Tetrahedron Letters No. 48, 4233 - 4234, 1975. Pergamon Press. Printed in Great Britain.

A FACILE SYNTHESIS OF PROPYLURE VIA LITHIUM TRIPROPYLTRIMETHYLSILYLETHYNYLBORATE

Kiitiro Utimoto, Mitsumasa Kitai, Mikio Naruse and Hitosi Nozaki

Department of Industrial Chemistry, Kyoto University, Yoshida, Kyoto, Japan

(Received in Japan 8 September 1975, received in UK for publication 13 October 1975)

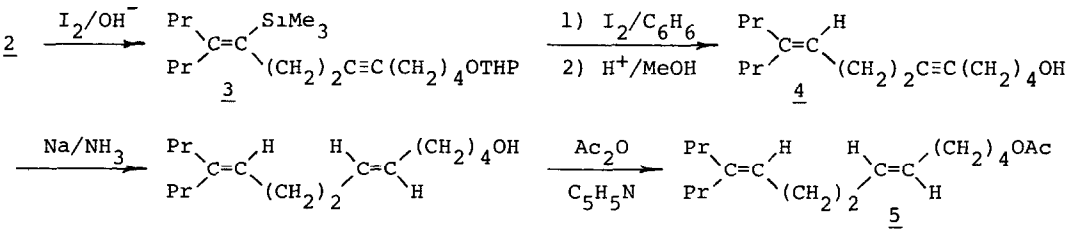
Reductive alkylation of acetylenes via lithium trialkylalkynylborates has provided useful methods for olefin synthesis [1] We now wish to report an application to synthesis of propylure.[2]

To a stirred solution of trimethylsilylacetylene (0.59 g, 6 mmol) in THF (6 ml) at -78° under argon, butyllithium in hexane (5 ml of 1.2 M solution) was added Stirring was continued at room temperature for 30 min, then tripropylborane (0.84 g, 6 mmol) was added to the solution at 0°. The mixture was stirred at room temperature for 2 h, added with tosylate 1 (1.14 g, 3 mmol in 3 ml of THF)[3] at -78°, and then heated at reflux for 16 h. Treatment of the whole mixture with 2 ml of 3 N sodium hydroxide and iodine (1.52 g, 6 mmol in 6 ml of THF)[5] at 0°, followed by stirring at room temperature for 2 h, afforded vinylsilane (3)[6,7] after column chromatography (Silica-gel, benzene) (0 84 g, 71% yield).

Treatment of the benzene solution of 3 with iodine[8] afforded the mixture of the alcohol 4 and the corresponding tetrahydropyranyl ether. Acid-catalyzed hydrolysis of the mixture gave the alcohol 4 (76% yield) [9] Propylure was obtained from 4 by Na/NH_3 reduction (84% yield) and acetylation (90% yield).[10,11]

$$HC{\equiv}CSiMe_3 \xrightarrow{BuLi} LiC{\equiv}CSiMe_3 \xrightarrow{Pr_3B} [Pr_3\bar{B}\text{-}C{\equiv}CSiMe_3]Li^+$$

$$\xrightarrow{TsO(CH_2)_2C{\equiv}C(CH_2)_4OTHP\ (1)} \underset{2}{\overset{Pr_2B}{\overset{Pr}{\diagdown}}C{=}C\overset{SiMe_3}{\diagup}\overset{(CH_2)_2C{\equiv}C(CH_2)_4OTHP}{\diagdown}}$$

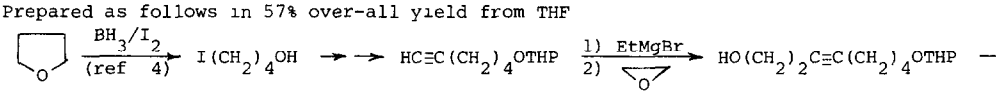


REFERENCES AND NOTES

1 See recent publications below and references cited therein (a) P Binger and R Koster, Synthesis, 350 (1974), (b) M Naruse, K Utimoto, and H Nozaki, Tetrahedron, 30, 3037 (1974), (c) A Pelter, C Subrahmanyam, R. J Laub, K J Gould, and C R Harrison, Tetrahedron Letters, 1633 (1975), (d) M Miyaura, T Yoshinari, M Itoh, and A Suzuki, ibid , 2961 (1974)

2 (a) W A Jones, M Jacobson, and D. F Martin, Science, 152, 1516 (1966), (b) K Eiter, E Truscheit, and M Boness, Liebigs Ann Chem , 709, 29 (1967), (c) G Pattenden, J Chem Soc (C), 2385 (1968), (d) M Stoll and I Flament, Helv Chim Acta, 52, 1996 (1969), (e) J C Stowell, J Org Chem , 35, 244 (1970), (f) A I Meyers and E. W. Collington, Tetrahedron, 27, 5979 (1971), (g) K Oshima, H Takahashi, H Yamamoto, and H Nozaki, J Amer Chem Soc , 95, 2693 (1973), (h) J Kossanyi, B Furth, and J-P Morizur, Tetrahedron Letters, 3459 (1973), (i) R J Anderson and C A Henrick, J Amer Chem Soc , 97, 4327 (1975) and references cited therein

3 Prepared as follows in 57% over-all yield from THF



4 L. H Long and G F Freeguard, Nature, 207, 403 (1965)

5 G Zweifel, H Arzoumanian, and C C Whitney, J Amer Chem Soc , 89, 3652 (1967).

6 The structure of this compound was determined spectrometrically, ir (neat) 1599, 1250, 1139, 1120, 1076, 1036, 838 cm^{-1}, nmr (CCl_4) δ ppm, 0 12 (9H, s), 0 90 (6H, t, J = 6 Hz), 1 3-1 8 (14H), 1 9-2 4 (10H), 3 2-3 8 (4H), 4.47 (1H, m) This vinylsilane 3 was obtained via 2 whose stereochemistry was not confirmed

Trisubstituted vinylsilanes can be prepared by this reductive alkylation of trimethylsilylacetylene 3-ethyl-4-trimethylsilyl-3-nonene (78% from Et_3B and $CH_3(CH_2)_4OTs$)[8] and 4-propyl-5-trimethylsilyl-8-methyl-4-nonene (80% from Pr_3B and $Me_2CHCH_2CH_2OTs$)

7 Analogous reductive trialkylation of acetylene via lithium trialkylalkynylborates has been achieved by successive treatment with oxirane and with iodine-alkaline [1b]

8 K Utimoto, M Kitai, and H Nozaki, Tetrahedron Letters, 2825 (1975)

9 The reaction of lithium tripropylethynylborate-ethylenediamine complex with tosylate 1 was expected to give the alcohol 4, but in this case elimination of 1 occurred predominantly

10 The structure was confirmed by mass spectrometry and comparison of ir and nmr spectra with those of the reported sample [2f] The authors are indebted to Professor A I Meyers, Colorado State University, for offering nmr and ir spectra of propylure

11 The authors wish to thank the Ministry of Education, Japan, for a Grant-in-aid (911506)