

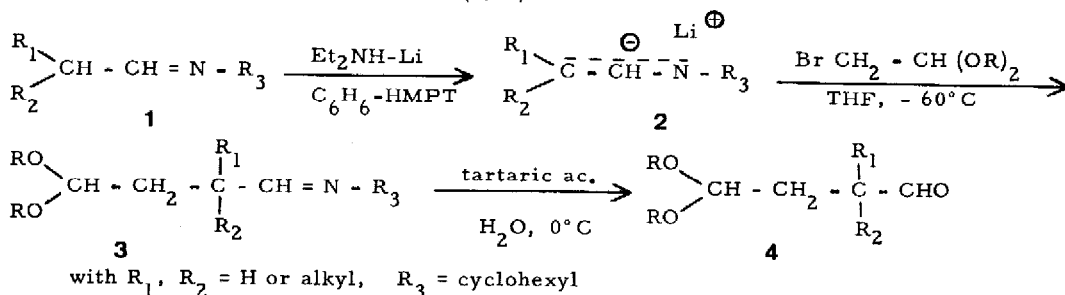
1, 4 - DIALDEHYDE MONOACETALS : A NEW SYNTHESIS OF DIHYDROTAGETONE

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Bi-functional compounds are specially attractive in organic synthesis when, by protecting one function, it is possible to change the first without modifying the second. We report in this paper a direct and fast synthesis of such compounds : the 1, 4-dialdehyde monoacetals. We have previously shown that the carbanions **2** are easily available from aldimines **1** by reacting them with "activated lithium amides" (1, 2).

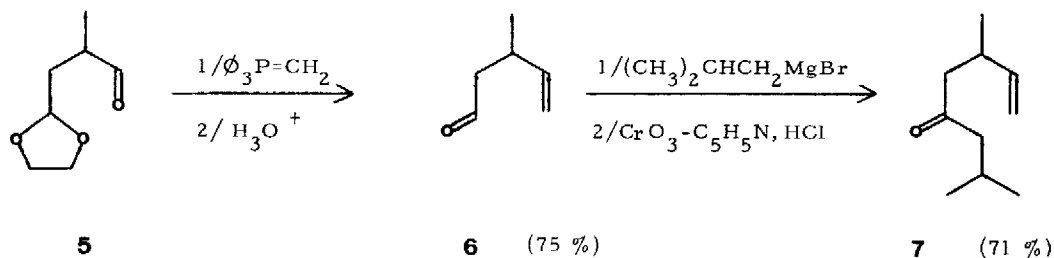


Though the bromine in an  $\alpha$  position to an acetal is not very reactive (3), it is possible in HMPT to substitute it even at low temperature. The reaction of the carbanion **2** with an  $\alpha$ -bromoacetal or dioxolane affords the acetal-imine **3** in good yields. A selective hydrolysis can be obtained by using a solution of tartaric acid at  $0^\circ\text{C}$  and the products **4** are isolated.

1, 4 - Dialdehyde monoacetals

$R_1$	$R_2$	R	B. p. $^\circ\text{C}/\text{mm Hg}$	Yield %	$R_1$	$R_2$	R	B. p. $^\circ\text{C}/\text{mm Hg}$	Yield %
$\text{CH}_3$	H	$-\text{CH}_2-$	40/0,05	79	$n\text{C}_4\text{H}_9$	H	$\text{C}_2\text{H}_5$	63/0,03	61
$\text{C}_2\text{H}_5$	H	$-\text{CH}_2-$	49/0,05	83	$n\text{C}_6\text{H}_{13}$	H	$-\text{CH}_2-$	92/0,05	81
$(\text{CH}_3)_2\text{CH}$	H	$-\text{CH}_2-$	60/0,05	68	$\text{CH}_3$	$\text{CH}_3$	$\text{C}_2\text{H}_5$	40/0,01	63
$n\text{C}_4\text{H}_9$	H	$-\text{CH}_2-$	69/0,01	85	$\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_5$	$-\text{CH}_2-$	63/0,05	68

To a stirred solution of diethylamide (0,06 mol) in HMPT is added a solution of aldimine (0,06 mol) in THF at  $-60^{\circ}\text{C}$ . The mixture is stirred and warmed up to  $-10^{\circ}\text{C}$  within two hours. The bromoacetal (0,05 mol) in THF is then added at  $-60^{\circ}\text{C}$ ; the mixture is allowed to warm up and hydrolysed at  $0^{\circ}\text{C}$  by stirring for five hours with aqueous tartaric acid. To illustrate our method we have prepared dihydrotagetone **7**. Several syntheses of this product have been reported (4)



The dioxolane aldehyde **5** prepared from propionaldimine by our method is reacted with a Wittig reagent to afford the aldehyde **6** after acid hydrolysis (bp  $110^{\circ}\text{C}/760$  mm Hg). This compound is then condensed with isobutyl magnesium bromide; the crude product is oxidized with pyridinium chlorochromate (5) and furnishes dihydrotagetone **7** (bp  $82^{\circ}\text{C}/15$  mm Hg). The overall yield from propanal is 42%. This attractive synthesis of dihydrotagetone outlines the synthetic value of 1,4-dialdehyde monoacetals. We thank D. G. R. S. T. for their financial support. (contrat 74-7-0940).

#### References and Notes :

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