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Green and Diasteroselective Oxidative Cyclization of Bisnaphthols to Spirans

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Hydrogen peroxide/MoO_3, as an efficient and clean oxidizing system was used to afford diasteroselective oxidative cyclization of bisnaphthols to spirans in ethanol at 60 °C with high yields. Bisnaphthols were prepared by the reaction of a series of aldehydes and 2-naphthol in the presence of a catalytic amount of $H_3[P(Mo_3O_{10})_4].nH_2O$ (HPA) in refluxing dichloromethane.

Keywords: Bisnaphtols, Spirans, MoO_3, Hydrogen peroxide, HPA

INTRODUCTION

Oxidative cyclization of bisnaphthols [aryldi-(2-hydroxy-1-naphthyl)methanes] (**1**) to spirans {arylnaphtho[2,1-*b*]furan-2(1H)-spiro-1'(2'H)-naphthalen-2'-one} (**2**,**3**) (Scheme 1) is an important reaction in biosynthesis of certain plant products [1]. Several oxidizing reagents for oxidation of bisnaphthols have been used to afford spirans. Dischendorfer used alkaline hypobromite to oxidize the bisnaphthol to a compound shown to be the spiran (**2**) in which the phenyl substituent was on the side of the molecule away from the carbonyl group [2]. It was also shown that some oxidants could produce the geometrical isomer (**3**) with the phenyl substituent on the same side as the carbonyl group [3]. Such a control over the stereochemistry is quite novel in oxidative cyclizations. Dean and co-workers discovered that a few oxidants were highly specific for one geometrical isomer or the other, though many had no specificity [4]. In their extended study, a selection of oxidants was used whose results showed that the reagents commonly used for phenolic coupling (and also peroxidase) had little specificity. It was also revealed that specificity was associated with "two-electron" oxidants operating through what are in fact substitution reactions rather than with "one-electron" oxidants [4]. A literature survey revealed that there was no report on utilizing green oxidants to afford spirans and therefore, using a green oxidizing agent such as H_2O_2 for this oxidation reaction would be desirable.

Aqueous hydrogen peroxide is an attractive oxidant because it is cheap, safely stored and handled, environmentally friendly, contains effective oxygen and produces only water as a byproduct, which is easy to deal with after reactions. There are many reports on oxidation reactions carried out by a combination of H_2O_2, and a catalyst that often increase the efficiency of the oxidant.

Aryldi-(2-hydroxy-1-naphthyl)methanes (**1**) have been synthesized by the reaction of aldehydes with 2-naphthol in the presence of acids [6]. On the other hand, aryldibenzoxanthenes have been synthesized without the intermediacy of aryldi-(2-hydroxy-1-naphthyl)methanes by heating the corresponding aldehydes and 2-naphthol in acetic acid/hydrochloric acid [7] or in the presence of a catalyst under neat conditions [8]. Despite these references for the preparation of dibenzoxanthenes, the literature survey shows that there are few reports on the synthesis of aryldi-(2-hydroxy-1-naphthyl)methanes from aldehydes and 2-naphthol. In continuation of our research on the oxidation of organic compounds [8], we report here our experiments in developing

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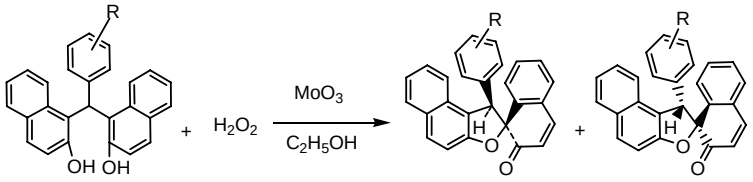


1 **2** **3**

Scheme 1

new procedures for oxidation of aryldi-(2-hydroxy-1-naphthyl)methanes (**1**) using our oxidizing system [5], aqueous hydrogen peroxide catalyzed by MoO_3 (Scheme 1).

EXPERIMENTAL

General Procedure for the Preparation of Bisnaphthols from 2-Naphthol in the Presence of HPA

In a round bottomed flask (25 ml) equipped with a condenser, a mixture of 2-naphthol (2 mmol), aldehyde (1 mmol) and HPA (0.04 mmol) in 1 ml dichloromethane was stirred magnetically at 40 °C for the time specified in Table 1. The progress of the reaction was followed by TLC. After the completion of the reaction, water (20 ml) was added to the reaction mixture and filtered. The solid residue was purified on a silica gel plate (eluent:n-hexane/EtOAc:10/3) to afford the pure bisnaphthol in excellent yield.

