and alkyl halides in the same manner as sulfides **9**.

***S,S*-Dimethylthioacetal of diethyl formylphosphonate (14a)** was obtained in 72% yield from **13** and methyl iodide: n^{24}_D 1.5200; ^{31}P NMR ($CDCl_3$) δ 20.0; ^{1}H NMR ($CDCl_3$) δ 1.32 (t, 6, CH_3CH_2OP, J_{HH} = 7.3 Hz), 2.22 (s, 3, CH_3S), 3.69 (d, 1, PCH, J_{PH} = 18.0 Hz), 4.18 (dq, 4, CH_3CH_2OP, J_{PH} = 8.2 Hz) (lit.[7b] n^{20}_D 1.5212).

***S*-Methyl-*S*-ethylthioacetal of diethyl formylphosphonate (14b)** was obtained in 70% yield from **13** and ethyl iodide: n^{26}_D 1.4946; ^{31}P NMR ($CDCl_3$) δ 18.5; ^{1}H NMR (CCl_4) δ 1.22 (t, 6, CH_3CH_2S, J_{HH} = 7.3 Hz), 1.25 (t, 6, CH_3CH_2OP, J_{HH} = 7.9 Hz), 2.25 (s, 3, SCH_3), 2.52 (q, 4, CH_3CH_2S), 3.58 (d, 1, PCH, J_{PH} = 17.7 Hz), 4.10 (dq, 4, CH_3CH_2OP, J_{PH} = 8.1 Hz). Anal. Calcd for $C_8H_{19}O_3PS_2$: C, 37.19; H, 7.41; P, 11.94. Found: C, 36.98; H, 7.30; P, 11.81.

Preparation of *O,S*-Dimethylthioacetal of Diethyl Formylphosphonate (16). To the freshly prepared mixture of potassium *tert*-butoxide (0.01 mol) in THF (15 mL) and *n*-butyllithium (0.01 mol) in hexane diethyl (methoxymethyl)-phosphonate (1.82 g, 0.01 mol) was added under an argon atmosphere at −78 °C. The reaction mixture was stirred at −78 °C for 30 min. Then sulfur (0.32 g, 0.01 mol) and methyl iodide (1.42 g, 0.01 mol) were added. The reaction mixture was warmed to room temperature. The bulk of the solvents was removed and the residue was treated with chloroform (50 mL) and washed with water. The chloroform solution was dried and evaporated to afford the crude **16**, which was chromatographed [benzene–acetone (9:1)] to give 1.2 g (53%) of pure **16**: n^{24}_D 1.4622; ^{31}P NMR ($CDCl_3$) δ 16.5; ^{1}H NMR ($CDCl_3$) δ 1.34 (t, 6, CH_3CH_2OP, J_{HH} = 7.4 Hz), 2.18 (s, 3, CH_3S), 3.46 (s, 3, CH_3O), 4.16 (dq, 4, CH_3CH_2OP, J_{PH} = 7.4 Hz), 4.33 (d, 1, PCH, J_{PH} = 11.8 Hz) (lit.[6b] n^{24}_D 1.4622).

Registry No. 4a, 683-08-9; **4b**, 78-38-6; **4c**, 1080-32-6; **5a**, 70660-05-8; **5b**, 70660-06-9; **5c**, 70660-07-0; **6**, 70660-08-1; **7**, 10419-77-9; **8a**, 70660-09-2; *dl*-**8b**, 70660-10-5; *meso*-**8b**, 70660-11-6; *dl*-**8c**, 70660-12-7; *meso*-**8c**, 70660-13-8; **9a**, 28460-01-7; **9b**, 54091-78-0; **9c**, 41760-64-9; **9d**, 22966-40-1; **9e**, 70660-14-9; **9f**, 70660-15-0; **9g**, 70660-16-1; **9h**, 70660-17-2; (*E*)-**10a**, 70660-18-3; (*Z*)-**10a**, 2764-94-5; (*E*)-**10b**, 70660-19-4; (*Z*)-**10b**, 70660-20-7; (*E*)-**10c**, 70660-21-8; (*Z*)-**10c**, 70660-22-9; **11a**, 451-40-1; **11b**, 93-55-0; **11c**, 1009-14-9; **13**, 70660-23-0; **14a**, 62999-70-6; **14b**, 70660-24-1; **15**, 32806-04-5; **16**, 59590-52-2; **17**, 70660-25-2; **18**, 70660-26-3; diethyl phosphonate, 762-04-9; triethyl phosphite, 122-52-1; thioacetic acid tetramethylammonium salt, 62698-51-5; benzaldehyde, 100-52-7; acetaldehyde, 75-07-0; butyrylaldehyde, 123-72-8; sulfur, 10544-50-0; sulfuryl chloride, 7791-25-5.

