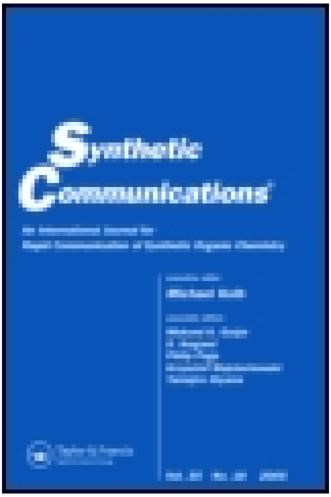

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

An Improved Procedure for the Synthesis of Terminal and Internal Alkynes from 10-Undecenoic Acid

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To cite this article: S. Narasimhan , H. Mohan & N. Palani (1991) An Improved Procedure for the Synthesis of Terminal and Internal Alkynes from 10-Undecenoic Acid, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 21:18-19, 1941-1949, DOI: 10.1080/00397919108021786

To link to this article: http://dx.doi.org/10.1080/00397919108021786

SYNTHETIC COMMUNICATIONS, 21(18&19), 1941-1949 (1991)

AN IMPROVED PROCEDURE FOR THE SYNTHESIS OF TERMINAL AND INTERNAL ALKYNES FROM 10-UNDECENOIC ACID

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Abstract: A remarkable solvent preference for dehydrobromination to yield 10-Undecynoic acid (5) and 9-Undecynoic acid (6) is observed in the case of 10,11-dibromoundecanoic acid (1). Thus, 10-Undecenoic acid can be easily and quantitatively converted to 6 in PEG-400, while 5 is produced in PEG-200. 5 can also be obtained in non-polar solvents with PEG-200/400 as a phase transfer catalyst.

Terminal and internal alkynoic acids dervied from 10-Undecenoic acid are valuable intermediates in the synthesis of pheromones such as E,E-10,12-Hexadecadienal[1], Z,E-9,11-tetradecadienyl acetate[2] and Z,E-9,12-tetradecadienyl acetate[3]. Earlier method reported for the synthesis of 10-Undecynoic acid (5) involved the use of sodamide in liquid ammonia at -78°C[4]; under similar conditions, only 38-49% yield was reported by Khan[5]; in a different method, the reaction had to be done for a longer time (12 hours)[6]. (The literature reported reaction conditions and

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Table 1: Literature data on dehydrobromination of (1):

S.No.	Base/ Solvent	Reaction time(h)/ temperature (°C)	Product	Yield (%)	Reference
1	$NaNH_2$/ liq. NH_3	- / -78	**5**	80	4
2	$NaNH_2$/ liq. NH_3	- / -78	**5**	38-49	5
3	KOH/PTC monoglyme	12 / 85	**5**	80	6
4	KOH	0.5/ 200	**6**	48.5	7
5	KOH	8 / 160	**5**	32	8

yield data are summarised in Table-1). The method reported for the preparation of 6 were accompanied by low yield[7]. This prompted us to study the dehydrobromination in detail and optimise the conditions for preparing 5 and 6.

It is known that dehydrobromination produces several intermediates (**2**–**4**): (Scheme: next page)

The exclusive formation of any of these species would be very valuable in pheromone synthesis. For example, the terminal vinyl bromide (**2**), if obtained in good yield, could be further used for coupling with the vinyl borane to produce Bombykol[9, 10]. Therefore, it is essential to study the reaction under different

SCHEME

$$BrCH_2CHBrCH_2(CH_2)_6CH_2COOH$$

1

$$\downarrow$$

$$BrCH{=}CHCH_2(CH_2)_6CH_2COOH + H_2C{=}CBrCH_2(CH_2)_6CH_2COOH$$

2 3

$$+ H_2C{=}C{=}CHCH_2(CH_2)_5CH_2COOH$$

4

$$\downarrow$$

$$HC{\equiv}CCH_2(CH_2)_6CH_2COOH + H_3CC{\equiv}CH_2(CH_2)_6CH_2COOH$$

5 6

conditions in order to optimise the formation of the preferred product.

Accordingly, we studied the dehydrobromation of 1 (obtained by the bromination of 10-Undecenoic acid) under different conditions and the products obtained in each case were analysed by ^{1}H-NMR[11] and ^{13}C-NMR. The results are indicated in Table-2.

