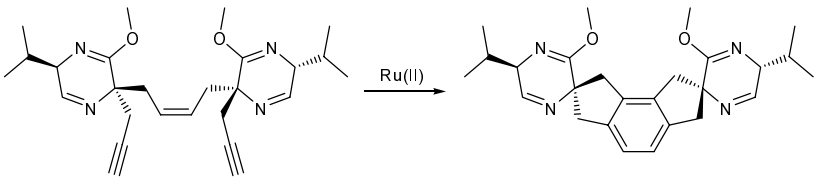
Table 8. (Contd.)

No.	Reaction	Δ	MW	Reference
40		40–100°C, 6–240 h, 32–87%	5–7 min, 45–89%	[198]
41		16 h, 82%	1 h, 62%	[199]
42		18 h, 62%	1 h, 64%	[200]
43		80°C, 24 h	1.5–2 min, 49–96%	[78]
44		5 min–6 h, 56–99%, *ee* = 56–99%	15–120 s, 96–99%, *ee* = 63–99%	[201, 202]
45			10 min, 77%	[175]
46		4 days, 70%	3 min, 73%	[203]
47		8 h, 79%	2 min, 87%	[179]
48		40–50°C, 12 h, 80–98%	12 min, 80–94%	[204]
49		7 days, 75 %	3–5 min, 11–95%	[106]

5.2. Cycloaddition and Other Reactions Involving Formation of Two C–C Bonds

Examples of MW-enhanced reactions leading to formation of two or more skeletal C–C bonds are collected in Table 9. Microwave irradiation facilitates condensations involving successive formation of two carbon–carbon bonds, in particular with formaldehyde (reaction nos. 50, 51), nitromethane (reaction no. 52), and vinyl ketones (reaction no. 53). Microwave irradiation is efficient in concerted cycloaddition processes leading to formation of six-membered rings, e.g., [2+4]-cycloaddition (reaction nos. 54–56) and [2+2+2]-cycloaddition (reaction no. 57). Retro-Diels–Alder reactions are also accelerated under microwave irradiation [205].

Table 9. Cycloaddition and other reactions involving formation of two skeletal C–C bonds

No.	Reaction	Δ	MW	Reference
50		9–24 h, 15–61%	30–60 min, 67–82%	[206]
51		1–3 h, 23–85%	5–15 min, 60–83%	[207]
52		90°C, 20 min, 27%	11 min, 70%	[208]
53		20°C, 2 days, 67%	15 min, 55%	[209]
54		138°C, 4 h, 67%	10 min, 87%	[2]
55		5–72 h, 14–70%	20–75 min, 21–42%	[97]
56		20–30 min, 40–45%	8–10 min, 80–90%	[210]
57		85°C, 14 h, 90%	20 min, 100%	[211]

5.3. Rearrangements

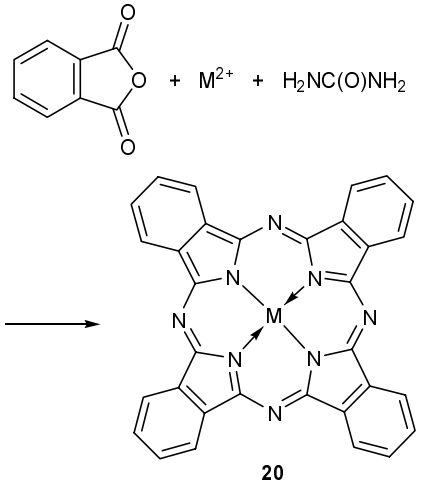
Microwaves accelerate various rearrangements, such as benzilic (Δ: 6 h, 32%; MW: 55 s, 93%) [212], pinacol (Δ: 15 h; MW: 15 min, 99%) [213], and Claisen (Δ: 10–16 h, 60–90%; MW: 4-6 min, 68–92%) [214]. The yields of *N*-methylbenzamide from acetophenone oxime (Beckmann rearrangement [215]) (9 min, 138°C, Δ: 17%, MW: 91%) and of hydroxynaphthalenecarbaldehyde from naphthyl acetate (Fries rearrangement) (7 min, Δ: 10%, MW: 95%) [216] strongly increase. Thia-Fries rearrangement of aryl sulfonates, catalyzed by silica gel-supported aluminum and zinc chlorides, also occurs at a higher rate under MW irradiation [217] (Δ: 120°C, 2 h, 12%; MW: 10 min, 87%).