Pyrylium Salts from Friedel–Crafts Acetylation of Isoparaffins

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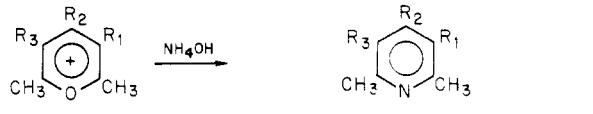
The first synthesis of pyrylium salts from acetylation of isoparaffins (isopentane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane) under Friedel–Crafts conditions is reported. The pyrylium salts are converted into the corresponding pyridines and the selectivity of the reaction is discussed. The influence of the $AcCl/AlCl_3$ ratio on the apparent selectivity is demonstrated.

Pyrylium salts are versatile synthons in preparative organic chemistry since they can be converted to several benzenoid derivatives and heterocyclic compounds.[1,2] Among the various synthetic routes, the diacylation of alkenes is a standard method for the preparation of alkyl-substituted pyrylium salts bearing two identical α substituents.[2] Various alkene precursors, such as alcohols or *tert*-alkyl halides, have been used with success.[2-6] We report the first examples of pyrylium salt synthesis from isoalkanes under Friedel–Crafts conditions. This study opens new prospects for the utilization of isoparaffins.

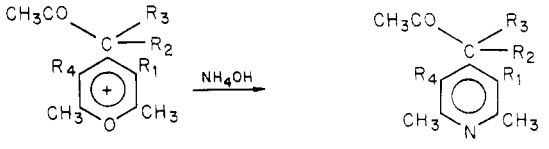
Results and Discussion

The acetylations were performed by acetyl chloride and aluminum chloride on four isoparaffins: isopentane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane, with and without chloroform. The isomeric hexanes were chosen to investigate possible rearrangements and fragmentations in the Friedel–Crafts medium.

Scheme I



1a, R_1 = H, R_2 = Me, R_3 = H
b, R_1 = H, R_2 = Et, R_3 = H
c, R_1 = H, R_2 = *i*-Pr, R_3 = H
d, R_1 = Me, R_2 = Me, R_3 = H
e, R_1 = H, R_2 = Pr, R_3 = H
f, R_1 = Et, R_2 = Me, R_3 = H
g, R_1 = Me, R_2 = Et, R_3 = H
h, R_1 = Me, R_2 = Me, R_3 = Me



2a, R_1 = H, R_2 = H, R_3 = H, R_4 = H
b, R_1 = H, R_2 = H, R_3 = Me, R_4 = H
c, R_1 = H, R_2 = Me, R_3 = Me, R_4 = H
d, R_1 = H, R_2 = H, R_3 = Et, R_4 = H
e, R_1 = Me, R_2 = H, R_3 = H, R_4 = H
f, R_1 = Me, R_2 = H, R_3 = Me, R_4 = H
g, R_1 = Et, R_2 = H, R_3 = H, R_4 = H
h, R_1 = Me, R_2 = H, R_3 = H, R_4 = Me

The conversion of alkylpyrylium salts into the corresponding pyridines is almost quantitative[1-6] and thus the pyridine mixture obtained upon treatment of the crude reaction medium by NH_4OH is representative of the

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(2) A. T. Balaban, W. Schroth, and G. Fisher, *Adv. Heterocycl. Chem.*, **10**, 241 (1969); A. T. Balaban, book dedicated to Professor Tilak's 60th birthday, in preparation.
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(4) (a) A. T. Balaban, A. Bota, F. Chiraleu, E. Sliam, A. Hanes, and C. Draghici, *Rev. Roum. Chim.*, **22**, 1003 (1977), and references therein; (b) A. T. Balaban and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **625**, 74 (1959); *J. Chem. Soc.*, 3553 (1961).
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(6) P. F. G. Praill and A. L. Whitear, *J. Chem. Soc.*, 3573 (1961).

