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DIOLS AS EFFECTIVE COCATALYSTS IN THE PHASE TRANSFER CATALYZED PREPARATION OF 1-ALKYNES FROM 1,2-DIHALIDES

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Abstract: Bis-tertiary diols accelerate bis-eliminations of HX from 1,2-dihalides in the presence of an onium salt as phase transfer catalyst and potassium hydroxide as base. PEG 400 catalyzes the same elimination, but isomerizations from 1-alkyne to mixtures with the 2-alkyne and the 1,2-diene occur easily.

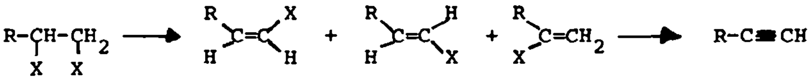
A recent paper from these two laboratories reported[1] that equimolar mixtures of lipophilic quaternary ammonium halides and certain diols allow the extraction of surprisingly high concentrations of "base" into non-polar organic media. The extracted base was shown to be the monoanion of the diol which seems to be partially self-solvated by intramolecular H-bonding. Although this finding is of some interest for phase transfer catalytic processes under basic conditions (review ref.[2]), a widespread application requires that the extracted species is a strong base and a poor nucleophile. The latter point can be met partially by using a bis-tertiary diols, e.g. pinacol. Unfortunately, no direct information is available on the first pK_a value of this compound or close analogues. Aqueous pKa values of primary alkanols are ~ 16.1, and the conjugate base of tert-butanol (aqueous $pK_a \sim 19$ [3]) is more basic. Various bis-primary diols [3,4] have pk_as of 15.1-15.4, and therefore one can estimate that the first pK_a of pinacol must be around 18. Thus, the monoanion of pinacol and related compounds should be a stronger base than the hydroxide ion in water. PTC experience with the latter shows that its basicity is enhanced in nonpolar media due to the absence of a large H-bonding solvent shell. It is open to question, how primary, secondary, and tertiary diol monoanions will behave under similar conditions. On one hand it is well known that most anions coextract a limited number (1-5 molecules) of water in PTC[2,5], but then tert-alkanols have an intrinsic higher acidity under non-solvated gas-phase conditions[6].

PTC elimination reactions have found a very wide interest[2,7,8,11]. This type of reaction therefore was considered a good model to test out the basic properties of the diols and to search for preparative improvements. Furthermore, the present work was undertaken to contrast the efficiency of a quaternary ammonium salt/diol mixture to the usefulness of a polyethylene glycol (PEG) as a catalyst.

RESULTS AND DISCUSSION

It was shown earlier[7b] that alkynes **5** can be prepared from 1,2-dibromoalkanes **1a** by heating with powdered potassium hydroxide and catalytic amounts of tetraoctylammonium bromide ($NOct_4Br$) in petroleum ether. Intermediates in this reaction are the bromoalkenes **2a**, **3a**, and **4a**, and the rates of further conversions to **5** are **2** > **4** > **3**[7a].

Working with 50% aqueous potassium hydroxide instead of powdered KOH, one obtains only **2a** - **4a**. If, however, alkanols are added to the reaction mixture, some alkyne **5** is formed in addition to **2a** - **4a** (Table 1). The performance of various alcohols is roughly parallel to their ability to extract basicity[7b]. Interestingly, the primary diols which carry the two OH-groups 6- 8 C-atoms



1 **2** **3** **4** **5**

a: X = Br, R = C_6H_{13}
b: X = Cl, R = C_6H_{13}

apart are more active than the tertiary diols and the n-alkanols. Ethanol is especially poorly suited, presumably because it is partitioned partly into the aqueous medium.

Table 1. Dehydrohalogenation of 1,2-dibromooctane 1a with 50% aqueous KOH (5.36 mmol 1a, 500 mmol KOH, 10^{-4} mol catalyst, 2 10^{-4} mol diol, 5 ml petroleum ether, 75°C, 2,5h)

Catalyst	Alkanol Cocatalyst	Alkyne % **5a**	Alkenes % **2a**-**4a**	Substrate % **1a**
$NOct_4Cl$	none	0	70	30
$NOct_4Cl$	EtOH	0	88	12
$NOct_4Cl$	n-$C_5H_{11}OH$	10	90	0
$NOct_4Cl$	n-$C_7H_{15}OH$	8	92	0
$NOct_4Cl$	$HO(CH_2)_6OH$	48	52	0
$NOct_4Cl$	$HO(CH_2)_8OH$	50	50	0
$NOct_4Cl$	2,5-hexandiol	50	50	0
$NOct_4Cl$	2-methyl-2,4-pentanediol	44	56	0
$NOct_4Cl$	2,3-dimethyl-2,3-butanediol	39	61	0
$NOct_4Cl$	2,5-dimethyl-2,5-hexanediol	39	61	0
	PEG 200	2	98	0
	PEG 1000	31	69	0

Other diols caused foaming and formation of emulsions, and therefore bis-tert-diols were selected for preparative work. Polyethylene glycols did not need the addition of an onium salt to extract basicity[1], but only the larger molecular weight one was very suitable for the elimination.

