Chemistry & Biology Interface, 2021, 11, 2, 57-60

RESEARCH PAPER ISSN: 2249 –4820

CHEMISTRY & BIOLOGY INTERFACE

An official Journal of ISCB, Journal homepage; www.cbijournal.com

Peterson Olefination in an Ionic Liquid: A Greener Approach

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Received 29 October 2020; Accepted 14 December 2020

Abstract: Excellent yielding olefin (2a-h) syntheses were performed from their respective β-hydroxyl-silyl compounds (1a-h) in an ionic liquid Ethylammonium nitrate (EAN). EAN has an inherent catalytic proficiency; the reactions were facilitated at room temperature. This effective and eco-friendly method is applicable for the preparation of natural products possessing terminal double bonds. Moreover, EAN was reused while following the specified method c for work up and product isolation from the reaction mixture. This methodology was performed at room temperature to obtain the products in an excellent yield about (75-87%). This reaction can be carried out on large scale having minimal product purification since the reaction did not require any additional catalyst.

Keywords: Peterson olefination, ionic liquid: Ethylammonium nitrate, olefin and greener approach

Introduction:

A large number of bioactive natural products are having alkene functional groups [1]. These can be achieved by various methods; Peterson olefination [2], Julia olefination [3], Johnson olefination [4] and Wittig reaction [5]. The Peterson olefination has fetched continuous interest from the synthetic organic chemists. Often these olefination reactions were carried out using more catalyst, and strong and excess of reagents. Recently reported syntheses of olefins were carried out using less loading with strong Bronsted acid $HNTf_2$ [6].

Because of their solvent properties, ionic liquids [7, 8, 9] are attracting increased attention. They afford significant environmental benefits and can contribute to green chemistry. Publications to date show replacing organic solvents by an ionic liquid can lead to remarkable improvements in well known procedures [7, 10]. EAN has many potential applications in protein chemistry. Broadly use an electrically conductive solvent in protein crystallography [11, 12]. Herewith reporting ionic liquid EAN

is mediated operationally simple, reusable, environment friendly, inexpensive and excellent yielding olefin compound by the Peterson olefination approach.

Experimental:

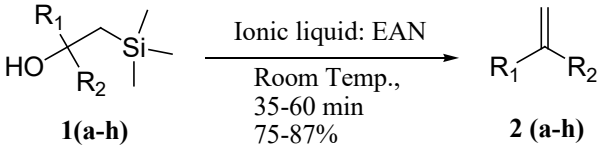
All reactions were performed under a nitrogen atmosphere. Ionic liquid EAN was prepared by the reported method. The required starting materials *β*-hydroxylsilyl (1a-1h) was prepared according to the method [7] given by Mark G. McLaughlin. All solvents were degassed before use. Neutral alumina TLC plate was used. ^{1}H NMR spectra were recorded on Bruker-400 (400 MHz).

Typical Experimental Procedure:

The following is a modification of the procedure outlined by Mark G. McLaughlin. The reaction of (Trimethylsilylmethyl) magnesium chloride (1.3 M solution in THF, 3 mmol) and aldehyde or ketone (1 mmol) gives crude compound of 2-(trimethylsilyl)-1, 1-disubstituted ethanol or 2-(trimethylsilyl)-1-monosubstituted ethanol. EAN (8 mmol) was added drop wise in reaction mixture, stirred at room temperature for 35-60 min. After completion of the reaction, methods a, b and or c was used for product isolation: (a) The reaction mixture was loaded directly on celite and isolation was carried out by eluting with n-hexane (2 X 15 ml). Eluted n-hexane fractions were combined then dried over sodium sulphate (3 g) and concentrated on rotary evaporator under reduced pressure to afford the product, (b) Reaction mixture was poured into ice-cold water (20 ml), and then filtered off obtained solid product and later purified by flash column chromatography or (c) Extraction with diethyl ether, the extract was dried over sodium sulphate (3g) and then concentrated on a rotary evaporator under reduced pressure to afford the product. The other layer contains an ionic liquid EAN, which can be reused after proper treatment.

