

Article

Highly Selective Vapor and Liquid Phase Transfer Hydrogenation of Diaryl and Polycyclic Ketones with Secondary Alcohols in the Presence of Magnesium Oxide as Catalyst

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Abstract: MgO has been shown to catalyze an almost quantitative hydrogen transfer from 2-octanol as the hydrogen donor to benzophenone to form benzhydrol, a useful intermediate product in the pharmaceutical industry. The hydrogen transfer from a series of alcohols to the carbonyl group of benzophenone, its ten derivatives, four polycyclic ketones, and 2-naphthyl phenyl ketone was carried out in liquid (LP) or vapor phase (VP). The dependence of reactivity on the structure of the hydrogen donor, reaction temperature, donor-acceptor ratio, amount of catalyst, and the type and position of substituents has been established. For both reaction modes, optimal conditions for selective synthesis of the alcohols were determined and side reactions were investigated. The results indicate that the reactivity of the ketone is suppressed by the presence of a methyl substituent in the ortho position to a much greater extent in LP mode. A scale-up was demonstrated in the liquid phase mode.

Keywords: magnesium oxide; transfer hydrogenation; benzophenones; 2-octanol; selective reduction



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1. Introduction

Much attention in research is focused on transfer hydrogenation reactions on different catalysts [1–4]. Although multiple studies using complex catalytic systems which include magnesium compounds have been recently reported [5,6] pure MgO is known for its basicity and is therefore able to serve as a catalyst for multiple reactions without any additives [7]. It is a cheap, nontoxic solid, which is easily separated from the post reaction mixture and can be reused. MgO has also been shown to catalyze transfer hydrogenation reactions of various carbonyl compounds into alcohols [8–13]. Similarly, other oxides, such as ZrO₂ [14–16] and Al₂O₃ [17], zeolites [18,19], as well as other systems [20–26] have been found to be active catalysts in hydrogen transfer. Reviews of the catalysts studied in such reactions are available in the literature [27,28]. Ethanol is often used as the hydrogen donor because it is cheap and easily available, although other alcohols are good alternatives. In the current paper, only secondary alcohols were studied and the scale-up is performed with 2-octanol, whose industrial synthesis requires the use of a sole raw material; namely, Castor Oil, a product of plant origin. These heterogeneous catalysts are environmentally friendly and can be applied in one-pot organic synthesis reactions which do not require the use of toxic and corrosive solvents, gaseous hydrogen under pressure, or expensive, moisture-sensitive and often hazardous hydride reagents. Moreover, they do not produce inorganic salts as waste and reactions can be carried out in the vapor phase mode under flowing conditions which is recommended by the rules of Green Chemistry [29]. An additional benefit of implementing this method, is that the obtained product is pure and the solid catalyst is easily separated from the post-reaction mixture. High selectivity of the reaction and ease of purification of a compound is especially important in the

pharmaceutical industry, in which benzhydrol is commonly used in the production of, e.g., antihistamines.

Reduction of carbonyl compounds has been one of the most fundamental processes in organic chemistry [30,31]. It is usually carried out in the presence of catalysts containing transition metals deposited onto a support, and pressurized gaseous dihydrogen is used as a reducing agent. A second common method of reducing a carbonyl group is the use of metal hydrides; mainly sodium borohydride. This compound, due to its mild reactivity, reduces carbonyl compounds in a water-alcohol solution instead of anhydrous ether solutions, which is a very convenient and an important simplification of the method of reduction. However, both these methods have disadvantages such as the risks associated with the use of gaseous hydrogen under pressure, expensive, moisture-sensitive and hazardous hydride reagents, inorganic salts as waste, and often the need for toxic and corrosive solvents.

The Meerwein–Ponndorf–Verley (MPV) reduction of aldehydes and ketones, a third method, is a classic example of a homogeneous route of hydrogen transfer reaction, which has been implemented to obtain various alcohols synthesized under mild conditions. A big advantage of the method is its selectivity, which enables a chemoselective reduction of α,β -unsaturated carbonyl compounds into unsaturated alcohols [32]. However, a major drawback of the method is the requirement to work in an anhydrous environment and the necessity to use a stoichiometric amount of aluminium alkoxides.

In contrast to the previously described methods a heterogeneous route of MPV reduction is freed from the abovementioned disadvantages and truly offers a green procedure for the synthesis of various alcohols. Catalytic transfer hydrogenation has been used in the reduction of many types of aldehydes and ketones: saturated [20,33,34], cyclic [21,35,36] and aralkyl [18,37,38], as well as α,β -unsaturated [8–10,39–42]. Although various carbonyl compounds have been reduced by this method, no systematic study of the reduction of diaryl ketones has been performed. Only benzophenone has been described in literature as the hydrogen acceptor. Ramana and Pillai have studied the reduction of the ketone in gas phase over alumina doped with Na^+ cations [43]. At 573 K and with the 2-propanol to benzophenone molar ratio (D/A) of 10, a 70% yield of benzhydrol has been observed. Vapour-phase transfer hydrogenation (TH) of benzophenone with 2-propanol (D/A = 3) has also been studied by Jyothi et al. [44]. At 473 K, in the presence of $6\text{MgO}\cdot\text{Al}_2\text{O}_3$ catalyst, 31% yield of benzhydrol has been noted. Hydrous zirconia, $\text{ZrO}_2\cdot n\text{H}_2\text{O}$ has shown a very high activity in TH of benzophenone with 2-propanol [45]. In its presence a quantitative yield of benzhydrol has been attained after 10 h of refluxing. On the other hand, very low activity of $2\text{MgO}\cdot\text{Al}_2\text{O}_3$ catalyst in the mentioned reaction with 2-propanol has been observed by Ruiz et al. After 24 h and at D/A = 30, a 4% yield of product has been found [20].

In the present work a thorough investigation of the reactivity of sixteen aromatic carbonyl compounds in the hydrogen transfer reduction by alcohols over magnesium oxide as the catalyst either in liquid or in vapor phase has been performed. The studied compounds were benzophenone and its ten derivatives, as well as four polycyclic ketones containing a benzene moiety, and 2-naphthyl phenyl methanone. The reduction of halogen containing derivatives of benzophenone and also 4-nitrobenzophenone was tested in order to determine if dehalogenation/denitrogenation reaction, which, very often accompanying the reduction of these compounds with a gaseous hydrogen in the presence of metallic catalysts, takes place under these reaction conditions. A broad spectrum of secondary alcohols as hydrogen donors from 2-propanol to 2-octanol was used due to the expected moderate reactivity of diaryl ketones in the liquid phase mode of TH reaction.