6. SYNTHESES OF SPECIFIC CLASSES OF ORGANIC COMPOUNDS

6.1. Organometallic Compounds

Microwave irradiation was used in the preparation of 2-arylmercurio-1,4-naphthoquinone from 1,4-naphthoquinone and arylmercury chloride (Δ: 6–11 h, 87–92%; MW: 4.5–7 min, 86–91%) [218]. Microwave irradiation considerably shortens the reaction time in the synthesis of phthalocyanine metal complexes **20** (Scheme 23; Δ: 3–5 ch, 55–80%; MW: 1–1.5 min, 65–90%) [219, 220].

Scheme 23.



20

M = Cu, Ni, Fe.

6.2. Heterocyclic Compounds

Microwave activation is successfully applied to syntheses of heterocycles (Table 10). It ensures high yields of aziridine (reaction no. 58) and azetidine derivatives (reaction nos. 59, 60). Pyrrolidin-2-ones were obtained by condensation of propionic acid with amines and isocyanides (reaction no. 61) or by reaction of substituted 2-(2-propynyl)-2-isocyanoacetates with 2-sulfanylethanol (Δ: 80°C, 6 h, 37%; MW: 5 min, 60%) [114]. Dihydropyrroles were prepared from 2-allyl-2-isocyanoacetates (reaction no. 62). Cyclization of *N*-allylanilines over montmorillonite in the absence of a solvent gives substituted dihydroindoles (Δ: 8–10 h; MW: 3–6 min, 71–85%) [221].

Pyrroles were synthesized by reaction of 1,3-diketones with anilines [222] or benzylamines [223] (MW: 0.5–5 min) or by condensation of α,β-unsaturated carbonyl compounds with amines and nitroalkanes (Δ: 15–18 h, 28–40%; MW: 5–10 min, 60–72%) [224]. 1,3-Dipolar cycloaddition of propynoic acid esters to ylides generated from *N*-phenacylpyridinium salts by the action of KF/Al_2O_3 afforded substituted indolizines (Δ: 3–6 h, 50–58%; MW: 7–10 min, 81–91%) [225]. Substituted 3-aminoindolizines were obtained by condensation of 2-aminopyridines with isocyanides and aldehydes, catalyzed by scandium trifluoromethanesulfonate (Δ: 72 h; MW: 10 min, 50–93%) [226].

α,β-Unsaturated carbonyl compounds react with hydrazines in glacial acetic acid to give *N*-acyldihydropyrazoles (Δ: 5.5–8 h; MW: 5–7 min, 73–88%) [227], and their reactions with arylhydrazines lead to *N*-aryldihydropyrazoles [228]. Fused *N*-aryldihydropyrazoles are obtained by reaction of benzofuran with arylhydrazines and aromatic aldehydes (reaction no. 63).

Heating of substituted (carbamoylamino)acetates in the presence of barium hydroxide results in cyclization with formation of substituted imidazolidine-2,4-diones (reaction no. 64). Condensation of *N*-methylglycine with akyl isothiocyanates gives 3-alkyl-1-methyl-2-thioxoimidazolidin-4-ones (Δ: 12 h, 67–92%; MW: 12 min, 75–92%) [204]. 4-Alkylidene-1*H*-4,5-dihydroimidazol-5-ones were obtained from carboximidates and aromatic aldehydes under solvent-free conditions (reaction no. 65). 4-Arylmethylidene-2-phenyl-4,5-dihydrooxazol-5-ones reacted with 2-amino-1,3,4-thiadiazoles in the presence of Al_2O_3 to form 4-arylmethylidene-1-(thiadiazolyl)-4,5-dihydroimidazol-5-ones (Δ: 7–8 h, 70–72%; MW: 5.5–6 min, 90–94%) [228].

Substituted imidazoles were synthesized by condensation of 1,2-dicarbonyl compounds with amines and aldehydes under MW irradiation in the absence of a solvent (Δ: 4 h; MW: 10 min, 72%) [229] or with amines and nitriles (reaction no. 66). 4-Alkylsulfanylimidazoles were obtained by condensation of aldehydes, thioamides, and alkyl bromides in the presence of ammonium acetate and sodium carbonate (Δ: 12 h, 26–96%; MW: 16 min, 21–96%) [230]. Substituted *o*-phenylenediamines reacted with alkyl isothiocyanates to afford 2-alkylaminobenzimidazoles (Δ: 4 h; MW: 9 min) [231]. Symmetric 3,5-diaryl-4-amino-1,2,4-triazoles were prepared by reaction of benzonitriles with hydrazine hydrochloride in the presence of excess hydrazine hydrate (Δ: 45–60 min, 61–97%; MW: 4–10 min, 58–96%) [232]. Reactions of benzonitriles with sodium azide afforded 5-aryltetrazoles (reaction no. 67).

