Microwave-mediated Newman–Kwart rearrangement in water†

Ina Hoffmann and Jürgen Schatz*

For the first time the unimolecular Newman–Kwart rearrangement is performed in pure water. The elevated temperatures required for the 1,3-aryl shift are easily accomplished by microwave irradiation. Differently functionalized substrates underline the expected influence on the reaction rate regarding the electronic and steric effects of the substituents. The utilization of supramolecular additives enables an increase in conversion. Besides, the conduction in a microwave reactor allows for a rapid collection of kinetic data affording the reaction rate constants of the rearrangement of distinct substrates as well as the Arrhenius constant and activation parameters of the conversion of 2- and 4-nitrophenyl-O-thiocarbamate.

Introduction

The thermally induced reaction of O-aryliothiocarbamates to their corresponding S-aryliothiocarbamates is commonly known as the Newman–Kwart rearrangement (NKR) and was first discovered in the 1960s. In light of the easy availability of various phenols 1, their facile conversion to N,N-dimethyl O-aryliothiocarbamates 2 as well as the readily achieved cleavage of the NKR product 3 by hydrolysis, methanolysis, or reduction, the NKR is one of the most synthetically attractive routes for the formation of thiophenols 4 from phenols 1 (Scheme 1). Both thiophenols and similarly accessible sulfur-containing compounds such as sulfoxides, sulfones, thioethers, and sulfonic acids contribute to a broad field of applications including agrochemicals, dyestuffs, medicinal chemistry, chiral ligands, molecular switches, organocatalysts, dendrimers and supramolecular assemblies. Not least, the NKR can be utilized for the synthesis of specific arenes from phenols 1 by desulfurization of the corresponding thiophenols 4.

The NKR proceeds via first-order kinetics and is based on an intramolecular migration of an aryl moiety from an oxygen atom to a sulfur atom (OAr → SAr), which is thermodynamically driven by the formation of a strong carbon–oxygen double bond and the simultaneous cleavage of the weaker carbon–sulfur double bond. This 1,3-aryl shift can also be considered as an intramolecular nucleophilic aromatic substitution with sulfur attacking the ipso-carbon atom. The rearrangement proceeds via a zwitterionic four-membered cyclic transition state (Fig. 1), requiring elevated temperatures in the range of 200–300 °C to accomplish the high activation energy (Ea, ΔG‡). Electron withdrawing groups (EWG) attached to the negative cyclo-hexadienyl moiety facilitate the OAr → SAr migration and therefore, either reduce the reaction temperature or reaction time. N,N-Dimethyl O-aryliothiocarbamates 2 bearing one EWG in ortho position can be even more easily converted due to the rotational restriction around the aryl–oxygen bond, which entails a loss in entropy and the associated higher order in the transition state. On the downside, doubly ortho, sterically hindered, and electron donating substituents (EDG) decrease the reaction rate and electron, therefore, require temperatures approaching 300 °C or prolonged reaction times. The general harsh reaction conditions not only cause undesired side

Scheme 1  (i) Dimethylthiocarbamoyl chloride (DMTCC), DABCO (NaH for less-acidic phenols), solvent, ≥50 °C; (ii) NKR: solvent or neat, Δ (conventional or microwave); (iii) aqueous NaOH, methanolic KOH, or LiAlH4.

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| OH | OMe2 | SMe2 | SH |  |
| R | R | R | R |  |
| 1 | 2 | 3 | 4 |  |