General Procedure for the Preparation of Spirans from Bisnaphthol with H_2O_2/MoO_3 System as Oxidizing Agent

In a round bottomed flask (50 ml) equipped with a condenser, a solution of substituted benzylidene-1,1'-bis-2-naphthol (1 mmol) in ethanol (1.5 ml) was prepared. Then, 30% H_2O_2 (1 ml), and MoO_3 (1 mmol) were added. The mixture was stirred magnetically at 60 °C for the appropriate time. The progress of the reaction was followed by TLC. After the completion of the reaction, water (20 ml) was added to the reaction mixture and filtered. The solid residue was recrystallized from EtOH to afford the pure product.

Selected spectroscopic data of spirans:

(Table 3, Entry 1):

Compound **2a**: IR (neat): 1677, 1628, 1484, 1459, 1248, 1088, 1024 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm): 5.4 (s, 1H), 6.5 (d, 1H), 7.0-7.9 (m, 15H). Compound **3a**: IR (neat): 1670, 1616, 1482, 1455, 1238, 1078, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm): 5.2 (s, 1H), 5.6 (d, 1H), 7.0-7.8 (m, 15H); ^{13}C NMR ($CDCl_3$) δ (ppm): 197.9, 158.8, 143.5, 136.5, 133.7, 131.1, 130.3, 130.2, 129.4, 129.0, 128.7, 127.9, 126.8, 125.3, 124.0, 123.2, 122.5, 117.8, 117.1, 111.8, 94.9, 63.9.

(Table 3, Entry 2):

Compound **2b**: IR (neat): 1680, 1628, 1462, 1372, 1043, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm): 5.9 (s, 1H), 6.3 (d, 1H), 6.4 (d, 1H), 7.0-8.0 (m, 14H); ^{13}C NMR ($CDCl_3$) δ (ppm): 198.2, 158.5, 145.0, 143.3, 134.8, 134.3, 134.0, 132.7, 131.2, 130.2, 129.4, 129.3, 129.0, 128.9, 128.8, 127.1, 124.6, 123.8, 123.4, 122.3, 119.9, 117.5, 94.5, 58.3. Compound **3b**: IR (neat): 1680, 1628, 1462, 1372, 1043, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm): 5.6 (s, 1H), 5.8 (s, 1H), 6.7 (d, 1H), 7.0-8.0 (m, 14H); ^{13}C NMR ($CDCl_3$) δ (ppm): 198.2, 158.5, 145.0, 143.3, 134.8, 134.3, 134.0, 132.7, 131.2, 130.2, 129.4, 129.3, 129.0, 128.9, 128.8, 127.1, 124.6, 123.8, 123.4, 122.3, 119.9, 117.5, 94.5, 58.3.

(Table 3, Entry 5):

Compound **2e**: IR (neat): 1674, 1622, 1454, 1370, 1038, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm): 6.0 (s, 1H), 6.2 (d, 1H), 6.4 (d, 1H), 7.1-7.9 (m, 14H); ^{13}C NMR ($CDCl_3$) δ (ppm): 198.4, 158.8, 145.3, 143.7 135.0, 134.6, 134.5, 132.9, 131.5, 130.5, 129.6, 129.4, 129.2, 129.0, 128.9, 127.4, 124.9, 124.5, 123.9, 123.6, 123.3, 122.5, 120.2, 117.8, 94.7, 58.5. Compound **3e**: IR (neat): 1674, 1622, 1454, 1370, 1038, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm): 5.6 (d, 1H), 5.8 (s, 1H), 6.7 (d, 1H), 7.1-7.9 (m, 14H); ^{13}C NMR ($CDCl_3$) δ (ppm): 198.6, 158.9, 145.5, 143.9, 135.2, 134.8, 134.9, 133.1, 131.6, 130.8, 129.8, 129.5, 129.5, 129.1, 129.0, 127.7, 125.1, 124.6, 124.2, 123.8, 123.4, 122.6, 120.3, 117.8, 94.9, 58.9.

