

PYRYLIUM SALTS FROM DIACETYLATION OF OLEFINS: SELECTIVITY IN $\text{AcCl}/\text{AlCl}_3$ MEDIUM.

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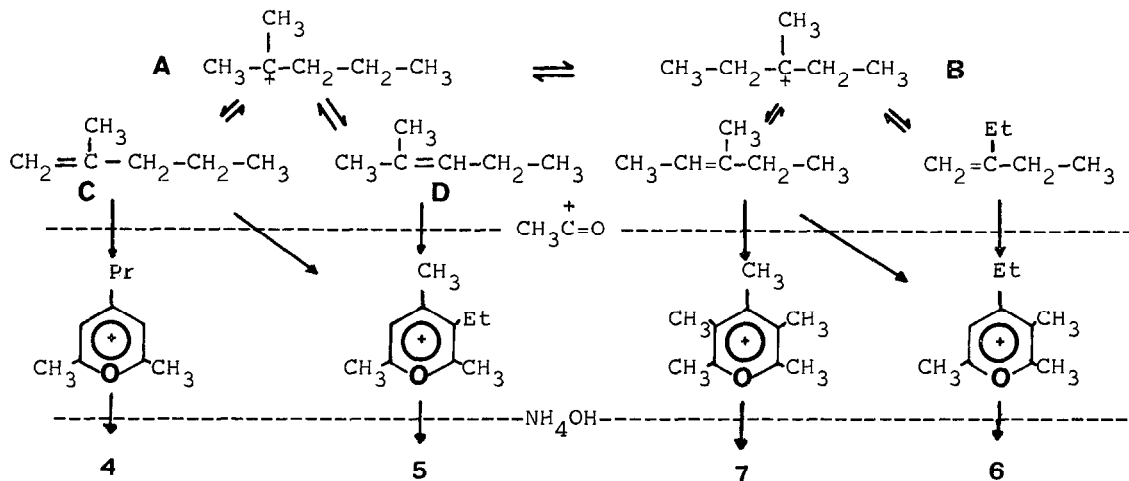
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Summary : it is shown that the selectivity of the reaction of diacetylation of olefins is governed by the ratio $\text{AcCl}/\text{AlCl}_3$ and not by the sole strength of the Lewis acid as previously postulated.

The reaction of diacetylation of olefins (or olefin precursors) is a standard method for preparing alkyl-substituted pyrylium salts bearing two identical α -substituents.¹

Isomeric pyrylium salts are obtained when an unsymmetrical olefin is treated with AcCl and a Lewis acid. It has been proposed that the selectivity of the reaction was controlled by the strength of the Lewis acid catalyst.^{1,2} Thus it was observed in all reports that acetylation with acetyl chloride and a strong Lewis acid such as aluminum chloride yields the less substituted pyrylium salt (e.g. which gives the pyridine 4) whereas weak Lewis acids yield the more substituted one (e.g. which gives the pyridine 5)^{2,3,4}.

Since the control of the selectivity is important for both practical and theoretical purposes, we report selected examples which show that the more substituted pyrylium salt is obtained even with an $\text{AcCl}/\text{AlCl}_3$ mixture, and that the determining factor in the selectivity is in fact the $\text{AcCl}/\text{AlCl}_3$ ratio



We have chosen 2-Me-pentenes since these olefins can give information on isomerization and cracking in the medium. Furthermore the behaviour of 2-Me-pentene has been reported recently^{4c}.

Pyrylium salts are converted into the corresponding pyridines in the crude reaction medium upon treatment with NH₄OH¹⁻⁵. Chloroform was used to avoid heterogeneity in the reaction medium.

The reaction mixture consists of pyridines 1-11 which are listed below in the increasing order of retention time on GLC⁶. Diacetylation and triacetylation of 2-Me-pentene afford respectively pyridines 4-5 and 8-10. Pyridines 6-7 result from the rearrangement of the dimethylpropyl carbenium ion (A) into the diethylmethyl carbenium ion (B)⁶. Pyridines 1,2 and 3 result from polymerization with further cracking in the medium.

The results are given in Table. It can be seen that the selectivity of the reaction S is strongly dependent on reaction conditions.