Fig. 1  Four-center 1,3-oxathietane transition state.
reactions and charring, but also pose a safety issue for the organic chemist. Notably, Harvey et al. performed the NKR at only 100 °C yielding quantitative conversions for several N,N-dimethyl O-aryltiocarbamates \( 2 \) by means of \([\text{Pd}(\text{Bu}_3\text{P})_2]\) as catalyst.\(^{14}\) In addition to that, Perkowski et al. utilized a commercially available photoxidant, which efficiently promoted the NKR at ambient temperature.\(^{15}\) A convenient alternative to at least circumvent the safety issue stemming from high reaction temperatures is the conduction of the rearrangement in a microwave (MW) reactor under small-scale autoclaves conditions.\(^{7,8,13,26}\) Further advantages compared to the conventional heating in an oil-bath are for instance the rapid access to high reaction temperatures as well as the fast cooling with compressed air at the end of the reaction, improved purity profiles, energy efficient in-core volumetric heating of the reaction medium, and practicability in terms of handling, i.e., accurate control of reaction parameters and if necessary, the rapid collection of several data points needed for a kinetic study.\(^{16,27}\) Moseley et al. investigated the NKR under MW irradiation and found no substantial difference between conventional heating and MW radiation.\(^{7}\) However, for the first time a solvent rate effect was experimentally described, showing an enhancement of the conversion with increasing polarity of the solvent. This is not surprising considering the highly polar transition state \( 5 \), which should be stabilized by polar solvents, and therefore enhance the reaction rate with decreasing \( E_A \). Addressing green chemistry, now the question arises to what extent water, possessing a dielectric constant \( (\varepsilon_r) \) of 78, is able to stabilize the transition state \( 5 \).\(^{18}\)

Over the last decades water has received increasing attention as solvent in organic synthesis and promoted an intriguingly diverse field of reactions ranging from pericyclic reactions over transition-metal catalysis to reactions with carbenes and radicals just to name a few.\(^{19–22}\) In addition to the obvious benefits towards organic solvents of being inexpensive, non-flammable, non-toxic, and readily available, in many cases water is able to enhance both the reaction rate and the reaction selectivity due to hydrophobic effects.\(^{23–25}\) One alternative way to increase the reaction rate and selectivity or rather overcome solubility issues of non-polar substrates in water, is the utilization of supramolecular additives such as cyclodextrines or calix\([n]\)arenes, which encapsulate the hydrophobic reactants in their cavities by non-covalent interactions while being watre-soluble themselves.\(^{26–33}\)

However, to our knowledge the sheer NKR has so far not been performed in pure water.\(^{24}\) Notably, owing to the fact, that the NKR can be conducted neat,\(^{5,8,13,23–40}\) this paper does not claim more environmentally benign reaction conditions, but rather demonstrates the attempt to lower \( E_A \) by means of the highly polar and green solvent water. In this context we decided to carry out the rearrangements in pure water by means of MW irradiation. Though water is known to be only a medium absorber (loss tangent (\( \tan \delta \)) = 0.123), it can be rapidly heated well above its boiling point in closed vessels and has already been successfully utilized in many microwave-assisted reactions.\(^{37,41,42}\)

In this paper, we report the effect of differently functionalized substrates utilizing electron-donating as well as electron-withdrawing substituents, the conversion dependency with and without MW irradiation, the influence of supramolecular additives (cf. Fig. 3), \( i.e. \) cucurbit[6]uril, imidazolilo- and sulfocalix[n]arenes, and finally, a more in-depth kinetic study of 2- and 4-nitrophenyl O-thiocarbamate investigating the effect of water in terms of a possible transition state \( 5 \) stabilization.

## Results and discussion

### Substrates and scope

The substrates utilized for NKR, \( i.e., \) O-aryltiocarbamates \( 2a–h \), were chosen to cover both sterically and electronic effects on the rearrangement (Table 1). Electron-withdrawing nitro-groups substituted in ortho-\( 2a, \) meta-\( 2c, \) and para-position \( 2b \) of the arene should display the conversion dependency on the substitution pattern within one group regarding both steric and electronic characteristics, whereas further EWGs as well as EDGs substituted in para-position should be compared purely regarding their electronic influence. Besides, all O-aryltiocarbamates \( 2a–h \) as well as S-aryltiocarbamates \( 3a–h \) are known from literature and the results, \( i.e., \) conversion and reaction rates can be well correlated with Hammet \( \sigma \) constants.\(^{44}\)

The syntheses of the substrates proceeded in a single-step reaction starting from readily available, less acidic phenols \( 1a–h, \) DABCO and dimethylthiocarbamoyl chloride (DMTCC) \( 6 \) according to the procedures of Moseley and DeCollo,\(^{{7,44}}\) Direct precipitation by addition of water afforded products in good to excellent yields (59–96%), most of them being highly crystalline with the exception of substrates \( 2d \) (4-CN), \( 2g \) (4-F), and \( 2h \) (4-OMe), which were recrystallized from ethanol.