(Table 3, Entry 7):

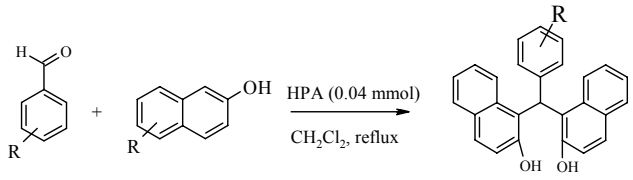
Compound **2g**: IR (neat): 1685, 1630, 1465, 1370, 1040, 1028 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm): 2.2 (s, 3H), 5.4 (s, 1H), 6.3

(d, 1H), 7.0-7.9 (m, 15H); ^{13}C NMR ($CDCl_3$) δ (ppm): 198.5, 158.9, 145.6, 143.1, 138.8, 136.6, 134.6, 131.0, 130.5, 130.1, 129.3, 129.0, 128.9, 128.5, 128.2, 127.9, 127.5, 126.6, 124.8, 123.0, 122.9, 116.7, 111.7, 95.7, 59.1, 20.8. Compound **3g**: IR (neat): 1685, 1630, 1465, 1370, 1040, 1028 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ (ppm): 2.3 (s, 1H), 5.2 (s, 1H), 5.6 (d, 1H), 7.0-7.9 (m, 15H); ^{13}C NMR ($CDCl_3$) δ (ppm): 198.4, 158.4, 143.8, 143.1, 137.4, 134.9, 130.7, 130.5, 130.2, 130.1, 129.3, 129.0, 128.8, 128.5, 126.6, 125.4, 124.8, 123.0, 122.8, 117.8, 119.9, 111.8, 95.2, 64.3, 21.0.

RESULTS AND DISCUSSION

First, aryldi-(2-hydroxy-1-naphthyl)methanes were synthesized efficiently by reaction of aromatic aldehydes with 2-naphthol in the presence of catalytic amounts of $H_3[P(Mo_3O_{10})_4]$-nH_2O (HPA) in refluxing dichloromethane (Scheme 2, Table 1). The experimental procedure for this reaction was remarkably simple and required no toxic organic solvents or inert atmospheres. However, the synthesis could not have been achieved in the absence of the catalyst. The reactions were complete in 1 h. The aromatic aldehydes containing electron-donating or electron-withdrawing groups underwent the conversion equally. It was observed that the yields of the products of aromatic aldehydes with substituents in 2-positions were low, while 2-nitrobenzaldehyde gave the corresponding product in high yield (Table 1, entry 2).

From among several possible oxidants, MoO_3 was chosen



(**1**)

Scheme 2

Table 1. Synthesis of Arylmethanebisnaphthols[a] from Aromatic Aldehydes and 2-Naphthol in the Presence of the Catalytic Amounts of HPA in CH_2Cl_2 under Reflux Conditions

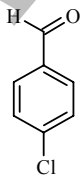
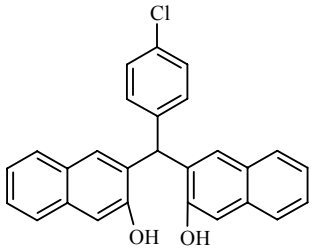
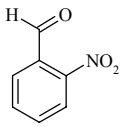
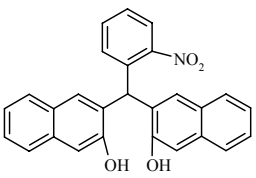
Entry	Aldehyde	Product[b]	M.p. (ºC)		Yield (%)[c]
			Found	Reported	
1			190	187.5-188	94
2			206-208	205-207	95

