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Synthesis of Alkyl Aryl Ethers by Catalytic Williamson Ether Synthesis with Weak Alkylation Agents

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Abstract:

For almost 70 years, there have been attempts to advance the Williamson ether synthesis process to allow the use of low-cost, noncarcinogenic, weak alkylating agents and avoid salt production. These attempts to produce a "green" version of Williamson ether synthesis have been based on the use of weak alkylating agents such as carboxylic acid esters at relatively high temperatures (approximately 200 °C) and pressures. However, none of the processes considered was suitable for industrial application because of the high concentration of the alkali metal carboxylates required. By increasing the temperature to above 300 °C, it has now proved possible to carry out Williamson ether synthesis as a homogeneous catalytic process. The large temperature increase significantly boosts the alkylating power of weak alkylating agents such as alcohols, carboxylic acid esters, and ethers derived from weak Brönsted acids, which are only weak alkylating agents at room temperature. At such temperatures, carboxylic acid esters such as benzoic acid methyl ester or acetic acid methyl ester demonstrate the alkylating power usually expected of alkylating agents derived from strong acids. In the catalytic cycle of this new process, for example, the low-cost alcohol methanol and phenol were converted into anisole and water at 320 °C via the intermediate methyl benzoate in the presence of catalytic quantities of alkali metal benzoate and phenolate. The catalytic Williamson ether synthesis (CWES) at high temperatures is especially well-suited for the production of alkyl aryl ethers such as anisole, neroline, and 4-methyl anisole which are of industrial importance. Selectivity values of up to 99% have been reached.

1. Introduction

Alkyl aryl ethers are important solvents and synthetic building blocks for the production of fragrances, cosmetics, pharmaceuticals, and dyestuffs, with the emphasis on derivatives of phenol, naphthalene, and dihydroxybenzenes.

Figures 1 and 2 show some examples of industrially important substances. Apart from anti-inflammatory agents such as Nabumetone and Naproxen and the sandalwood fragrance *trans*-3-isocamphyl-cyclohexanol,[1] anisole derivatives are of considerable importance as UV absorbers in skin protection products. Further growth in this market is expected in the future as a result of the depletion of the ozone layer and the increased awareness on the part of customers of the damage caused by the sun's rays.

The knowledge required for the synthesis of asymmetric ethers was developed in the mid-19th century. The processes concerned include Williamson ether synthesis,[2] which can be used for the production of alkyl aryl ethers:

$$\mathrm{Ar{-}O{-}Na + RX \rightarrow Ar{-}O{-}R + NaX}$$

Ar = substituted phenyl, naphthyl

$\mathrm{RX = (CH_3)_2SO_4, CH_3Cl, CH_3Br}$

The process consists of the conversion of an alcoholate with alkyl derivatives of Brönsted acids. However, to ensure satisfactory reaction rates at temperatures below 100 °C, the alkyl derivatives of strong Brönsted acids such as alkyl halogenides and alkyl sulfates need to be used. Strong alkylating agents are often carcinogenic and therefore call for extensive health and safety precautions. In addition, an inorganic salt which needs to be disposed of is a byproduct of the process. Although this noncatalytic synthesis process is relatively simple, it therefore results in considerable cost.

In view of the disadvantages described above, the objective for many years has been to carry out Williamson ether synthesis with weak alkylating agents which (1) are not carcinogenic and (2) avoid the production of waste salts to the greatest possible extent. The first solutions to this problem were proposed in the 1930s. As explained below, these approaches were pursued continuously until a variant suitable for industrial-scale use was developed.

2. Williamson Ether Synthesis Using Weak Alkylating Agents

2.1. Noncatalytic Williamson Ether Synthesis. The term "alkylating agent" for Williamson ether synthesis is extended to include the alkyl derivatives of weaker Brönsted acids. Such alkylating agents include the esters of weak acids such as acetic acid or benzoic acid, as well as alcohols and dialkyl ethers, which can be seen as mono- or dialkyl derivatives of the Brönsted acid water, and finally alkyl aryl ethers, the alkyl derivatives of hydroxy aromatics. There are however considerable differences between the acidities of the various classes of Brönsted acids (Table 1).