For our initial substrate screenings we decided to conduct the NKR of substrates \( 2a–h \), all being completely insoluble in water at room temperature, at 180 °C and determine the conversions after 20 min (Table 2). At this temperature solely the rearrangements of 2-nitro \( 2a \) (>99%) and 4-nitrophenyl-\( O-\)

### Table 1 Synthesis of O-aryltiocarbamates \( 2a–h \) from phenols \( 1a–h^a \)

| Entry | \( R \)     | \( t \) [h] | Yield [%] | NKR substrate |
|-------|------------|------------|-----------|---------------|
| 1     | 2-NO\(_2\) | 3.8        | 92        | \( 2a \)      |
| 2     | 4-NO\(_2\) | 2.5        | 91        | \( 2b \)      |
| 3     | 3-NO\(_2\) | 5.8        | 93        | \( 2c \)      |
| 4     | 4-CN      | 3.0        | 88        | \( 2d \)      |
| 5     | 4-COMe\(^b\) | 1.5     | 96        | \( 2e \)      |
| 6     | 4-Br       | 2.5        | 84        | \( 2f \)      |
| 7     | 4-F        | 5.0        | 83        | \( 2g \)      |
| 8     | 4-OMe      | 3.7        | 59        | \( 2h \)      |

\(^a\) Reaction conditions: phenol \( 1 \) (1 eq.), DMTCC \( 6 \) (1.1 eq.), DABCO (1.3 eq.), NMP, 50 °C;\(^{7} \) \( b \) DMTCC \( 6 \) (1.2 eq.), DABCO (2.5 eq.), DMF, 65 °C.\(^{44}\)
Table 2: NKR of O-arylthiocarbamates 2a–h at given temperatures and substituent relating Hammett σ constants

| Entry | R     | σ   | Conv. [%] at 180 °C | Conv. [%] at 200 °C | Conv. [%] at 210 °C |
|-------|-------|-----|---------------------|---------------------|---------------------|
| 1     | 2-NO₂  | —   | > 99 (89)           | —                   | —                   |
| 2     | 4-NO₂  | +0.778 | 79                 | —                   | —                   |
| 3     | 3-NO₂  | +0.710 | 0                  | 0                   | 0⁰                 |
| 4     | 4-CN   | +0.628 | 9                  | 46                  | 81                 |
| 5     | 4-COMe | +0.516 | 15                 | 42                  | 64                 |
| 6     | 4-Br   | +0.232 | 2                  | 3                   | 4                  |
| 7     | 4-F    | +0.062 | 0                  | 0                   | 0                  |
| 8     | 4-OMe  | —0.268 | 0                  | 0                   | 0                  |

*a Reaction conditions: O-arylthiocarbamate 2a–h (500 μmol, 0.2 M), MW irradiation, H₂O (2.5 mL), 20 min, b Isolated yield in parentheses. c 220 °C. d Apart from conversion some product degradation occurred.

The solvent-free conduction yielded a conversion of 88% after 10 min at 180 °C. Besides, the determined reaction rate constants (k) reveal the neat reaction to be about two and a half times slower than the MW-mediated rearrangement. Overall, the usage of MW energy and water as reaction medium for the NKR appears to be an effective combination as has already been shown in many reactions before.⁴⁴,⁴⁵ In addition to that, this method is generally beneficial in terms of easy workup and safe reaction control.