2. Results and Discussion

2.1. The Catalyst

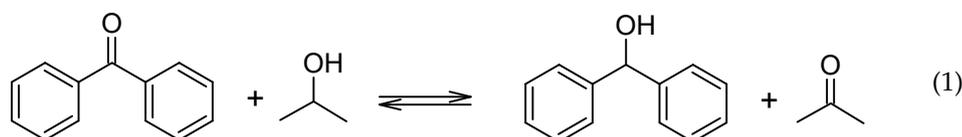
The specific surface area of the catalyst precursor, i.e., $\text{Mg}(\text{OH})_2$, is $30.4\text{ m}^2\cdot\text{g}^{-1}$ and the pore volume is $0.17\text{ cm}^3\cdot\text{g}^{-1}$. Structural examination by powder X-ray diffraction has shown that the precursor comprises a single phase: as synthesized, the magnesium

hydroxide crystallizes in the trigonal system, in the P3m1 space group as exhibited by brucite. The TG-DTA analysis revealed that T_{\max} for the decomposition of $\text{Mg}(\text{OH})_2$ is 692.2 K and the weight loss (320–873 K) 30.61% (exp), 30.89% (calc).

The specific surface area and pore volume determined for the calcined catalyst, MgO, were $129.2 \text{ m}^2 \cdot \text{g}^{-1}$ and $0.40 \text{ cm}^3 \cdot \text{g}^{-1}$, respectively. The XRD results indicate the presence of a single phase in the catalyst sample. The obtained MgO crystallized in the cubic system in the Fm3m space group (periclase). The strength of the surface acid-base sites of MgO as determined by the indicator studies are: $(\text{H}_0) > +4.8$; $7.2 \leq (\text{H}_-) < 33.0$. The concentration of acidic sites equals $8 \mu\text{mol} \cdot \text{g}^{-1}$ (titrant: Et_3N), whereas that of basic sites is $1360 \mu\text{mol} \cdot \text{g}^{-1}$ (titrant: PhCOOH).

2.2. Liquid-Phase Transfer Hydrogenation of Diaryl Ketones

For our studies on hydrogen transfer in the liquid phase conducted in the presence of magnesium oxide as a catalyst from secondary alcohols to diaryl ketones, unsubstituted diphenyl methanone (benzophenone) was selected along with ten of its derivatives containing the following: alkyl-, halo-, hydroxy-, methoxy- and nitro- groups. The course of the reaction is exemplified by the following equation:



The dependence of the structure of the hydrogen donor, the reactant molar ratio and the catalyst weight on the conversion of benzophenone, and the yield of the product have been determined. The results of the activity measurements when different isomers of heptan- x -ols ($x = 2, 3$ or 4) were used as the hydrogen donor are collected in Figure 1. In the case of heptan-2-ol, the yield of benzhydrol after 1 h of reaction was 45%, whereas when heptan-3-ol and heptan-4-ol were used, the yield of the product was 14 and 2%, respectively. Therefore, it can be concluded that the shift of the hydroxy group to the middle of the molecule causes a decrease in its reactivity. This trend is maintained for all three studied times of the reaction. After 6 h of reaction, the differences in the reactivity were less pronounced, with the yield of benzhydrol equal to 73, 69 and 39% for $x = 2, 3$, and 4 in heptan- x -ol (Figure 1).

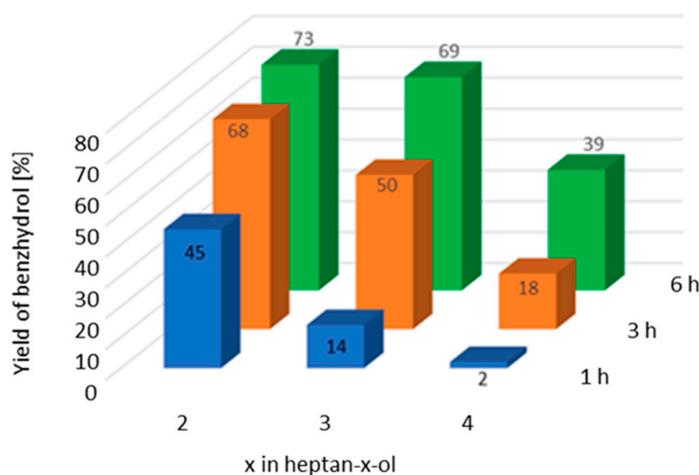


Figure 1. Liquid phase transfer hydrogenation of benzophenone with heptan- x -ols ($x = 2, 3$ or 4) in the presence of MgO. Reaction conditions: $W_{\text{MgO}} = 250 \pm 5 \text{ mg}$, 3.125 mmol of ketone, $D/A = 8$, selectivity $>98\%$.

The results obtained with heptan- x -ols show that the most meaningful comparison between donors which differ in the length of the aliphatic chain would be between alcohols

with the OH group in the same position. Therefore, seven straight chain secondary aliphatic alcohols with the OH group attached to the second carbon atom were used as hydrogen donors in the reaction with benzophenone. Since they all have much lower boiling points than benzophenone itself (b.p. 579 K) and they were added in substantial excess, their boiling points determined the reaction temperature. The results reveal that there is a strong dependence of the product yield on the boiling point of the donor. Previous studies in which the activity of some donors was tested at the same temperature, i.e., for two of them the temperature was lower than their boiling points, in order to ensure separation of the effect of donor from the reaction temperature have shown that the yield is the highest at the boiling point temperature of the donor and negligible at lower temperatures [38]. Therefore, in the present work, as well as in most of the literature on LP transfer hydrogenation, all liquid phase activity tests were carried out at the boiling point of each donor, which means that it is not possible to separate the effect of the type of donor and reaction temperature. The yield of benzhydrol after 1 h of reaction are shown in Figure 2 and indicate that by increasing the length of the chain, and therefore the reaction temperature, the yield increases. Under the studied reaction conditions with 2-octanol as the hydrogen donor ($D/A = 8$, 6 h) an almost quantitative yield of benzhydrol has been observed. It is noteworthy that the order of introduction of substrates and the catalyst into the reaction chamber plays an important role in the reaction. When the catalyst is first dosed with the donor, and then the acceptor is introduced, a much higher yield of the product is observed. A reversed order of introducing of reactants, first acceptor then 2-octanol, leads to a yield of benzhydrol equal to 75% after 1 h of reaction, as opposed to 97% (Figure 2).

