

A Caveat on the Use of 2-Chloro-4,6-dimethoxy-1,3,5-triazine for the Synthesis of 4,4-Dimethyl-2-R-2-Oxazolines¹

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Abstract: The reported synthesis of 4,4-dimethyl-2-R-2-oxazolines from carboxylic acids and 2-amino-2-methyl-1-propanol (**1**) using 2-chloro-4,6-dimethoxy-1,3,5-triazine (**2**) via direct coupling/cyclisation is questioned. The results reported herein indicate that the products are actually ω -hydroxyamides resulting from dehydrative R-COOH/**1** (peptide) coupling *only*, which has been known to be mediated by **2** for some time.

Keywords: Oxazoline, triazine, coupling reactions, amides, amino alcohols, 4,5-dihydro-2-oxazole.

INTRODUCTION

2-Oxazolines (*i.e.*, 4,5-dihydro-2-oxazoles) are an important class of naturally occurring and synthetic organic heterocycles [1]. The group has found application in a number of roles in coordination chemistry [2], asymmetric synthesis [3-4], and in natural products chemistry [5-6]. In addition, the recent intense study of chiral oxazolines as ligands in enantioselective Lewis acid catalysis is a particularly significant area of research within heterocyclic chemistry and organic synthesis in general [2]. The achiral 4,4-dimethyl-2-oxazolines (Fig. (1): R = aryl or alkyl) are also a well-studied sub-class of oxazolines, as they are a robust derivative of the carboxylic acid group. Hence, such acids are often protected in the form of oxazolines for use in HPLC, GC and MS analysis. The conversion of carboxylic acids into 2-oxazolines is often used for the trace analysis of naturally occurring carbonyl compounds [1, 7]. In synthetic chemistry, Meyers and others have found that 2-aryl-2-oxazolines can be used as highly regio- and enantioselective directing groups for the *ortho*-lithiation of aryl rings [1, 3b, 3d-f, 8].

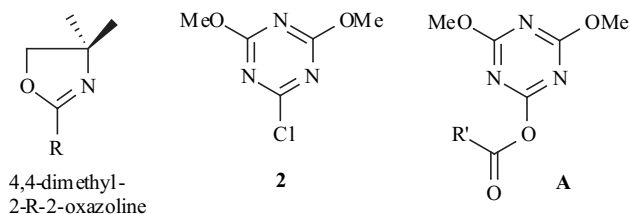


Fig. (1).

The 4,4-dimethyl-2-oxazoline group has been produced by a number of synthetic methods. These include (although certainly not an exhaustive list) such protocols as: (i) the

high temperature ($\geq 180^\circ\text{C}$) treatment of carboxylic acids with neat 2-amino-2-methyl-1-propanol (**1**) [1, 7]; (ii) SOCl_2 (or MsCl or TsCl) mediated cyclisation of *N*-(2-hydroxyethyl)amides [1, 5a, 9]; (iii) the reaction of imidate esters with HCl salts of **1** [6h]; (iv) phosphine-mediated coupling of benzoic acids and **1** [10]; (v) the application of microwave technology to produce oxazolines from *N*-acylbenzotriazoles [11a], (vi) the use of resin-bound amides in a combinatorial approach [11b]; and (vii) metal halide (Lewis acid) catalyzed reaction of organonitriles with **1** [7, 12]. Although all of these methods can be employed to give oxazolines (in varying yields), typically high temperatures and long reaction times are required. In addition, many of these methodologies are not tolerant to sensitive functional groups and thus more general synthetic protocols are still desirable. This problem has been partially solved by the recent development of a number of mild and highly efficient promoters to facilitate oxazoline ring formation such as the Vilsmeier reagent [13a], the Burgess Reagent [13b-c], DAST [13d-f], Deoxo-Fluor [13f-h], zeolites [13i] and/or naturally occurring clay materials [13j]. Unfortunately, many of these reagents are expensive and must be used in a stoichiometric fashion and, in some cases, at low temperature. Thus, there is still a need for the development of new, cheap and effective methods for the synthesis of simple and complex 2-oxazoline compounds.