Substituted *o*-hydroxybenzaldehydes react with phenacyl *p*-toluenesulfonates to give 2-aroylbenzofurans (reaction no. 68). Intramolecular cyclization of

Table 10. Syntheses of heterocyclic compounds

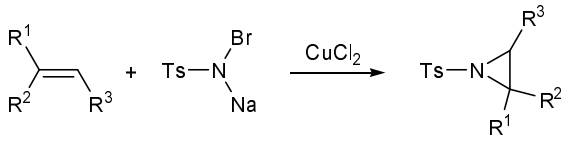
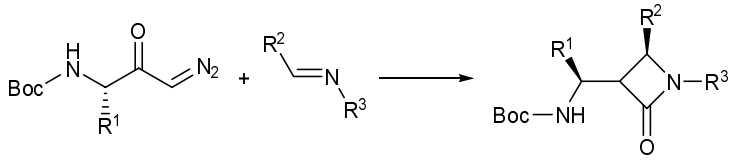
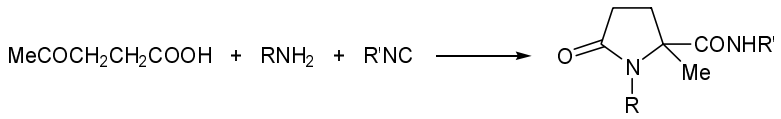
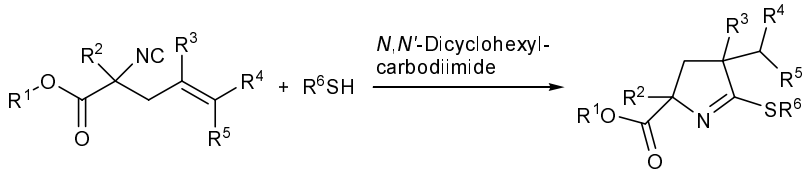
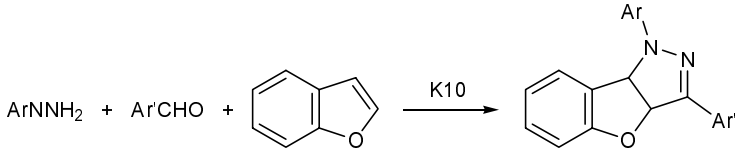
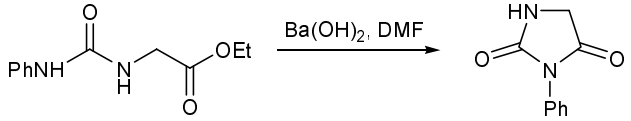
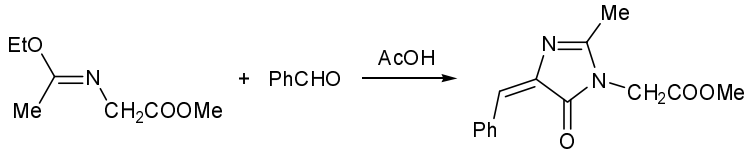
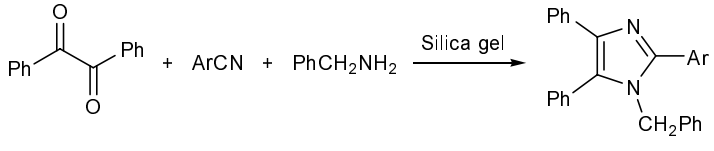
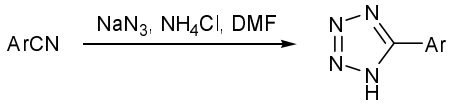
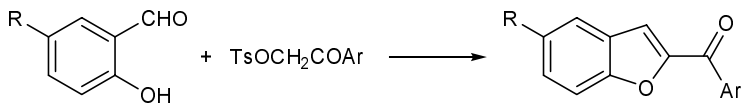
No.	Reaction	Δ	MW	Reference
58		25°C, 12 h, 68%	12 min, 88%	[256]
59		50°C, 48 h, 65%	15 min, 80%	[257]
60		2 h, 0–76%	20-30 min, 40–85%	[258]
61		48 h	30 min, 17–90%	[259]
62		110°C, 5 h, 40%	5 min, 78%	[260]
63		0–10%	4–7 min, 60–75%	[261]
64		48 h, 51%	4 min, 88%	[262]
65		70°C, 3.5 h, 96%	5 min, 98%	[263]
66		29 h, 82%	8 min, 87%	[264]
67		7–96 h, 35–97%	10–25 min, 36–98%	[182]
68		15 min–24 h	1.5–3.5 min, 89–96%	[265]

Table 10. (Contd.)