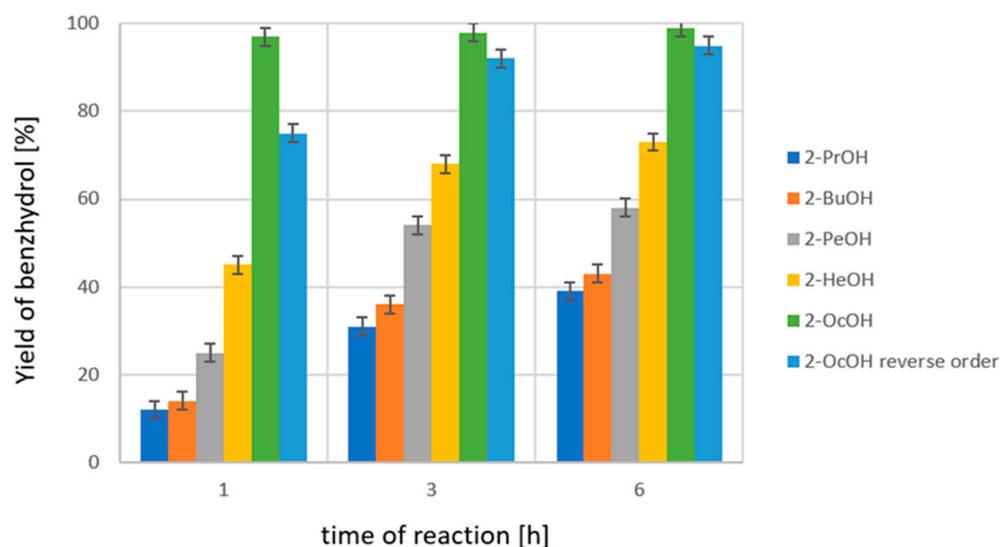


Figure 2. Liquid phase transfer hydrogenation of benzophenone with different 2-alkanols at normal pressure in the presence of MgO catalyst. Reaction conditions: $W_{MgO} = 250 \pm 5$ mg, 3.125 mmol of ketone, $D/A = 8$, selectivity $>98\%$.

The results of activity measurements carried out with 2-octanol as the hydrogen donor and seven different donor-acceptor ratios on the yield of benzhydrol are presented in Figure 3. It can be seen that when the $D:A$ ratio is 4, a yield of 86% is noted after 1 h of reaction. A higher yield is noted for the donor-acceptor ratios of 6 and 8, i.e., 93% and 97%, respectively. The maximum yield of benzhydrol (99%) was attained after 6 h of reaction with 250 mg of MgO for a ratio equal to 8. Further increase of the D/A parameter leads to slightly lower yields (98–90%) of the product although the high selectivity ($>98\%$) was retained. In light of these results, the optimal donor to acceptor ratio is 8:1.

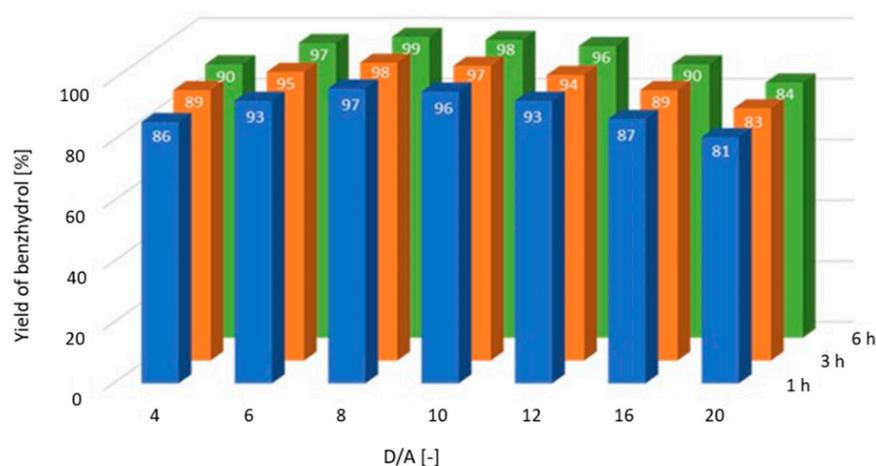


Figure 3. Influence of the donor-acceptor molar ratio on the reaction yield in liquid phase transfer hydrogenation of benzophenone with 2-octanol in the presence of MgO. Reaction conditions: $W_{\text{MgO}} = 250 \pm 5$ mg, 3.125 mmol of ketone, selectivity >98%.

Figure 4 contains the results of studies performed to determine the effect of the weight of the catalyst used on the yield of benzhydrol. When 25 mg of MgO are used, the yield of the desired product is only 35% after 1 h of reaction. After two more hours, a yield of 55% is noted, which shows that the additional time is needed. However, the yield of benzhydrol after 6 h of reaction is only 5% higher than that observed after 3 h. This shows that doubling the time does not help to increase the yield of the product. In contrast, the use of 100 mg of the catalyst instead of 25 mg leads to a substantial increase of the product yield (Figure 4). It can be seen that even after 1 h of the test, a 91% yield of benzhydrol is attained, which is substantially more than after 6 h of reaction with the smaller amount of catalyst. It can be stated that the yield of benzhydrol increases with an increase of the amount of the catalyst until reaching a plateau (98–99%), which starts at 250 mg of MgO (Figure 4).

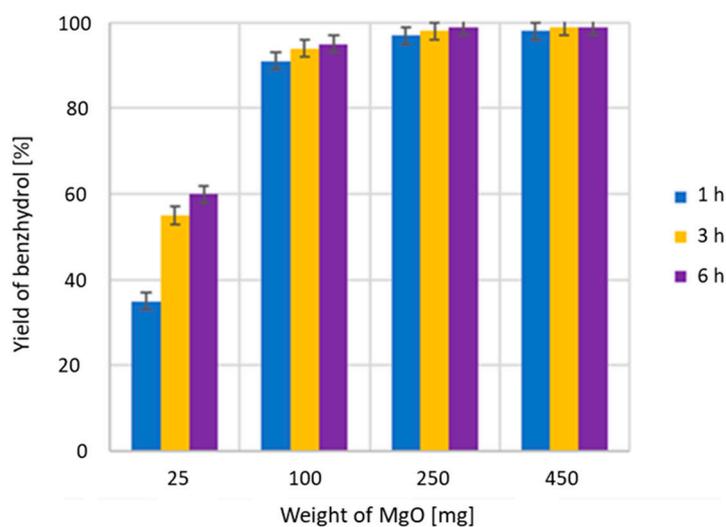


Figure 4. Influence of the weight of MgO on the reaction yield in liquid phase transfer hydrogenation of benzophenone with 2-octanol in the presence of MgO catalyst. Reaction conditions: $W_{\text{MgO}} = \text{var}$, 3.125 mmol of ketone, $D/A = 8$, selectivity >98%.

The catalyst was tested repeatedly with a total of 4 batches of benzophenone. Under the reaction conditions MgO does not react to form any soluble magnesium-containing compounds and it is not soluble itself. Therefore, the same portion of MgO was used in consecutive tests directly after separation from reactants. In each cycle, the yield of the

desired product was determined after 1, 3 and 6 h of reaction. It was observed that in the second cycle, the efficiency of the reduction of benzophenone slightly decreased from 99 to 97% after 6 h of reaction (Figure 5). Further drops in activity were noticed in each of the two subsequent cycles, but overall, this parameter did not have as great of an impact on the yield of benzhydrol as the other studied variables. In the fourth repetition of the cycle under these conditions, benzhydrol was obtained with a yield of 91%.

