IAU-ARAK

J. Iran. Chem. Res. 4 (2011) 51-57

Journal of the Iranian Chemical Research

www.iau-jicr.com

4-Chloro-3,5-dioxaphosphacyclohepta[2,1-α;3,4-α']dinaphthalene (BINOL-PCl) as a Bulky and Efficient Reagent for the Transformation of Symmetric and Asymmetric Benzoins to Corresponding Benziles

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Received 18 January 2011; received in revised form 15 February 2011; accepted 28 February 2011

Abstract

4-Chloro-3,5-dioxaphosphacyclohepta[2,1-α;3,4-α']dinaphthalene (BINOL-PCl) was found to be an efficient, bulky and selective reagent for the transformation of symmetric and asymmetric benzoins to the corresponding benziles at 0 °C to room temperature under nitrogen atmosphere in good yield.

Keywords: : 4-Chloro-3,5-dioxaphosphacyclohepta[2,1-α;3,4-α']dinaphthalene**;** Transformation reagent; Benzoin; Benzil.

1. Introduction

Many several biological compounds obtained from α-diketones such as: 5,5-diphenylhydantoin [1], pyrazine derivatives [2,3] and other related biological compounds, are important in organic synthesis. Some benzil analogues (benzil possessing of substituent on its phenyl ring(s)) play as inhibitors of mammalian carboxylesterases [4]. α-Diketones can also be utilized for the preparation of a variety of organic compounds [5]. Moreover benzil derivatives are an important class of compounds, which have been reported for their application as inhibitors of the acid corrosion of mild steel [6] as photosensitive agents in photo curable coatings [7] and also as natural compounds [8].

Methyl or methylene groups α to a carbonyl can be oxidized with selenium dioxide to give, respectively, α-keto aldehyde and α-diketones [9]. These compounds can also be prepared straightforward by oxidation of α-hydroxy ketones in the presence of dinitrogentetraoxide complex of iron (III) and cupper(II) [10], tetrabutylammonium periodate in aprotic organic solvent [11] cupper(II) in alkaline [12], dimethyl sulfoxide (DMSO)-SbCl5 (1:1) complexes [13], thallium (III) nitrate (TTN) [14], polyvinylpyridinium dichromate [15], cupper (II) acetate, ammonium nitrate or pyridiniumchlorochromate as an oxidant with microwave assisted [16], nickel acetate [17] and etc. Selective oxidation of benzylic alcohol to the corresponding carbonyl compounds under solvent-free conditions [18], solid phase oxidation of organic compounds with benzyltriphenylphosphonium dichromate [19], 1,4-dibenzyl-1,4-diazoniabicyclo [2.2.2] octane chlorochormate (DBDABOCC) [20], direct oxidation of benzoin to benzil with air catalyzed by

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mesoporous materials [21] and also conversions of unsymmetrical benzoins in basic media [22] are reported. Previously, we reported the selectively oxidation of benzoins to benziles on the surface of alumina and/or silica gel [23] and selectively conversion of benzoins to the benziles by using *p*-toluenesulfonic acid [24] with heating under solvent-free condition in excellent yield.

4-Chloro-3,5-dioxaphosphacyclohepta [2,1-α; 3,4-α'] dinaphthalene (**2**) not only has been used for the preparation of asymmetric phosphites in enantioselective synthesis [25] but also used for the conversion of primary and secondary alcohols to the corresponding iodides and tertiary alcohols regio- and/or stereo selectively to olefin(s) via formation of corresponding phosphites [26]. As we searched there is no report of transformation of benzoins to the benziles via BINOL-PCl in the literature. In this research, we reported the new route for the conversion of symmetric and asymmetric benzoins to the corresponding benziles in the reaction with BINOL-PCl as bulky and reactive reagent.

