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R = aryl, alkyl

[Rh(dppp)₂]Cl

Ionic liquids

$$R\text{-CHO} \xrightarrow[\text{Ionic liquids}]{[Rh(dppp)_2]Cl} R\text{-H} + CO$$

Yield up to >99%
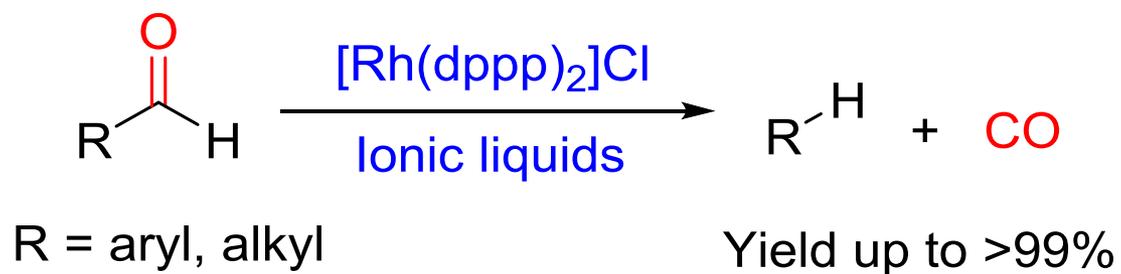
Ionic liquids as recyclable and separable reaction media in Rh-catalyzed

decarbonylation of aromatic and aliphatic aldehydes

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Abstract

Ionic liquids (ILs) have been applied as recyclable reaction media in the decarbonylation of aldehydes in the presence of a rhodium-phosphine complex catalyst. The performance of several new catalytic systems based on imidazolium-based ILs and $[Rh(dppp)_2]Cl$ (dppp: 1,3-diphenylphosphinopropane) were excellent in the decarbonylation of both aromatic and aliphatic aldehydes providing >99 yield of benzenes and alkanes, respectively. The catalytic performance depended, however, strongly on the employed IL and its thermal stability. In addition, the ILs afforded good catalyst immobilization as well as a biphasic system with the product allowing recovery and reuse of the employed catalyst.

Keywords: Aldehydes; decarbonylation; rhodium; ionic liquids; homogeneous catalysis.

1. Introduction

Selective catalytic decarbonylation is an important transformation in both synthetic chemistry and biology enabling oxygen removal from aldehydes as carbon monoxide (CO) [1-4]. Such catalytically obtained CO may find use in organic tandem reactions as *in-situ* source of CO, thus avoiding hazardous CO gas as an external reagent [5-

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11]. Additionally, selective decarbonylation can be a viable method for upgrading carbohydrates and furfurals (e.g., 5-hydroxymethylfurfural) into bio-fuels as well as intermediate structures and chemical building blocks in bio-refineries [12].

The decarbonylation reaction was conducted successfully for the first time in the early 1960's by cleaving organic molecules with stoichiometric amounts of Wilkinson's rhodium complex catalyst, [RhCl(PPh$_3$)$_3$], under mild conditions [13,14]. This approach required large amounts of reactants and the catalyst could not be reused. Later significantly improved catalytic performance was shown to be obtained with the catalyst system at elevated temperatures in high boiling solvents, where CO abstraction from the rhodium center is facilitated [15]. Recently, the development of more proficient homogeneous Rh decarbonylation catalysts has been thoroughly investigated by Madsen and co-workers [17-19]. Here it was found that that a superior - but not recoverable - catalytic system could be obtained with two equivalents of dppp (1,3-diphenylphosphinopropane) phosphine ligand and one equivalent of [Rh(COD)Cl]$_2$ (COD: 1,5-cyclooctadiene) in diglyme as reaction media, when the reaction was completed at temperatures above 165 °C. Subsequently, good results with alternative catalyst systems based on Ir complexes and other ligands have also been reported [20-23].