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Table I. Acetylation of Isoparaffins in $AcCl/AlCl_3$ Medium

	run	T, °C	t, h	paraffin[b]	$AlCl_3$[b]	CH_3COCl[b]	$CHCl_3$[c]	pyridines[a]
isopentane	1	25	18	0.1	0.2	0.8	0	2.9
	2	35-45	5.5	0.5	0.2	0.3	0	7.5
	3	27	18	0.5	0.4	0.4	0	8.9
2-methylpentane	4	35	14	0.1	0.2	0.8	0	3.75
	5	35	23	0.3	0.6	0.6	0	4.75
	6	35	23	0.1	0.2	0.2	200	1.05
	7	25	5.5	0.4	0.65	0.4	0	2.0
3-methylpentane	8	35	23	0.1	0.2	0.2	200	0.4
	9	44	5	0.4	0.35	0.51	0	8.8
	10	38	7.5	0.4	0.37	0.83	0	13.5
	11	41	4	0.4	0.65	0.4	0	2.82
	12	53	5.5	0.4	0.39	0.8	0	11.4
2,3-dimethylbutane	13	35	23	0.1	0.2	0.2	200	0.25
	14	35	18	0.1	0.2	0.8	0	3.5

[a] In grams of pure isolated pyridines after acid and base treatments. [b] In moles. [c] In cm^3.

Table II. Product Ratios[a] of Pyridine Derivatives Obtained by Acetylation of Isoparaffins

run	1a	1b	1c	1d	1e	1f	1g	1h	2a	2b	2c	2d	2e	2f	2g	2h
1	1.9	25.2		12.9					0.5	27.8			31.6			
2	1.6	17.6		67.9						6.5			6.4			
3		1		92						trace			trace			
4	2.6	4			28.7	8.7	3.6	2.1				20.8		5	20.7	3
5	0.8				21.8	25.9	1.8	3.2				10.8		3.6	28.6	3.6
6						100										
7	4.2	1.9			4.9	85		2.9				1				
8						90										
9	0.5				8.2	43.5	7	12				6.6		6.2	10.7	3.2
10	12.6	1.9			17.8	5.2	10.5	5.5				13.1		13.3	15.1	3.6
11	6				3.9	85.2		2.9					1			
12	1.2				28.3	8	14	7.3				10.4		8.6	17.9	3.9
13						92.5										
14	10.7		22.4						1.8		42					

[a] The given selectivities are obtained from GLC. The amount of pure isolated pyridines is given in grams in Table I.

pyrylium salt mixture (Scheme I). All the pyridines **1a–h** and **2a–h** were identified by conventional methods (GC/MS, IR, ^1H and ^{13}C NMR) and compared with samples obtained from classical synthesis starting from alcohols[2,4a] or *tert*-alkyl halides.[2,4a] They are listed according to the increasing order of retention time on GLC.[7] The experimental conditions are given in Table I and the results in Table II. It may be seen that an $AcCl/AlCl_3$ mixture is effective in bringing about the diacetylation and triacetylation of isoparaffins to pyrylium salts under mild conditions.

The treatment of isopentane by $AcCl/AlCl_3$ (runs 1–3) affords mainly four pyrylium salts which were transformed into pyridines **1b,d** and **2b,e**. Pyridines **1b,d** are formed from the diacetylation of 2-methylbutenes generated in situ from the isoparaffin, whereas **2b,e** result from the triacetylation of the same alkenes according to Scheme II.[2,8] It can be seen that the product distribution is strongly dependent on the experimental conditions. When the ratio $AcCl/AlCl_3$ is larger than unity, a large amount of triacetylation products are formed (run 1) and the apparent selectivity of the resultant alkylpyridines favors the formation of the less substituted pyridine **1b**. The occurence of traces of 2,4,6-trimethylpyridine (**1a**) and its analogue **2a** indicates that isobutene has been formed in the reaction medium. Isobutene could arise from oligomerization with further cracking in the medium. When the ratio $AcCl/AlCl_3 = 1$ (run 3), the more substituted pyridine **1d** is obtained almost exclusively together with traces of **1b** and **2b,e**. Isopentane has been treated with $AcCl/AlCl_3$ mixture in chloroform by Tabushi et al.[9] They have obtained in low yield the conjugated ketone corresponding to monoacetylation of a mixture of 2-methylbutenes. They did not look for the pyrylium salts. Tabushi's results are in accord with the low reactivity and the poor yields in chloroform (vide infra).