2. Experimental

2.1 Instrument and materials

Melting points were taken with a digital melting point apparatus (Electrothermal) and were uncorrected. IR spectra were determined in the region 4000-400 cm^{-1} on a NEXUS 670 FT-IR spectrometer by preparing KBr pellets. The ^1H NMR spectra were measured in $CDCl_3$ at 300 MHz, using Bruker 300 FT-NMR spectrometer referencing tetramethylsilane as internal standard. The data are reported as singlet (s), doublet (d), multiplet (m) and coupling constants in Hz. In this work, benzoins **3a-g** [31] and racemic 2,2'-dihydroxy-1,1'-dinaphthalene (BINOL) **1** [30] were synthesized in our laboratory based on reported literatures. Triethylamine, phosphorus trichloride and used solvents were purchased from Merck and Aldrich and used after drying without further purification.

*2.2. Typical procedure for the syntheses of reagent BINOL-PCl **2.***

In a 250 mL two necked round bottom flask, equipped with an ice-bath and magnetically stirrer, freshly redistilled phosphorus trichloride (1.5 mL, 17.2 mmol) was dissolved in 25 mL of dry diethyl ether under nitrogen atmosphere. To this solution was added BINOL **1** (3.67 g, 13 mmol) in 100 mL of dry diethyl ether, followed by triethylamine (4.3 mL, 14.9 mmol) dropwise, and the solution was stirred for 20 h at 0 °C. The reaction mixture was then filtered, and the residue was washed with 5 ml of dry diethyl ether. The solvent was evaporated under vacuum from the filtrate to yield pale yellow solid (BINOL-PCl **2**, 70%). Owing to the reactivity and instability of **2**, this compound was used to reaction with benzoins without further purification.

*2.3. Typical procedure for the conversion of benzoins **3a-g** to the corresponding benziles **4a-g**.in the presence of BINOL-PCl **2**.*

Compound **2** (9 mmol) was dissolved in dry acetonitrile (30 mL) in a two necked round bottom flask equipped with an ice-bath, magnetic stirrer under nitrogen atmosphere. The solution of benzoin **3** (9 mmol) and triethylamine (18 mmol) in dry acetonitrile (30 mL) was added dropwise into round bottom flask at 0 °C, then stirred at room temperature under nitrogen atmosphere for 48 h. Reaction progress was monitored by TLC and the TLC solvent was the mixture of ethyl acetate 20% and cyclohexane 80% (v/v). The salt of triethylammonium hydrochloride precipitate was then filtered off. The solvent was removed from crude reaction mixture at reduced pressure. The reaction products were separated by silica gel column chromatography. Spectroscopic and physical data of **2** and obtained benziles are shown in below.

*2.4. 4-Chloro-3,5-dioxaphosphacyclohepta[2,1-α;3,4-α']dinaphthalene (BINOL-PCl **2**)*

Pale yellow solid (lit.[25,29]). IR (KBr): 3100 (C–H, ar.), 1620 (C=C), 1590 (C=C), 1210 (P-O), 720 (P-Cl); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3-7.7 (m, 8H), 8.0-8.3 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 134.0, 131.5, 129.5, 128.4, 127.5, 124.5, 124.0, 123.9, 118.8; ^{31}P NMR (121 MHz, $CDCl_3$) δ (s, 178.8).

*2.5. 1,2-Diphenylethane-1,2-dione (**4a**)*

Green solid, mp 95 °C (lit.[10,11] 95 °C); IR (KBr) 3100 (C–H, ar.), 1680 (C=O), 1595 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.5 (t, 4H), 7.7 (t, 2H), 8.0 (d, 4H, *J*= 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 134.9, 133.0, 129.9, 129.0.

*2.6. 1,2-Bis-(4-methoxyphenyl)ethane-1,2-dione (**4b**)*

Green solid, mp 133 °C (lit.[10,11] 132-135 °C); IR (KBr) 3050 (C–H, ar.), 2900, 2800 (C–H, aliph.), 1670 (C=O), 1595 (C=C), 1160 (C–O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.0 (s, 3H), 7.2 (d, *J*= 9 Hz, 2H), 8.2 (d, *J*= 9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7, 142.1, 131.7, 130.0, 129.7, 57.2.

*2.7. 1,2-Bis-(4-methylphenyl)ethane-1,2-dione (**4c**)*

Green solid, mp 103 °C (lit.[10,11] 105 °C); IR (KBr) 3040 (C–H, ar.), 2920 (C–H, aliph.), 1665 (C=O), 1606 (C=C), 1165 (C–O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.4 (s, 3H), 7.3 (d, *J*= 8.1 Hz, 2H), (d, *J*= 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 146.0, 130.7, 130.0, 129.7, 21.9.