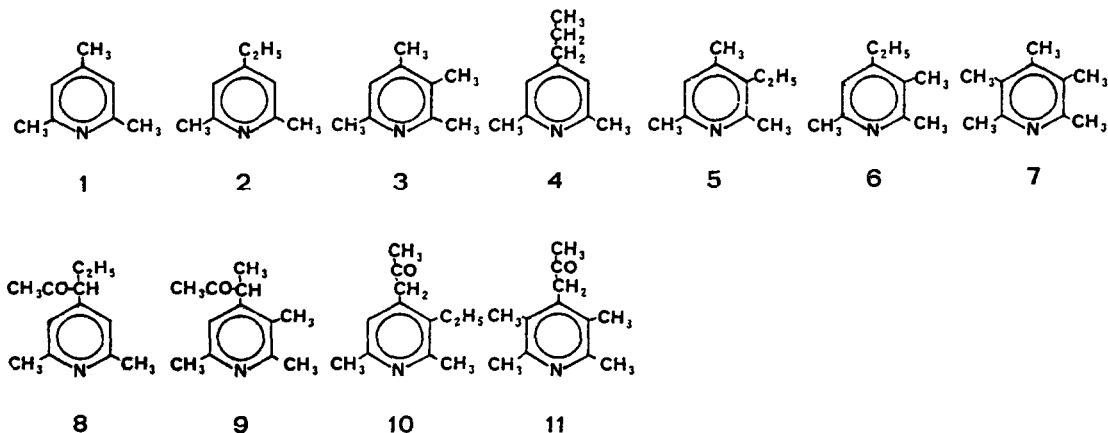


TABLE : Biacetylation of 2-Me-pentenes in $\text{AcCl}/\text{AlCl}_3$ medium.

	Reactants ^a			Pyridines (% GLC) ⁷											Selectivity	
	Olefin	AcCl	AlCl ₃	1	2	3 + 4	5	6	7	8	9	10	11	S ^e = 5/4 + 5	d	
1	0.13	0.65	0.13	0.1	1.2	42.5	9.3	6.1	1.6	11.	0.9	25.1	2.1	18	6:5	
2	0.10	0.30	0.20	3.3	6.1	41.6	16.9	3.3	4.4	16.1	-	8.3	-	29	5.1	
3	0.10	0.20	0.20	2.	0.6	25.	58.2	2.9	6.7	2.3	-	2.3	-	70	3:2	
4	0.10	0.30	0.30	2.6	0.7	25.4	62.3	1.0	4.4	0.7	-	1.4	-	71	2.	
5 ^b	0.10	0.30	0.30	2.4	0.5	23.3	57.4	1.3	1.3	-	-	-	-	71	4.1	
6 ^c	0.10	0.30	0.30	0.6	0.5	21.	68.3	0.3	4.7	-	-	-	-	76	3.7	

a) 2-Me-2-pentene otherwise indicated; in mole; The olefin is added dropwise in the mixture $\text{AcCl}/\text{AlCl}_3/\text{CHCl}_3$ (200 ml) at 0°C. (1 hour); the mixture is then allowed to react 2 hrs at 35°C; the mixture is treated with 300 ml NH_4OH 34%. b) 2-Me-1-pentene; c) 2-Cl-2-Me-pentane; d) Grams of pyridine. e) see note 6.

Run 1 corresponds to the experimental conditions given in reference 4c (except chloroform). Our results confirm that the less substituted pyrylium salt is obtained in this case but a large amount of triacetylation product is also found. The same trends are observed in run 2 in which the $\text{AcCl}/\text{AlCl}_3$ ratio is 1.5. The more substituted pyrylium salt is obtained as soon as the $\text{AcCl}/\text{AlCl}_3$ ratio is 1. Traces of triacetylation products are found. The more substituted pyrylium salt is obtained starting either from 2-Me-2-pentene (Run 4) or from 2-Me-1-pentene (Run 5) with a very similar products distribution. This shows that the isomerization of the two olefins is fast in the medium. Run 6 shows that 2-Cl-2-Me-pentane as olefin precursor leads to the more substituted pyrylium derivative when $\text{AcCl}/\text{AlCl}_3 = 1$. Pyridines 6 and 7 which result from the carbenium ion B are obtained in low yields; thus the isomerization $\text{A} \rightleftharpoons \text{B}$ is slow compared to the acetylation of C and D. However the selectivity $\frac{7}{(6+7)}$ parallels the one observed for 4 and 5 (Runs 1, 3, 6).

Actually our results show that the selectivity of the reaction of acetylation of olefins is governed by the ratio $\text{AcCl}/\text{AlCl}_3$ and not by the sole strength of the Lewis acid as previously postulated. It is clear that the structure of the acetylium ion-Lewis acid complex is involved in the selectivity changes. Further work to define quantitatively the relative importance of the reaction parameters is underway.

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References and Notes.

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- ⁶Chromosorb P AW, 5 % KOH; 20 % Apiezon L. Pyridines 3 and 4 are not resolved on these columns thus the given selectivity S in the Table is actually the lower limit of this value. However n.m.r. analysis of 3 + 4 Shows that 3/3 + 4 never exceed 5%. Authentic samples of 2, 3 have been prepared by diacylation of 2-Me-2-butanol with HClO₄, Ac₂O³ whereas 6 and 7 have been obtained from 3-Me-3-pentanol.
- ⁷4-iPr-2,6-DiMe-pyridine is not observed in appreciable yields. This is consistent with the slow rate of isomerization of A or B into Dimethylisopropyl carbenium ion
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