Tetrahedron, Vol. 37, pp. 1653 to 1658, 1981
Printed in Great Britain.

0040-4020/81/091653-06$02.00/0
Pergamon Press Ltd.

A CONVENIENT ROUTE TO ALKYNES VIA PHASE TRANSFER CATALYSIS

(APPLICATIONS OF PHASE TRANSFER CATALYSIS, PART 19[1])

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(Received in Germany 16 December 1980; received in UK 23 February 1981)

Abstract - High yield, rapid formations of alkynes from vic-dibromides are possible using powered potassium hydroxide and catalytic amounts of lipophilic phase transfer catalysts. Reasons are given why molar amounts of expensive catalysts were necessary in earlier procedures.

A recently published Organic Synthesis procedure for the preparation of 3,3-diethoxy-1-propyne (1)[2] (*cf.*[3]) prompts us to present our own, more convenient method to make this and other alkynes by phase transfer catalysis (PTC)[4].

$$BrCH_2\text{-}CHBr\text{-}CH(OEt)_2 \longrightarrow \underset{\mathbf{1}}{HC\equiv C\text{-}CH(OEt)_2}$$

In the published PTC-synthesis of 1, larger than molar amounts of the rather expensive catalyst tetrabutylammonium hydrogen sulfate must be used[2]. This makes a multi-step recovery procedure of the ammonium salt necessary.

Attempts of the previous authors to use only catalytic amounts of tetrabutylammonium hydrogen sulfate or other catalysts like $(C_4H_9)_4N^{\oplus}Br^{\ominus}$, $(C_4H_9)_4N^{\oplus}J^{\ominus}$, triethylbenzylammonium chloride,or hexadecyltrimethylammonium bromide failed[3c]. Our procedure for β-eliminations, however, works with catalytic amounts of tetraoctylammonium bromide, 18-crown-6, or even Aliquat 336[5]. It even surpasses our previous PTC-method to generate alkynes (dihalides/potassium-*tert*-butoxide/18-crown-6)[6] in simplicity and cheapness, although its scope is more limited.

Our results are shown in table 1. The formation of alkynes involves the stepwise elimination of two molecules of hydrogen bromide. We could demonstrate that the relative rates of eliminations from the intermediate bromoalkenes are in this order:

2-bromoalkene > (Z)-1-bromoalkene > (E)-1-bromoalkene (*cf.*[6]). Thus, a (slow) *syn*-elimination must be possible under these conditions.

Table 1: Preparation of alkynes from 0.1 mol *vic.*-dibromides, 0.25 mol solid KOH 1 mMol tetraoctylammonium bromide in petroleum ether.

alkyne	yield[7]	time/°C
$HC\equiv C-CH(OEt)_2$	79%	6h/80°C
$C_6H_5-C\equiv C-C_6H_5$	96%	1h/80°C
$(p-Cl)-C_6H_4-C\equiv C-(p-Cl)-C_6H_4$	84%	8h/20°C
$C_6H_5-C\equiv CH$	98%	1h/80°C
$(p-CH_3)-C_6H_4-C\equiv CH$	96%	8h/35°C
$n-C_4H_9-C\equiv CH$	92%	6h/90°C
$n-C_6H_{13}-C\equiv CH$	95%	6h/90°C
$n-C_{14}H_{29}-C\equiv CH$	88%	6h/90°C
$(CH_3)_3C-C\equiv CH$	86%	6h/90°C

Alkynes from dichlorides or chloroalkenes can be prepared similarly, but yields are generally lower after comparable reaction times. Thus, E/Z-2-chlorovinyl ethyl ethers give only 47% ethoxyacetylene, 2,2-dichloro-3,3-dimethylbutane and 2-(1,1-dichloroethyl)-thiophene yield only 38 or 56% of the respective alkynes after 8h at 90°C. In all cases unreacted starting materials and/or chloroalkenes were recovered in addition to the alkynes.