*2.8. 1,2-Difuran-2-yl-ethane-1,2-dione (**4d**)*

Light green solid, mp 162 °C (lit.[10] 162-164 °C); IR (KBr) 3150 (C–H, ar.), 3130 (C–H, ar.), 1650 (C=O), 1450 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.7 (m, 1H), 7.6 (m, 1H), 7.8 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 153.6, 149.4, 124.7, 113.1.

*2.9. 1-(3-Methoxyphenyl)-2-phenylethane-1,2-dione (**4e**)*

Green solid, mp 66 °C (lit.[32] 65 °C); IR (KBr) 3076 (C–H, ar.), 3013 (C–H, ar.), 2840 (C–H, aliph.), 1659 (C=O), 1594 (C=C), 1484 (C=C), 1174 (C−O), 1157 (C−O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.8 (s, 3H), 7.1 (m, 1H), 7.1 (s, 1H), 7.4–7.3 (m, 5H), 7.6–7.5 (m, 1H), 7.9 (d, 1H, *J*=7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6 (2CO), 160.2, 135.0, 134.5, 133.2, 130.3, 130.0, 129.0, 123.3, 121.9, 113.0, 55.5.

*2.10. 1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (**4f**)*

Green solid, mp 65 °C (lit.[32] 65 °C); IR (KBr) 3065 (C–H, ar.), 3015 (C–H, ar.), 2939 (C–H, aliph.), 2844 (C–H, aliph.), 1668 (C=O), 1650 (C=O), 1570 (C=C), 1451 (C=C), 1182 (C−O), 1162 (C−O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.9 (s, 3H), 7.0 (d, 2H, *J*=9 Hz), 7.5 (m, 2H), 7.7 (m, 1H), 8.0–7.9 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 193.2, 165.0, 134.8, 133.8, 132.4, 130.0, 129.1, 125.9, 114.4, 55.6.

*2.11. 1-(Furan-2-yl)-2-phenylethane-1,2-dione (**4g**)*

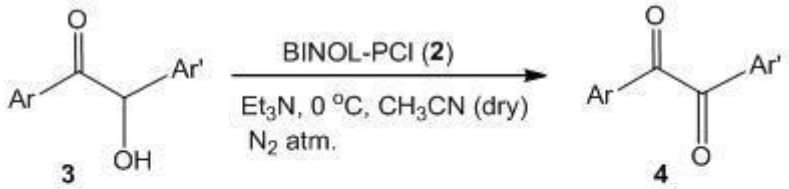
Green solid, IR (KBr) 3065 (C–H, ar.), 3015 (C–H, ar.), 2939 (C–H, aliph.), 2844 (C–H, aliph.), 1668 (C=O), 1650 (C=O), 1570 (C=C), 1451 (C=C), 1182 (C−O), 1162 (C−O); ^{1}H NMR

(300 MHz, $CDCl_3$) δ 6.5 (m, 1H), 7.2 (m, 1H), 7.5 (m, 3H), 7.7 (m, 1H), 7.8 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.0, 194.5, 153.6, 149.3, 134.0, 130.0, 128.6, 127.5, 120.0, 113.0.

3. Results and Discussion

The preparation of 4-chloro-3,5-dioxaphosphacyclohepta[2,1-α;3,4-α']dinaphthalene (BINOL-PCl, **2**), the compound 2,2'-dihydroxy-1,1'-dinaphthalene (BINOL, **1**) was first reacted with fresh phosphorous trichloride in dry diethyl ether under nitrogen atmosphere according to previously reported method [27]. This reagent (cheap, reactive) was easily prepared and a bulky source of reagent in the reaction with hydroxyl functional group (Scheme 1). Previously, we reported the reaction of **2** with primary and secondary alcohols then consequently with iodine obtained to produce the corresponding alkyl iodide in dichloromethane via phosphites **5.** No carbonyl compounds were obtained [26]. Tertiary alcohols were transformed selectively (stereo- and/or regioselective) to the corresponding olefin(s) under the same condition [26].