Fig. 2 Influence of supramolecular additives on conversion based on the NKR of 4-acetylphenyl-O-thiocarbamate 2e (reaction conditions: 2e (500 μmol, 0.2 M), additive (0.5 mol%), MW, H₂O (2.5 mL), 20 min, 200 °C).
Supramolecular additives

In recent studies we could show that supramolecular additives such as sulfocalix[n]arenes can efficiently increase the catalytic activity of Suzuki and metathesis reactions performed in pure water.27,46 The ability to solubilize hydrophobic reactants and an improved mass transfer are characteristics, which make water-soluble calix[n]arenes valuable for reactions in aqueous media or neat water. This tempted us to investigate the influence of macrocyclic additives on the NKR. Therefore we chose the rearrangement of 4-acetylphenyl-O-thiocarbamate 2e at 200 °C in 20 min (42% conversion, cf. Table 2) and added three different host compounds at a concentration of 0.5 mol% (Fig. 2 and 3). The reactions with cucurbit[6]uril 8 and SC6C3 7a resulted in hardly increased conversions of 43% and 45%, respectively, whereas the employment of SC8C8 7b gave an 21% improvement versus the rearrangement without additive. As described above, at elevated temperatures water acts as pseudo-organic solvent and is able to dissolve non-polar substrates. Owing to the fact that the substance probe is automatically cooled with compressed air after the reaction and thus, the organic product precipitated from water at ambient temperature, it is not detectable if the reactant had been fully dissolved afore. Therefore, we assume that SC8C8 7b contributes to an additional stabilization of the transition state 5 and an either fully or faster solubilization by encapsulating the hydrophobic NKR substrate in its cavity. A possible reason for the conversion difference of the two sulfocalix[n]arenes 7a, b may be an enhanced surface-activity of SC8C8 7b due to its larger hydrophobic tails. In general, the increased conversion might also derive from an enlarged loss tangent, i.e. the addition of salts, in our case 0.5 mol% SC8C8 7b, improves the MW absorbance due to ionic conduction.

In a second experiment, cationic imidazolio calix[4]arenes (9–11) were employed to possibly stabilize the transition state 5 of the NKR of 3-nitrophenyl-O-thiocarbamate 2c at 180 °C (cf. Fig. 3). However, none of the cations initiated the rearrangement, which underlines that the electronically disfavored 3-nitro substrate 2c requires higher temperatures to overcome the activation barrier.

Kinetic study

**Reaction rates.** The unimolecular NKR proceeds via a first-order reaction. The reaction rate constants were ascertained by applying eqn (1) to at least five experimentally determined
data points. Besides, all rearrangements were conducted employing substrate concentrations of 0.2 M.

\[
[A]_t = [A]_0 \times e^{-kt}
\]  

(1)

As described in literature, substituents differing in their electronic characteristics, have a strong impact on the reactivity of the NKR and additionally, are in good agreement with the Hammett \( \sigma \) constants. This correlation could also be seen for the rearrangement in pure water (vide supra) and should now be further investigated regarding the corresponding reaction rates. For this purpose, several NKRs of para-substituted substrates, i.e. nitro-2b, cyano-2d, acetyl-2e, and bromophenyl-O-thiocarbamate 2f, were conducted at 200 °C. The rate constant of the substrate bearing the nitro group in ortho position 2a was extrapolated from measurements at 140–180 °C using eqn (2) (cf. Fig. 7). Fig. 4 shows the exponential curves of the respective reactants displaying a reaction rate enhancement in the order 2-nitro > 4-nitro > 4-cyano > 4-acetyl > 4-bromo, which is still in line with the substituent constants of Hammett and former literature (cf. Fig. 5). The \( \sigma \) values, the corresponding rate constants, and the half-lives are depicted in Table 4. The rearrangement of substrate 2a is additionally promoted due to the steric restriction in the ortho position and would be completely converted in about three minutes. As opposed to that, the quantitative rearrangement of 4-bromophenyl-O-thiocarbamate 2f would be feasible within five days.