It is known that the acidity of water, a weak Brönsted acid, increases with temperature. If the temperature of water is increased from 0 to 100 °C, its pK_a value decreases from approximately 15 to approximately 12. The reason for this increase in acidity is the weakening of the O−H bond with rising temperature. To achieve adequate alkylation performance with weak alkylating agents, it can therefore be assumed that it is necessary to use high temperatures and, therefore, to work at high pressures.

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[1] Bauer, K.; Garbe, D.; Surburg, H. *Common Fragrance and Flavor Materials*, 3rd ed.; WILEY-VCH: (ISBN 3-527-28850-3) 1997; p 76.

[2] Williamson, A. *Justus Liebigs Ann. Chem.* **1851**, *77*, 37−49, 81, 373.

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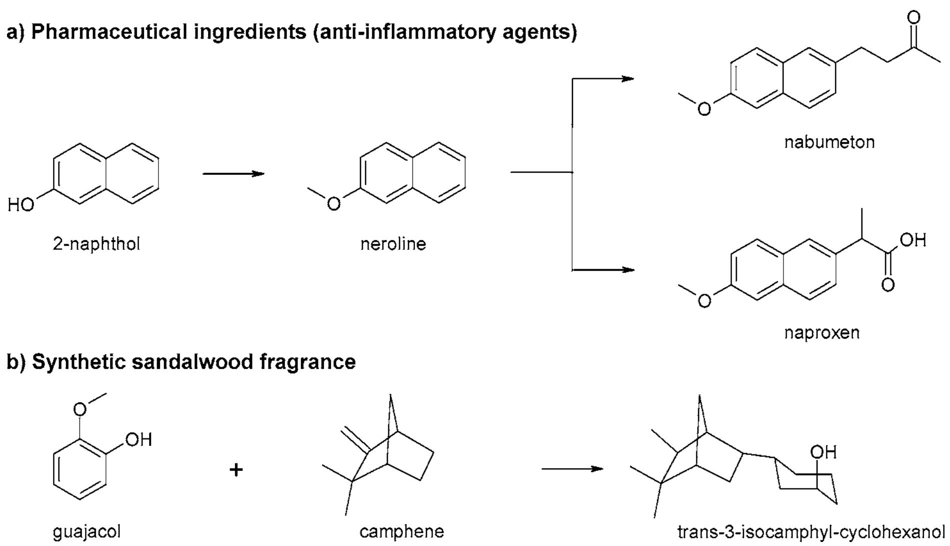

