A CONVENIENT ROUTE TO ALKynes VIA PHASE TRANSFER CATALYSIS

APPLICATIONS OF PHASE TRANSFER CATALYSIS, PART 19

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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 \((1)\) \((2)\) \((3)\) prompts us to present our own, more convenient method to make this and other alkynes by phase transfer catalysis (PTC) \(^4\).

\[
\text{BrCH}_2\text{CHBr-CH(OEt)}_2 \rightarrow \text{HOCCH-C-CH(OEt)}_2^1
\]

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 \((\text{C}_4\text{H}_9)_4\text{N}^\text{+}\text{Br}^\text{-}\), \((\text{C}_9\text{H}_{18})_4\text{N}^\text{+}\text{Br}^\text{-}\), triethylbenzylammonium chloride, or hexadecytrimethylammonium bromide failed \(^3\). Our procedure for \(\beta\)-eliminations, however, works with catalytic amounts of tetaoctylammonium bromide, 18-crown-6, or even Aliquat 336 \(^5\). It even surpasses our previous PTC-method to generate alkynes (dihalides/potassium-tetra- 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) \textit{g} \textit{ly} \textit{c} -elimination must be possible under these conditions.

(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 small.

<table>
<thead>
<tr>
<th>alkyne</th>
<th>yield</th>
<th>time/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC≡C-CH(OEtf)₂</td>
<td>79%</td>
<td>6h/80°C</td>
</tr>
<tr>
<td>C₆H₅-C≡C-C₆H₅</td>
<td>96%</td>
<td>1h/80°C</td>
</tr>
<tr>
<td>(p-Cl)-C₆H₄-C≡C-(p-Cl)-C₆H₄</td>
<td>84%</td>
<td>8h/20°C</td>
</tr>
<tr>
<td>C₆H₅-C≡CH</td>
<td>98%</td>
<td>1h/80°C</td>
</tr>
<tr>
<td>(p-CH₃)-C₆H₄-C≡CH</td>
<td>96%</td>
<td>8h/35°C</td>
</tr>
<tr>
<td>n-C₄H₉-C≡CH</td>
<td>92%</td>
<td>6h/90°C</td>
</tr>
<tr>
<td>n-C₆H₁₃-C≡CH</td>
<td>95%</td>
<td>6h/90°C</td>
</tr>
<tr>
<td>n-C₁₄H₂₉-C≡CH</td>
<td>88%</td>
<td>6h/90°C</td>
</tr>
<tr>
<td>(CH₃)₃C-C≡CH</td>
<td>85%</td>
<td>6h/90°C</td>
</tr>
</tbody>
</table>

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.

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⁻ 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 \([NR_4^+ \text{halide}^-]\) even if a large excess of alkali metal hydroxide is present\(^8,9\). 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 \(N(n-C_6H_{13})_4Cl^+\) in benzene with an equal volume of 50% sodium hydroxide leads to a solution of 0.028 M \([N(n-C_6H_{13})_4OH^-]\) in benzene\(^8\). The reason for this difference seems to rest in the poor solubility of the hydroxides of small ammonium cations. Thus, relative extractability \(\text{OH}^-\) vs. \(\text{halide}^-\) and relative solubility \([NR_4^+ \text{OH}^-]\) vs. \([NR_4^+ \text{halide}^-]\) 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-stoichiometric 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 \(E_1\text{CB}\)) could be partially responsible for PTC eliminations. The observed effects do not support this
as the sole process, however.

ACKNOWLEDGEMENTS

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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 CC1$_4$ 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 of the petroleum ether should be different from that of the alkyne. Therefore, two variants were used: Variant A: petroleum ether b.p. 80-100°C; variant B: petroleum ether b.p. > 200°C.

A solution or suspension of 0.1 mol dibromide in 100 ml petroleum ether (see above) and 1 mmol tetracylammonium bromide (or Aliquat 336, or 18-crown in the preliminary experiments) was added to 0.25 mol (14g) powdered potassium hydroxide. The mixture was filtered after stirring for 1-8 hours at 20-90°C (see table 1). Depending on relative boiling points, either the solvent was distilled off and the residue was recrystallized or distilled (variant A), or the product was distilled directly out of the reaction mixture and subsequently redistilled (variant B).

Compounds prepared:

3,3-diethoxy-1-propyne, b.p. 90-94°C/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°C (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), procedure...
A convenient route to alkynes

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.

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


5) Aliquat 336 is a technical grade tricaprylammonium chloride.


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


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


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