**Arrhenius and activation parameters.** The more thorough investigation of both nitro substrates 2a and 2b involve the prior determination of various reaction rate constants at different temperatures (Fig. 6 and 7), whose correlation is given in the Arrhenius eqn (2).

\[
k = A \times e^{-\frac{E_A}{RT}}
\]  

(2)

| Entry | R          | \( k \) [s\(^{-1}\)] | \( t_{1/2} \) [s] | \( \sigma \) |
|-------|------------|-------------------------|-------------------|-------------|
| 1     | 2-NO\(_2\) | 3.30 \times 10^{-2}     | 21.0              | —           |
| 2     | 4-NO\(_2\) | 1.42 \times 10^{-2}     | 48.8              | +0.778      |
| 3     | 4-CN      | 8.95 \times 10^{-4}     | 774               | +0.628      |
| 4     | 4-COMe    | 6.51 \times 10^{-4}     | 1.07 \times 10^{2} | +0.516      |
| 5     | 4-Br      | 1.15 \times 10^{-5}     | 6.04 \times 10^{1} | +0.232      |

\* Extrapolated from measurements at 140–180 °C using \( k = 4.06 \times 10^{-12} \) s\(^{-1}\) \times \exp(-128 \text{ kJ mol}^{-1}/R \times 473.15 \text{ K}) (cf. Fig. 7).
The evaluation of the $\Delta S^\ddagger$-values is not as straightforward. On the one hand the entropy of activation is increasing with extending reaction rate constant. This correlation is given in the Eyring eqn (6) and is also in line with our obtained results for the ortho-2a and para-nitro substrate 2b. Similar $\Delta S^\ddagger$-correlations had been found for the NKR of 2- and 4-methylphenyl-O-thiocarbamate, which was ascribed to the restriction of the free rotation around the carbon-oxygen bond in the ground state.12

$$k = \frac{k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{\frac{\Delta H^\ddagger}{RT}}$$

(6)

On the other hand, the activation entropy decreases with higher order in the transition state, i.e. loss of rotational and translational degrees of freedom, as compared to the initial state and becomes more negative with higher restriction. However, this conflicts with the lower negative activation entropy and the accelerated reaction rate constant of the sterically more restricted 2-nitrophenyl-O-thiocarbamate 2a.

**Experimental section**

**General**

Chemicals were purchased from commercial sources and used without further purification. O-Arylthiocarbamates 2a–h were prepared according to the published procedure.7–11 Imidazolio calix[4]arenes 9–11 were utilized by the courtesy of Dr. Markus Frank47 and alkylated sulfocalix[η]arenes 7a, b were utilized by the courtesy of Silvia Onodi.48 Maldi-ToF spectra were recorded on a Shimadzu Biotech AXIMA Confidence and El spectra were recorded on a Finnigan MAT 95 XP from Thermo Scientific. IR spectroscopy was performed on a Varian 660-IR spectrometer. NMR spectra were recorded in CDCl$_3$ using a Bruker Avance 400 operating at 400.13 MHz for $^1$H-NMR and 100.62 MHz for $^{13}$C-NMR. Chemical shifts (δ) are indicated in parts per million (ppm) relative to the internal standard (δ$_{\text{Me}}$ = 7.24 ppm, δ$_{\text{C}}$ = 77.23 ppm). The conversions of the Newman–Kwart rearrangements were determined by comparing the integrated proton signals of the methyl groups of O-2a–h and S-aryl-N,N-dimethylthiocarbamate 3a–h. All conventional NRks (with exception of the solvent-free experiment) were stirred at highest rate using a MR Hei-Tec from Heidolph®.

**Microwave-mediated Newman–Kwart rearrangement**

The microwave-assisted reactions were performed employing an Initiator+ from Biotage® (fourth generation microwave synthesizer). For a general procedure, O-aryl-N,N-dimethylthiocarbamate (500 μmol) and H$_2$O (2.5 mL) were placed in a sealed 2–5 mL vial. The reactant was stirred for a fixed time of 30 s and subsequently heated to the selected temperature not exceeding 400 W. All data on the reaction time exclude the heating time. After the sample was stirred at the respective temperature and time, it was automatically cooled down to approximately 50 °C and was afterwards allowed to further cool down to room temperature. The product was extracted with CDCl$_3$ (3 × 600 μL) and subsequently used for $^1$H-NMR analysis.

As was expected, for one the reaction rates increase with higher temperatures and for another the beneficial steric acceleration of the ortho substrate 2a is mirrored in the reaction rates, being lower for the para substrate 2b at every temperature.