Here are some practical notes for running such reactions:

(a) The temperature should be lower than 100°C to slow down the decomposition of the ammonium salt[8]. (b) Isomerisation of the 1-alkyne can be avoided if there is no large excess of base present. (c) The boiling range of the petroleum ether should be very different from that of the alkyne formed to allow for easy separation.

DISCUSSION

Whereas in previous procedures molar or higher amounts of catalysts were necessary, only 10 mol-% are used in the present process. Now large, lipophilic catalysts are used, while formerly more hydrophilic quaternary ammonium salts were advocated. The reason for the different performance of the two classes of PTC catalysts seems to be the relative extractability of hydroxide. Competitive extraction of hydroxide is difficult generally as the extraction constant of $OH^{\ominus}$ is some powers of ten smaller than the ones of the halides[8].

This, however, must not be the only factor involved. After equilibrating an organic solution of a rather hydrophilic ammonium salt (e.g. benzyl triethylammonium chloride) with excess concentrated aqueous sodium hydroxide, only trace amounts of base can be titrated in the organic layer. This can be generalized: Small quaternary ammonium ions are extracted almost exclusively as [$NR_4^{\oplus}$ $halide^{\ominus}$] <u>even if a large excess of alkali metal hydroxide is present</u>[8,9]. By way of contrast, large lipophilic quaternary ammonium cations can carry a limited, but appreciable quantity of hydroxide ions into a nonpolar medium: Equilibration of 0.1 M $N(n\text{-}C_6H_{13})_4^{\oplus}Cl^{\ominus}$ in benzene with an equal volume of 50% sodium hydroxide leads to a solution of 0.028 M [$N(n\text{-}C_6H_{13})_4^{\oplus}$ $OH^{\ominus}$] in benzene[8]. The reason for this difference seems to rest in the poor solubility of the hydroxides of small ammonium cations. Thus, <u>relative extractability</u> $OH^{\ominus}$ vs. $halide^{\ominus}$ and <u>relative solubility</u> [$NR_4^{\oplus}$ $OH^{\ominus}$] vs. [$NR_4^{\oplus}$ $halide^{\ominus}$] together seem to determine the catalytic efficiency of various phase transfer catalysts.

Once accepting this concept, it is easy to understand, why at least molar amounts of $N(C_4H_9)_4HSO_4$ must be applied in the eliminations: The halide formed is always present in sub-stochiometric amounts and cannot block up the extraction of hydroxide. The sulfate formed by neutralizing the hydrogen sulfate is not extracted at all (cf.[4]). With the very lipophilic catalysts, there will always be some hydroxide extraction as long as the excess of aqueous hydroxide is large relative to the halide formed.

Unfortunately, no data are available at present to evaluate various possible catalysts according to solubilities, extractabilities, and efficiency in elimination reactions. It is hoped that such informations can be presented from this laboratory in the future.

It must be noted here that there are at least two possible mechanisms of phase transfer catalysis in the presence of alkali metal hydroxide: (i) The one considered so far involving the extraction of hydroxide ions into the organic medium. (ii) Deprotonation of the organic substrate at the interphase, followed by detachment of the absorbed substrate anion by the catalyst cation and transport into the depth of the organic phase for further transformations. Mechanisms (ii) has been advocated first by Makosza for PTC-alkylations[10] and by one of the present authors for PTC dihalocarbene generations[11]. Supporting evidence for this mechanism has accumulated since [4a, 9, 12], and a very recent kinetic study of PTC alkylation comes to the same conclusion[13]. It is not known presently whether such a deprotonation at the interphase (which would shift the elimination towards E_1cB) could be partially responsible for PTC eliminations. The observed effects do not support this as the sole process, however.

ACKNOWLEDGEMENTS

This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. We thank Mr. Uwe Fastabend for technical assistance.