Recently, Bandgar and Pandit reported [14] the use of 2-chloro-4,6-dimethoxy-1,3,5-triazine (Fig. (1): compound **2**) as a simple, mild and highly efficient promoter for the synthesis of 4,4-dimethyl-2-oxazolines. Their "one-pot" approach involves the direct treatment of **2**/NMM (NMM = *N*-methylmorpholine) with a carboxylic acid followed by addition of **1** and stirring at room temperature [14]. This simple approach appears to have solved many of the above problems in oxazoline synthesis, as NMM is a cheap reagent and **2** is readily produced in large quantities [15, 16]. In addition, the methodology is apparently tolerant to the presence of sensitive functional groups. However, we have closely re-examined this procedure and unfortunately, in our hands, we find that the published procedure yields ω -hydroxyamides (*i.e.*, the amide resulting from the coupling of R-COOH with **1**), as the only major product [16, 17].

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RESULTS AND DISCUSSION

Our initial investigation into the use of **2** for the synthesis of 2-oxazolines was prompted by our requirements for a number of substituted aryl- and alkyl-2-oxazolines for a QSAR study. The published procedure [14] calls for the dissolution of **2** in CH_2Cl_2 followed by addition of NMM at a temperature of between 0 and 5°C. This action forms a suspension of the resulting salt as described [14]. Treatment of this material by R-COOH is surmised to yield the highly reactive 2-acyloxy-4,6-dimethoxy-1,3,5-triazine (Fig. (1): **A**) intermediate [14, 17], that upon treatment with **1** gives, after warming to room temperature (RT) and stirring for several hours, the oxazoline. Mechanistically, this latter development seems somewhat unusual; since the intermediate amide formed from **A** must thereafter undergo an intramolecular dehydrative cyclisation at RT to form the oxazoline. Typically, this kind of cyclisation requires the addition of a Lewis acid catalyst (e.g., ZnCl_2) and elevated temperatures (e.g., refluxing PhCl) or an additional step in which the terminal -OH functionality has been converted into a better leaving group (e.g., Ts) [1-5, 10, 12]. We have repeated the published protocol [14] using both commercial and synthetic sources of **2** and have found that the product formed and isolated is invariably the *amide* and not the oxazoline. We have used benzoic acid itself and a number of its derivatives (*p*-F, Cl, OMe, Me, NO_2 , *m*-Me, Cl, Me), a variety of other carboxylic acids as described [14] (e.g. cinnamic acid) and others (maleic, fumaric acids, etc.). All reactions appear to give only the amide [18-19] in very good yield (in fact, this is a simple and facile method for amide production: [17]). As an example (Scheme (1): R = *p*- $\text{C}_6\text{H}_4\text{NO}_2$), the treatment of 4-nitrobenzoic acid under identical conditions to that reported [14] yielded a product (**3**) having a considerably *higher* mp (116-117°C) and notably different ^1H NMR spectrum than that reported for 4,4-dimethyl-2-(*p*-nitrophenyl)-2-oxazoline (**4**: mp = 96-97°C) [20]. We have further taken this apparent amide and produced a completely new product (the desired oxazoline: [21]) by treatment of the amide (**3**) with 10 mol% ZnCl_2 in PhCl at reflux temperature (24 h) [19]. The properties of this latter material are fully consistent (mp, NMR, IR) with that reported for **4** [11a, 20], which we further checked by comparison to an authentic sample of **4** produced by the classical two-step SOCl_2 route [22].

Further support for the notion that the reported method [14] does not directly yield oxazolines can be found in the disclosures by Kaminski in the mid-1980's [17]. In this work, the use of **2**/NMM to give *amides* from R-COOH and primary amines, in a very similar fashion to that reported by Bandgar and Pandit, was clearly demonstrated. Kaminski's methodology can also be employed with *N*-protected L-serine (i.e., Scheme (1): R = $\text{HOCH}_2\text{CH}\{\text{NH}(\text{Boc})\}$) as the

source of carboxylic acid [17b]. In this case, the primary hydroxyl functionality is not protected but there is neither reported evidence that this -OH group reacts further with the resulting amide (intramolecularly) to give an oxazoline nor any indication of an intermolecular reaction to yield higher molecular weight by-products.

