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REACTIVITY OF SOME α-AND α,γ - UNSATURATED SILANES TOWARDS ACETALS IN THE PRESENCE OF A LEWIS ACID.

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SUMMARY: α-and α,γ-unsaturated silanes undergo titanium tetrachloride-induced alkylation of acetals.

Allyltrimethylsilanes have been reported to react with various electrophiles in the presence of a Lewis acid with regiospecific rearrangement in the allylic part (1)(2)(3).

We have now studied the reactivity of the following silanes :

1 $C_6H_5-CH=CH-CH_2-Si(CH_3)_3$ (4) ; 2 $CH_3-C\equiv C-CH_2-Si(CH_3)_3$ (5) ;
3 $CH_2=CH-CH=CH-CH_2-Si(CH_3)_3$ (6) ; 4 $nC_4H_9-C\equiv C-CH=CH-CH_2-Si(CH_3)_3$ (7) ;

towards the acetals :

5 $(CH_3)_2CH-CH_2-CH(OC_2H_5)_2$; 6 $C_6H_5-CH(OCH_3)_2$.

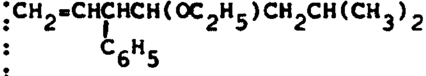
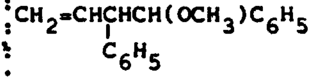
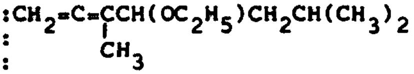
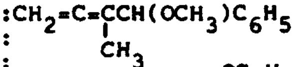
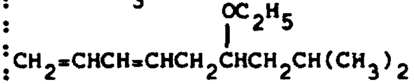
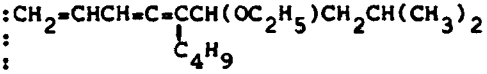
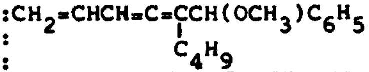
These silanes, in a sense, resemble the allylic silanes and thus could undergo titanium tetrachloride - induced alkylation of an acetal. We have found that this is indeed the case.

In a typical reaction, to an acetal 5 or 6 (6mmol) in dry dichloromethane (8ml), titanium tetrachloride (2mmol) and a silane 1, 2, 3 or 4 (4mmol) are successively added at - 78°C; the mixture is stirred under the conditions given in the following table and then hydrolysed. The structures of these etheroxydes are in a good agreement with those observed in the reaction of 3 and 1 with carbonyl compounds (6)(8) and of propargylic silanes with sulfonating agents (9)(10)(11) or chloral (12). The products which are obtained are isomerically pure and were characterized by their combustion analysis, and by ir and ^1H nmr spectroscopy. Yields are fair to good.

It is clear that a new and very useful method for the preparation of β-ethylenic, α-allenic, β,δ-diethylenic and α-vinylallenic etheroxydes is in hand.

Other investigations of the chemical reactivity of these silanes and related compounds towards other electrophiles are at present under progress.

$TiCl_4$ - Induced alkylation of acetals by α-and α,γ-unsaturated silanes

Silane	Acetal	Conditions	Product	Yield %	n_D^{20}
1	5	-78°C, 10min., -78°C to -45°C, 20 min.	 $CH_2=CH\underset{C_6H_5}{\underset{\vert}{C}}HCH(OC_2H_5)CH_2CH(CH_3)_2$	86	1,4900
1	6	-78°C, 10 min., -78°C to + 15°C, 20 min.	 $CH_2=CH\underset{C_6H_5}{\underset{\vert}{C}}HCH(OCH_3)C_6H_5$	83	-(a)
2	5	-78°C, 10 min., -78°C to -45°C, 10 min.	 $CH_2=C=\underset{CH_3}{\underset{\vert}{C}}CH(OC_2H_5)CH_2CH(CH_3)_2$	92	1,4432
2	6	-78°C, 20 min.,	 $CH_2=C=\underset{CH_3}{\underset{\vert}{C}}CH(OCH_3)C_6H_5$	85	1,5305
3	5	-78°C, 10 min.,	 $CH_2=CHCH=CHCH_2\overset{OC_2H_5}{\overset{\vert}{C}}HCH_2CH(CH_3)_2$	65	1,4610
3	6	-78°C, 10 min.,	$CH_2=CHCH=CHCH_2CH(OCH_3)C_6H_5$	79	1,5306
4	5	-78°C, 10 min., -78°C to -45°C, 20 min.	 $CH_2=CHCH=C=\underset{C_4H_9}{\underset{\vert}{C}}CH(OC_2H_5)CH_2CH(CH_3)_2$	90	1,4740
4	6	-78°C, 10 min., -78°C to -45°C, 20 min.	 $CH_2=CHCH=C=\underset{C_4H_9}{\underset{\vert}{C}}CH(OCH_3)C_6H_5$	88	1,5350

a) recrystallised from diethylether, F = 102°C.

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