EXPERIMENTAL

Melting points were determined on a Dr. Tottoli apparatus and are uncorrected. Boiling points were observed in a kugelrohr apparatus. All compounds were characterized by GC and spectroscopic methods. ^{1}H-NMR-Spectra (CCl_4, TMS as internal standard) were recorded with a Varian EM 360 or Bruker WH 80 instrument, IR Spectra with a Beckmann Acculab 8 spectrometer in CCl_4 solution. Analytical gas chromatography was performed with a Carlo Erba 4200 chromatograph (3m-column with OV101, 10% on chromosorb w).

Materials: All phase transfer catalysts were commercially available. Technical grade petroleum ether and potassium hydroxide were used. The following starting materials were prepared according to published procedures: 2,3-dibromo propionaldehyde diethylacetal[2], stilbene dibromide[14], 1,2-dibromo-1,2-di-(p-chlorophenyl)-ethane[15], styrene dibromide[16], 1-(p-tolyl)-1,2-dibromoethane[17], 1,2-dibromohexane[16], 1,2-dibromoctane[16], 1,2-dibromohexadecane[18], 1,2-dibromo-3,3-dimethylbutane[19], 2,2-dichloro-3,3-dimethylbutane[20], E/Z-2-chlorovinyl ethyl ether[21], E/Z-2-bromovinyl ethyl ether[22], 2-(1,1-dichloroethyl)-thiophene[23].

GENERAL PROCEDURE

For easy separation of the product alkyne from solvent, the boiling range the petroleum ether should be different from that of the alkyne. Therefor two variants were used: Variant A: petroleum ether b.p. 80-100°C; variant petroleum ether b.p. > 200°C.

A solution or suspension of 0.1 mol d bromide in 100 ml petroleum ether (se above) and 1 mmol tetraoctylammonium bromide (or Aliquat 336, or 18-crown- in the preliminary experiments) was added to 0.25 mol (14g) powdered potassium hydroxide. The mixture was fi tered after stirring for 1-8 hours a 20-90°C (see table 1). Depending on relative boiling points, either the solvent was distilled off and the re sidue was recrystallized or distille (variant A), or the product was dist led directly out of the reaction mix ture and subsequently redistilled (variant B).

Compounds prepared:

3,3-diethoxy-1-propyne, b.p. 90-94° 150 Torr (lit.[2] 95-96°C/170 Torr), procedure B.

tolane, m.p. 61°C (lit.[24] m.p. 61°C procedure A.

di-(p-chlorophenyl)-ethyne, m.p. 17 (lit.[25] m.p. 178-179°C), procedure

phenylacetylene, procedure B.

p-tolylacetylene, b.p. 55°C/15 Torr (lit.[26] b.p. 52°C/11 Torr), procedu

1-hexyne, b.p. 71°C (lit.[27] b.p. 71,3° C), procedure B.

1-octyne, b.p. 125°C (lit.[27] b.p. 126,2°C), procedure B.

1-hexadecyne, b.p. 95°C/0.1 Torr (lit.[27] b.p. 284°C), procedure A.

3,3-dimethyl-1-butyne, b.p. 37°C (lit.[28] b.p. 37°C), procedure variant B gave 7.1g (86%) from 24.4g 1,2-dibromo- 3,3-dimethylbutane. In another experiment 15,5g 2,2-dichloro-3,3-dimethyl-butane yielded only 38% in 8 hours at 90°C.

ethoxyacetylene, b.p. 51°C (lit.[29] b.p. 51°C). 31.2g (0.2 mol) E/Z-2-bromovinyl ethyl ether yielded 9.0g (64%) according to procedure B in 8 hours reaction time at 90°C. Starting with 21.1g E/Z-2-chlorovinyl ethyl ether only 6.6g (47%) were obtained under the same set of conditions.

2-ethinyl-thiophene, b.p. 34°C /13 Torr (lit.[30] b.p. 31°C/3,5 Torr), 18.1g 2-(1,1-dichloroethyl)-thiophene yielded 6.0g (58%) according to procedure B in 8 h reaction time at 90°C.