In their brief report, Bandgar and Pandit detail specifically the synthesis of 2-(*p*-chlorophenyl)-4,4-dimethyl-2-oxazoline (Scheme (1), **5**: R = *p*- $\text{C}_6\text{H}_4\text{Cl}$) [14]. Some of the reported data (mp) is consistent with our isolated (87%) *amide* (Fig. (2): compound **6**) [18, 23]. Further, compound **5** is known to be, like many 2-aryl-2-oxazolines, a *low melting* solid at standard temperature and pressure [11a, 24] and not a moderately high melting compound as reported [14]. We have made **5** independently from *p*-chlorobenzoic acid under conditions (SOCl_2 ; two-steps) similar to that reported many years ago [8a, 22] and have isolated **5** as a slightly yellow oil which solidifies slowly to a waxy material on standing (lit. mp: 33-34°C [24] and as an oil in ref. [11a]). The spectroscopic properties match those recently reported by Katritzky *et al.* [11a], but are inconsistent with those reported by Bandgar *et al.* for their *presumed* oxazoline **5** [14]. Our synthesis of **5** from isolated **6**, using $\text{ZnCl}_2/\text{PhCl}/\Delta$ as detailed above for **4** [12a, 23], yielded **5** which was identical in all respects to that obtained *via* other original methods [8a, 11a, 22] and in an isolated yield of 70% [18].

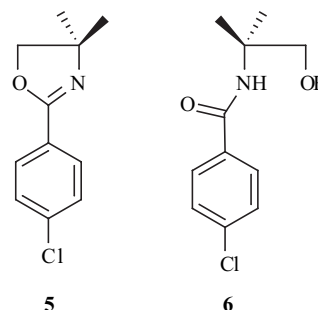
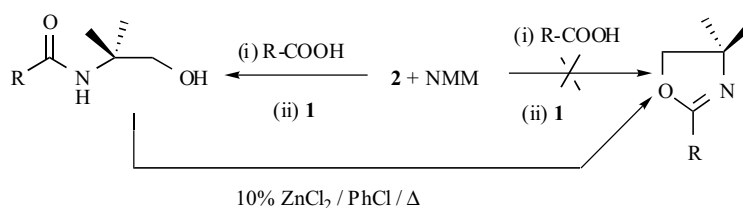


Fig. (2).

CONCLUSIONS

In conclusion, we have found that the synthetic protocol [14] used to produce 4,4-dimethyl-2-oxazolines in a single reaction vessel from carboxylic acids and 2-amino-2-methyl-1-propanol leads instead to high yields of ω -hydroxyamides. We feel, however, that this is an underused and synthetically attractive approach to amide bond formation [17], especially in light of the high water solubility of the by-product triazines. The amides isolated in this way can be readily cyclised to give the desired oxazolines using typical protocols [1, 3, 10b, 10c, 12a].



Scheme 1.