Figure 1. **Sample applications of alkyl aryl ethers.**

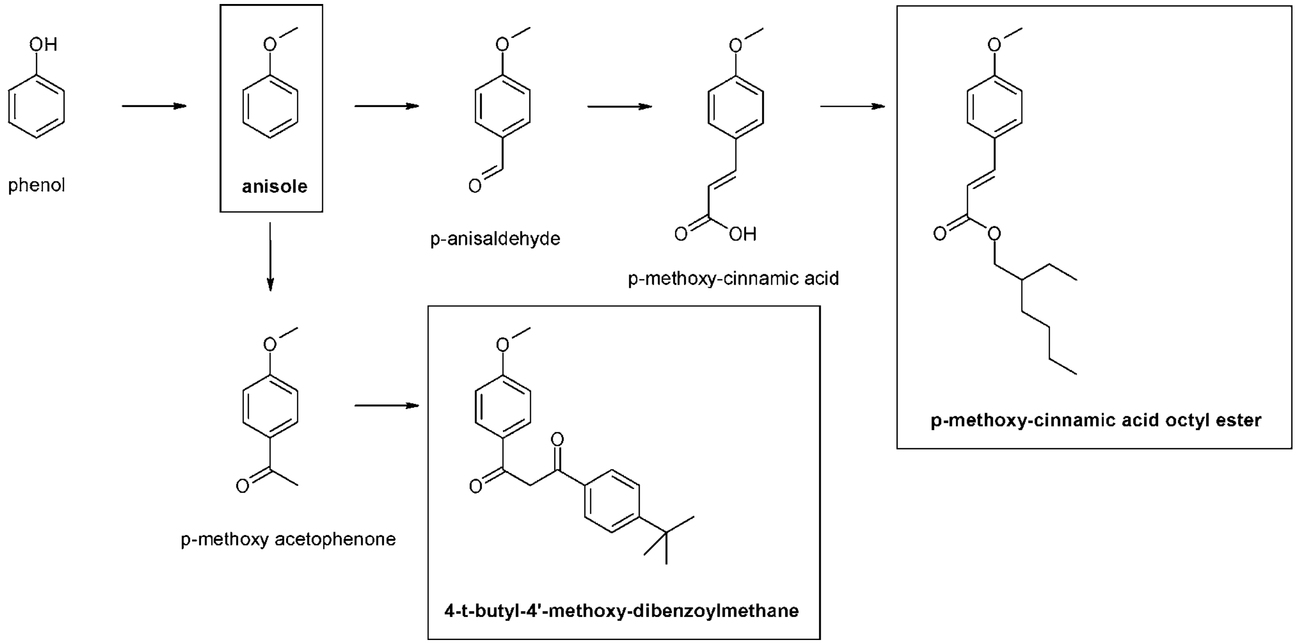

Figure 2. **Anisole-based UV absorbers for skin protection products.**

This approach to Williamson ether synthesis, high-temperature alkylation with a weak alkylating agent, laid the foundations for the process of Zerbe and Jage[4] in 1935 for the synthesis of anisole from sodium or potassium phenolate with methanol and carbon monoxide at 180 °C and elevated pressures.

step 1:

$$CH_3OH + CO \rightleftharpoons CHOOCH_3$$

step 2:

$$CHOOCH_3 + PhONa \rightleftharpoons PhOCH_3 + CHOONa$$

In step 1, formic acid methyl ester, a relatively weak alkylating agent, is formed in situ. This is directly converted by a classical Williamson ether synthesis reaction step (step 2).

The reaction must be kept at 180 °C, because, at higher temperatures, the equilibrium of step 1 shifts towards the entropic side of the equation, according to Fischer and Tropsch.[5] In other words, only small quantities of formic acid methyl ester, which is required as the alkylating agent, are formed. On the other hand, below 180 °C, step 2 (the ether synthesis reaction) is relatively slow.

After a reaction time of approximately 3 h, anisole yields above 80% were obtained. A disadvantage of this process is that it is necessary to work in an environment essentially free from water with equimolar quantities of alkali. It was also observed that the amount of anisole produced only corresponded to the quantity of phenolate in the reaction mixture. When sodium phenolate was used in catalytic quantities, no excess anisole was observed.

This is in line with the classical Williamson ether synthesis reaction. It is conceivable that this observation, which is well understood nowadays and which only applies

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(3) Linde, D. R. Handbook of Chemistry and Physics, 80th edition; CRC Press: (ISBN 0-8493-0480-6) 1999−2000; (8-44)−(8-56).

(4) Zerbe, C.; Jage, F. *Brennstoff-Chemie No. 5* **1935**, *16*, 88−92.

(5) Fischer, F.; Tropsch, H. *Ges. Abh. Kenntn. Kohle* **1922**, *6*, 382.

Table 1. **pK_a values of weak Brönsted acids [3]**

Brönsted acid	pK_a value	measurement temp (°C)
water	14.00	25
p-cresol	10.17	25
phenol	9.89	20
2-naphthol	9.51	25
carbonic acid	6.35	25
	10.33	25
acetic acid	4.76	25
benzoic acid	4.19	25
2- naphthoic acid	4.17	25
formic acid	3.75	20
1-naphthoic acid	3.70	25
phthalic acid	2.89	25
	5.51	25
terephthalic acid	3.51	25
	4.82	16
salicylic acid	2.97	19
	13.40	18
malonic acid	2.83	25
	5.69	25

at the relatively low temperature required for this reaction, prevented the development of similar homogeneous catalytic processes.

In 1939, King and Wright described the synthesis of anisole from equimolar quantities of potassium phenolate and methyl benzoate or dimethyl phthalate at temperatures of 180−200 °C under pressure:[6]

$$PhOK + PhCOOCH_3 \rightarrow PhOCH_3 + PhCOOK$$

In the case of methyl benzoate, the anisole yield after 3 h was 63%. A yield of 75% was obtained with phthalic acid methyl ester, which is significantly more reactive (see acidity values in Table 1). In contrast to the process of Zerbe and Jage, thermally stable esters of aromatic carboxylic acids were used as alkylating agents in this case.