By using above synthetic method and appropriate substrates, following compounds (2a- 2h) were synthesized.

Scheme 1. EAN mediated synthesis of olefin from β-hydroxylsilyl compound.



1(a-h) **2 (a-h)**

Results and Discussion:

Work was initiated by using compound 2-(trimethylsilyl)-1, 1-diphenylethanol (1e) which was synthesized from benzophenone and $TMSCH_2MgCl$ (trimethylsilylmethylmagnesium chloride) by the reported method [6]. For the conversion of compound 2-(trimethylsilyl)-1,1-diphenylethanol (1e) into compound 1,1-diphenylethene (2e), use of stoichiometric amount of EAN only confirmed formation of the product by stirring after 10 hr. The progress of the reaction and yield of the product were checked by increasing the amount of EAN from 5 equivalents to 8 equivalents. When EAN 5 equivalents was used, it was found that 10% of the substrate remains unreacted even after stirring 3 hr at room temperature. The reaction was further carried out by using EAN 8 equivalents; it was observed that substrate (1e) to product (2e) conversion increased satisfactorily within 45 minutes. This increase in EAN equivalence helped out in making the reaction mixture homogenized. Further work up of the reaction mixture by method a and or c yielded the 1, 1-diphenyl ethylene 87%. Having optimized reaction conditions, the scope of ionic liquid EAN for the conversion of β-hydroxylsilyl compounds into alkenes were carried out by the Peterson olefination approach. The reaction did not require any additional catalyst because the ionic liquid EAN acted as solvent and catalyst

Table 1: Reaction conditions and spectral characterization of synthesized olefins.

Product no.	R_1	R_2	Reaction time (min)	Work up method	Yield (%)	^{1}H NMR (400 MHz, CDCl3) δ ppm
2a	4-CN Ph	Me	45	a & c	87	7.61 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 5.47 (s, 1H), 5.46–5.24 (m, 1H), 2.17 (s, 3H).
2b	4-Br Ph	Me	55	a	76	7.42–7.31 (m, 4H), 5.34 (s, 1H), 5.12–5.09 (m, 1H), 2.11 (s, 3H).
2c	3,4-Dichloro Ph	Me	60	a & c	78	7.52 (d, *J* = 2.1 Hz, 1H), 7.39–7.26 (m, 2H), 5.37 (s, 1H), 5.14 (s, 1H), 2.11 (s, 3H).
2d	Naphth	Me	45	b & c	75	7.86–7.77 (m, 4H), 7.64 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.46 – 7.41 (m, 2H), 5.52 (s, 1H), 5.20 (s, 1H), 2.25 (s, 1H).
2e	Ph	Ph	45	a & c	87	7.35–7.28 (m, 10H), 5.47 (s, 2H).
2f	Ph	2-F Ph	45	c	80	7.35–7.27 (m, 7H), 7.16–7.06 (m, 2H), 5.77 (d, *J* = 1.1 Hz, 1H), 5.43 (s, 1H).
2g	4-CN Ph	H	35	a	77	7.62–7.50 (m, 2H), 7.49–7.47 (m, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.45 (d, *J* = 10.9 Hz, 1H).
2h	4-Br Ph	H	35	a & c	75	7.47–7.42 (m, 2H), 7.30–7.28 (m, 2H), 6.66 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.78–5.73 (m, 1H), 5.29 (d, *J* = 10.9 Hz, 1H).

Spectral data (^{1}H NMR) in accordance to previously published data [6, 12].

as reported earlier [8].

Conclusions:

This effective and eco-friendly method was used for the preparation of terminal alkenes by Peterson olefination approach. This methodology was performed at room temperature to obtain the products of excellent (about 75-87%) yields. It is scalable approach having minimal product purification. This method may be useful for the preparation of natural products having terminal double bonds, since the reaction did not require any additional catalyst.

Acknowledgement:

Hangarge R. V. is grateful to the Emeritus Professor Dr. Shingare M. S., Principal Dr. Kanade K. G. and Vice Principal Dr. Nikumbh A. B., Annasaheb Awate College, Manchar for providing facilities for the support of this work.

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