Scheme 1 Preparation of BINOL-PCl (**2**) and conversion of alcohols to corresponding phosphites [26].



Ar = Ar' = Ph (**a**)
Ar = Ar' = *p*-MeO-Ph (**b**)
Ar = Ar' = *p*-Me-Ph (**c**)
Ar = Ar' = 2-Furyl (**d**)
Ar = *m*-MeO-Ph, Ar' = Ph (**e**)
Ar = *p*-MeO-Ph, Ar' = Ph (**f**)
Ar = Ph, Ar' = 2-Furyl (**g**)

Scheme 2 Conversion of benzoins to the corresponding benziles in the presence of **2**.

In this study we observed that the reagent **2** is able to transform benzoins to the corresponding benziles in good yield (Scheme 2). In this work, our initial attempt was failed (based on our previous report [26]) to synthesis 2-iodo-1,2-diarylethanones (**7a-g**) in the reaction of **2** with benzoins (**3**) via phosphite intermediates (**6**) instead benziles (**4a-g**) were observed in good yields (Scheme 3).

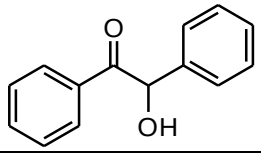
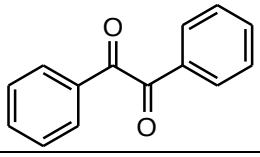
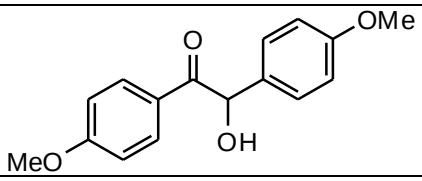
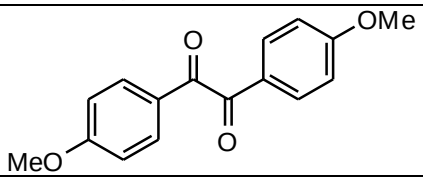
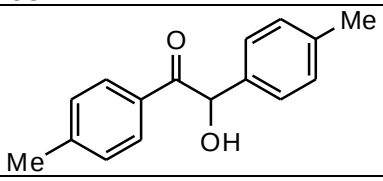
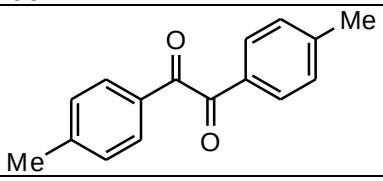
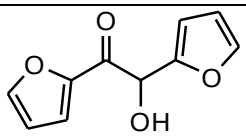
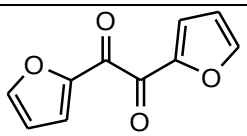
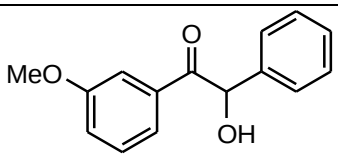
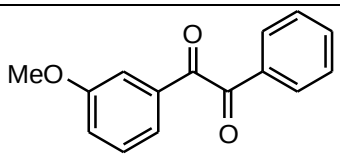
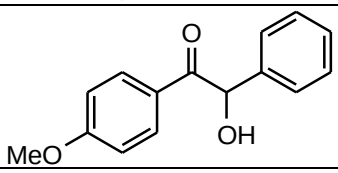
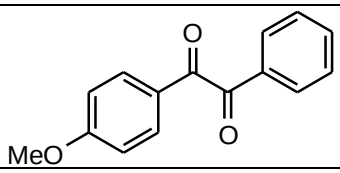
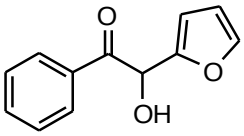
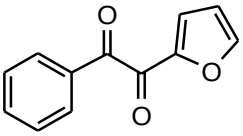
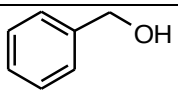
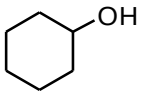
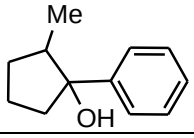
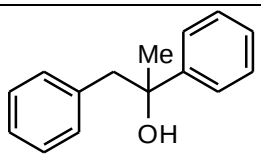
Scheme 3 Proposed mechanism of the effect of adjacent carbonyl group in transformation of **6a** to **4a** as representative.