Table 1. Continued

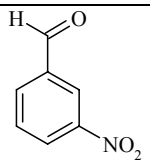
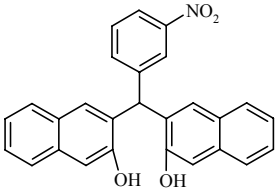
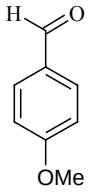
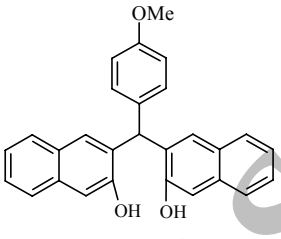
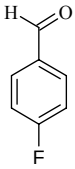
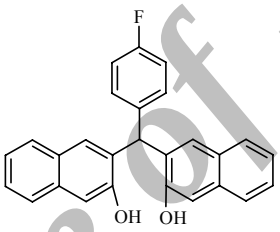
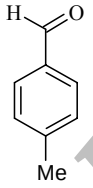
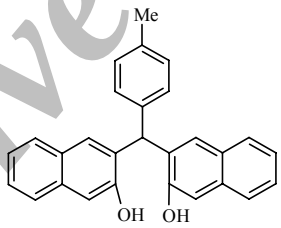
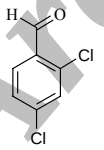
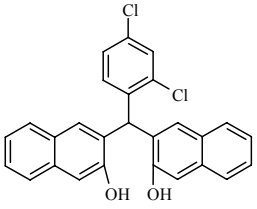
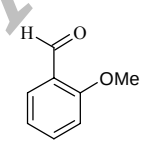
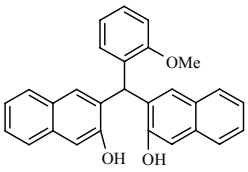
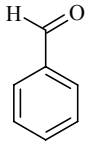
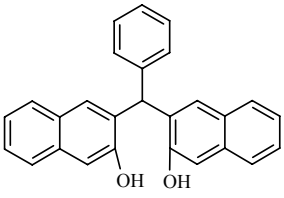
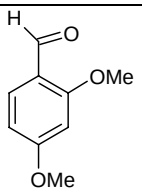
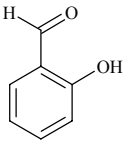
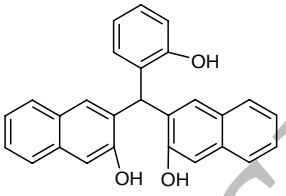
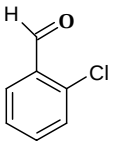
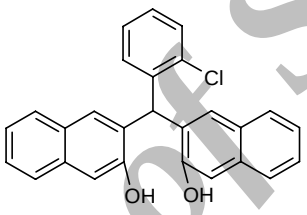
3			189-190	189-191	97
4			178	-	60
5			110	109-110	65
6			165	-	85
7			153	-	55
8			191	189-190	59
9			200	-	51

Table 1. Continued

10		N.R	-	-	-
11			-	-	<10
12			130	-	45

[a]The reaction time is 1 h. [b]The products were characterized by comparison of their melting points and ^{1}H NMR and ^{13}C NMR spectroscopic data with those reported in literature. [C]Isolated yields.

Table 2. The Catalyst Amount and Solvent Effect on the Oxidative Reaction of Phenyldi-(2-hydroxy-1-naphthyl)methane with H_2O_2/MoO_3 System

Entry	Oxidizing system	MoO_3 (%mol)	Solvent	Time (h)	Yield (%)[a]
1	H_2O_2	0	EtOH	10	N.R[b]
2	MoO_3	100	EtOH	10	N.R[b]
3	H_2O_2/MoO_3	100	CH_3CN	3	30
4	H_2O_2/MoO_3	100	$ClCH_2CH_2Cl$	3	10
5	H_2O_2/MoO_3	50	EtOH	3	62
6	H_2O_2/MoO_3	100	$CH_3COOC_2H_5$	3	10
7	H_2O_2/MoO_3	100	EtOH	3	85
8	H_2O_2/MoO_3	100	CH_3COCH_3	3	65

[a]Isolated yield. [b]No reaction.

based on our recent study utilizing hydrogen peroxide together with MoO_3 as an efficient and chemoselective oxidative system in oxidizing sulfides [5]. After examining various amounts of MoO_3, we found that one equivalent of MoO_3 was the best choice. The effect of solvents on the oxidation reaction was also examined by the reaction of phenyldi-(2-hydroxy-1-naphthyl)methane with H_2O_2/MoO_3 in different solvents at 60 °C and it was found that EtOH was the best solvent (Table 2).

A range of aryldi-(2-hydroxy-1-naphthyl)methanes with

different substituents was subjected to the developed reaction procedure to afford the products with high diasteroselectivity and high yields. It proved to be compatible with some functional groups on aromatic aldehyde and proceeded under neutral conditions. In addition, the results in Table 3 indicate that the electronic effects in the phenyl substituent hardly affected the orientation of the reaction. Therefore, the selectivity is presumed to be caused mainly by steric effects.