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REFERENCES AND NOTES

- [1] (a) Wiley, R.H.; Bennett Jr., L.L. *Chem. Rev.*, **1944**, *49*, 447; (b) Frump, J.A. *Chem. Rev.*, **1971**, *71*, 483; (c) Reumann, M.; Meyers, A.I. *Tetrahedron*, **1983**, *41*, 837; (d) Gant, T.G.; Meyers, A.I. *Tetrahedron*, **1994**, *50*, 2297; (e) Inoue, K. *Prog. Polym. Sci.*, **2000**, *25*, 453.
- [2] (a) Gómez, M.; Muller, G.; Rocamora, M. *Coord. Chem. Rev.*, **1999**, *193-195*, 769 and references therein; (b) Fache, F.; Schulz, E.; Tommasino, M.L.; Lemaire, M. *Chem. Rev.*, **2000**, *100*, 2159 and references therein; (c) Pfaltz, A. *J. Heterocyclic Chem.*, **1999**, *36*, 1437.
- [3] (a) Langlois, Y. *Curr. Org. Chem.*, **1998**, *2*, 1; (b) Meyers, A.I.; Lutomski, K.A. *J. Am. Chem. Soc.*, **1982**, *104*, 879; (c) Liddell, R.; Whiteley, C. *J. Chem. Soc., Chem. Commun.*, **1983**, 1535; (d) Meyers, A.I.; Hanagan, M.A.; Trefonas, L.M. *Tetrahedron*, **1983**, *39*, 1991; (e) Hulme, A.N.; Meyers, A.I. *J. Org. Chem.*, **1994**, *59*, 952; (f) Meyers, A.I. *Acc. Chem. Res.*, **1978**, *11*, 375.
- [4] Meyers, A.I. *J. Heterocyclic Chem.*, **1998**, *35*, 991.
- [5] (a) Black, D.St.C.; Wade, M.J. *Aust. J. Chem.*, **1972**, *25*, 1797; (b) Meyers, A.I.; Willemsen, J.J. *Chem. Commun.*, **1999**, 1573.
- [6] For example: (a) Shioiri, T.; Hamada, Y.; Kato, S.; Shibata, M.; Kondo, Y.; Nakagawa, H.; Kohida, K. *Biochem. Pharmacol.*, **1987**, *36*, 4181; (b) Akhmedzhanova, V.I.; Batsrunén, D.; Shakirov, R.Sh. *Khim. Priir. Soedin.*, **1993**, *29*, 873 [*Chem. Nat. Compds.*, **1993**, *29*, 778]; (c) Boden, C.D.J.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1*, **2000**, 875; (d) Boden, C.D.J.; Norley, M.C.; Pattenden, G. *Tetrahedron Lett.*, **1996**, *37*, 9111; (e) Wipf, P.; Fritch, P.C. *J. Am. Chem. Soc.*, **1996**, *118*, 12358; (f) Wipf, P.; Uto, Y. *Tetrahedron Lett.*, **1999**, *40*, 5165; (g) Norley, M.C.; Pattenden, G. *Tetrahedron Lett.*, **1998**, *39*, 3087; (h) Wipf, P.; Miller, C.P.; Grant, C.M. *Tetrahedron*, **2000**, *56*, 9143; (i) Crimmins, M.T.; Tabet, E.A. *J. Org. Chem.*, **2001**, *66*, 4012.
- [7] (a) Liebich, H.M.; Schmieder, N.; Wahl, H.G.; Wöll, J. *J. High Res. Chromatogr.*, **1994**, *17*, 519; (b) Dobson, G.; Christie, W.W. *Trends Anal. Chem.*, **1996**, *15*, 130; (c) Viron, C.; Saunois, A.; André, P.; Perly, B.; Lafosse, M. *Anal. Chim. Acta*, **2000**, *409*, 257; (d) Destaillets, F.; Wolff, R.L.; Angers, P. *Lipids*, **2001**, *36*, 319.
- [8] (a) Gschwend, H.W.; Hamdan, A. *J. Org. Chem.*, **1975**, *40*, 2008; (b) Meyers, A.I.; Mihelich, E.D. *J. Org. Chem.*, **1975**, *40*, 3159; (c) Reed, J.N.; Snieckus, V. *Tetrahedron Lett.*, **1983**, *24*, 3795; (d) Evans, P.A.; Nelson, J.D.; Stanley, A.L. *J. Org. Chem.*, **1995**, *60*, 2298; (e) Green, L.; Chauder, B.; Snieckus, V. *J. Heterocyclic Chem.*, **1999**, *36*, 1453; (f) Tahara, N.; Fukuda, T.; Iwao, M. *Tetrahedron Lett.*, **2002**, *43*, 9069.
- [9] Hoyeyda, H.R.; Karunaratne, V.; Rettig, S.J.; Orvig, C. *Inorg. Chem.*, **1992**, *31*, 5408.
- [10] (a) Vorbrüggen, H.; Krolkiewicz, K. *Tetrahedron Lett.*, **1981**, *22*, 4471; (b) Bolm, C.; Weickhardt, K.; Zehnder, M.; Ranff, T. *Chem. Ber.*, **1991**, *124*, 1173; (c) Witte, H.; Seelinger, W. *Justus Liebigs Ann. Chem.*, **1974**, *68*, 996.
- [11] (a) Katritzky, A.R.; Cai, C.; Suzuki, K.; Singh, S.K. *J. Org. Chem.*, **2004**, *69*, 811; (b) Pirrung, M.C.; Tumej, L.N. *J. Comb. Chem.*, **2000**, *2*, 675.
- [12] (a) Button, K.M.; Gossage, R.A.; Phillips, R.K.R. *Synth. Commun.*, **2002**, *32*, 363; (b) Banks, J.T.; Button, K.M.; Gossage, R.A.; Hamilton, T.D.; Kershaw, K.E. *Heterocycles*, **2001**, *55*, 2251; (c) Button, K.M.; Gossage, R.A. *J. Heterocyclic Chem.*, **2003**, *40*, 513; (d) Koch, G.; Lloyd-Jones, G.C.; Loiseleur, O.; Pfaltz, A.; Prétôt, R.; Schaffner, S.; Schneider, P.; von Matt, P. *Recl. Trav. Chim. Pays-Bays*, **1995**, *114*, 206.
- [13] (a) Wuts, P.G.M.; Northuis, J.M.; Kwan, T.A. *J. Org. Chem.*, **2000**, *65*, 9223; (b) Wipf, P.; Miller, C.P. *Tetrahedron Lett.*, **1992**, *33*, 907; (c) Lamberth, C. *J. Prakt. Chem.*, **2000**, *342*, 518; (d) Burrell, G.; Evans, J.M.; Jones, G.E.; Stemp, G. *Tetrahedron Lett.*, **1990**, *31*, 3649; (e) Lafargue, P.; Guenot, P.; Lellouche, J.-P. *Heterocycles*, **1995**, *41*, 947; (f) Phillips, A.J.; Uto, Y.; Wipf, P.; Reno, M.J.; Williams, D.R. *Org. Lett.*, **2000**, *2*, 1165 (*Corrigendum*: **2003**, *4*, 4743); (g) De Angelis, M.; Campiani, G. *Tetrahedron Lett.*, **2004**, *45*, 2355; (h) Scarone, L.; Sellanes, D.; Manta, E.; Wipf, P.; Serra, G. *Heterocycles*, **2004**, *63*, 773; (i) Cwik, A.; Hell, Z.; Hegedüs, A.; Finta, Z.; Horváth, Z. *Tetrahedron Lett.*, **2002**, *43*, 3985; (j) Jnaneshwara, G.K.; Deshpande, V.H.; Lalithambika, M.; Ravindranathan, T.; Bedekar, A.V. *Tetrahedron Lett.*, **1998**, *39*, 459.