The recovery and recycling of the catalysts is still a challenge in homogeneous catalysis [24]. This is also the case for Rh-catalyzed decarbonylation reaction where - to the best of our knowledge – only Blum et al. have reported so far a sol-gel entrapped catalyst that could be recycle up to seven times without any loss of activity in aldehydes decarbonylation [25]. The use of ILs has emerged as a promising alternative in order to overcome the problems associated to homogeneous catalysis. Ionic liquids have in several reactions been demonstrated to be viable reaction media

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where catalyst immobilization is facilitated by phase-separation of the IL-catalyst phase and the product phase, including Rh-catalyzed alkene hydroformylation [26] and methoxycarbonylation [27]. Beside catalyst separation, such IL reactions are in many cases also more benign and green compared to traditional processes using organic solvents due to inherent IL properties such as, e.g. negligible vapor pressure, good thermal stability and tunable coordination properties [28]. Furthermore, ILs can also relatively easy be designed to accommodate functional groups which can provide the ILs with auxiliary reactivity [29].

In this study, we present for the first time the use of ILs as reaction media in the Rh-phosphine complex catalyzed decarbonylation of aromatic and aliphatic aldehydes to make benzene derivatives and alkanes, respectively (Scheme 1). Furthermore, it is demonstrated that the use of an IL yields a biphasic system which can be recovered and reused in successive reaction cycles.
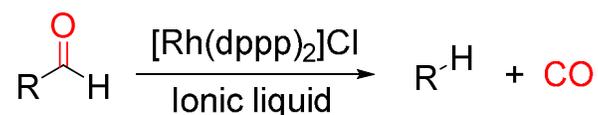
Scheme 1. Decarbonylation reaction with IL catalyst system.

2. Experimental

2.1 Materials

All chemicals were purchased from Sigma-Aldrich and used without purification unless otherwise noted, including the ILs. The precursor metal compound [Rh(dppp)$_2$]Cl used for catalyst preparation were prepared under an inert atmosphere of Argon (grade 5.0, Air Liquide) as described in literature [28].

2.2 Catalytic reactions

A 10 ml flask was charged with 1.0 ml of IL (or solvent) and the desired amount of [Rh(dppp)$_2$]Cl was subsequently added to obtain a chosen metal loading. The solution was then stirred for initially 30 min to ensure complete solvation, where after 55 µl mesitylene (internal standard) was added and the mixture stirred for another 1 h at 165 °C with a water cooling unit preventing evaporation of the mesitylene. The aldehyde substrate was then added to the reaction mixture and left for a desired time period under continuous stirring. After reaction, 3 ml of deionized water and 3 ml of diethylether were added to the IL mixture, the ethereal phase decanted off and dried with magnesium sulfate and finally analyzed by GC-FID (HP 5890 Series II chromatograph, SGE BP1 non-polar 100% dimethyl polysiloxane capillary column 50 m x 0.32 mm x 0.25 mm). Standard curves with authentic products and mesitylene (internal standard) were used to quantify product yields.

2.2 Recycling experiments

The recycling experiments where performed as the regular catalytic reactions, but at the end of each reaction run the product was separated and the remaining substrate and/or products in the IL phase were extracted with diethylether. The yield and conversion were calculated by means of GC-FID analysis. The IL-catalyst solution was subsequently applied directly for the next reaction run.

3. Results and Discussion

The decarbonylation of aldehydes was conducted in batch reactions at 165 °C in runs of 8 h or 24 h using catalyst systems composed of imidazolium-based ILs and [Rh(dppp)$_2$]Cl as pre-catalyst. This pre-catalyst was chosen because it has been reported to facilitate decarbonylation of aldehydes in a wide variety of solvents and temperatures [12-15,17-19]. The product yield was found to depend both on the IL composition, catalyst concentration and substrate as reported below.