For both carbamates the Arrhenius constant ($A$) and $E_A$ were determined by plotting the $k$-values according to eqn (3) (cf. Fig. 8 for 2-NO$_2$ substrate 2a) and the activation parameters, i.e. activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$), were calculated using eqn (4) and (5):

$$\ln k = \ln A - \frac{E_A}{RT}$$

(3)

$$\Delta H^\ddagger = E_A - RT$$

(4)

$$\Delta S^\ddagger = R \left( \ln \frac{A}{T} - \frac{k_B}{h} \ln \frac{1}{h} \right)$$

(5)

Table 5 shows the results for both systems. $E_A$ and the activation enthalpy, which is smaller by the product of $RT$, are each higher for the 2-NO$_2$ substrate 2a. Moreover, the comparison with the values of Gilday et al., who performed the NKR of 2-nitrophenyl-O-thiocarbamate in poorly polar dichlorobenzene, even reveals the $E_A$ in water to be higher by the factor of 12 kJ mol$^{-1}$ diminishing the assumption of a possible transition state stabilization.46 On the contrary, comparing our results of the rearrangement of 4-nitrophenyl-O-thiocarbamate 2b with literature, where the NKR has also been conducted in a highly polar solvent, i.e. dimethylacetamide, the activation barrier could be reduced by approximately 11 kJ mol$^{-1}$ in pure water.
Preparative Newman–Kwart rearrangement

2-Nitrophenyl-1,1,3,3-tetramethyl-5-thiocarbamate 3a. H$_2$O (2.5 mL) and 2-nitrophenyl-1,1,3,3-tetramethyl-5-thiocarbamate 2a (113 mg, 500 μmol) were placed in a sealed 2–5 mL vial. The reactant was stirred for a fixed time of 30 s and subsequently heated to 180 °C. After stirring 10 min at this temperature, the sample was automatically cooled down to approximately 50 °C and was afterwards allowed to further cool down to room temperature. The product was extracted with DCM (3 × 600 μL) and dried over MgSO$_4$. DCM was removed by a rotatory evaporator and the product was dried under high vacuum. 101 mg (447 μmol) were placed in a sealed 2 mL and subsequently used for 1H-NMR analysis.

Conventional Newman–Kwart rearrangements

**Neat.** 2-Nitrophenyl-1,1,3,3-tetramethyl-5-thiocarbamate 2a (113 mg, 500 μmol) was placed in an open vessel and put inside a heat-on plate, which was pre-heated to 180 °C. After the respective reaction period, the sample was allowed to cool down to room temperature. The product was dissolved in CDCl$_3$ (600 μL) and subsequently used for 1H-NMR analysis.

**Pressure tube.** 2-Nitrophenyl-1,1,3,3-tetramethyl-5-thiocarbamate 2a (113 mg, 500 μmol) and H$_2$O (2.5 mL) were placed in a sealed pressure tube and put inside a heat-on plate, which was pre-heated to 180 °C. After 10 min, the sample was allowed to cool down to room temperature. The product was extracted with CDCl$_3$ (3 × 600 μL) and subsequently used for 1H-NMR analysis.

**Reflux.** 2-Nitrophenyl-1,1,3,3-tetramethyl-5-thiocarbamate 2a (113 mg, 500 μmol) and H$_2$O (2.5 mL) were placed in a flask with attached reflux condenser and put inside an oil-bath, which was pre-heated to 180 °C. After 10 min, the sample was allowed to cool down to room temperature. The product was extracted with CDCl$_3$ (3 × 600 μL) and subsequently used for 1H-NMR analysis.

