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# IODINE MEDIATED SYNTHESIS OF ALKYL TERTIO-ALKYL ETHERS

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Mixed alkyl t-alkyl ethers have been prepared by the selective coupling of the alcohol precursors. Dehydration was promoted by iodine under hydrogen pressure at 100°C.

Alkyl t-alkyl ethers (mainly t-butyl and t-amyl) are currently considered as possible gasoline additives due to their high energy content and high octane number which confer effective anti-knock properties. The most important ether is methyl t-butyl ether (MTBE) which is industrially prepared by the reaction of methanol with isobutene in the presence of ion exchange resins[1]. There are numerous other procedures, all of which involve acid catalysis to create the t-butyl carbocation. Most of these preparations are state-of-art techniques requiring long addition times of t-butanol to the other alcohol[2].

We report here a dehydration method allowing the synthesis of t-alkyl ethers in acceptable yields in very short times. The procedure is based on the selective coupling of a tertiary and another alcohol which may be primary or secondary :

$$ROH + R'OH \xrightarrow{catal.} ROR' + H_2O \quad (R' : \text{tertiary}).$$

The catalyst is iodine[3], which is known to act as a mild Lewis acid in the dehydration of tertiary alcohols to alkenes[4]. Interestingly, iodine was used in the synthesis of mixed arylmethyl-alkyl ethers[5] ; however, no t-butyl ether could be synthesized.

In this paper, the preparation of ethyl tertiobutylether (ETBE) was studied as the reference reaction, with the generality of the reaction demonstrated by the synthesis of a range of asymmetric ethers. Since we have found that closed reaction systems produced much higher yields of the mixed ether, the experiments were carried out in autoclaves under hydrogen pressure. Fig. 1 and 2 portray the pressure and the temperature effect on the reaction yield.

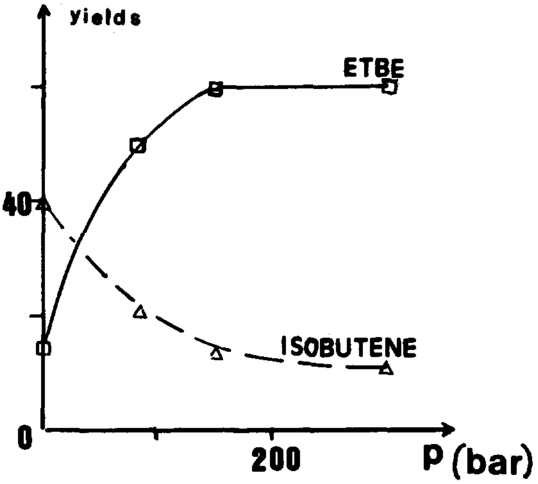


Fig. 1 : Pressure effect (T : 104°C)
(no diethyl ether is formed)
ETBE (ethyl t-butylether)

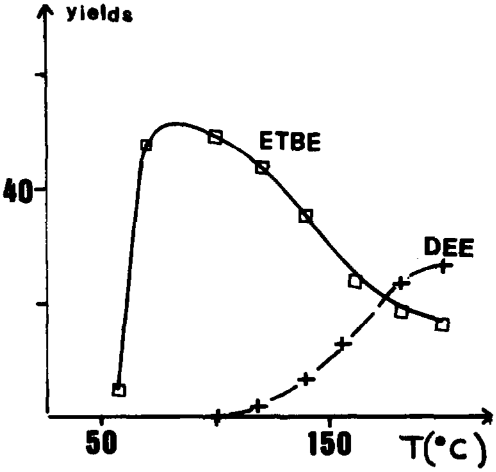


Fig. 2 : Temperature effect
(P : 80 bar)
DEE (Diethylether)

As exemplified in Fig. 1, the synthesis of ethyl t-butylether is enhanced by autoclaving, presumably because the dehydration product, isobutene, is confined within the reactor. Temperature is a critical parameter (Fig. 2), since it controls the generation of isobutene. Highest yields of ethyl t-butylether were obtained between 70-100°C, while higher temperatures promoted the formation of the symmetrical ether, diethyl ether, together with isobutene.

The equilibrium is reached very rapidly, e.g. at 100°C and 80 bar hydrogen pressure, 10 minutes are sufficient. Iodine can be replaced by hydrogen iodide, with less success, however. Alkaline iodides are inefficient, while organic iodides lead only to low yields of ethyl t-butylether.

Adopting the following experimental conditions (R'OH : ROH = 1 : 1 - molar ratio -, total volume : 4 ml, iodine : 1.5 mmol, T : 100°C, hydrogen : 80 bar, t : 30 min), we prepared numerous mixed t-alkyl ethers (Table).