3.1 Influence of the ionic liquid composition

Five ILs (Scheme 2) were tested in the decarbonylation of *p*-toulaldehyde to produce toluene from *p*-toluladehyde using 3 mol% of the prepared [Rh(dppp)$_2$]Cl complex as pre-catalyst. The results are depicted in Figure 1.
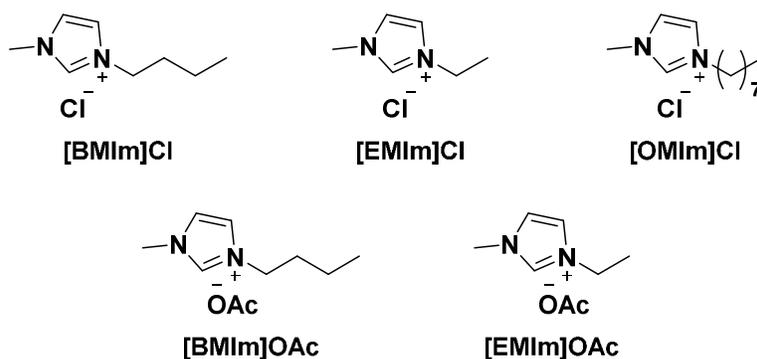
Scheme 2. ILs tested in the studied decarbonylation reaction ([BMIm]: 1-butyl-3-methylimidazolium, [EMIm]: 1-ethyl-3-methylimidazolium, [OMIm]: 1-methyl-3-octylimidazolium).

The highest reaction rate and product yield (48%) was achieved when [BMIm]Cl was used as reaction media and the lowest yield (16%) when [BMIm]OAc was applied. By changing the IL cation from [BMIm]$^+$ to [EMIm]$^+$ a similar trend in rate and yield was

observed with Cl^- as anion (30% yield) compared to using OAc^- as anion (23% yield). The better performance of the chloride-based ILs can most be attributed to the higher thermal stability of these ILs (see supporting information, S1), which will ensure that the active complex remains solubilized. Concerning the alkyl chain length in the imidazolium moiety, the best result (48%) was obtained for the chlorides with the $[BMIm]^+$ cation having an intermediate chain length. For the acetates the $[EMIm]^+$-based IL gave higher yield than the $[BMIm]^+$-based (23 and 16 %, respectively).
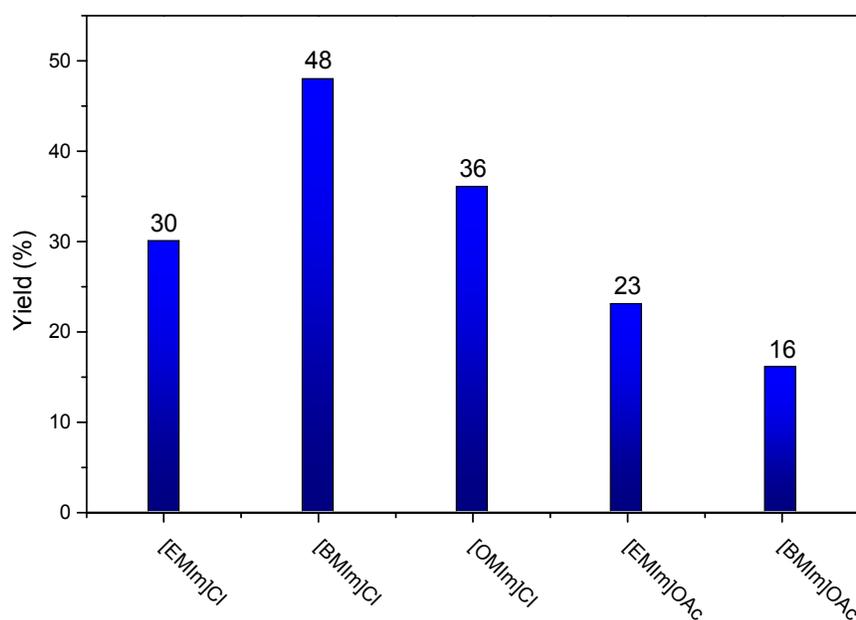

Figure 1. Decarbonylation of *p*-tolualdehyde in different ILs. Reaction conditions: IL (1 ml), aldehyde (8.5 mmol), mesitylene (0.4 mmol), 3 mol% [Rh(dppp)$_2$]Cl, 165 °C, 8 h.