Conclusions

In conclusion, we have shown that the microwave-mediated Newman–Kwart rearrangement (NKR) can be successfully performed in pure water. Substrates bearing electron-withdrawing substituents could be converted within short reaction times, whereas electron-donating groups demonstrated the limit of the reaction in water due to the immense pressure build-up with increasing temperature needed for a rearrangement. While this issue is a topic of current investigation, a possible answer was given by sulfonamides, whose addition facilitated the reaction affording higher conversions. Notably, based on our kinetic survey, a transition state stabilization could be ascribed to the reaction of the 4-NO$_2$ carbamate and in addition, the reaction rates of the NKR of the 2-NO$_2$ carbamate exceeded those of some commonly used organic solvents. Finally, control studies revealed a conclusive microwave (MW) effect for the rearrangement in water plus higher reaction rates than the solvent-free NKR.

The fusion of MW irradiation and water, as environmentally benign reaction medium, not only affords quantitative Newman–Kwart rearrangements, but simultaneously meets two key principles of green chemistry, i.e. “energy-efficient synthesis” and “safer solvents”.* The transfer to a pilot or production scale is an important topic, which has to be studied in future.

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References

1. M. S. Newman and H. A. Karnes, *J. Org. Chem.*, 1966, 31, 3980–3984.
2. H. Kwart and E. R. Evans, *J. Org. Chem.*, 1966, 31, 410–413.
3. J. D. Edwards and M. Piana, *J. Chem. Soc.,* 1965, 7338–7344.
4. W. Walter and K. D. Bode, *Angew. Chem., Int. Ed.*, 1967, 6, 281–293.
5. G. Lloyd-Jones, J. Moseley and J. Renny, *Synthesis*, 2008, 661–689.
6. C. Zonta, O. De Lucchi, R. Volpicelli and L. Cotarca, *Top. Curr. Chem.*, 2007, 275, 131–161.
7. J. D. Moseley, R. F. Sankey, O. N. Tang and J. P. Gilday, *Tetrahedron*, 2006, 62, 4685–4689.
8. M. Burns, G. C. Lloyd-Jones, J. D. Moseley and J. S. Renny, *J. Org. Chem.*, 2010, 75, 6347–6353.
9. K. Miyazaki, *Tetrahedron Lett.*, 1968, 9, 2793–2798.
10. A. Kaji, Y. Araki and K. Miyazaki, *Bull. Chem. Soc. Jpn.*, 1971, 44, 1393–1399.
11. A. Mondragón, I. Monsalvo, I. Regla and I. Castillo, *Tetrahedron Lett.*, 2010, 51, 767–770.
12. H. M. Relles and G. Pizzolato, *J. Org. Chem.*, 1968, 33, 2249–2253.
13. J. D. Moseley and P. Lenden, *Tetrahedron*, 2007, 63, 4120–4125.
14. J. N. Harvey, J. Jover, G. C. Lloyd-Jones, J. D. Moseley, P. Murray and J. S. Renny, *Angew. Chem., Int. Ed.*, 2009, 48, 7612–7615.
15. A. J. Perkowski, C. L. Cruz and D. A. Nicewicz, *J. Am. Chem. Soc.*, 2015, 137, 15684–15687.
16. J. P. Gilday, P. Lenden, J. D. Moseley and B. G. Cox, *J. Org. Chem.*, 2008, 73, 3130–3134.
17. C. O. Kappe, *Angew. Chem., Int. Ed.*, 2004, 43, 6250–6284.
18. A. Lubineau, J. Augé and Y. Queneau, *Synthesis*, 1994, 741–760.
19. C.-J. Li and L. Chen, *Chem. Soc. Rev.*, 2006, 35, 68–82.
20 U. M. Lindström, Organic Reactions in Water, Blackwell Publishing, Singapore, 2007.