To obtain higher conversion to the alkyne **5a**, powdered KOH was used. Figures 1 and 2 show reaction diagrams for 1,2-dibromo- and 1,2-dichlorooctane in the absence and the presence of pinacol. The cocatalytic effect is much stronger with the slow reacting chloro-compound.

In Table 2 yields are summarized in bis-eliminations from activated, non-activated, and sterically hindered dibromides. Here 2,5-dimethyl-2,5-hexanediol was the cocatalyst because this compound

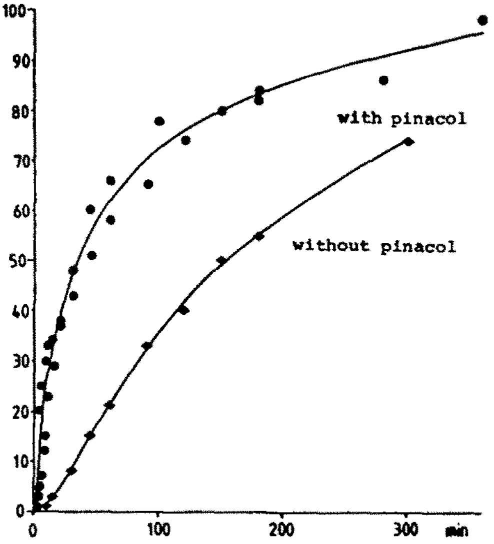


Figure 1

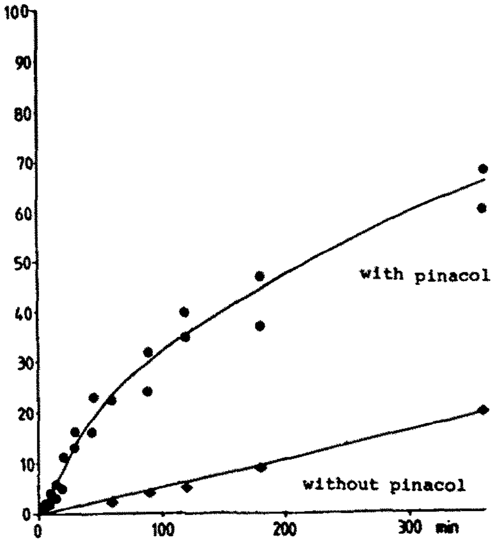


Figure 2

Figures 1 and 2: Conversion of 1,2-dibromooctane or 1,2-dichlorooctane, respectively, with powdered potassium hydroxide in the presence or absence of pinacol (75°C, 5 fold molar excess of KOH, 2 mol-% $NOct_4Br$ 4 mol-% pinacol (when present) petroleum ether as solvent)

Table 2. Bis-eliminations from dibromides in the presence of powdered KOH, catalyst, and 2,5-dimethyl-2,5-hexanediol. (50 mmol substrate, 500 mmol powdered KOH, 1 mmol catalyst, 2mmmol diol).

Substrate	Product	Base	Catalyst	Temp. °C	Rk.-Time h	Solvent	Yield %
dibromostyrene	PhC≡CH	50% aq.KOH	$NOct_4Br$	80-90	4.5	—	80[a]
$C_4H_9CHBrCH_2Br$	$C_4H_9C≡CH$	KOH powder	$NOct_4Br$	80-90	0.25	—	88
$C_5H_{11}CHBrCH_2Br$	$C_5H_{11}C≡CH$	KOH powder	$NOct_4Br$	80-90	0.25	—	85
$C_6H_{13}CHBrCH_2Br$	$C_6H_{13}C≡CH$	KOH powder	$NOct_4Br$	80-90	0.5	—	88[b]
1-adamantyl-2,2-dibromoethane	adamantylacetylene	KOH powder	$POct_4Cl$	110	5.0	toluene	60
$(CH_3)_3C-CHBrCH_2Br$	tert-Bu-C≡CH	KOH powder	$POct_4Cl$	100	0.75	—	80
1,2-dibromo-cyclohexane	95:5 1,3- and 1,4-cyclohexadiene	KOH powder	$NOct_4Br$	80-90	0.75	—	63[c]

[a] without diol: 70%, [b] without diol in 3h: 77%, [c] without diol: 40%.