- [14] Bandgar, B.P.; Pandit, S.S. *Tetrahedron Lett.*, **2003**, *44*, 2331.
- [15] Cronin, J.S.; Ginah, F.O.; Murray, A.R.; Copp, J.D. *Synth. Commun.*, **1996**, *26*, 3491.
- [16] Compound **2** can be purchased commercially; we employed both commercial and synthetic sources [15] of **2** with no change in our results.
- [17] (a) Kaminski, Z.J. *Tetrahedron Lett.*, **1985**, *26*, 2901; (b) Kaminski, Z.J. *Synthesis*, **1987**, 917.
- [18] Our ω -hydroxyethylamide (**6**) was identified by the presence of an IR stretching frequency around 1639 cm^{-1} and a very broad absorption, assigned to the $\nu(\text{OH})$ stretching frequency, above 3200 cm^{-1} . IR frequency values of greater than 1600 cm^{-1} are not reported in ref. [14]. In addition, we observe a single slightly broad ^1H NMR resonance at $\delta_{\text{H}} = 6.30$ ppm. This has been assigned to the amide N-H proton (also see data given in reference [23] below).
- [19] The synthesis and characterisation of 4,4-dimethyl-2-(*p*-nitrophenyl)-2-oxazoline is typical of our results. A sample of **2** (1.32 g; 7.5 mmol) was dissolved in CH_2Cl_2 (*ca.* 30 mL) and cooled to 0-5°C while the mixture was stirred *via* a teflon stir bar. NMM (~0.8 mL) was added dropwise and the mixture stirred for 30 min.; a procedure that resulted in the formation of a white precipitate. To the cooled mixture was added a 15 mL solution (CH_2Cl_2) of *p*-nitrobenzoic acid (1.25 g, 7.5 mmol) in a dropwise fashion over a period of *ca.* 5 min. The solution then slowly clarified over a 2 h period; **1** was then added (2.1 mL; 22 mmol). The solution was then stirred overnight at RT and became notably turbid. The resulting mixture was then treated with 10% aq. NaHCO_3 and the organic layer separated, washed twice with water and then dried with Na_2SO_4 , filtered and evaporated to dryness to give a light tan coloured powder. Yield: 0.35 g (19%). mp 116-117°C. NMR (CDCl_3): $\delta_{\text{H}} = 8.30$ (d, 2H, $J = 8.8$ Hz, ArH), 7.92 (d, 2H, $J = 8.8$ Hz, ArH), 6.30 (s, br, 1H, N-H), 3.86 (t, 1H, $J = 2.0$ Hz, OH), 3.73 (d, 2H, $J = 2.0$ Hz, CH_2), 1.47 (s, 6H, CH_3). This material was then dissolved in PhCl (10 mL) in the presence of ZnCl_2 (10 mol%) and heated to reflux temperature for 24 h. The contents of the reaction vessel were then evaporated to dryness and the residue recrystallised from CH_2Cl_2 /pet. ether to give oxazoline **4** in the form of a white powder. Yield: 0.30 (95%). mp 96.5-99°C (lit. [20]: 97-98°C). NMR (CDCl_3): $\delta_{\text{H}} = 8.28$ (d, 2H, $J = 8.9$ Hz, ArH), 8.13 (d, 2H, $J = 8.9$ Hz, ArH), 4.19 (s, 2H, CH_2), 1.43 (s, 6H, CH_3). [lit. [20]: 8.3 (d, 2H), 8.1 (d, 2H), 4.1 (s, 2H), 1.4 (s, 6H); lit [11a]: 8.25 (d, 2H, $J = 8.4$ Hz), 8.10 (d, 2H, $J = 8.4$ Hz), 4.16 (s, 2H), 1.40 (s, 6H)].
- [20] Clarke, D.S.; Wood, R. *Synth. Commun.*, **1996**, *26*, 1335.
- [21] Analysis (^1H NMR, mp) of our isolated oxazoline **4** matches fully with the data reported independently by Clarke and Wood [20] and Katritzky *et al.* [11a]. We also synthesized **4** independently using a modification of the original SOCl_2 route reported by Leffler and Adams involving a two-step procedure *via* the isolated amide **3** [22]. Compound **4** and the intermediate amide synthesised by this earlier method were fully consistent [20] with the two products reported above using **2** as amide bond-forming agent.
- [22] Leffler, M.T.; Adams, R. *J. Am. Chem. Soc.*, **1937**, *59*, 2252.
- [23] Data for presumed **5** described in [14]: mp 79°C; ^1H NMR (field strength and solvent not stated): $\delta_{\text{H}} = 7.8$ (d, 2H, $J = 8.5$ Hz, ArH), 7.6 (d, 2H, $J = 8.5$ Hz, ArH), 4.1 (s, 2H, OCH_2), 1.42 (s, 6H, CH_3); IR (cm^{-1} ; KBr): 720, 950, 1470, 1510, 1600 (higher frequency values not given); *n.b.*: MS and analytical data given are consistent with **5**. Data for **6** isolated here: mp 74.5-78.5°C; IR (thin film KBr: medium intensity bands unless otherwise stated): 750, 840, 870, 950, 1470 (s), 1530 (s), 1585, 1639 (s), 1710 (w), 2860, 2920, 2960, 3500 (br, s) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3):