21 C.-J. Li and T.-H. Chan, Comprehensive Organic Reactions in Aqueous Media, John Wiley & Sons, Inc., Hoboken, 2nd edn, 2007.
22 S. Kobayashi, Science of Synthesis: Water in Organic Synthesis, Georg Thieme Verlag, Stuttgart, 2nd edn, 2012.
23 M. Seßler and J. Schatz, Chem. Unserer Zeit, 2012, 46, 48–59.
24 I. Hoffmann and J. Schatz, Nachr. Chem., 2013, 61, 748–753.
25 R. Breslow, Acc. Chem. Res., 1991, 24, 159–164.
26 M. Baur, M. Frank, J. Schatz and F. Schildbach, Tetrahedron, 2001, 57, 6985–6991.
27 I. Hoffmann, B. Blumenröder, S. Onodi née Thumann, S. Dommer and J. Schatz, Green Chem., 2015, 17, 3844–3857.
28 F. Hapiot, J. Lyskawa, H. Bricout, S. Tilloy and E. Monflier, Adv. Synth. Catal., 2004, 346, 83–89.
29 S. Shimizu, T. Suzuki, Y. Sasaki and C. Hirai, Synlett, 2000, 1664–1666.
30 D. Kirschner, M. Jaramillo, T. Green, F. Hapiot, L. Leclercq, H. Bricout and E. Monflier, J. Mol. Catal. A: Chem., 2008, 286, 11–20.
31 E. Monflier, G. Fremy, Y. Castanet and A. Mortreux, Angew. Chem., Int. Ed., 1995, 34, 2269–2271.
32 S. Shimizu, S. Shirakawa and Y. Sasaki, Angew. Chem., Int. Ed., 2000, 39, 1256–1259.
33 T. Brendgen, T. Fahlbusch, M. Frank, D. T. Schühle, M. Seßler and J. Schatz, Adv. Synth. Catal., 2009, 351, 303–307.
34 N. Lal, L. Kumar, A. Sarswat, S. Jangir and V. L. Sharma, Org. Lett., 2011, 13, 2330–2333.
35 V. Albrow, K. Biswas, A. Crane, N. Chaplin, T. Easun, S. Gladiali, B. Lygo and S. Woodward, Tetrahedron: Asymmetry, 2003, 14, 2813–2819.
36 S. Cossu, O. De Lucchi, D. Fabbri, G. Valle, G. F. Painter and R. A. J. Smith, Tetrahedron, 1997, 53, 6073–6084.
37 D. Fabbri, G. Delogu and O. De Lucchi, J. Org. Chem., 1993, 58, 1748–1750.
38 M. Hori, T. Kataoka, H. Shimizu, M. Ban and H. Matsushita, J. Chem. Soc., Perkin Trans. 1, 1987, 1, 187.
39 V. Novakova, M. Miletin, T. Filandrová, J. Lenčo, A. Růžička and P. Zimčík, J. Org. Chem., 2014, 79, 2082–2093.
40 R. Romagnoli, P. G. Baraldi, M. D. Carrion, O. Cruz-Lopez, M. Tolomeo, S. Grimaudo, A. Di Cristina, M. R. Pipitone, J. Balzarini, A. Brancale and E. Hamel, Bioorg. Med. Chem., 2010, 18, 5114–5122.
41 V. Polshettiwar, R. S. Varma, V. Cadierno, P. Crochet, S. E. Garcia-Garrido, A. Fihri, C. Len, H. Zhao, C. Marestín, R. Mercier and B. Baruwati, Aqueous Microwave Assisted Chemistry: Synthesis and Catalysis, RSC Publishing, Cambridge, 2010.
42 D. Dallinger and C. O. Kappe, Chem. Rev., 2007, 107, 2563–2591.
43 T. V. DeCollo and W. J. Lees, J. Org. Chem., 2001, 66, 4244–4249.
44 R. W. Hoffmann, Aufklärung von Reaktionsmechanismen, Georg Thieme Verlag, Stuttgart, 1976.
45 C. R. Strauss and R. S. Varma, Top. Curr. Chem., 2006, 266, 199.
46 J. Tomasek, M. Seßler, H. Gröger and J. Schatz, Molecules, 2015, 20, 19130–19141.
47 M. Frank, Imidazolium-substituierte calix[4]arene: von molekularen Rezeptoren zu stabilen carbenen und Kreuzkupplungsreaktionen, translated “Imidazolium substituted calix[4]arenes: from molecular receptors to stable carbenes and cross-coupling reactions”, University Ulm, 2004.
48 S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki and O. Manabe, J. Org. Chem., 1986, 108, 2409–2416.
49 P. T. Anastas and J. C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.