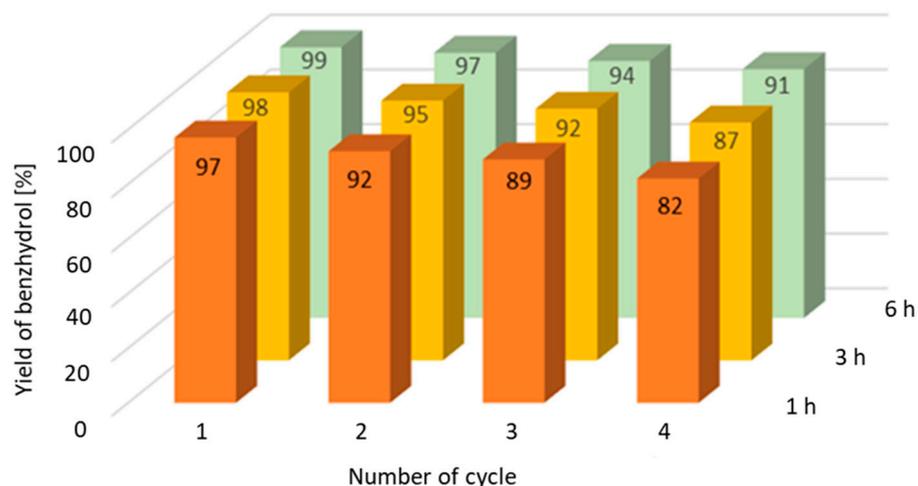


Figure 5. Recycling test of MgO in liquid phase transfer hydrogenation of Ph₂CO with 2-octanol. Reaction conditions: W_{MgO} = 250 ± 5 mg, 3.125 mmol of ketone, D/A = 8, selectivity >98%.

The results of activity tests of some derivatives of benzophenone under the optimized conditions, i.e., 250 mg of MgO used, 2-octanol as the hydrogen donor, D:A = 8, are shown in Table 1. The presence of a methyl substituent in the 2-position of one of the rings resulted in a significant decrease (Table 1 lines 1 and 2) in the reactivity of the ketone, manifested by a 27% yield of the alcohol after 3 h of reaction. Extending the reaction time to 6 h allowed us to obtain (2-methylphenyl) phenyl methanol with 75% yield. It can be seen that the presence of a methyl group in the 3 or 4 positions of one of the ketone rings (Table 1 lines 3 and 4) had a very slight effect on its reactivity; after 3 h of reaction, the yields of the alcohols were 88 and 94% for (3-methylphenyl) phenyl methanone and (4-methylphenyl) phenyl methanone, respectively.

As shown in the catalytic test, the presence of two methyl substituents in ortho positions in one of the ketone rings ((2,4,6-trimethylphenyl) phenyl methanone; Table 1 line 5) leads to a lack of reactivity of the ketone during 6 h under reaction conditions. The reason for such behavior is undoubtedly the presence of a steric hindrance in the close vicinity of the carbonyl group. This is similar to the case of the non-reactivity of 1-(2,4,6-trimethylphenyl)-1-ethanone (acetylmesitylene) in reaction with secondary alcohols in the liquid phase in the presence of MgO described in our previous work [38].

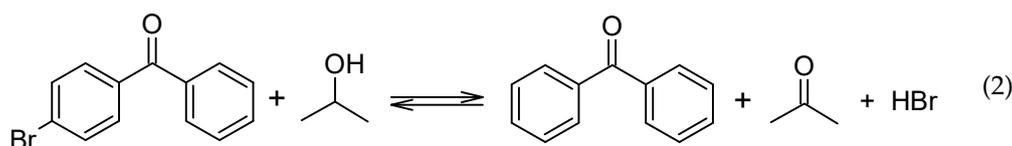
The transfer hydrogenation of benzophenone derivatives containing halogens (Table 1 lines 6–8) in the para position was carried out with a donor:acceptor ratio of 16. Under such conditions, the yield of benzhydrol from the unsubstituted ketone was 87% after 1 h of reaction. It can be seen that the type of halogen used has an impact on the yield of benzhydrol with values of 68%, 82% and 87% noted for fluorine, chlorine and bromine, respectively. These values indicate that the extent of the electron withdrawing effect plays a role in the interaction of the ketone with the catalyst and/or the donor.

Table 1. Liquid phase transfer hydrogenation of substituted Ph₂CO with 2-octanol in the presence of MgO catalyst.

Line No.	Substituent	Yield of Alcohol ^{a,b} [%]/Reaction Time [h]		
		1	3	6
1	-	97	98	99
2	2-Me	5	27	75
3	3-Me	74	88	96
4	4-Me	81	94	99
5	2,4,6-triMe	0	0	0
6	4-F ^c	68 ^d	88	87 ^e
7	4-Cl ^c	82 ^f	85	83 ^g
8	4-Br ^c	87 ^{h,i}	84	79
9	j	3 ^k	10	18
10	4-OMe	43	76	78
11	4-OH	0	0	0
12	4-NO ₂	-	6 ^{l,m}	20 ^{l,n}
13	2-NpPh ^o	39	87	94

^a—Reaction conditions: WMgO = 250 ± 5 mg, 3.125 mmol of ketone, D/A = 8; ^b—Selectivity > 98% or stated otherwise; ^c—D/A = 16; ^d—For 1, 3 and 6 h the conversions of 69, 90 and 91% were noted, respectively; ^e—Formation of Ph₂CO was not observed during 6 h; ^f—For 1, 3 and 6 h the conversions 84, 87 and 89% were noted, respectively; ^g—After 6 h 0.2% yield of Ph₂CO was noted; ^h—For 1, 3 and 6 h the conversions 92, 93 and 96% were noted, respectively; ⁱ—Yields of Ph₂CO were 3.4, 3.8 and 4.4% after 1, 3 and 6 h, respectively; ^j—2-PrOH as hydrogen donor, D/A = 16; ^k—For 1, 3 and 6 h yields of Ph₂CO 1.4, 1.7 and 2.0% were noted, respectively; ^l—PhCH(OH)Ph-NO₂; ^m—Also 1.1% PhCOPh-NH₂ and 1.3% of mixture of Ph₂CO and PhCH(OH)Ph; ⁿ—Also 1.5% PhCOPh-NH₂ and 2.3% of mixture of Ph₂CO and PhCH(OH)Ph; ^o—2-Naphthyl phenyl ketone as hydrogen acceptor.

It has been observed that for (4-bromophenyl) phenyl methanone, the yield of the alcohol decreased in time. The corresponding conversions of the substrate were 92, 93 and 96% for 1, 3 and 6 h of the reaction (Table 1 point h). It was determined that a dehalogenation reaction was occurring, in which 3.4, 3.8 and 4.4% of the substrate were converted to Ph₂CO (Table 1 point i). The course of the dehalogenation reaction on the example of 4-bromobenzophenone is described by Equation (2):



Hydrogen bromide formed in the reaction is chemically bonded to magnesium oxide. In contrast, in the case of the F-substituted ketone the formation of Ph₂CO was not observed during 6 h under reaction conditions (Table 1 point e). When (4-bromophenyl) phenyl methanone reacted with 2-propanol instead of 2-octanol, the yield of the alcohol was only 3% after 1 h of reaction (Table 1 line 9). Additional 2 h of reaction led to an overall alcohol yield of 10%, and after a total of 6 h of reaction the value reached 18%.