The treatment of 2-methylpentane (runs 4–7) by $AcCl/AlCl_3$ follows the same trends as those evidenced in the isopentane case. The more substituted pyrylium salts and low quantities of triacetylated products are formed when $AcCl/AlCl_3 \leq 1$ (runs 6, 7) while the reverse is observed when $AcCl/AlCl_3 > 1$ (run 4). Run 5 is reported to underline the extreme importance of the homogeneity of the reaction medium on the selectivity: in run 5 $AcCl/AlCl_3 = 1$ but it was impossible to have efficient mixing and thus accumulation of AcCl on the upper part of the reactor leads to an effective $AcCl/AlCl_3$ ratio larger than unity, which accounts for the large amount of triacetylated compounds and the poor apparent selectivity of this run. Apart from the expected pyridines **1e,f** derived from 2-methylpentenes, pyridines **1a,b,g,h** are also formed in low yields. Pyridines **1g,h** result from the isomerization of the dimethylpropylcarbenium ion into the diethylmethylcarbenium ion (Scheme III). It is worth noting that the selectivities in products formed after the isomerization closely parallel those observed in the expected compounds.

(7) Chromosorb P AW, 5% KOH, 20% Apiezon L; on these columns all the given pyridines are resolved except **1d,e** which have been determined by GLC/MS coupling.

(8) Products resulting from triacetylation were evidenced for the first time by Balaban et al. (A. T. Balaban, P. T. Frangopol, A. R. Katritzky, and C. D. Nenitzescu, *J. Chem. Soc.*, 3889 (1962)), and it was shown that triacetylation products cannot result from the already formed pyrylium salts, thus supporting Scheme II. A further report on triacetylation was given in A. T. Balaban, A. Bota, and I. I. Staniou, *Rev. Roum. Chim.*, 21, 1183 (1976).

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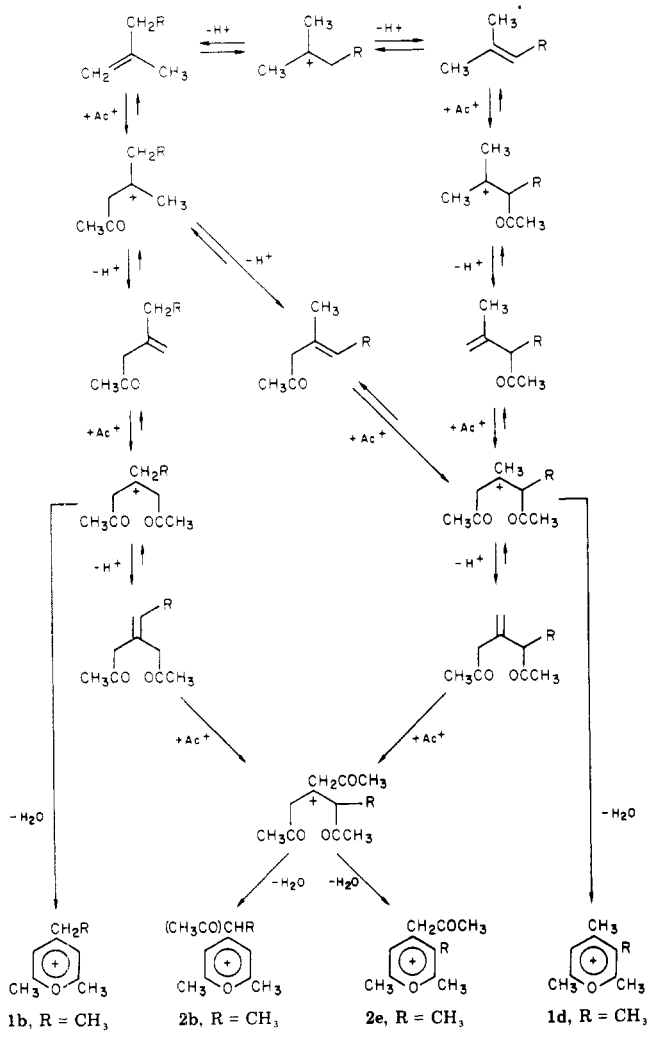
Scheme II