The main difference between these two methods and classical Williamson ether synthesis process is that weak alkylating agents are used for ether synthesis and that an organic salt is formed instead of an inorganic salt. However, these two processes do not achieve the objective of minimizing the production of salt in the process.

2.2. First Steps to a Catalytic Williamson Ether Synthesis with Weak Alkylating Agents. In 1971, the synthetic process described by King and Wright was modified by Ashai Chemicals Industry Co., Ltd. (ACI).[7] Instead of an aromatic carboxylate, the modified process uses alcohols as indirect alkylating agents. In the patent mentioned, low cost methanol is preferred. The salt of an aromatic or aliphatic carboxylic acid is used as a catalyst (RCOOM).

In this system, catalytic quantities of phenolate and alkyl carboxylate are produced (steps 1 and 2). At 240 °C, these substances react to form the ether required with a high degree of selectivity in accordance with the Williamson ether synthesis process (step 3):

step 1 (alcoholate formation)

$$ArOH + RCOOM \rightleftharpoons ArOM + RCOOH$$

step 2 (esterification)

$$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$$

step 3 (ether synthesis)

$$RCOOR' + ArOM \rightleftharpoons ArOR' + RCOOM$$

sum

$$ArOH + R'OH \rightleftharpoons ArOR' + H_2O$$

After a reaction time of 10 h an anisole yield of 93% was obtained by this process.

If a soluble salt such as potassium benzoate is used (M = K), this reaction can be implemented as a homogeneous catalytic process. In contrast to classical Williamson ether synthesis, only a mild methylating agent is used. As a further advantage, water is produced instead of large quantities of potassium carboxylate. This process therefore requires no carcinogenic compounds and does not produce any waste.

The approach taken is especially elegant because methanol, a very weak alkylating agent, is converted in situ into a methyl carboxylate with significantly higher alkylating power.

In Table 1 one can see the considerable difference between the strength of the two corresponding Brönsted acids: water (pK_a value 14.00) and benzoic acid (pK_a value 4.17).

A disadvantage of this process is the fact that a phenol and a carboxylate must be used in equimolar proportions with a very high excess of alcohol. Although the metal carboxylate has a catalytic effect, high salt contents were used in the examples. This is a considerable obstacle to the simple processing of the reaction mixture and the regeneration of the catalyst.

Further process variants were developed by Rhone Poulenc. In these variants, phenol, bivalent phenols, and methanol were converted into ethers at approximately 200 °C under pressure in the presence of sodium acetate and acetic acid.[8−10] The sequence of steps in the reaction is the same as that with the Ashai process mentioned above. In a further variant, potassium iodide is added to improve reactivity.[11]

This catalytic process still has a considerable disadvantage, since a large (tetramolar) excess of the catalyst, sodium acetate, with respect to phenol must be used.

2.3. Catalytic Williamson Ether Synthesis (CWES) at High Temperatures. The authors[12] have succeeded in eliminating all the disadvantages of the processes described above by significantly increasing the reaction temperature to >300 °C under pressure and using phenol and methanol in equimolar proportions.

At these high temperatures, which result in a considerable increase in alkylation power, it is possible to use the homogeneous catalyst, consisting of a carboxylic acid and KOH (in situ preparation of the potassium carboxylate), in

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(6) King, H.; Wright, E. V. *J. Chem. Soc.* **1939**, *256*, 1168−1170.

(7) Asahi Chemical Industry Co., Ltd, JP 43-45852 (Saburo Scnoo, Toshi Kato, Kunihiko Ishii).

(8) Rhone Poulenc Spec Chim (FR), EP 0037353, 1981 (Ratton Serge).