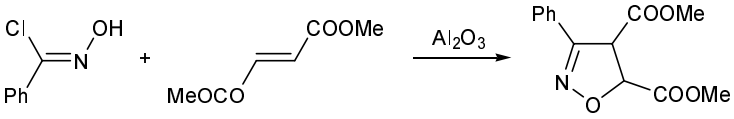
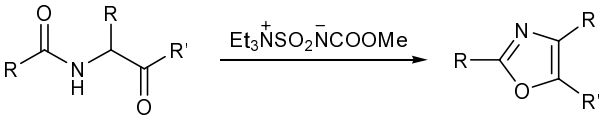
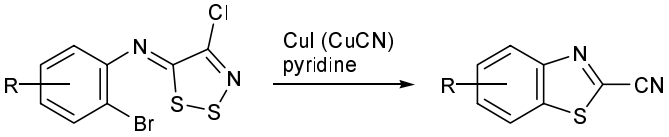
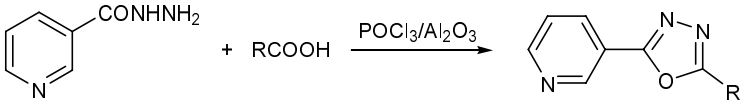
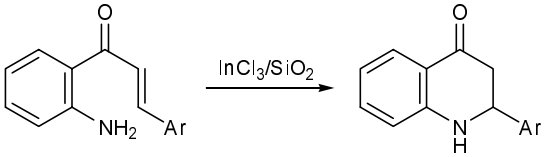
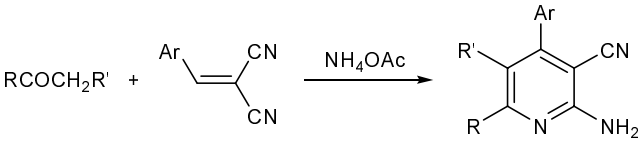
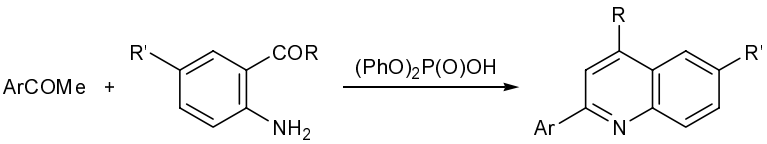
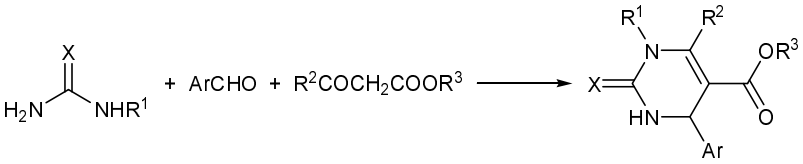
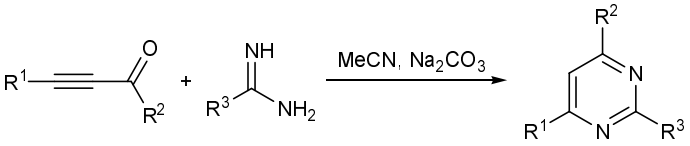
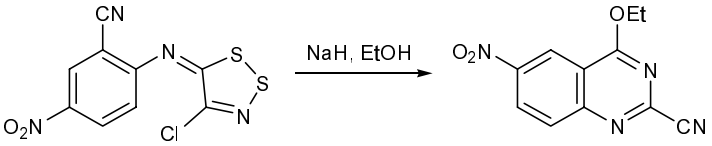
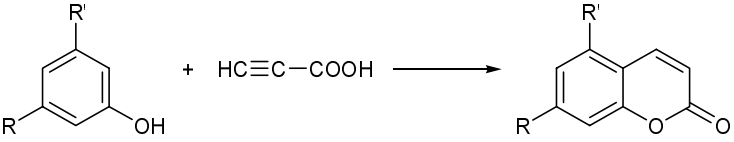
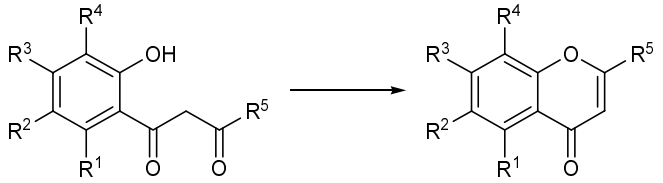
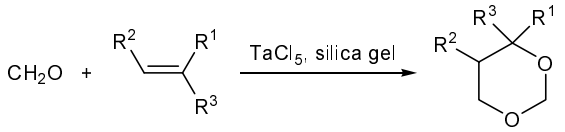
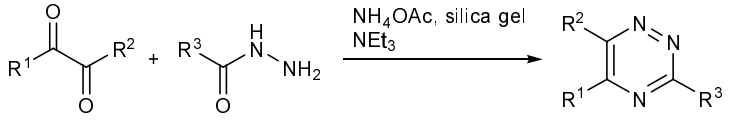
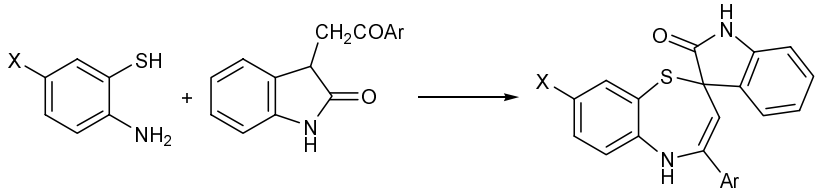
No.	Reaction	Δ	MW	Reference
69		30 min, 40%	30 min, 85%	[266]
70		2 h, 3–77%	1–20 min, 72–100%	[267]
71		45–90 min, 50–84%	10–20 min, 53–87%	[268, 269]
72		4–9 h, 63–86%	7–15 min, 79–96%	[270]
73		2–6 h, 10–75%	1.5–5 min, 55–90%	[238]
74		5–6 h, 46–69%	3–4 min, 69–78%	[271]
75		5.5 h, 70%	4 min, 78%	[272]
76		1–8 h, 15–68%	1–2 min, 65–99%	[47, 273–276]
77		2 h, 60–95%	40 min, 82–98%	[91]
78		11 h, 37%	80 min, 61%	[269]
79		24 h, 6%	15 min, 41%	[246, 247]