FOOTNOTES AND REFERENCES

1) Part 18: E.V. Dehmlow and S. Barahona-Naranjo, J. Chem. Res., submitted.

2) A. Le Coq and A. Gorgues, Organ. Synth. 59, 10 (1980).

3)a) A. Gorgues, C.R. Acad. Sc. Paris 278c, 287 (1974). b) A. Gorgues, and A. Le Coq, Tetrahedron Lett. 1976, 4723. c) A. Gorgues, and A. Le Coq, Bull. Soc. Chim. France II 1976, 125.

4)a) E.V. Dehmlow, and S.S. Dehmlow, Phase Transfer Catalysis, Verlag Chemie, Weinheim, Deerfield Beach (Florida), Basel 1980. b) W.P. Weber, and G.W. Gokel, Phase Transfer Catalysis in Organic Synthesis, Springer-Verlag, Berlin, Heidelberg, New York 1977. c) Ch. M. Starks, and Ch. Liotta, Phase Transfer Catalysis, Principles and Technique, Academic Press, New York, San Francisco, London 1978.

5) Aliquat 336 is a technical grade tricaprylammonium chloride.

6) E.V. Dehmlow, and M. Lissel, Liebigs Ann. Chem. 1980, 1.

7) Isolated yields. All compounds are known. They were fully characterized by the usual physical methods.

8) E.V. Dehmlow, M. Slopianka, and J. Heider, Tetrahedron Lett. 1977, 2361.

9) E.V. Dehmlow, and M. Lissel, Liebigs Ann. Chem., in press.

10) M. Makosza, Pure Appl. Chem. 43, 439 (1975).

11) E.V. Dehmlow, Angew. Chem. 89, 521 (1977), Angew. Chem. Intern. Ed. Engl. 16, 493 (1977).

12) R. Le Goaller, M.A. Pasquini, and J.L. Pierre, Tetrahedron 36, 237 (1980).

13) R. Solaro, S. D'Antone, and E. Chiellini, J. Org. Chem. 45, 4179 (1980).

14) L.I. Smith and M.M. Falkof, Organ. Synth. Coll. Vol. III, J. Wiley & Sons, New York, Sydney 1955, p.350.

15) E. Späth, Monatsheft Chem. 35, 474 (1914).

Verlag der Wissenschaften, Berlin (1974).

17) A.F. Titley, J. Chem. Soc. 1926, 508.

18) S.L. Langedijk, and D.L. Stedehander, Rec. Trav. Chim. Pays-Bas 56, 526 (1937).

19) W.L. Collier, and R.S. Macomber, J. Org. Chem. 38, 1367 (1973).

20) P.D. Bartlett, and L.J. Rosen, J. Am. Soc. 64, 543 (1942).

21) D.H. van Dorp, J.F. Arens, and O. Stephenson, Rec. Trav. Chim. Pays-Bas 70, 289 (1951).

22) L. Brandsma, Preparative Acetylenic Chemistry, Elsevier Publ. Comp. Amsterdam, London, New York 1971, p. 190.

23) A. Vaitukunas, and F.F. Nord, J. Org. Chem. 19, 902 (1954).

24) P. Ruggli, and F. Lang, Helv. Chim Acta 21, 38 (1938).

25) W.L. Walton, J. Am. Chem. Soc. 69, 1544 (1974).

26) V. Prey, and H. Berbalk, Monatsh. Chem. 82, 990 (1951).

27) Selected Values of Thermodynamic Properties of Hydrocarbons and Related Compounds, Thermodynamic Res Cent., API 44 Hydrocarbon Project, Texas A & M University, College Station, Texas 1978.

28) H.N. Miller, K.W. Greenlee, J.M. Derfer, and C.E. Boord, J. Org. Chem. 19, 1882 (1954).

29) W.F. Truce, and D.L. Goldhamer, J. Am. Chem. Soc. 64, 5798 (1959).

30) H. Keskin, R. Miller, and F.F. Nord, J. Org. Chem. 16, 5798 (1959).