3.2 Influence of the catalyst loading and the substrate

Decarbonylation of *p*-tolualdehyde was next performed with different amounts of [Rh(dppp)$_2$]Cl pre-catalyst in [BMIm]Cl to examine the effect of catalyst loading. The [BMIm]Cl was selected for further use as it proved superior in the initial IL screening (vide infra). The obtained results are showed in Table 1. As expected, the yield of

toluene increased gradually from 20 to >99 % when the amount of added catalyst was increased from 2 to 5 mol% in 8 h reactions (Table 1, entries 1-4). Furthermore, the IL system proved more efficient than the analogous system based on diglyme, which is the best performing decarbonylation system reported so far [18]. Hence, after 24 h of reaction 80 % toluene yield was obtained with the ILs system, whereas only 71 % was achieved with pure diglyme (Table 1, entries 5 and 7). A mixture of [BMIm]Cl and dyglyme (1:1 volume) was further selected as reaction media in order to facilitate generation of a biphasic mixture that could allow ease separation of the product. Here a comparable product yield of only 56 % was obtained after 24 h of reaction (Table 1, entry 6), suggesting the interphase reaction to be significantly slower than both the reaction with IL solvent and the one with diglyme. Importantly, the reaction mixtures where IL were present seemed to provide more stable Rh-complex catalyst systems than the system with diglyme alone, where darkening of the solution, due to Rh catalyst decomposition, was clearly observed after reaction (Figure 2).

Table 1. Decarbonylation of aldehydes in different reaction media[a]

Entry	Catalyst (mol%)	Solvent	Substrate	Yield (%)
1	2	[BMIm]Cl	*p*-tolualdehyde	20
2	3	[BMIm]Cl	*p*-tolualdehyde	48
3	4	[BMIm]Cl	*p*-tolualdehyde	97
4	5	[BMIm]Cl	*p*-tolualdehyde	>99
5[b]	1	Diglyme	*p*-tolualdehyde	71
6[b,c]	1	Diglyme:[BMIm]Cl	*p*-tolualdehyde	56
7[b]	1	[BMIm]Cl	*p*-tolualdehyde	80

8	3	[BMIm]Cl	*o*-tolualdehyde	>99
9	3	[BMIm]Cl	*m*-tolualdehyde	>99
10	3	[BMIm]Cl	*p*-anisaldehyde	62
11	3	[BMIm]Cl	1-nonanal	>99

[a] Reaction conditions: Solvent (1 ml), aldehyde (8.5 mmol), mesitylene (0.4 mmol), catalyst [Rh(dppp)$_2$]Cl, 165 °C, 8 h. [b] 24 h reaction as in ref. 18; [c] [BMIm]Cl:diglyme = 1:1.

Figure 2. Pictures of the post-reaction mixtures with only [BMIm]Cl (left), 1:1 mixture of diglyme:[BMIm]Cl (middle) and pure diglyme (right).

In order to evaluate the steric and electronic influence of the substrates in the decarbonylation reaction, alternative aromatic aldehydes were also tested with the [BMIm]Cl-catalyst system (Table 1,entries 8-10). To enable direct comparison of the catalyst activity with the different substrates the catalyst loading was selected to be 3 mol% to provide moderate yields like obtained in the case of *p*-tolualdehyde (48 %, Table 1, entry 2). The best results were obtained with *o*-tolualdehyde and *m*-tolualdehyde, where almost quantitative yield was achieved (Table 1, entries 8 and 9). The comparable yield obtained with a more electron-donating methoxy-group substituted in the para position was 62 % (Table 1, entry 10). These results suggest that substitution in the *ortho*- and the *meta*-positions induce steric hindrance, which eases the migratory extrusion step in the decarbonylation mechanism (as well as the reductive elimination step) that has been proposed to be the rate determining with the applied catalyst [17].

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The Rh-based catalyst system could also be applied in decarbonylation of aliphatic aldehydes, as exemplified for 1-nonanal where an excellent yield of >99 % 1-octane was obtained under the same reaction conditions used to obtain toluene from *ortho-* and *meta*-tolualdehyde (Table 1, entry 11).