Table 10. (Contd.)

No.	Reaction	Δ	MW	Reference
80		6–24 h, 65–98%	1–8 min, 72–98%	[277, 278]
81		10–13 h, 78–82%	3–5 min, 78–90%	[279]
82		6–24 h, 30–65%	5–15 min, 69–92%	[280]
83		4–6 h, 51–62%	7–15 min, 49–65%	[281]

aryl phenacyl ethers leads to 2-arylbenzofurans (Δ: 10 h; MW: 2–6 min, 76–92%) [233]. Furan ring is also formed by intramolecular cyclization of 2-propynyl enol ethers (Δ: 14 h, 52%; MW: 18 min, 65%) [234].

1,3-Dipolar cycloaddition of nitrones to cinnamonitrile gives isoxazolidine derivatives (Δ: 60°C, 21 days, 30%; MW: 2 h, 30%) [66]. Likewise, benzohydroximoyl chloride and dimethyl fumarate give rise to dimethyl 3-phenyl-4,5-dihydroisoxazole-4,5-dicarboxylate (reaction no. 69). Substituted oxazoles (reaction no. 70) and benzothiazoles (reaction no. 71) were obtained in high yields under MW irradiation. Reactions of *o*-aminophenols with benzaldehydes [231] or benzoyl chlorides [235] lead to formation of substituted benzoxazoles (Δ: 24 h, 85%; MW: 15 min, 92%). Aromatic acid hydrazides are converted into 1,3,4-oxadiazoles by the action of phosphoryl chloride (reaction no. 72). Metathesis of allyl(3-butenyl)amines over ruthenium catalyst gives tetrahydropyridine derivative (Δ: 24 h, 100%; MW: 10 min, 100%) [236]. Fused heterocycles containing a tetrahydropyridin-2-one [228, 237, 238] or 1,4-dihydropyridine fragment [239, 240], e.g., 2-aryl-1,2,3,4-tetrahydroquinolin-4-ones (reaction no. 73), were synthesized under conditions of MW activation. Condensation of ketones with arylmethylidenemalononitriles gave substituted pyridines (reaction no. 74). Quinolines were obtained by condensation of acetophenones with *o*-aminophenyl ketones (reaction no. 75). Other polycyclic systems including a pyridine ring were also synthesized under MW irradiation [241–243].

Microwave-activated reaction of diphenylamine with acetic acid in the presence of zinc chloride gives 79% of 9-methylacridine in 5 min [244], while the classical synthesis requires 4 h (yield 50%). Microwave irradiation accelerates cascade reactions of aromatic aldehyde oximes with dimedone, leading to *N*-hydroxyacridines (Δ: 100°C, 70–85 min, 76–88%; MW: 5–6 min, 80–92%) [245]. The formation of tetrahydropyrimidine derivatives (reaction no. 76) and other systems containing a tetrahydropyrimidine fragment [101, 240] occur at a higher rate under MW irradiation. Substituted pyrimidines were obtained by reaction of alkynyl ketones with carboximidamides (reaction no. 77).