Table 3. Synthesis of Spirans from Bisnaphthols Using H_2O_2/M_OO_3 System in EtOH at 60 ºC

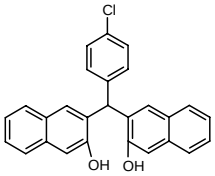
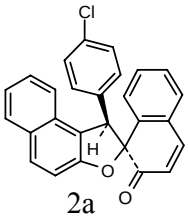
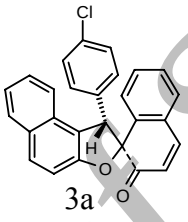
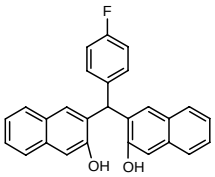
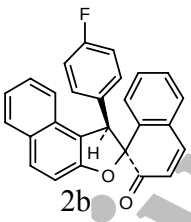
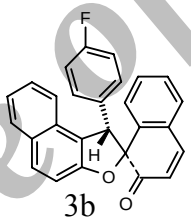
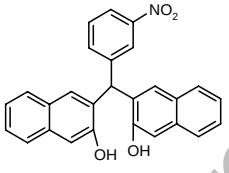
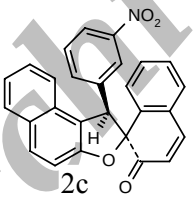
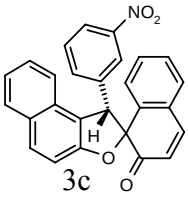
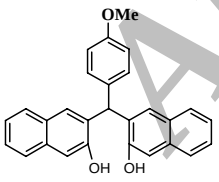
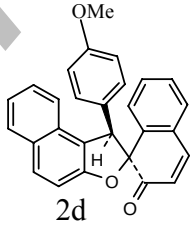
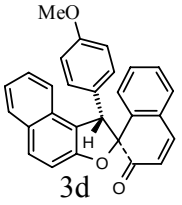
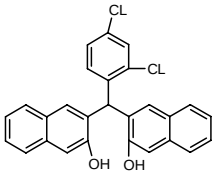
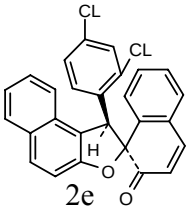
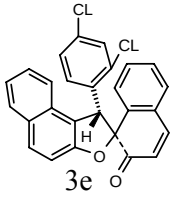
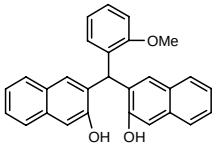
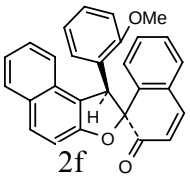
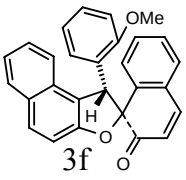
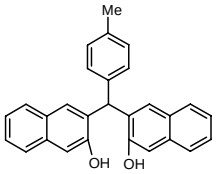
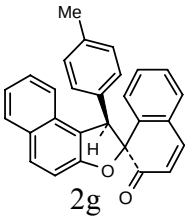
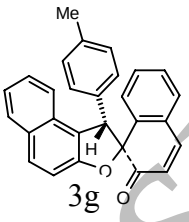
Entry	Substract	Product **2**	Product **3**	M.p. (°C) Found **2**	M.p. (°C) Found **3**	M.p. (°C) Reported [Ref.] **2**	M.p. (°C) Reported [Ref.] **3**	Total yield Yield(**2**)/Yield (**3**)
1		 2a	 3a	264	239	-	-	85 25/27
2		 2b	 3b	144	214	145 [4]	214 [4]	92 20/80
3		 2c	 3c	225	241	227 [4]	241 [4]	85 40/60
4		 2d	 3d	196	226	195 [4]	227 [4]	58 63/37
5		 2e	 3e	195	204	-	-	65 25/75

Table 3. Continued

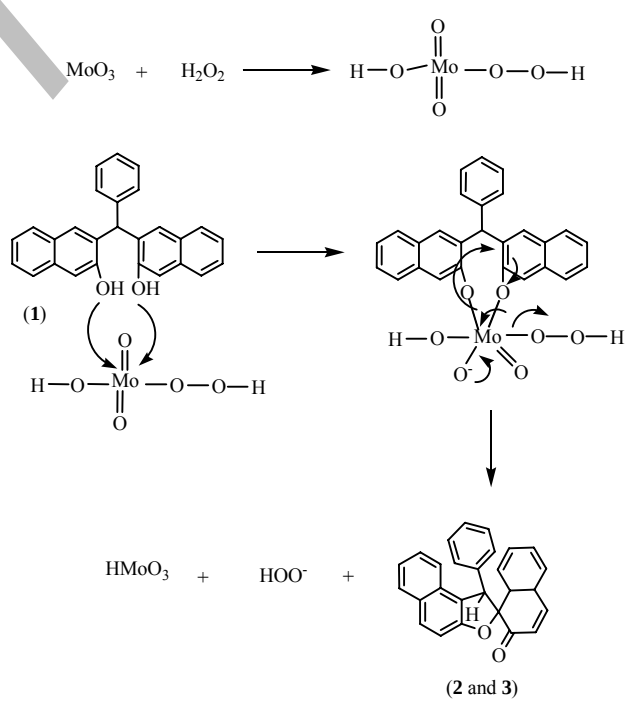
6				195	230	194 [4]	229 [4]	55 65/35
7				155	228	-	-	67 48/52

Interestingly, 2,4-dimethoxybenzaldehyde gave no corresponding product under the same reaction conditions.

