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# CATHODIC CLEAVAGE OF THE TRITYLONE GROUP FROM PROTECTED ALCOHOLS

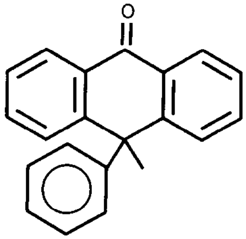
## SELECTIVE PROTECTION OF THE PRIMARY OR SECONDARY HYDROXYL GROUP IN 1,4-PENTANE DIOL[1)]

Claus van der Stouwe, and Hans J. Schäfer

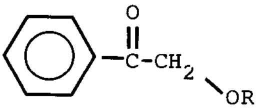
Organisch-Chemisches Institut der Universität
Orléans-Ring 23, D 44 Münster, Germany

Alcohols protected with the tritylone group can be deprotected cathodically under mild and neutral conditions. The combination of the tritylone and the p-cyanobenzyl group allows the selective protection of either the primary or secondary hydroxyl group in 1,4-pentane diol.

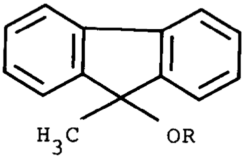
The tritylone group (1) has been introduced by Barnett[2)] for the protection of alcohols. It resembles the trityl group[2)], but is more stable towards acid and hydrogenation. Of disadvantage are the vigorous conditions for its deprotection: Wolff-Kishner reduction at 200° C in strong alkaline medium, which are not tolerated by many functional groups. As it had been shown that alcohols can be cathodically split off from phenacyl-(2)[3)] and 9-methylfluorenyl ethers (3)[4)], the tritylone group bearing similar structural features was expected to be electroactive too.



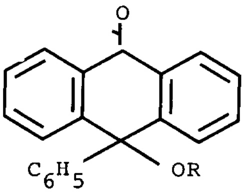
$\underline{\underline{1}}$



$\underline{\underline{2}}$



$\underline{\underline{3}}$



$\underline{\underline{4}}$

Indeed tritylone ethers ($\underline{\underline{4}}$) show reduction peaks at $E_p$ = -1.30 to -1.36 V (vs. Ag/AgCl), at which they are cleaved at room temperature under neutral conditions to afford alcohols ROH (Table).

Table: Preparation and cathodic cleavage of tritylone ethers

| Tritylone ether $\underline{\underline{4}}$<br>R | yield (%)[a] | Reduction potential[b]<br>$E_p$ (V) of $\underline{\underline{4}}$ | ROH-yield (%) by<br>cathodic reduction of $\underline{\underline{4}}$[c] |
|---|---|---|---|
| n-Butyl- | 35 | -1.32 | 85[d] |
| n-Octyl- | 92 | -1.36 | 84[d] |
| n-Decyl- | 87 | -1.34 | 81[d] |
| Cyclohexyl- | 55 | -1.32 | 84[d] |
| β-Cholesteryl- | 60* | -1.30 | 66*[e] |

a) Equimolar amounts of ROH and tritylone alcohol ($\underline{\underline{4}}$, R = H) in benzene were refluxed in a water separator with catalytic amounts of p-toluenesulfonic acid

b) Experimental conditions: $10^{-3}$ $\underline{M}$ $\underline{\underline{4}}$ in a 0.1 $\underline{M}$ $TBABF_4$ methanol or methanol/dioxane* (1:1) solution at a hanging mercury drop cathode vs. Ag/AgCl.