4-Aminoquinazolines were synthesized in good yields by reaction of *p*-aminobenzonitrile with aromatic cyanides (reaction time 2 min) [90] (the reaction with benzonitrile at 200°C takes 20 h, yield 39%). 2-Cyanoquinazolines were obtained in better yields

under MW irradiation (reaction no. 78). Microwave activation was also used to prepare from anthranilic acid polycyclic systems containing a quinazoline fragment (Δ: 120°C, 48 h, 50%; MW: 90 min, 95%) [141].

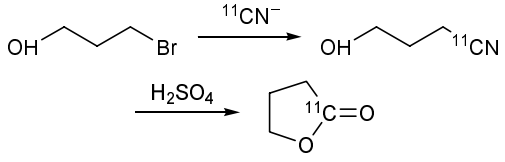
Substituted coumarins and dihydrocoumarins are formed in reactions of phenols with α,β-unsaturated carboxylic acids (Δ: 4 h, 73%; MW: 10 min, 72%) [246, 247], methyl acetoacetate (Δ: 4–20 h, 45–79%; MW: 2–10 min, 69–82%) [248], or propynoic acid (reaction no. 79). Barbituric acids reacted with triethyl orthoformate and substituted acetonitriles to give bicyclic 2*H*-chromen-2-ones (Δ: 1–6 h, 35–70%; MW: 2–8 min, 55–95%) [242]. Coumarins were also prepared from substituted *o*-hydroxybenzaldehydes and carboxylic acids or their esters (Δ: 100–120°C, 6–20 h; MW: 3–8 min, 58–82%) [249–251]. *o*-(1,3-Dioxoalkyl)phenols were converted into substituted 4*H*-chromen-4-ones (reaction no. 80).

1,3-Dioxanes were synthesized by the Prins reaction (reaction no. 81). Microwave irradiation accelerates other condensation processes leading to formation of 1,3-thiazine [252], 1,4-thiazine [253], and 1,3-oxazin-6-one skeletons [254]. 1,2,4-Triazines were obtained from 1,2-diketones and carboxylic acid hydrazides (reaction no. 82). Microwave activation was successfully applied to the synthesis of hexahydro-1,2,3,4-tetrazines [255] and spiro-fused benzothiazepines (reaction no. 83).

6.3. Syntheses of Labeled Compounds

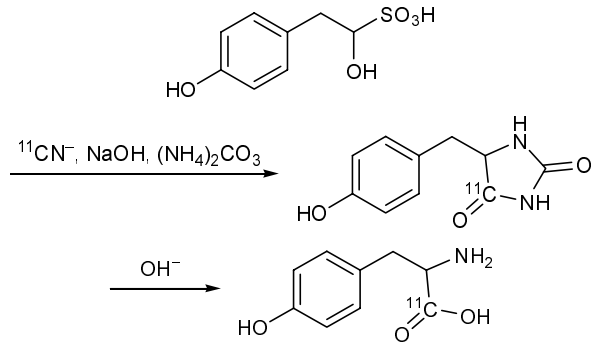
Microwave enhancement of organic reactions is of specific importance in the synthesis of labeled compounds, for the lifetime of some isotopes is comparable with or shorter than the time of reactions performed under classical conditions. In many cases, e.g., in the synthesis of compounds labeled with short-lived ^{11}C, ^{122}I, and ^{18}F isotopes, classical procedures cannot be used. The radiochemical yield is very sensitive to the reaction time. For example, the amount of radioactive atoms in ^{11}C-labeled compounds decreases by 29% every 10 min [18]; therefore, the overall duration of syntheses of ^{11}C-labeled compounds should not exceed 1 h.

Scheme 24.



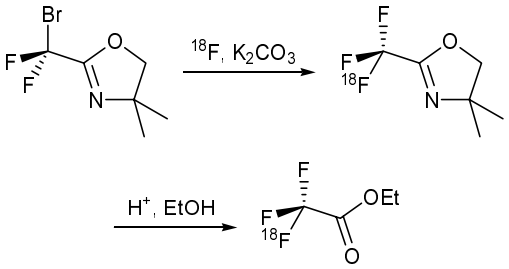
Microwave irradiation shortens the time of cyanodehalogenation of 3-bromo-1-propanol by a factor of 15, as compared to classical heating [282] (Scheme 24). The subsequent hydrolysis of 4-hydroxybutyronitrile is also accelerated to an appreciable extent. The two-step synthesis of ^{11}C-labeled D,L-tyrosine [282] takes 1 min against 20 min without MW irradiation (Scheme 25).