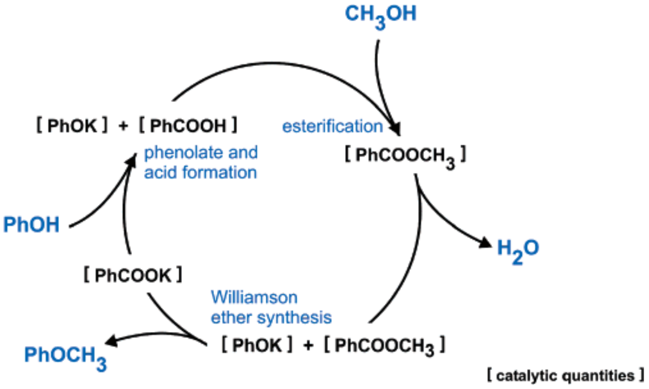
(9) Rhone Poulenc Rech (FR), EP 0046719, 1982 (Ratton Serge).

(10) Rhone-Poulenc Industries (FR), U.S. Patent 4,487,975, 1984 (Ratton Serge).

(11) Rhone Poulenc Spec Chim (FR), FR 2513632, 1983 (Ratton Serge).

(12) (a) Biller, E.; Surburg, H. Unpublished experiments. (b) Haarmann & Reimer GmbH (DE) and RÜTGERS VFT AG (DE), WO 01/27060 A1, 2001 (Biller, E., Fuhrmann, E., Hagena, D., Janneck, H. G., Talbiersky, J., Walther, L.).

genuinely catalytic quantities (approximately 4 mol %). The catalytic cycle shown below for anisole illustrates the principle of this new process:



The catalytic system is formed by the substances shown in the circle: potassium phenolate, methyl benzoate, benzoic acid, and potassium benzoate. The ester and the phenolate react in accordance with Williamson ether synthesis at catalytic concentration levels. Anisole (the output from the cycle) is finally formed from phenol and methanol (the inputs to the cycle), with water as a byproduct.

In contrast to the batch process, a continuous process variant provides very high yields with reference to space and time, making the industrial use of the process economically viable. In addition, the reaction product can be reprocessed by distillation without salt precipitation, because of the low salt concentration of the catalytic system. The stable catalyst remains in the distillation residue, which is recirculated.

The selectivity of the process is approximately 99%. In contrast to the classical Williamson ether synthesis process, the only byproduct is water, which does not pose a problem. This new ether synthesis, appropriately described as a homogeneous, catalytic Williamson ether synthesis, (CWES) represents a successful adaptation of an established process to modern environmental protection requirements. It meets some important principles of “Green Chemistry”[13a] such as the following:

(1) prevent waste
(2) design less hazardous chemical systems
(3) use catalysts
(4) maximize atom economy
(5) avoid chemical derivatives

A typical example for the batch type production of anisole with CWES is given in the following section:

A mixture of phenol (2.27 mol), methanol (2.27 mol), benzoic acid (0.07 mol), and potassium hydroxide (0.08 mol) is transferred to a 600 mL, stirred autoclave. The homogeneous mixture is allowed to react for 6 h at a temperature of 320 °C. Under these conditions, the internal pressure (steam pressure) of the autoclave reaches 60 bar. After cooling the apparatus down to room temperature, the homogeneous reaction mixture is analysed by gas chromatography.

The analytical results of this experiment are given in Table 2.

Table 2. **Analytical results of a typical CWES anisole batch synthesis; GC results (free from water)**

compound	concentration/weight %
methanol	10.6
low boiling compounds	0.05
anisole	42.1
phenol	43.8
o-cresol	0.31
methyl anisole	0.05
benzoic acid	1.80
methyl benzoate	1.18
high boiling compounds	0.11
water content (Karl Fischer method)	6.8

A modern variant of the original Williamson ether synthesis (WES) allows the use of the methyl groups of carcinogenic dimethyl sulfate (DMS), minimizing alkylating agent consumption and salt production.[13b]

Comparing this improved process with CWES, the figures for the production of one ton of anisole are as follows, clearly confirming the advantages of CWES:.

process	alkylating agent	alkylating agent quantity	alkali consumption	salt produced
WES	DMS	0.73 t	0.32 t	0.82 t
CWES	methanol	0.30 t	0.00 t	<0.001 t

With less than 1 g of waste per kg of product, CWES has an outstanding position in the fine chemicals sector in terms of waste avoidance.[14]

3. Results and Discussion of CWES

3.1. Model Tests on the Correlation of the Acidity and Alkylation Power of Weak Alkylating Agents in Catalytic Williamson Ether Synthesis. Tests were made to determine whether the alkylation power of weak alkylating agents at high temperatures and low water concentrations can also be derived from the strength of the Brönsted acid.