Significant differences in the reactivity of (4-methoxyphenyl) phenyl methanone and (4-hydroxyphenyl) phenyl methanone were observed in the tested reaction (Table 1 lines 10 and 11). The former compound was reduced to the corresponding alcohol with a 76% yield, whereas the latter was non-reactive. The reason for the observed lack of reactivity is undoubtedly the presence of a phenolic hydroxy group in the molecule of the latter, whose acidic properties in conjunction with the high basicity of the magnesium oxide surface resulted in an acid-base reaction and catalyst deactivation.

In the reduction of 4-nitrobenzophenone, next to the main product, an equimolar mixture of benzophenone and benzhydrol was formed (Table 1 line 12). The yield of PhCH(OH)Ph-NO₂ was 6 and 20% after 3 and 6 h of reaction, respectively. The other components of the reactant stream were also identified. After 3 h under reaction conditions,

the liquid phase also contained 1.1% PhCOPh-NH₂ and 1.3% of mixture of Ph₂CO and PhCH(OH)Ph, whereas after 6 h, the corresponding values were: 1.5% PhCOPh-NH₂ and 2.3% of mixture of Ph₂CO and PhCH(OH)Ph.

In order to determine if a heavier ketone, i.e., one with more rings in its structure can be reduced using this method, a test was conducted with 2-naphthyl phenyl ketone as the hydrogen acceptor (Table 1 line 13). It has been shown that the yield of the appropriate alcohol was 39%, 87% and 94% after 1, 3 and 6 h of reaction, respectively.

The occurrence of dehalogenation of (4-halophenyl) phenyl methanones during the course of the hydrogen transfer reaction in the liquid phase was taken up in further research. (4-Bromophenyl) phenyl methanone was selected for the test, i.e., the ketone which underwent the above-mentioned side reaction with the highest yield. Catalytic tests were carried out with three hydrogen donors: 2-propanol, 2-pentanol and 2-octanol. The test results are summarized in Table 2. It can be seen that the occurrence of the ketone debromination reaction was found in the case of all the hydrogen donors used and the yield of the tested reaction increased slightly with temperature. It was shown that at the highest reaction temperature (454 K) the dehalogenation product yield did not exceed the value of 5% after 6 h, with a hydrogen transfer reaction product yield of 67%.

Table 2. Liquid phase transfer hydrogenation of 4-bromobenzophenone with various secondary alcohols in the presence of MgO catalyst.

Donor	T [K]	Yield of PhCH(OH)Ph-Br ^a [%]/Reaction Time [h]		
		1	3	6
2-PrOH	355	2.5/1.4 ^b	10.2/1.7	17.9/2.0
2-PeOH	393	31.1/2.3 ^b	59.5/2.5	73.7/2.7
2-OcOH	454	66.7/3.4 ^b	70.7/3.8	66.5/4.4

^a—Reaction conditions: W_{MgO} = 250 ± 5 mg, 3.125 mmol of ketone, D/A = 16; ^b—Yield of PhCOPh.

2.3. Vapour-Phase Transfer Hydrogenation of Diaryl Ketones

The study of the hydrogen transfer reaction to diphenyl methanones in the gas phase was limited to the unsubstituted ketone and its monosubstituted methyl derivatives. The reason was the high boiling point of ketones under normal pressure (benzophenone, b.p. 579 K) and the need to work in the temperature regime in which they occur in the gas phase. Therefore, the choice of reaction temperatures was rather limited and the catalytic tests were performed in the temperature range of 573–723 K (Table 3).

Table 3. Liquid phase transfer hydrogenation of polycyclic derivatives of cyclopentanone with secondary alcohols in the presence of MgO catalyst.

Line No.	Substituents	Conversion [%]/Yield of Alcohol [%] ^a			
		573 K	623 K	673 K	723 K
1	-	90/89	90/89	76/68	72/43
2	- ^b	89/88	91/89	-	-
3	- ^c	62/62	68/67	54/51	39/16
4	- ^d	52/52	61/57	66/59	60/44
5	2-Me	75/74	75/73	69/62	67/44
6	3-Me	90/89	88/83	81/78	74/46
7	4-Me	89/88	85/80	78/56	78/41

^a—Reaction conditions: D/A = 8, LHSV = 3 h⁻¹, N₂ = 3 dm³ h⁻¹; ^b—Repeated test with a spent catalyst;

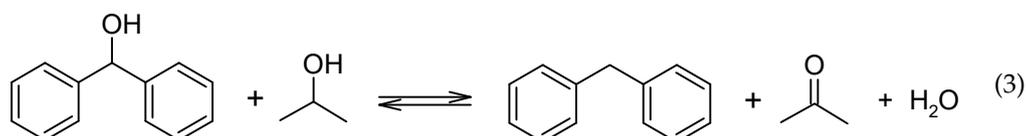
^c—D/A = 6; ^d—Ethanol as hydrogen donor.

The conversion of benzophenone and yield of alcohol observed for vapor phase transfer hydrogenation with 2-propanol as the donor at 573 K, with a donor-acceptor ratio of 8, were 90 and 89% (Table 3 line 1), respectively. When the test was performed again with

recycled MgO, the results were 89 and 88% (Table 3 line 2), respectively. When the donor-acceptor ratio was 6, the conversion of benzophenone and yield of benzhydrol dropped substantially; both were equal to 62% (Table 3 line 3). The lowest benzophenone conversion and alcohol yield (both 52%) were noted when the hydrogen donor was changed from 2-propanol to ethanol (Table 3 line 4). However, unlike the results obtained with 2-propanol, the values noted in the reaction with ethanol did not exhibit a drop at 673 K. In fact, both went up. Upon further increase in temperature (to 723 K), the conversion and the alcohol yield dropped with ethanol as the hydrogen donor.

The influence of the presence of a methyl group in the ortho position was pronounced regardless of the reaction temperature. For example, at 573 K the conversion of benzophenone dropped from 90% to 75% and the yield of alcohol decreased from 89% to 74% (Table 3 line 5). However, the discrepancy was much smaller than in the case of that observed in the liquid phase (Table 1). It is noteworthy that in the case of (3-methylphenyl) phenyl methanone (Table 3 line 6), no effect of the methyl substituent on the conversion and alcohol yield is detected in the vapor phase. A similar observation was made for (4-methylphenyl) phenyl methanone, which indicates that only the ortho position causes a steric hindrance which impedes the reaction (Table 3 line 7).