Scheme 25.



The time from the start of synthesis of ^{18}F-labeled compounds to their use should not exceed 2 h. Microwave-enhanced fluorodebromination of polyhalogenated compounds under conditions of phase-transfer catalysis not only ensured shorter reaction time but also allowed the use of excess substrate to be avoided; as a result, the radiochemical yield increased [283] (Scheme 26). Other examples of the application of MW irradiation in the synthesis of labeled compounds were reported in [284–288].

Scheme 26.



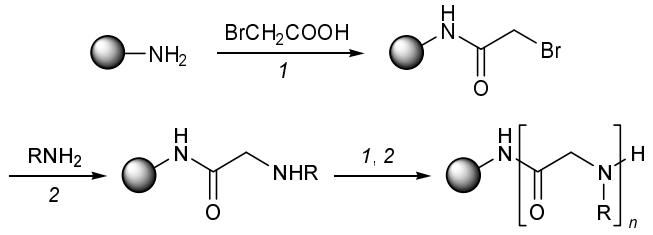
6.4. Syntheses of Biologically Active and Natural Compounds and Combinatorial Chemistry

Wide application of microwave irradiation in combinatorial chemistry is determined by the fact that shortening of reaction time is very important for building up of combinatorial libraries including several tens or hundreds compounds. Microwave irradiation was used in combinatorial chemistry for the first time while synthesizing a series of substituted pyridines by

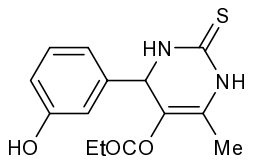
the Hantzsch reaction [289]. Libraries of substituted 1,3,5-triazines [290], dihydropyrimidines [275], 2-(arylamino)benzimidazoles [291], bicyclic dihydropyrimidinones [292], sulfanyl-1*H*-imidazoles [230], benzoxazoles [231], etc. were obtained with the aid of MW technique.

Microwave irradiation accelerates the synthesis of peptoids [293] over the Rink resin (Scheme 27); here, each step takes 15 s. To attain comparable yields under conventional conditions (37°C), step (*1*) requires 45 min, and step (2), 1 h.

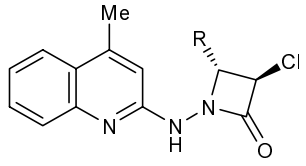
Scheme 27.



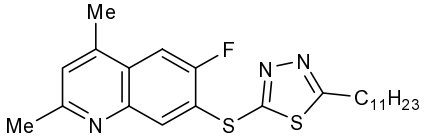
Microwave-assisted modification of the Akabori hydrazinolysis was successfully used to analyze cyclopeptides [294]. Microwave irradiation was used in the synthesis of monastrol (**21**) which inhibits kinesin Eg5 [295], β-lactams **22** [296], quinoline **23** [297] and cephalosporin [298] possessing antibacterial properties, macrocyclic peptides [299], dipeptides [300], steroids [301], and other natural compounds [302], as well as in the hydrolysis of peptides [303] and adenosine triphosphate [304]. Enzymatic reactions were also shown to proceed at a higher rate under microwave irradiation [61].



21



22



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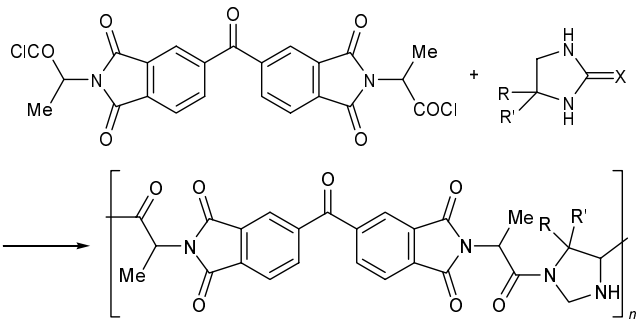
6.5. Large-Scale Organic Syntheses and Synthesis of Polymers

The possibility of enhancing large-scale chemical processes by MW irradiation was demonstrated using sulfonation of anilines as an example [305]. The presently used procedure involves prolonged (10–13 h) heating of anilinium hydrogen sulfate at 180–220°C under reduced pressure. Insofar as the reaction mixture (which solidifies during the process) is characterized by a low heat conductivity, the layer of anilinium hydrogen sulfate should not exceed 8 cm in thickness to facilitate removal of water. Microwave irradiation makes it possible to shorten the reaction time to 40–45 min. The industrial procedure for the synthesis of poly(ε-caprolactam) utilizes high pressure and temperature (250–270°C, 12–24 h). Fang *et al.* [306] described MW-assisted synthesis of poly(ε-caprolactam) in a nitrogen atmosphere under normal pressure at 250°C (2 h). The catalytic polymerization process for manufacture of another industrially important polymer, poly(ε-caprolactone), requires from 10 h to several days. Under microwave irradiation, the polymerization is complete in 30 min at 80–210°C (yield 90%, average molecular weight 124000 a.m.u.) [307].