For the model reaction, 300 g of a mixture of phenol, methylating agent, and KOH (molar ratio 1:0.72:0.036) were allowed to react at various temperatures for 6 h in a 600 mL stainless steel autoclave. The alkylating agents used were methanol, 4-methyl anisole, neroline, dimethyl phthalate, methyl acetate, and methyl benzoate.

Figure 3a and b show that the evaluation in terms of anisole formation (anisole produced compared to the quantity of alkylating agent used) in the selected temperature range of 280−340 °C, with KOH as a catalyst, was as follows:

4-methyl anisole, neroline $\gg$ methanol (Figure 3a)

dimethyl phthalate > $PhCOOCH_3$, CH_3COOCH_3 (Figure 3b)

These results confirm the expectations based on the acidity series. However, this model is not adequate for detailed consideration of acidity relationships, since a number of other factors also play a role. These include the different polarities of the reaction mixtures, the different stabilities of the carboxylic acids produced, and, especially at high temper-

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(13) (a) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998; p 30. (b) BASF AG (DE), EP 0459242, 1991 (Houben, J., Weber, W.).

(14) Sheldon, R. A. *Chem. Technol.* **1994**, *24*, 38.

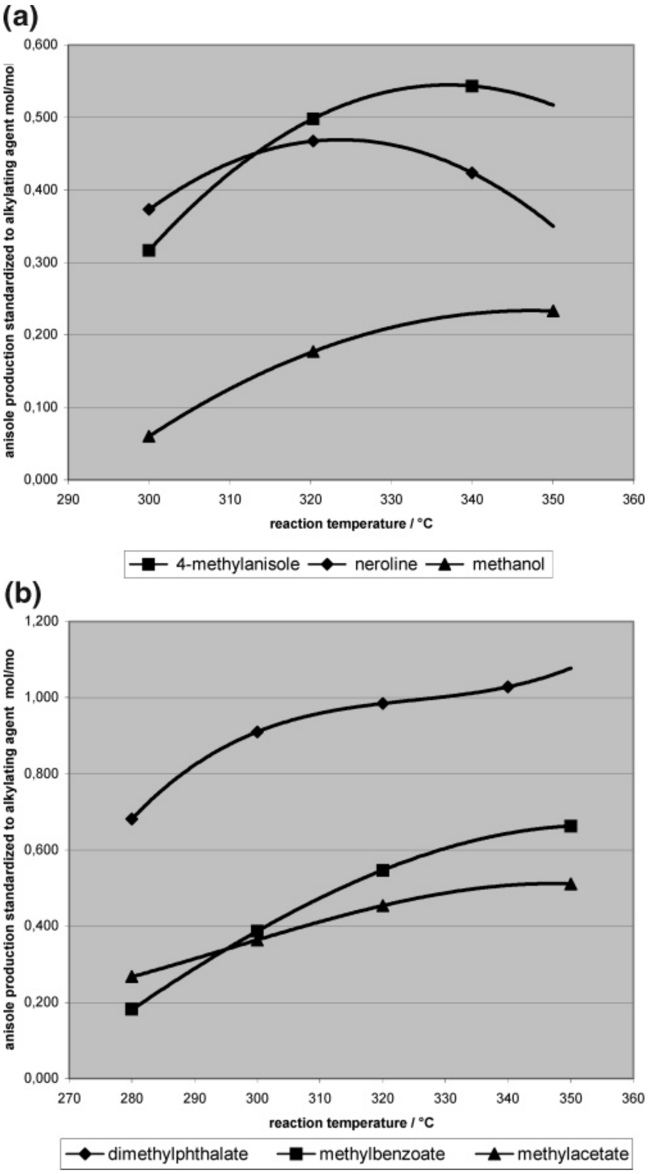

Figure 3. **(a) Anisole production as a function of alkylating agent quantities (methyl aryl ether and methanol) (discontinuous autoclave experiments with 6 h reaction time in each case). (b) Anisole production as a function of alkylating agent quantities (carboxylic acid ester) (discontinuous autoclave experiments with 6 h reaction time in each case).**

atures, the limited thermal stability of the ether, resulting in C-alkylation of the aromatic ring. It is especially the latter that causes the dip in the curve (Figure 3a) at high temperatures (see also Table 5).