Previously, the selectively conversion of benzoins to the corresponding benziles is carried out by using *p*-toluenesulfonic acid (PTSA) under solvent-free condition [24]. We have reported that the adjacent carbonyl group is necessary for the oxidation of hydroxyl group in benzoins in the presence of PTSA according based to references [24,28]. Benzoin **3a** is known to undergo an interesting transformation to tetraphenylfuran (25%), benzil **4a** (45%), 2,3,5,6-tetraphenyl-[1,4]dioxine (**9a**) and other characterized compounds when refluxed with PTSA in dry xylene with azeotropic removal of water [28]. Kar *et al.* has shown that the adjacent carbonyl group is necessary in the oxidation of benzoin **3a** to benzil **4a** in the presence of PTSA in boiling xylene. The adjacent carbonyl group can attack to the second protonated benzoin lead to **9a** and benzil **4a** [28].Therefore, comparison of the transformation of benzoins to the corresponding benziles in acidic condition as PTSA and in the presence of reagent **2** (in this research), demonstrated that the adjacent carbonyl group is necessary for those transformations.

The proposed mechanism for the transformation of **3a** into **4a** through intermediate **6a** is shown in Scheme 3. In the reaction with reagent **2**, the formation of intermediate **8a** proceeds by the condensation of **3a** with phosphite **6a** to form a carbon-oxygen bond with removal of cyclic hydrogen phosphonate [29] (Scheme 3). Unfortunately, all attempts failed to separate or characterize phosphites **6a-g**, instead phosphites derived from alcohols (1°, 2° and 3°) were obtained in good yield [26]. According to the Scheme 3 in these reactions, the adjacent carbonyl group is necessary for the transformation of benzoins to the corresponding benziles (similar to PTSA condition). The possible pathway (path *a*) for the formation of **4a** is depicted in Scheme 3. Intramolecular tautomerization and cleavage of the carbon-oxygen bond of intermediate **8a** lead to the formation of **4a** (path *a*). No **9a** was observed (path *b*) whereas the transformation of benzoin **3a** in acidic condition (PTSA) afforded 5% of **9a** [28]. These observations indicated that the **6a** is the key intermediate and condensed with second benzoin molecule afforded benzil via intermediate **8a** (Scheme 3). All the benziles obtained from corresponding benzoins in the presence of reagent **2** are summarized in Table 1. The results are compared with those of the reaction of alcohols (**10-13**) with **2** under the same conditions.

The main advantages of these reactions are: (a) BINOL **1** is easily prepared [30] (b) a bulky and reactive reagent **2** (c) selective conversion of benzoins to the corresponding benziles (d) alcohols converts to corresponding phosphites and (e) neither aldehydes nor ketones reacts with **2** under the same conditions.

Table 1
Conversion of Benzoins to corresponding benziles in the presence of reagent **2**.

Compd.	Reactants	product structure (**4**)	Yield (%)[a]
3a			60
3b			70
3c			65
3d			75
3e			70
3f			70
3g			75
10		[b]	-
11		[b]	-
12		[c]	-
13		[d]	-

[a] Isolated yield.
[b] Corresponding phosphite **5** [26].
[c] Regioselective, mixture of two alkenes were obtained [26].
[d] Stereoselective, mixture of two alkenes (*E*- and *Z*-isomers) were obtained [26].

Acknowledgements

We thank to the Urmia University Research Council for the financial support of this work. The authors also gratefully acknowledge to financial supporting of the Tabriz Payam-e-Noor University.