The effect of the temperature on the conversion and yield of alcohol for the studied compounds is presented in Table 3 (lines 1–7). When 2-propanol is used as the hydrogen donor, the highest conversions in the reaction for all tested ketones were observed at the temperature of 623 K. They reached 85–90%, except for the 2-methyl derivative (Table 3 line 5) for which 75% conversion was recorded. Moreover, very high (>94%) selectivities were found in the reduction of ketones to the corresponding alcohols at this temperature. As the reaction temperature increased, the conversion of all ketones dropped and the selectivity of reduction to alcohols significantly decreased, especially at the temperature of 723 K; it has been shown to be caused by a side reaction in which the primary reduction product, diphenylmethanol, undergoes a subsequent reaction with the participation of the hydrogen donor, hydrogenolysis, in which it is converted to diphenylmethane according to the equation shown below:



The water formed in the reaction interacts with the catalyst causing its partial temporary deactivation, which in turn reduces the conversion of the ketone. It was calculated that for the two higher temperatures, i.e., 673 K and 723 K, the amount of water forming was $87 \mu\text{mol}\cdot\text{h}^{-1}$ and $319 \mu\text{mol}\cdot\text{h}^{-1}$, respectively. Despite a similar conversion, a substantially lower yield of benzhydrol was noted for the higher temperature. Catalyst deactivation has been shown to be reversible in the catalytic test; upon returning to lower reaction temperatures, the catalyst regained its previous high activity.

It was observed that the selectivity of the reaction at the two higher temperatures is strongly influenced by the donor. When 2-propanol was used, a substantial drop of the selectivity to the alcohol noted when the temperature was changed from 673 K to 723 K. A smaller drop of selectivity was observed when ethanol was used as the hydrogen donor. Although the selectivity to the alcohol with both studied donors were the same (89%) at 673 K, the selectivities noted at 723 K were 60% and 73% for 2-propanol and ethanol, respectively.

The time-on-stream tests carried out at 573 K with benzophenone as the hydrogen acceptor, 2-propanol as the donor, and a D/A = 8, have shown that magnesium oxide was highly active in the reaction for 6 h in the reactant stream (Figure 6). The determined conversion over time was 90 and 88% after 1 and 6 h of the test, respectively. A similar profile was noted for the yield of diphenylmethanol, after 6 h the product was obtained

with a yield of 87%. It should be emphasized that the selectivity of the hydrogen transfer reaction was equal to 99% throughout the entire test.

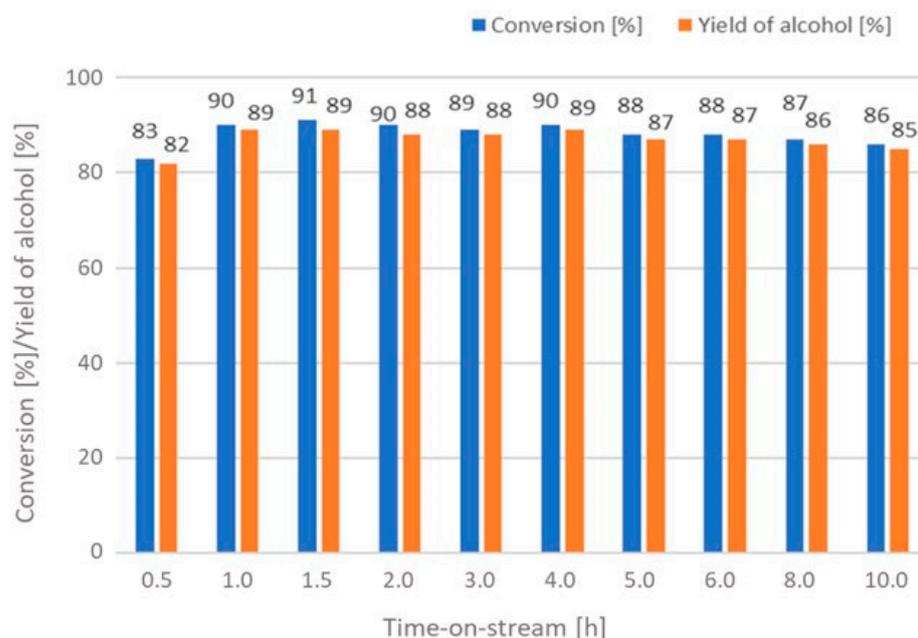


Figure 6. Vapor phase transfer hydrogenation of benzophenone with 2-propanol in the presence of MgO catalyst. Time-on-stream test. Reaction conditions: $T = 573\text{ K}$, $D/A = 8$, $LHSV = 3\text{ h}^{-1}$, $V_{N_2} = 3\text{ dm}^3\text{ h}^{-1}$.

2.4. Liquid-Phase Transfer Hydrogenation of Polycyclic Ketones

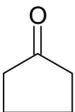
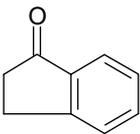
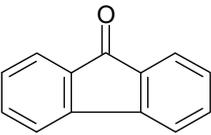
In the part of the research devoted to the transfer of hydrogen to polycyclic ketones, two groups of ketones were selected as research objects:

- cyclopentanone derivatives with one or two fused benzene rings: benzocyclopentanone (1-indanone) and dibenzocyclopentadienone (fluorenone);
- cyclohexanone derivatives with one or two fused benzene rings: benzocyclohexanone (1-tetralone) and dibenzocyclohexadienone (anthrone).

It was expected that this change in the structure of ketone molecules, i.e., hydrogen acceptors, would have an influence on the reactivity of their carbonyl groups in the reaction. Moreover, the lower acidity of hydrogen atoms in the α position in the case of monobenzocycloalkenones, was expected to cause an increase in the selectivity of the reaction towards the formation of the appropriate carbinols. In order to assess the reactivity of the selected ketones, their reactivity in the hydrogen transfer reaction was carried out in the liquid phase and it was compared with the reactivity of cyclopentanone and cyclohexanone, respectively, under these conditions.

Table 4 contains the value obtained for group I polycyclic ketones, i.e., the ones containing the cyclopentanone core. In the case of cyclopentanone, the conversion was 25, 39 and 48% after 1, 3, and 6 h of reaction, respectively. The yield of alcohol, however, was only 1, 2 and 3% after 1, 3 and 6 h under reaction conditions. This shows very poor selectivity towards the alcohol. In contrast, both of the ketones with fused benzene rings exhibit a much higher selectivity of the reaction towards the corresponding carbinol. The selectivity determined for benzocyclopentanone and dibenzocyclopentadienone was 98% compared to only 6% for cyclopentanone. It is noteworthy that a lack of by-products was observed in the case of benzocyclopentanone, despite the fact that its molecule contains hydrogen atoms in the α position to the carbonyl group, which could potentially undergo acid-base transformations. It is highly probable that the fusion of cyclopentanone and the benzene rings results in such a change in the charge distribution in the newly formed compound that the hydrogen atoms in the α position to the carbonyl group lose their acidic properties.

Table 4. Liquid phase transfer hydrogenation of polycyclic derivatives of cyclopentanone with secondary alcohols in the presence of MgO.