Microwave procedures were developed for the synthesis of optically active polyamides and polyimides [308–310] which are used in chromatographic separation of enantiomer mixtures. For example, polymers including hydantoin fragments [308] were obtained in 10 min, while classical reactions require more than 5 h (Scheme 28).

Scheme 28.

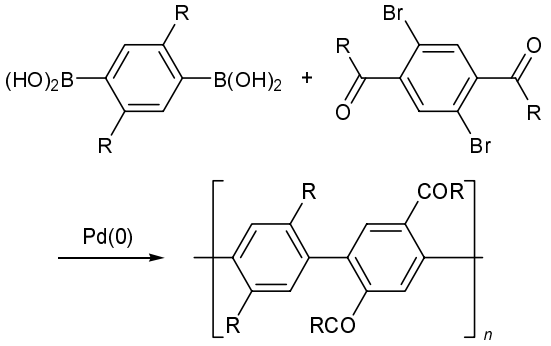


Conjugated polyphenylenes are electroluminescent polymers necessary for various branches of industry. The existing methods of their synthesis under catalysis by nickel complexes are long (up to 24 h) and laborious. Moreover, these procedures are difficult to reproduce owing to sensitivity of the initial monomers and resulting polymers to atmospheric oxygen and other impurities. Microwave irradiation ensured preparation of highly pure poly(9,9-dihexylfluorene) in 10 min (yield 99.5%) [311].

Advantages of microwave heating were demonstrated in the synthesis of semiconducting polymers

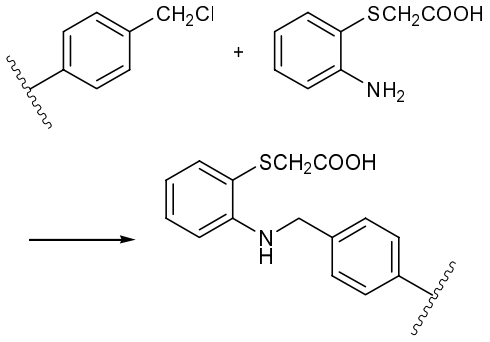
according to the Suzuki reaction [312]. The classical procedure requires 3 days, while MW-enhanced process is complete in 12 min (Scheme 29). Analogous results were obtained in the preparation of a copolymer from 9,9-disubstituted 3,6-dibromofluorenes and 5,5'-bis(trimethylstannyl)-2,2'-bithienyl according to Stille [312]. The reaction time shortened from 3 days to 9 min.

Scheme 29.



Microwave irradiation was used in the synthesis of resins [313] capable of chelating metal ions (Scheme 30). Such resins are used for analytical determination of lead. Radical polymerization of 4-nitrophenyl acrylate, initiated by 2,2'-azobis(isobutyronitrile), gave polymers with a narrower molecular weight distribution, as compared to those obtained by conventional heating [314]. Microwave-assisted living radical polymerization in the preparation of modified resins was reported [315]. The reaction time shortens from 20 h to 10–40 min. Microwave irradiation also accelerates radical polymerization of methyl methacrylate [316].

Scheme 30.



Depending on the heating mode, not only the rate of polymerization but also the composition and properties of the resulting polymers can be varied. Copolymerization of isosorbite with α,ω-dihalogen derivatives [317] and alkanedisulfonates [318] under MW irradiation takes 30 min (yield 63%) against 24 h on heating. The average molecular weight of the copolymer increases, and the composition of polymeric products changes. Polymers formed upon conventional heating contain hydroxy groups in the terminal positions, while those obtained in the microwave-enhanced reaction contain unsaturated fragments in the terminal positions [317].

As a rule, all reactions occurring on heating are facilitated by MW irradiation, and only in a few cases MW irradiation produces no appreciable effect on the reaction time. Almost any thermal reaction can be effected by MW irradiation, saving time and/or raising the yield. Microwave activation techniques make experiments simpler and less expensive, provide better results, and improve ecological parameters.

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