It is evident from Table-2 that, employing either excess of a weaker base (five equivalents of potassium carbonate) or two equivalents of potassium hydroxide results in the formation of 40% of 5 (entries 1-4), the remaining being a mixture of 2, 3 and 4. There was no reaction in the presence of bases such as triethyl

Table 2: Dehydrobromination of 10,11-dibromoundecanoic acid(1):[a]

S.No.	Base (equiv)		solvent/ reaction time(h)	% product[b] 2+3+4[c]	 5	 6
1	K_2CO_3	(5)	PEG - 200/2	58	42	--
2	K_2CO_3	(5)	PEG - 400/2	65	35	--
3	KOH	(2)	PEG - 200/2	60	40	--
4	KOH	(2)	PEG - 400/2	61	39	--
5	KOH	(4)	PEG - 200/2	25	75(73)	--
6	KOH	(4)	PEG - 200/3	28	62(60)	10
7	KOH	(4)	PEG - 400/1	5	17	78(75)
8	KOH	(4)	PEG - 400/2	5	--	95(93)
9	KOH	(4)	PEG - 400/0.5[d]	10	--	90(88)
10	KOH	(4)	cyclohexane/2[e]	30	70(67)	--
11	KOH	(4)	cyclohexane/2[f]	32	68(65)	--

a All reactions are carried out at 125°C, unless specified.

b Based on ^{1}H-integration of peaks due to $\underline{H}C{\equiv}CC\underline{H}_2$ and $\underline{H}_3CC{\equiv}CC\underline{H}_2$ with respect to $C\underline{H}_2COOH$; values in the paranthesis indicate isolated yields.

c Due to the complexities in the vinyl region in the ^{1}H-NMR spectrum, individual species (**2**, **3** and **4**) could not be estimated.

d Reaction temperature: 200°C

e Reaction temperature: 80°C; PEG-200

f Reaction temperature: 80°C; PEG-400

amine and pyridine. Also, no appreciable reaction was observed with potassium hydroxide in non-polar solvents.

With excess of potassium hydroxide, <u>5</u> is formed predominantly in PEG-200 (entries 5-6) and <u>6</u> is obtained in major amounts in PEG-400 (entries 7-9). Although <u>6</u> is produced initially, it appears that the isomerisation reaction is faster in PEG-400 producing <u>6</u> exclusively in two hours (entry 8), while it is only 10% in PEG-200 after three hours (entry 6). This could be attributed to the more polar nature of the solvent, viz., PEG-400. Hence, it is possible that more of <u>5</u> could be obtained in a non-polar solvent.

It should be noted that there is no reaction in hexane probably due to the heterogenous nature of the reaction medium. Hence, employing a phase transfer catalyst could facilitate dehydrobromination. This is demonstrated in the dehydrobromation of <u>1</u> in cyclohexane with PEG-200 (or PEG-400) being employed only as a phase transfer catalyst, instead of Aliquat-330[6], wherein <u>6</u> is not at all formed (entries 10-11). Also, under these conditions, 1,2-dibromodecane produced 1-decyne in 70% yield.

Interestingly, a facile, quantitative conversion of <u>1</u> to <u>6</u> occurs in PEG-400 at 200°C in just thirty minutes (entry 9). This is in contrast to the procedure reported earlier[7].

The results indicate that optimum conditions could be obtained for the preparation of 5 and 6, but more studies are needed for the synthesis of the vinyl bromide (**2**). In the presence of a phase transfer catalyst (even PEG-400), non-polar solvents are useful to produce terminal alkynes, in general.

All reagents were of commercial quality from freshly opened containers. Melting points are uncorrected. ^{1}H-NMR and ^{13}C-NMR were recorded on a JEOL GSX 400 NMR Spectrometer. IR spectra were recorded on a Bruker FT-IR IFS 85 Spectrophotometer.

EXPERIMENTAL

10-Undecynoic acid (5):

(i) A slurry of potassium hydroxide (22.4g, 400mmol) in PEG-200 (100mL) is stirred and heated to 125°C, to get a clear solution. Maintaining this temperature, 1 (34.4g, 100mmol) is added in drops. Two hours after the addition of 1, the reaction mixture is cooled, neutralised with concentrated hydrochloric acid (checked with pH paper). The mixture is extracted with chloroform:hexane (1:3 v/v, 4x100mL). The organic extracts are combined, washed with brine (2 x 100mL), water (2 x 100mL) and dried over anhydrous sodium sulfate. The evaporation of solvent yields a reddish-brown liquid, which is distilled to obtain the pure product. b.p. 180°C/15mm. The distillate crystallised on standing. m.p.42°C (Ref[12] m.p.42°C). Yield: 13.7g (75%).