The products were characterized by comparing their melting points and ^{1}H NMR and ^{13}C NMR spectroscopic data with those reported in literature. In all cases, less than 15% of xanthenes were obtained.

The structural assignments were examined by ^{1}H NMR and ^{13}C NMR studies. The geometrical isomers (**2**) showed a doublet around 6.1 ppm (vinylic hydrogen), while the other isomers (the less hindered isomers) (**3**) indicated a resonance of nearly 5.4 ppm. In addition, the geometrical isomers (**2**) were yellow in color, while the other isomers (**3**) were pale yellow or cream. The ratio of **2**/**3** changed from 0.25 to 0.67. The products (**2**) and (**3**) were not affected by the oxidant when the reactions continued for a longer period.

This observation reveals that the reactions are not reversible. A tentative proposed mechanism for this oxidation reaction is shown in Scheme 3.



Scheme 3

CONCLUSIONS

We have developed a method for the synthesis of aryldi-(2-hydroxy-1-naphthyl)methanes from aromatic aldehydes and 2-naphthol in the presence of the catalytic amounts of HPA in refluxing CH_2Cl_2 in high yields in 1 h. Aryldi-(2-hydroxy-1-naphthyl)methanes were efficiently and oxidatively cyclized to arylnaphtho[2,1-*b*]furan-2(1H)-spiro-1'(2H)-naphthalen-2'-one diasteroselectively in the presence of H_2O_2/MoO_3 system in ethanol at 60 °C.

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REFERENCES

[1] a) A.C. Day, J. Nabney, A.I. Scott, J. Chem. Soc. (1961) 4067; b) B. Akermark, H. Erdtman, C.A. Wachtmeister, Acta Chem. Scand. 13 (1959) 1855; c) H. Erdtman, C.A. Wachmeister, in Festschrifte Artur Stoll, Birkhauser, Basle, 1957, p. 144; d) C.W. Hassall, J.R. Lewis, J. Chem. Soc. (1961) 2312; e) T.A. Davidson, A.I. Scott, J. Chem. Soc. (1961) 4075.

[2] O. Dischendorfer, Ber. 59 (1926) 774.

[3] a) F.M. Dean, H.D. Locksley, J. Chem. Soc. (1963) 393; b) D.J. Bennett, F.M. Dean, A.W. Price, J. Chem. Soc. (C) (1976) 1557.

[4] D.J. Bennett, F.M. Dean, G.A. Herbin, D.A. Matkin, A.W. Price, M.L. Robinson, J. Chem. Soc., Perkin Trans 1 (1980) 1978.

[5] M.M. Khodaei, K. Bahrami, M. Khedri, M. Can. J. Chem. 85 (2007) 7.

[6] a) M.S. Kharasch, R. Marker, J. Am. Chem. Soc. 48 (1926) 3130; b) J.P. Poupelin, G. Saint-Ruf, R. Lacroix, G. Narcisse, O. Foussard-Blampin, G. Uchida-Ernouf, Eur. J. Med. Chem. Ther. 3 (1978) 381; c) A. Khoramabadi-zad, Z. Kazemi, H.A. Rudbari, J. Korean. Chem. Soc. 46 (2002) 6.

[7] a) R.M. Ion, Progr. Catal. 2 (1997) 55; b) L. Cleisen, Liebigs Ann. Chem. 271 (1887) 2371; c) O. Koki, K. Taketoshi, Bull. Chem. Soc. Jpn. 49 (1976) 1167; d) R. Damiens, R. Delaby, Bull. Soc. Chim. Fr. (1952) 976; e) R. Wizinger, Y. Al-Attar, Helv. Chim. Acta 30 (1947) 189; f) J.V. Allan, D.D. Giannini, T.H. Whitesides, J. Org. Chem. 47 (1982) 820.

[8] A.R. Khosropour, M.M. Khodaei, H. Moghanian, Synlett (2005) 955.