In the case of dimethyl phthalate, one must be aware that the relatively acidic first carboxyl group dominates the reaction at lower temperatures (<300 °C) as compared with the less acidic second group. However, as the graph shows, the second group also plays a considerable role in the reaction at higher temperatures.

In addition, the free carboxylic acid produced during alkylation with esters leads to a decrease in the equilibrium concentration of the potassium phenolate, which slows down the reaction. This effect does not occur if methanol and alkyl aryl ethers are used.

Table 3. **Suitability of weak acids for catalytic Williamson ether synthesis (based on own experiments and data from literature)**

	fulfillment of selection criteria			
carboxylic acid	strength	ester formation (methanol and acid)	stability at 320 °C	solubility at 25 °C
formic acid	+	−	−	+
acetic acid	+	+	+	+
carbonic acid	+	−	−	−
oxalic acid	+	−	−	+
benzoic acid	+	−	−	+
salicylic acid	+	+		+
phthalic acid	+	+	+	+
terephthalic acid	+	+	+	(−)
1-naphthoic acid	+	+	+	+
2-naphthoic acid	+	+	+	+
malonic acid	+	−	−	−

All these results also show that temperatures in excess of 300 °C are absolutely necessary for a reasonable reaction rate of the phenolate at a catalytic level with weak alkylation agents.

3.2. Selection Criteria for the Employed Reagents. (a) Carboxylic Acids. Carboxylic acids must meet the following criteria for use in the catalytic Williamson ether synthesis:

(1) significant ester formation under the prevailing alkaline reaction conditions;

(2) thermal and chemical stability (of acids, salts, and esters);

(3) esters with adequate alkylation power;

(4) solubility of acids and salts;

(5) low corrosion potential.

These criteria severely limit the choice of carboxylic acids which are suitable. Thus, formic acid esters (see the Zerbe/Jage process mentioned above), dialkyl carbonates, salicylic esters, malonates, and oxalates have high alkylation potential but cannot be used because of their lack of thermal stability at 320 °C (Table 3). In addition, nitrocarboxylic acids are converted into the corresponding amino carboxylic acids in the presence of methanol.

(b) Hydroxy-Substituted Aromatics. Using methanol, relatively high selectivities (>99% in the case of anisole) can be obtained for monohydroxy aromatics such as β-naphthol, phenol, and alkyl phenols such as *o*- and *p*-cresol. Conversion rates of phenols are of the order of 40−55% (see also Table 4).

In principle, CWES can also be used with bivalent phenols such as catechol, but lower temperatures must be used and selectivity is reduced.

(c) Alcohols. Among aliphatic alcohols, methanol gives the highest reactivity and selectivity for catalytic Williamson ether synthesis. In the case of methanol, possible secondary reactions such as the formation of dimethyl ether, the production of formic acid or water and carbon monoxide by the Guerbet reaction, or disproportionation to methane and formaldehyde, which must be taken into consideration in the case of benzyl alcohol (disproportionation to toluene and benzaldehyde), are of negligible importance.

Table 4. **Ratio of O-alkylation (1) to C-alkylation (2) in the CWES at 320 °C**[a]

hydroxy aromatic	alcohol	molar ratio (1):(2)
phenol	methanol	117
p-cresol	methanol	80
3,5-DMP	methanol	28
phenol	ethanol	11
phenol	*n*-butanol	1.2
phenol	*tert*-butanol	1.6×10^{-2}
phenol	benzyl alcohol	3.2×10^{-4}

[a] Reaction conditions: 300 g of reagent mixture in 600 mL stainless steel autoclave, 320 °C, 6 h, hydroxy aromatic/alcohol/KOH/benzoic acid in a ratio of 1:1:0.04:0.036.

In addition, as will be demonstrated below, benzyl alcohol leads to a high degree of direct alkylation of the ring.