$\delta_{\text{H}} = 7.69$ (d, 2H, $J = 8.8$ Hz, ArH), 7.42 (d, 2H, $J = 8.8$ Hz, ArH), 6.30 (s, br, 1H, N-H), 3.71 (s, 2H, OCH₂), 1.43 (s, 6H, CH₃). Data for **5** isolated here by treatment of **6** (ZnCl₂/PhCl/ Δ): mp <30°C: oil (lit mp's: 33-34°C [24]; oil [11a]); IR (cm⁻¹; thin film KBr: medium intensity bands unless otherwise stated): 670, 725 (s), 840 (s), 960, 1010 (s), 1080, 1060 (s), 1305, 1350, 1395, 1485 (s), 1590, 1641 (s), 1720, 2890, 2920, 2980 (s); ¹H NMR

(300 MHz, CDCl₃): $\delta_{\text{H}} = 7.89$ (d, 2H, $J = 8.8$ Hz, ArH), 7.39 (d, 2H, $J = 8.8$ Hz, ArH), 4.13 (s, 2H, OCH₂), 1.40 (s, 6H, CH₃); lit. data [11a]: $\delta_{\text{H}} = 7.87$ (d, 2H, $J = 8.7$ Hz), 7.37 (d, 2H, $J = 8.7$ Hz), 4.11 (s, 2H), 1.38 (s, 6H).

[24]

Boyd, R.N.; Rittner, R.C. *J. Am. Chem. Soc.*, **1960**, *82*, 2032.

[25]

Shono, T.; Kise, N.; Nomura, R.; Yamanami, A. *Tetrahedron Lett.*, **1993**, *34*, 3577.