3.3 Catalyst recyclability

One of the major issues in homogeneous catalysis is the recovery and reutilization of the normally expensive precious metal catalyst. With this in mind, we examined the recyclability of the [BMIm]Cl IL-catalyst system in three consecutive experiments with *p*-tolualdehyde and 5 mol% of the Rh catalyst. The results are shown in Figure 3.
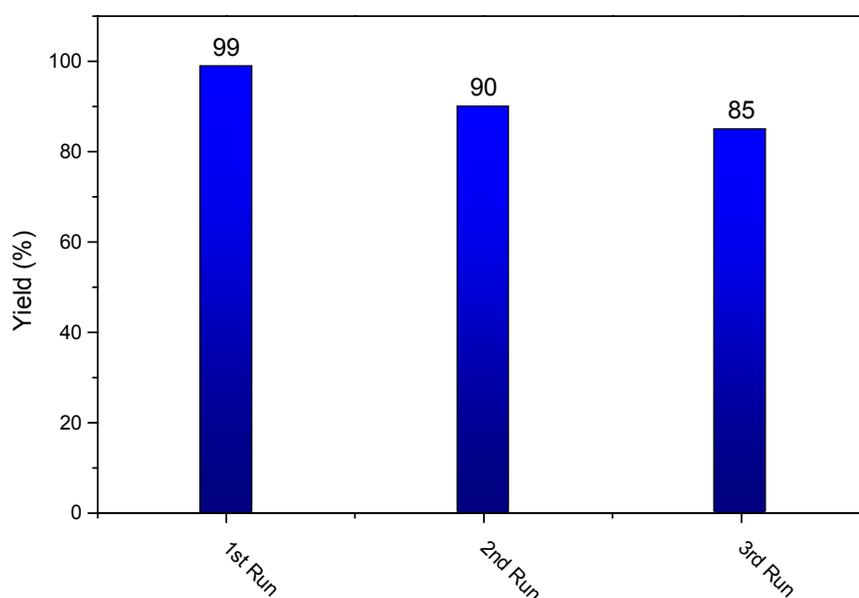

Figure 3. Recyclability of the IL catalytic system in the decarbonylation of *p*-tolualdehyde. Reaction conditions: [BMIm]Cl (1 ml), *p*-tolualdehyde (8.5 mmol), mesitylene (0.4 mmol), 5 mol% [Rh(dppp)$_2$]Cl, 165 °C, 8 h.

As it is shown, the catalytic system could be recovered and reused for the three consecutive reactions. The gradual observed drop in conversion upon reuse could be

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attributed to loss of IL and therefore catalyst during the IL phase recovery. The use of the IL provided a biphasic system due to immiscibility of the product in the IL phase and efficient catalyst immobilization. At this point, it is worthy to point out that no signs of decomposition of the ionic liquid (BMimCl) were evidenced by ^{1}H NMR analysis just comparing a pure sample of the employed ionic liquid and the re-used ionic liquid phase (see supporting information S2 and S4). In addition, no ionic liquid was found in the ether phase after extraction, thus ensuring a good recyclability and immobilization of the catalyst in the ionic liquid phase (see supporting information S2 and S3). In Figure 4, a picture of the orange colored IL phase after the three reaction cycles is shown. Since, no sign of catalyst decomposition or Rh black are observed it can be assumed that the IL stabilizes the catalytic species involved in the reaction.

Figure 4. [BMIM]Cl-catalyst phase after three reaction cycles in the decarbonylation of *p*-tolualdehyde.

4. Conclusions

Ionic liquids have been applied as reaction media for the first time in the homogeneous decarbonylation of aldehydes with [Rh(dppp)$_2$]Cl as catalyst. The performance of the catalytic system with [BMIm]Cl was excellent in the decarbonylation of both aromatic and aliphatic aldehydes allowing to obtain >99 % product yield. Five different ILs were tested at similar reaction conditions and their

catalytic performance correlated with thermal stability and ion composition demonstrating both the anion and the cation to play a role. Furthermore, the ILs provided a biphasic system with excellent catalyst immobilization allowing recovery and successful reuse of the IL-catalyst system at least three times. Notably, during these consecutive runs the product was easily obtained by decantation without impurities. In perspective, selective decarbonyaltion with ILs as reaction and separable media could potentially be implemented as a key methodology to remove oxygen in biomass valorization.

Acknowledgements

References

(1) T. M. Cheesbrough, P. E. Kolattukudy *Proc. Natl. Acad. Sci. USA* 1984, **81**, 6613-6617.

(2) M. Dennis, P. E. Kolattukudy *Proc. Natl. Acad. Sci. USA* 1992, **89**, 5306-5310.

(3) A. Schirmer, M. A. Rude, X. Li, E. Popova, S. B. del Cardayre *Science* 2010, **329**, 559-562.