3.3. Selectivity of CWES with Respect to the Oxygen Alkylation of Hydroxy Aromatics. In principle, the alkylation of hydroxy-substituted aromatics may produce either the ether (1) or the alkylated phenol (2):

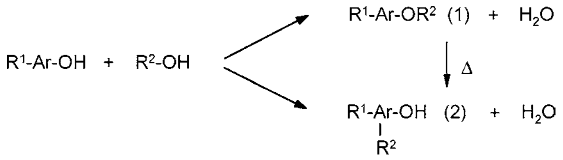

Table 4 shows the ratio of O-alkylation to C-alkylation for different reagents. This ratio was determined by the GC–MS method without considering possible competing reactions.

At the selected temperature of 320 °C, the results shown in Table 4 indicate that the more stable the carbenium ion, the greater the tendency of the alcohol to undergo ring alkylation. This observation is in agreement with the obvious decrease in the yield of phenol ethers in favor of ring-alkylated phenols. This shift becomes more pronounced as the stability of the alkyl group attached to the oxygen increases. Thus, in the case of anisole, there is no significant shift towards phenol even at a reaction temperature of 320 °C. On the other hand, it is known that *tert*-butyl phenyl ether is largely replaced by 4-*tert*-butyl phenol even if it is only distilled without a catalyst.[15] In addition, if (1-phenylethyl)phenyl ether is kept at 200 °C for 5 h, the products include a mixture of 85% *ortho*- and 15% *para*-(1-phenylethyl) phenol in addition to styrene and phenol.[16]

Table 5. **Temperature dependence of O- (1) and C-alkylation (2) at CWES conditions (see Table 3)**

hydroxy aromatic	alcohol	temp/(°c)	(1):(2)
phenol	methanol	340	42
phenol	methanol	320	117
phenol (1 mol)	benzyl alcohol (1 mol)	320	3.2×10^{-4}
phenol (1 mol)	benzyl alcohol (1 mol)	270	1.73
2- naphthol (1 mol)	benzyl alcohol (2 mol)	270	9.8×10^{-3}
2- naphthol (1 mol)	benzyl alcohol (2 mol)	240	0.17

With decreasing temperatures (Table 5), the tendency even of stable carbenium ions such as that of benzyl alcohol towards oxygen alkylation increases significantly. Surprisingly, at the reaction conditions selected (temperatures considerably above 200 °C), phenyl benzyl ether, for example, remains relatively stable.

At least in the case of the selected examples investigated (Table 4), the following rule appears to apply: as the polarizability (softness) of the π-electron in the aromatic ring and the charge distribution (softness) of the carbenium ion increase (for example, as a result of +I-substitution effects), so does the tendency towards ring alkylation. Conversely, as the charge concentration (hardness) of the carbenium ion increases, there is a growing tendency for the hard, strongly basic oxygen anion to be alkylated. This is in line with the theory of J. O. Edwards and R. G. Pearson.[17]

4. Conclusion and Outlook

CWES certainly cannot replace the classical Williamson ether synthesis in all applications and is subject to definite limitations, especially as a result of the thermal instability of certain alkyl aryl ethers. Nevertheless, this environmentally benign process is well suited for the highly efficient production of ethers which are important for industry and have high market volumes. These include anisole, 4-methyl anisole, and neroline. In such cases, methanol, a low-cost, noncarcinogenic alkylating agent, can be used and the only byproduct, instead of salt, is water.

The process is already being used on an industrial scale for the continuous production of anisole at the Castrop-Rauxel plant of RÜTGERS Chemicals AG.

As described, the significant increase in the reactivity of alkylating agents based on Brönsted acids observed at higher temperatures cannot only be used for ether synthesis. It may also prove useful in other areas such as the selective ring alkylation of hydroxy aromatics.

Finally, the strong increase in the acidity of weak Brönsted acids at high temperatures and pressures which can be derived from the experiments may open up new prospects for acid catalysis.

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(15) Smith, R. A. *J. Am. Chem. Soc.* **1933**, *55*, 3720. Natelson, S. *J. Am. Chem. Soc.* **1934**, *56*, 1583.

(16) Hart, H.; Eleuterio, H. S. *J. Am. Chem. Soc.* **1954**, *76*, 519.

(17) Edwards J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, *84* (6). Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.