Ketone	Donor	Yield of Alcohol [%] ^a /Reaction Time [h]		
		1	3	4
	2-PrOH	1 ^b	2	3
	2-PrOH	8 ^c	12	14
	2-OctOH	43 ^c	45	45
	2-PrOH	49 ^d	74 ^c	78
	2-OctOH	82 ^c	82	78

^a—Reaction conditions: $W_{\text{MgO}} = 250 \pm 5$ mg, 3.125 mmol of ketone, D/A = 8; ^b—Conversion of cyclopentanone was 25, 39 and 48% after 1, 3 and 6 h of reaction, respectively; ^c—Selectivity into carbinol was higher than 98%; ^d—Yield after 30 min of reaction.

Fluorenone, in which two benzene rings are fused with the cyclopentanone ring, shows a much higher reactivity in the hydrogen transfer reaction to form the corresponding carbinol than benzocyclopentanone (Table 4). In the latter case, after 6 h of reaction with 2-propanol, a carbinol yield of 14% was obtained compared to a 78% yield in the reduction of fluorenone.

The impact of the hydrogen donor on the reactivity and selectivity of the reaction with the group I ketones was also studied. Both 2-propanol and 2-octanol were used as donors for the reaction with the two cyclopentanone derivatives (Table 4). In both cases, the yield of the alcohol was much higher in the reaction with 2-octanol.

The inverse relationship of reactivity to structure was noted for group II ketones (Table 5). Benzocyclohexenone showed four times lower reactivity with 2-propanol than cyclohexanone under the same conditions. After 6 h of reaction with 2-propanol, only a 14% yield of benzocyclohexenol was recorded. A similar yield of this alcohol (59%) as that of cyclohexanol (61%) was obtained by replacing 2-propanol as the donor with the much higher boiling 2-octanol. On the other hand, benzocyclohexenone was reduced to the alcohol with a higher selectivity (>98%) than cyclohexanone (81%). This proves, as in the case of benzocyclopentanone, that the fusion of the cyclohexanone molecule and the benzene ring reduces the acidity of the hydrogens at the α -carbon, thus inhibiting the possibility of the substrate aldol condensation reaction.

It was found that dibenzocyclohexadienone (anthrone) had no measurable reactivity when reacting with 2-propanol in the presence of magnesium oxide as the catalyst (Table 5). It was also impossible to observe its reactivity at a much higher temperature (454 K) obtained by changing the hydrogen donor from 2-propanol to 2-octanol. The reason for the lack of reactivity of the ketone is its transformation in the presence of the catalyst with basic properties, into its enol form that is not susceptible to reduction, which is described by Equation (4):

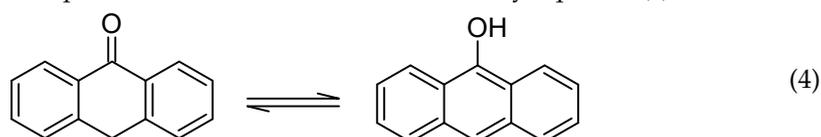
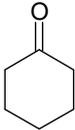
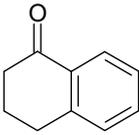
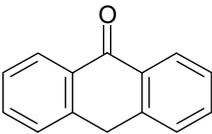


Table 5. Liquid phase transfer hydrogenation of polycyclic derivatives of cyclohexanone with secondary alcohols in the presence of MgO.

Ketone	Donor	Yield of Alcohol [%] ^a /Reaction Time [h]		
		1	3	4
	2-PrOH	52 ^b	58	61
	2-PrOH	10 ^c	13	14
	2-OcOH	53 ^c	58	59
	2-PrOH	0	-	0
	2-OcOH	0	-	0

^a—Reaction conditions: $W_{MgO} = 250 \pm 5$ mg, 3.125 mmol of ketone, D/A = 8. ^b—Conversion of cyclohexanone was 58, 68 and 75% after 1, 3 and 6 h of reaction, respectively. ^c—Selectivity into carbinol was higher than 98%.

3. Materials and Methods

3.1. Preparation of MgO and Its Characterization

The method of preparation of the catalyst can be found in [12]. The fraction of MgO used for the tests carried out in these studies was 0.40–0.63 mm for vapor and 0.16–0.40 mm for the liquid phase.

The procedures of the following characterization, such as nitrogen physisorption, X-Ray Diffraction, TG-DTA-MS measurements and determination of the acid-base sites (types and concentration [46]), along with details of the instruments, are provided in our previous publication [10].

3.2. Hydrogen Acceptors

Benzophenone (99%, Aldrich, Munich, Germany) was crystallized twice from ethanol. The purified product was 99.7% (GC) pure.

The following derivatives of benzophenone were used: 2-methyl- (98%), 3-methyl- (99%), 4-methyl- (99%), 4-chloro- (99%), 4-bromo- (98%), 4-hydroxy- (98%) and 4-methoxybenzophenone (97%), all from Aldrich. For purification, they were crystallized from ethanol or distilled under reduced pressure.

4-Fluorobenzophenone was prepared by dropping benzoyl chloride to a suspension of $AlCl_3$ as catalyst in boiling fluorobenzene (an excess) and heating the reaction mixture under reflux for 13 h. Yield of distilled product 84%, b.p. 427–9 K/15 hPa (exp), 432–4 K/17 hPa (lit), purity 99.4% (GC) (including 2.2% of 2-fluorobenzophenone), m.p. 314–318 K (exp), 320–2 K (lit).

2,4,6-Trimethylbenzophenone was synthesized in our laboratory in the reaction of benzoyl chloride with mesitylene in the presence of anhydrous $AlCl_3$ and purified by distillation under reduced pressure. Yield 73%, m.p. 308 K (exp), 307–8 K (lit), purity 99.4% (GC).

4-Nitrobenzophenone was prepared by acylation of benzene with 4-nitrobenzoyl chloride in the presence of anhydrous $AlCl_3$. A crude product was mixed with charcoal and crystallized thrice from methanol-toluene solution. Yield 54%, m.p. 408–409 K (exp), 404–6 K (lit), purity 99.0% (GC).

Fluorenone (98%, Aldrich) (dibenzocyclopentadienone) was crystallized twice from ethanol, mp. 355 K (exp), 355–6 K (lit), purity 99.1% (GC).

1-Indanone (>99%, Aldrich) (benzocyclopentenone) was distilled under reduced pressure b.p. 390-1 K/15 hPa (exp), 387-8 K/13 hPa (lit), solidifies upon standing, m.p. 313-4 K (exp), 314-6 K (lit), purity 99.3% (GC).

1-Tetralone (>97%, Aldrich) (benzocyclohexenone) was distilled under reduced pressure, b.p. 396-8 K/15 hPa (exp), 394-5 K/13 hPa (lit), final purity 98.3% (GC).

Anthrone (dibenzocyclohexadienone) was obtained by reduction of anthraquinone (97%, Aldrich) with metallic tin and hydrochloric acid in boiling acetic acid as a solvent according to procedure described in [47]. The crude product mixed with charcoal was crystallized twice from a mixture of benzene-*n*-hexane (3: 1 *v/v*), m.p. 427-9 K (exp), 429 K (lit), purity 98.9% (GC).