(ii) A mixture of potassium hydroxide (4.48g, 80mmol), cyclohexane (20mL), PEG-200/400 (2mL) and $\underline{1}$ (6.88g, 20mmol) is stirred at 80°C for two hours. A similar work-up as given above followed by distillation yields $\underline{5}$, which crystallises on standing. Yield: 2.6g (70%).

IR (CCl$_4$): ν = 3300(**H-C**≡**C**), 3150(**OH**), 2250(C≡C), 1717(**C=O**)cm^{-1}

^{1}H-NMR (CDCl$_3$/TMS): δ =
1.35-1.5 (**m**, **12H**),
1.95 (**t**, **1H**, $\underline{H}C\equiv C$)
2.175 (**m**, **2H**, $C\equiv CC\underline{H}_2$)
2.35 (**t**, **2H**, $C\underline{H}_2COOH$)
10.85 (**s**, **1H**, $COO\underline{H}$) ppm.

^{13}C-NMR (CDCl$_3$/TMS): δ =
18.701 (t, $\equiv C\underline{C}H_2$),
24,590-29.946 [t, ($\underline{C}H_2$)$_6$],
34.077 (t, $HOOC\underline{C}H_2$),
68.260 (**d**, $H\underline{C}\equiv$),
84.517 (s, $HC\equiv\underline{C}$),
180.540 (**s**, $\underline{C}OOH$) ppm.

9-Undecynoic acid (6):

(i) A slurry of potassium hydroxide (22.4g, 400mmol) in PEG-400 (100mL) is stirred and heated to 125°C to get a clear solution. Maintaing this temperature, $\underline{1}$, (34.4g, 100mmol) is added in drops. Two hours after the addition of $\underline{1}$, the reaction mixture is cooled, neutralised with concentrated hydrochloric acid (checked with pH paper) and extracted with choloform: hexane (1:3 v/v, 4 x 100mL) mixture. The extracts are combined, washed with brine (2 x 100mL), water (2 x 100mL) and dried over anhydrous sodium sulfate; the solvent evaporated to give a reddish-brown liquid, which is distilled. b.p.128°C/0.4mm. The distillate solidified immediately. m.p.58°C (Ref[13] m.p.58°C). Yield: 16.94g (93%).

(ii) At 200°C, the reaction is complete in thirty minutes; a similar work-up procedure yields <u>**6**</u> in 88% yield (16g).

IR (CCl_4): ν = 3150(**OH**), 2250(**C≡C**), 1715(**C=O**)**cm**$^{-1}$.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.35-1.5 (**m, 10H**),
1.763 (**t, 3H,** $\underline{H}_3CC{\equiv}C$),
2.12 (**m, 2H,** $C{\equiv}CC\underline{H}_2$),
2.35 (**t, 2H,** $\underline{H}_2CCOOH$),
10.85 (**s, 1H,** $COO\underline{H}$) ppm.

^{13}C-NMR ($CDCl_3$/**TMS**)**:** δ = 3.461 (**q,** $H_3\underline{C}C{\equiv}$),
18.701 (**t,** ${\equiv}C\underline{C}H_2$),
24.651-28.977 [**t,** $(\underline{C}H_2)_5$],
34.107 (t, $\underline{C}H_2COOH$),
75.455 (**s,** $H_3C\underline{C}{\equiv}C$),
79.280 (**s,** $C{\equiv}\underline{C}CH_2$),
180.312 (**s,** $\underline{C}OOH$) ppm.

<u>**Acknowledgement:**</u> The authors thank Prof.T.R.Govindachari, Director, CAR for encouragement, Mr.M.S.Moni (RSIC, IIT, Madras) for ^{1}H-NMR and ^{13}C-NMR spectra and Dr.Geetha Gopalakrishnan (CAR) for IR spectra. HM thanks DST, Government of India for financial support.

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(Received in UK 22 May, 1991)