References

[1] R.L. Hudkins, D.L. DeHaven-Hudkins, Bioorg. Med. Chem. Lett. 4 (1994) 2185-2188.
[2] G. Bonde, N.J. Gaikwad, Bioorg. Med. Chem. 12 (2004) 2151-2161.
[3] B. Jiang, X.-H. Gu, Bioorg. Med. Chem. 8 (2000) 363-371.
[4] R.M. Wadkins, J.L. Hyatt, X. Wei, K.J.P. Yoon, M. Wierdl, C.C. Edwards, C.L. Morton, J.C. Obenauer, K. Damodaran, P. Beroza, M.K. Danks, P.M. Potter, J. Med. Chem. 48 (2005) 2906-2915.
[5] B.S. Jursic, D.M. Neumann, K.L. Martin, E.D. Stevens, Org. Lett. 4 (2002) 811-813.
[6] B.I. Ita, O.E. Offiong, Mater. Chem. Phys. 70 (2001) 330-335.
[7] Matsuschita Electric Industrial Co. Ltd. Jpn. Kokai Tokkyo Koho, 8198203, 1981; Chem. Abstr. 1981, 95, 188163v.
[8] L.R. Hillis, R.C. Ronald, J. Org. Chem. 50 (1985) 470-473.
[9] J. March, Advanced Organic Chemistry Reaction Mechanisms, and Structure, John Wiley & Sons, New York, Chapt. 19 (1985)
[10] N. Iranpoor, H. Firouzabadi, M.A. Zolfigol, Bull. Chem. Soc. Jpn. 71 (1998) 905-909.
[11] H. Firouzabadi, A.R. Sardarian, H. Badparva, Bull. Chem. Soc. Jpn. 69 (1996) 685-691.
[12] H.A. Cannon, B.G. Sheldon, K.E. Harding, L.E. Letterman, D.G. Fulton, W.G. Nigh, J. Org. Chem. 38 (1973) 2020-2023.
[13] J. Yamamoto, S. Ito, T. Tsuboi, T. Tsuboi, K. Tsukihara, Bull. Chem. Soc. Jpn. 58 (1985) 470-472.
[14] A. Mckillop, B.P. Swann, M.E. Ford, E.C. Taylor, J. Am. Chem. Soc. 95 (1973) 3641-3645.
[15] B. Tamami, N. Goudarzian, Polymer Bull. 23 (1990) 295-298.
[16] K. Alok, M. Apra De, N. Karchaudhuri, J. Chem. Res (S) (1999) 246-247.
[17] G.S. Hammond, S.W. Chin-hua, J. Am. Chem. Soc. 95 (1973) 8215-8222.
[18] A.R. Hajipour, S.E. Mallakpour, I.M. Baltork, S. Khoee, Chem. Lett. (2000) 120-121.
[19] A.R. Hajipour, I.M. Baltork, Phos. Sulfor and Silicon 164 (2000) 145-151.
[20] I.M. Baltork, A.R. Hajipour, A. Ghahramankhani, Indian J. Chem. Sec. B 39(11) (2000) 863-866.
[21] B. Li, J. Wang, J. Fu, J. Wang, C. Zou, Catal. Commun. 9 (2008) 2000-2002.
[22] S.P. Ivonin, A.V. Lapandin, ARKIVOC viii (2005) 4-9.
[23] N. Noroozi-Pesyan, A.H. Dabbagh, Molecules 10 (2005) 1364-1368.
[24] N. Noroozi-Pesyan, A.H. Dabbagh, J. Iran. Chem. Res. 1(2) (2008) 123-127.
[25] M. Ostermeier, B. Brunner, C. Korff, G. Helmchen, Eur. J. Org. Chem. (2003) 3453-3459.
[26] N. Noroozi-Pesyan, J. Khalafy, H. Khani-Meinagh, Turk. J. Chem. 33 (2009) 527-543.
[27] A. Vogel, Textbook of Practical Organic Chemistry, (VOGEL'S), 4rd Ed., Longman, 1978.
[28] S.K. Kar, A. Kar, J. Org. Chem. 42 (1977) 390-391.
[29] A.H. Dabbagh, N. Noroozi-Pesyan, A.R. Najafi-Chermahini, B.O. Patrick, B.R. James, Can. J. Chem. 85 (2007) 466-474.
[30] F. Toda, K. Tanaka, S. Iwata, J. Org. Chem. 54 (1989) 3007-3009.
[31] S.I. Walter, S.B. Juhannes, Org. React.(N.Y.) 4 (1948) 269-304.
[32] A. Giraud, O. Provot, J.-F. Peyrat, M. Alami, J.-D. Brion, Tetrahedron 62 (2006) 7667-7673.