3.3. Hydrogen Donors

The hydrogen donor in each reaction was one of the following commercially available alcohols: ethanol (anhydrous, p.a., 99.8%), propan-2-ol (p.a., 99.8%) both from POCh Poland (Gliwice, Poland), 2-butanol (>99%), 2-pentanol (98%) and 2-octanol (97%), all three from Aldrich. Their purification has been described by us before [12]. The final purities of the last two alcohols were 98.9 and 98.4%, respectively. 2-Heptanol, 3-heptanol and 4-heptanol were prepared by the reduction of the appropriate ketones with sodium borohydride in a water-methanol solution. After fractional distillation through a 50 cm long Vigreux column their purities exceeded 99.5, 98.9 and 99.4% (GC), respectively. All distilled alcohols were kept dry in Schlenk-type containers under nitrogen.

3.4. Catalytic Activity Measurements

In both modes of reaction, the transfer of the hydrogen is reversible. The values obtained from the GC determinations are therefore the resultant numbers of both the forward and backward reaction.

Vapor phase. The experiments were carried out in a tubular glass reactor which contained a fixed-bed with 250 ± 5 mg of MgO. A protective atmosphere was used when placing the catalyst in the reactor, as well as when ramping the temperature. The measurements were conducted between 573–723 K. After the desired temperature stabilized, the reagents were supplied to the reactor with a microdosing pump (LHSV = 3 h⁻¹). The molar ratio of the hydrogen acceptor and hydrogen donor in the solution was 1:8. The conversion was determined based on the composition of the reaction products after 60 min of reaction. The reason for the delay was the fact that the catalyst is very active at the beginning and produces approximately 10% of products of aldol condensation of 2-octanone, but decreases sharply with the time of reaction and after 30 or so minutes it is no more than 1% and a steady state is reached. In order to get a representative sample, the products were collected for 30 min and then tested.

Liquid phase. The tests were performed in a glass reactor, whose description has been given elsewhere [38], into which approximately 250 mg (± 5 mg) of MgO was poured. Also for this mode of reaction a protective atmosphere was used when introducing the catalyst into the reactor. Next, the alcohol, ketone (usually 3.125 mmol) and internal standard were sequentially added to the reactor along with a magnetic bar, and the reactor was placed in a hot oil bath thermostat. The time of the beginning of the reaction was determined based on when the boiling point of the stirred mixture was reached. The side arm of the reactor was used to obtain samples for analysis (c.a. 0.05 cm³). After centrifuging (20 min, 3200 rpm) the liquid from above the catalyst was introduced into the gas chromatograph.

Tests with recycled catalyst. In order to determine if the catalyst loses its activity in the reaction over time, the catalyst was recycled. After performing a 6 h test, the reactor was emptied and its content was centrifuged in order to remove as much of the liquid as possible. Without any additional treatment, the spent catalyst was suspended in a known volume of hydrogen donor and transferred back to the reactor. A known amount of benzophenone was added and the test was repeated. Such procedure was applied three times.

Scaling-up. In a two-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser, 10.1 g (0.25 moles) of a freshly calcined MgO catalyst (0.10–0.25 mm of grain diameter) was loaded and mixed with 130.2 g (1 mole, 159 cm³) of 2-octanol. Benzophenone (22.8 g, 0.125 moles) was added in one portion to the suspension under stirring. The flask was heated in an electric mantle and the mixture was refluxed for 6 h. The extent of reaction was monitored by GC. After cooling to room temperature, the reaction mixture was separated by centrifuging and the catalyst was washed with diethyl ether (3 × 20 cm³). The washings were added to a main organic fraction and the solvent was distilled off. The residue was distilled under reduced pressure until the temperature of the vapors reached 383 K at 27 hPa. The crude product (23.5 g) was crystallized from ethanol, yield 20.5 g (89%), m.p. 336–7 K (exp), 338 K (lit).

3.5. Analytical Determinations

The identification and quantification of each of the reaction products was performed by GC using a high-resolution gas chromatograph (KONIK, Barcelona, Spain) with a TRACER WAX capillary column (l = 30 m, i.d. = 0.25 mm) and Flame Ionized Detector. High boiling ketones like 4-nitrobenzophenone, 2-naphthyl phenyl ketone, anthrone and fluorenone, and the products derived from them were analyzed using a chromatograph (HP-6890, Hewlett-Packard, Palo Alto, CA, USA.) equipped with HP-1 column (length 60 m, 0.25 mm i.d.), FID. The compounds were identified by GC-MS (HP-6890N with a 5973N mass detector, Palo Alto, CA, USA.) and by comparison of the retention time with that of a standard sample. Tetradecane, *t*-butylbenzene or 1,3,5-tri-*i*-propylbenzene were used as the internal standard for quantitative analysis.

4. Conclusions

Both vapor and liquid phase transfer hydrogenation of aromatic ketones with the use of secondary alcohols as the hydrogen donors has been successfully performed. It has been found that in the presence of MgO benzophenone is selectively reduced in a liquid phase by secondary aliphatic alcohols to benzhydrol with the yield, which itself depends strongly on several factors. Various secondary alcohols from 2-propanol to 2-octanol, whose boiling points range from 355 to 454 K have been investigated in this reaction. Quantitative yields of benzhydrol (98–99%) have only been observed for 2-octanol, the highest boiling hydrogen donor used. By changing the 2-octanol-benzophenone molar ratio, at a given duration of reaction (6 h), it was found that the maximum yield of benzhydrol is reached for D/A equal to 8. Altering the amount of catalyst used, the optimal mass was determined to be 250 mg for 3.125 mmol of the starting ketone. These conditions were used for the scale up. It has also been shown that the catalyst can be reused up to four times with no substantial loss of conversion or selectivity.

Different derivatives of benzophenone with single substituents were used to study the impact of the type and position of the substituent on the activity and selectivity of the reaction. In short, the highest activity was noted for the unsubstituted ketone and all substituents lower the activity to a different extent. From the three studied halogens, fluorine exerted the most pronounced effect on the yield of the alcohol. The presence of a methoxy group in the para position caused a decrease of the yield of alcohol, whereas the presence of an OH group renders the ketone completely unreactive. The side reactions were studied in detail for the Br-substituted benzophenone. It was shown that the choice of the hydrogen donor had a pronounced influence on the selectivity. The highest activity and selectivity were observed for 2-octanol.

In the vapor phase studies it was demonstrated that in the lower region of the studied reaction temperatures (573–623 K) high conversions of benzophenone and its 3- and 4-methyl derivatives (85–90%), as well as high selectivities to the appropriate carbinols can be attained. The time-on-stream test showed that magnesium oxide exhibits stable activity and excellent selectivity in vapor phase transfer hydrogenation of benzophenone with 2-propanol.

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