Yields could not be improved even by variyng pressure, temperature or reaction time, since the mixed ether is subject to cleavage reactions, which are well documented[6].
In order to limit the reverse reaction, the experiments were carried out in water-immiscible solvents. Use of alkanes was beneficial only for the synthesis of alkyl t-butyl ethers. For example, ethyl t-butylether was obtained in 75% yield, when octane was used as the reaction medium. In the case of 2-propanol, the yield reached 14% instead of 8% in the absence of octane. The yield remained unaffected in the case of 2-methyl-1-propanol reaction, regardless of the choice of solvents.

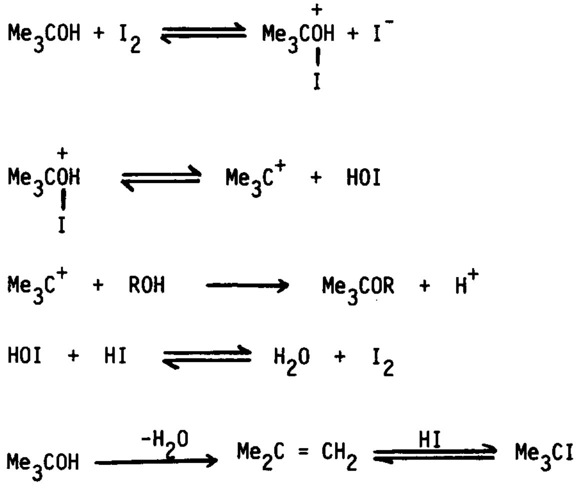
TABLE

Synthesis of t-alkyl ethers.

| R'OH | ROH | ROR' Yield (%) | ROR' Selectivity[a] (%) |
|---|---|---|---|
| 2-Methyl-2-propanol | methanol | 50 | 78 |
| | ethanol | 51 | 82 |
| | 1-propanol | 52 | 75 |
| | 2-propanol | 8 | 23 |
| | 1-butanol | 48 | 72 |
| | 2-methyl-1-propanol | 60 | 80 |
| | 1-pentanol | 60 | 75 |
| | allyl alcohol | 40 | 55 |
| 2-Methyl-2-butanol | methanol | 42 | 48 |
| | ethanol | 30 | 40 |
| | allyl alcohol | 12 | 21 |
| 1-Methyl-1-cyclohexanol | methanol | 18 | 40 |

[a] Other products include the olefin(s) derived from R'OH and minor amounts of RI.

The reaction sequence is derived from the scheme proposed earlier for the iodine dehydration of t-alcohols to alkenes[4,7] and may also involve t-butyl iodide :



$$Me_3COH + I_2 \rightleftharpoons Me_3C\underset{I}{\overset{+}{O}}H + I^-$$

$$Me_3C\underset{I}{\overset{+}{O}}H \rightleftharpoons Me_3C^+ + HOI$$

$$Me_3C^+ + ROH \longrightarrow Me_3COR + H^+$$

$$HOI + HI \rightleftharpoons H_2O + I_2$$

$$Me_3COH \xrightarrow{-H_2O} Me_2C = CH_2 \overset{HI}{\rightleftharpoons} Me_3CI$$

$$Me_3CI \rightleftharpoons Me_3C^+ + I^-$$

$$Me_3COR \xrightarrow{HI} Me_3COH + RI$$

$$Me_3COH \xrightarrow{HI} Me_3CI + H_2O$$

The proposed scheme is supported by the following results :

i) t-butyl iodide reacts readily with ethanol to give ethyl t-butylether, ethyl iodide and t-butanol, whereas $C_2H_5I$ couples poorly with t-butanol.

ii) RI is formed in minor amounts in all runs ($CH_3I$ from $CH_3OH$, $C_2H_5I$ from $C_2H_5OH$...).

iii) Facile cleavage of any t-alkyl ether occurs with hydroiodic acid.

Use of other potential dehydration or coupling agents gave poor results ($KHSO_4$ [8], $H_3PO_4$, $Ni(acac)_2$ [9], $ZnCl_2$ [10]).

## CONCLUSION.

Mixed ethers involving t-alkyl groups can be synthesized in closed systems by iodine-catalyzed coupling of a tertiary alcohol with a primary or a secondary alcohol under hydrogen pressure. The yield is dependent on the coupling ability of the primary alcohol and the reactivity of the t-alkyl ether produced towards HI. In some cases, the addition of hydrocarbons is beneficial for the synthesis of the ether.

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