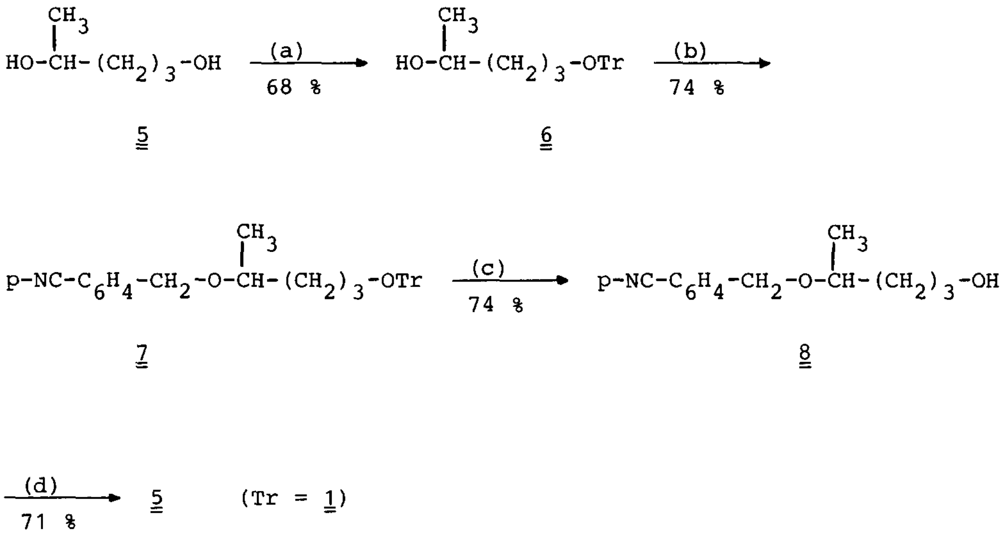
c) For electrolysis conditions see experimental procedure.

d) Isolated by bulb to bulb distillation.

e) Isolated by liquid chromatography.

The combination of the tritylone- with the more cathodically reduced p-cyanobenzyl-group$^{5)}$ allows the selective protection of either the primary (6) or the secondary hydroxyl group (8) in a diol (Scheme). 1,4-Pentane diol (5) served as a model diol.

Scheme:



$$\overset{\displaystyle CH_3}{\overset{|}{HO\text{-}CH}}\text{-}(CH_2)_3\text{-}OH \xrightarrow[68\ \%]{(a)} \overset{\displaystyle CH_3}{\overset{|}{HO\text{-}CH}}\text{-}(CH_2)_3\text{-}OTr \xrightarrow[74\ \%]{(b)}$$

5 6

$$p\text{-}NC\text{-}C_6H_4\text{-}CH_2\text{-}O\text{-}\overset{\displaystyle CH_3}{\overset{|}{CH}}\text{-}(CH_2)_3\text{-}OTr \xrightarrow[74\ \%]{(c)} p\text{-}NC\text{-}C_6H_4\text{-}CH_2\text{-}O\text{-}\overset{\displaystyle CH_3}{\overset{|}{CH}}\text{-}(CH_2)_3\text{-}OH$$

7 8

$$\xrightarrow[71\ \%]{(d)} 5 \qquad (Tr = 1)$$

(a) Tritylone alcohol, benzene, toluenesulfonic acid, reflux;

(b) NaH in ether, p-cyanobenzylbromide;

(c) -1.4 V vs. Ag/AgCl at Hg-cathode;

(d) -2.1 V vs. Ag/AgCl at Hg-cathode.

Tritylone alcohol reacts preferentially with the primary hydroxyl group in 5 to afford the monoprotected diol 6, that subsequently was further protected with p-cyanobenzylbromide to 74 % 7. The diprotected diol 7 yields on controlled potential electrolysis at -1.4 V (vs. Ag/AgCl) 74 % 8, that can be deprotected to 71 % 5 on electrolysis at -2.1 V (vs. Ag/AgCl). Other combinations of electroactive protecting groups, e.g. the tribromo- (-0.7 V vs. SCE) and the trichloroethoxy-carbonyl group ($E_p$ = -1.85 V vs. SCE)6) or the tritylone and the tosyl group ($E_p$ = -2.2 V vs. SCE)7) gave unsatisfactory results.

Cathodic cleavage of tritylone ethers: 2 g (4.68 mMol) tritylone decyl ether in 50 ml 0.1 m LiBr methanol is electrolysed in a divided cell (working electrode: mercury pool, counter electrode: platinum sheet) at 20° C and controlled potential (-1.4 V vs. Ag/AgCl) until 1900 Asec were consumed. For work up methanol was evaporated and the residue taken up in ether. Bulb to bulb distillation afforded 0.6 g (3.8 mMol, 81 %) decanol, liquid chromatography yields 1.06 (3.9 mMol, 83 %) tritylone alcohol (Fp. 215-216° C lit.2) 213-214° C).

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