extracted the highest concentration of basicity. The following facts deserve mention: With powdered KOH, the first elimination is fast, immediate, and exothermic. When starting with activated dibromides like dibromostyrene, extensive polymerization occurs, and therefore 50% aqueous potassium hydroxide is prefered in these cases. The new method is a significant improvement over classical ones in the case of hindered compounds like adamantylacetylene, where KOH/triglycol was used at 200°C and a reaction time of 9 h[9]. Elimination from trans-dibromocyclohexane gives a 95:5 mixture of 1,3- and 1,4-cyclohexadiene in 63% yield, and the process can compete well with older ones[10]. Experiments towards the preparation of ethoxyacetylene were in vain. Here the diol monoanion presumably acts as a nucleophile. Eliminations from dichlorides were less satisfactory. Reactions were slower and the isolated yields were much lower than from the dibromides inspite of the better diol catalysis mentioned above.

Under the conditions used (KOH powder, $NOct_4Br$, diol), only tiny amounts of diol ethers could be detected. Furthermore the wellknown isomerization of the 1-alkynes to 1,2-dienes and 2-alkynes was not observed. The situation changed when PEG 400 was used as the sole catalyst. A change in product ratio was observed depending on reaction variables such as the quality and condition of the KOH (powder, scales, or pellets), reaction time, temperature, intensity of mixing, and the amount of PEG. Although the reaction rate seemed to be faster than in the NR_4X/diol catalyzed reaction a strong tendency towards **5a** $\rightleftarrows$ **6a** $\rightleftarrows$ **7a** isomerization was difficult to control. In Table 3 some typical results are given.

$C_6H_{13}\text{-}C{\equiv}CH$	$C_5H_{11}\text{-}CH{=}C{=}CH_2$	$C_5H_{11}\text{-}C{\equiv}C\text{-}CH_3$
5a	**6a**	**7a**

Table 3. Eliminations from 100 mmol dibromooctane **1a** in the presence of PEG 400 and potassium hydroxide.

Base	Amount of Base (mmol)	Amount of PEG (mmol)	Temper. °C	React. Time	Conversion	Products
KOH pellets a)	250	5	60	4h	93%	5a
KOH scales b)	250	2.5	60-70	4h	66%	5a
KOH scales b)	250	2.5	80-90	0.25h	68%	5a
KOH scales b)	250	2.5	80-90	4h	77%	90% 5a, 7% 6a, 3% 7a
KOH powder c)	500	2.5	80-90	0.25h	90%	43% 5a, 30% 6a, 27% 7a
KOH powder c)	500	2.5	60-70	4h	75%	73% 5a, 15% 6a, 12% 7a

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a) analytical grade, 85% assay. 1-hexyne, 1-decyne, and phenylacetylene were obtained in similar yields under these conditions.

b) 85% assay.

c) prepared from the KOH scales by ball milling under exclusion of moisture.

In a further experiment, pure 1-octyne (**5a**) was equilibrated under the reaction conditions (500 mol powdered KOH, 2.5 mmol PEG 400, 60-70°C, 4h) yielding a mixture of 23% **5a**, 14% of allene **6a**, and 59% 2-octyne (**7a**).

Quite clearly for terminal alkyne preparation it is essential to keep the reaction temperature low and the PEG concentration at 5 mol-%, and to distill the product from the reaction mixture as it is formed.

In conclusion, the preparation of 1-alkynes by PTC eliminations works safest with a combination of an onium halide and 2,5-dimethyl-2,5-hexanediol or a similar bis-tert-diol. The use of PEG 400/KOH pellets can be recommended only if the reaction variables are controlled carefully.

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EXPERIMENTAL

General procedure for the eliminations of Table 1:

5.36 mmol **1a** were mixed with 50 mmol 50% KOH, 2 mol-% $NOct_4Cl$, 4 mol-% of the alkanol (or 2% of the PEG alone), 5.36 mmol anisol (gas chromatographic standard), and 5 ml petroleum ether (b.p. 70-85°C). The mixture was heated for 2.5 h. Thereafter the mixture was separated, the organic phase was filtered through Na_2SO_4, and was analyzed by gas chromatography. Test mixtures had a reproducibility of ± 1%.

General procedure for the eliminations of Table 2:

500 mmol powdered KOH were mixed with 1 mmol onium salt catalyst and 2 mmol 2,5-dimethyl-2,5-hexanediol. When the dibromide was added an immediate exothermic reaction occured normally. The mixture was heated at the temperature given in the table. Volatile alkynes were distilled directly from the mixture. In other cases, the mixture was poured into water after the times given in the table. The products were distilled after separation and drying.

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