(4) D. Das, B. E. Eser, J. Han, A. Sciore, E. N. G. Marsh *Angew. Chem. Int. Ed.* 2011, **50**, 7148-7152.

(5) C. M. Jensen, K. B. Lindsay, R. H. Taaning, J. Karaffa, A. M. Hansen, T. Skrydstrup *J. Am. Chem. Soc.* 2005, **127**, 6544-6545.

(6) G. K. Min, D. Hernandez, A. T. Lindhardt, T. Skrydstrup *Org. Lett.* 2010, **12**, 4716-4719.

(7) P. Hermange, A.T. Lindhardt, R. H. Taaning, K. Bjerglund, D. Lupp, T. Skrydstrup *J. Am. Chem. Soc.* 2011, **133**, 6061-6071.

(8) S. T. Friis, R. H. Taaning, A. T. Lindhart, T. Skrydstrup *J. Am. Chem. Soc.* 2011, **133**, 18114-18117.

(9) K. Bjerglund, A. T. Lindhardt, T. Skrydstrup *J. Org. Chem.* 2012, **77**, 3793-3799.

(10) D. U. Nielsen, K. Neumann, R. H. Taaning, A. T. Lindhardt, A. Modvig, T. Skydstrup *J. Org. Chem.* 2012, **77**, 6155-6165.

(11) A. T. Lindhardt, R. Simonssen, R. H. Taaning, T. M. Gogsig, G. N. Nilsson, G. Stenhagen, C. S. Elmore, T. Skrydstrup *J. Label Compd. Radiopharm.* 2012, **55**, 411-418.

(12) R. N. Monrad, R. Madsen *J. Org. Chem.* 2007, **72**, 9782-9785.

(13) J. Tsuji, K. Ohno, *Tetrahedron Lett.* 1965, **6**, 3969-3971.

(14) K. Ohno, J. Tsuji*, J. Am. Chem. Soc.* 1968, **90**, 99-107.

(15) D. H. Doughty, L. H. Pignolet, *J. Am. Chem. Soc.* 1978, **100**, 7083-7085.

(16) C. M. Beck, S. E. Rathmill, Y. J. Park, J. Chen, R. H. Crabtree, *Organometallics* 1999, **18**, 5311-5317.

(17) P. Fristrup, M. Kreis, A. Palmelund, P.-O. Norrby, R. Madsen, *J. Am. Chem. Soc.* 2008, **130**, 5206-5215.

(18) E. Taarning, R. Madsen, *Chem. Eur. J.* 2008, **14**, 5638-5644.

(19) M. Kreis, A. Palmelund, L. Bunch, R. Madsen *Adv. Synth. Catal.* 2006, **348**, 2148-2154.

(20) F. M. A. Geilen, T. Vom Stein, B. Engendahl, S. Winterle, M. A. Liauw, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* 2011, **50**, 6831-6834.

(21) T. Iwai, T. Fujihara, Y. Tsuji, *Chem. Commun.* 2008, 6215-6217.

(22) S. Maetani, T. Fukuyama, N. Suzuki, D. Ishihara, I. Ryu, *Chem. Commun.* 2012, **48**, 2552-2554.

(23) A. Modak, A. Deb, T. Patra, S. Rana, S. Maity, D. Maiti, *Chem. Commun.* 2012, **48**, 4253-4255.

(24) D.J. Cole-Hamilton, R.P.Tooze (Eds.), Catalysis by Metal Complexes "Homogeneous Catalysis-Adventages and Problems", volume 30, pp 1-8, Springer-Netherlands, **2006**.

(25) S. Dahoah, Z. Nairoukh, M. Fanun, M. Schwarze, R. Schomäcker, J. Blum, *Journal of Molecular Catalysis A: Chemical*, 2013, **380**, 90-93.

(26) M. Haumann, A. Riisager, *Chem. Rev.*, 2008, **108**, 1474-1497.

(27) E. J. Garcia-Suarez, S. G. Khokarale, O. N. Van Buu, R. Fehrmann, A. Riisager, *Green Chem.* 2014, **16**, 161-166.

(28) P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley, 2007.

(29) B. R. James, D. Mahajan, *Can. J. Chem.* 1979, **57**, 180 -187.

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