Furthermore, we have already shown that the reaction of acetylation of pure 2-methylpentenes with an $AcCl/AlCl_3$ mixture affords rearrangement products.[3b]

In the treatment of 3-methylpentane with $AcCl/AlCl_3$ (runs 8–12), a large amount of pyridines resulting from the isomerization of the initial carbenium ion is observed. In chloroform, run 8, the only obtained pyridine results from isomerization with a high selectivity but a low yield. The isomerization of diethylmethylcarbenium ion into the dimethylisopropylcarbenium ion is known to be slow, whereas the isomerization into the dimethylpropylcarbenium ion is fast.[10,11] This may explain why we do not observe pyridine **1c**, which would result from the isomerization of diethylmethylcarbenium ion into dimethylisopropylcarbenium ion.

The treatment of 2,3-dimethylbutane by an $AcCl/AlCl_3$ mixture gives mainly the two expected pyridines resulting from the diacetylation (**1c**) and triacetylation (**2c**) of 2,3-dimethylbutene (runs 13, 14). Little rearrangement is observed in a medium of high activity such as in run 14 but a high percentage of trimethylpyridine **1a** is found. The use of chloroform as solvent dramatically changes the selectivity of the reaction, since the only pyridine results from isomerization of the initial carbenium ion into the dimethylpropylcarbenium ion (run 13). In chloroform, the reactivity of the medium is so low that the rearrangement is total and the observed pyridine can be used as an indication of the relative ease of the attack of the various olefins in the medium. It is interesting to point out that the three isomeric hexanes lead in chloroform to the same pyridine with a high selectivity but a low yield. This observation allows the use of a crude hexane cut from petrochemical plants for the preparation of substituted pyridines.

In the literature, various attempts to acetylate isoparaffins have been reported in an $AcCl/AlCl_3$ medium.[9,12] Depending on experimental conditions, saturated or unsaturated ketones have been obtained. These ketones result from the monoacetylation of the olefins, followed by reduction or elimination reactions. It is clear that in several instances pyrylium salts should have been obtained but they were certainly missed in the aqueous phase since interest was focused on the organic layer. It is interesting to note that a long time elapsed before the first pyrylium salt was identified in the classical acetylation of olefins.[4,6] The key step in all these acetylations consists of the generation of a carbenium ion from the isoparaffins by hydride exchange between some protosolvated or Lewis-acid-complexed acylium ion or possibly by acid-catalyzed ($HCl-AlCl_3$) hydride abstraction (Scheme IV).[13,14] Whatever the exact mechanism of the hydride abstraction, the result is that the carbenium ion issued from the isoparaffin is the same as that derived from alcohols or *tert*-alkyl halides and thus can be transformed into olefins which are then acetylated.

Conclusion

Pyrylium salts have been prepared from isoparaffins as carbenium ion precursors and transformed in pyridines in a one-pot synthesis. We have shown that the selectivity of the reaction is strongly dependent on the nature of the initial carbenium ion and on the $AcCl/AlCl_3$ ratio. The transformation of isoparaffins into pyrylium salts, which are important synthons in preparative chemistry, is an interesting use of these substrates.

Experimental Section

General Procedures. Anhydrous aluminum chloride, isopentane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane (Fluka puriss) were used without further purification. $CHCl_3$ and CH_3COCl were purified by distillation before use. Analysis of the reaction mixture by GLC was performed on an Intersmat IGC 16 (FID) equipped with a 3.5 m × $^1/_8$ in. i.d. stainless steel column packed with Chromosorb P AW 80/100, 5% KOH, 20% Apiezon L. A temperature of 160 °C was held for 6 min after which the temperature range 160–210 °C was programmed to increase at 6 °C/min. Nitrogen pressure was 2 bars. The preparative GLC's were performed on a F and M Scientific 700 laboratory chromatograph equipped with a thermal conductivity detector and a 3.5 m × $^1/_4$ in. i.d. stainless steel column (isotherm). Mass spectra have been obtained for pure samples on an AEI MS 50 and for mixtures on a Varian MAT 111. The ^1H NMR and ^{13}C NMR spectra were run, respectively, on a Varian XL 100 in deuteriochloroform or carbon tetrachloride

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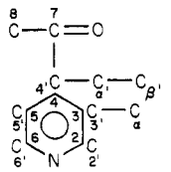
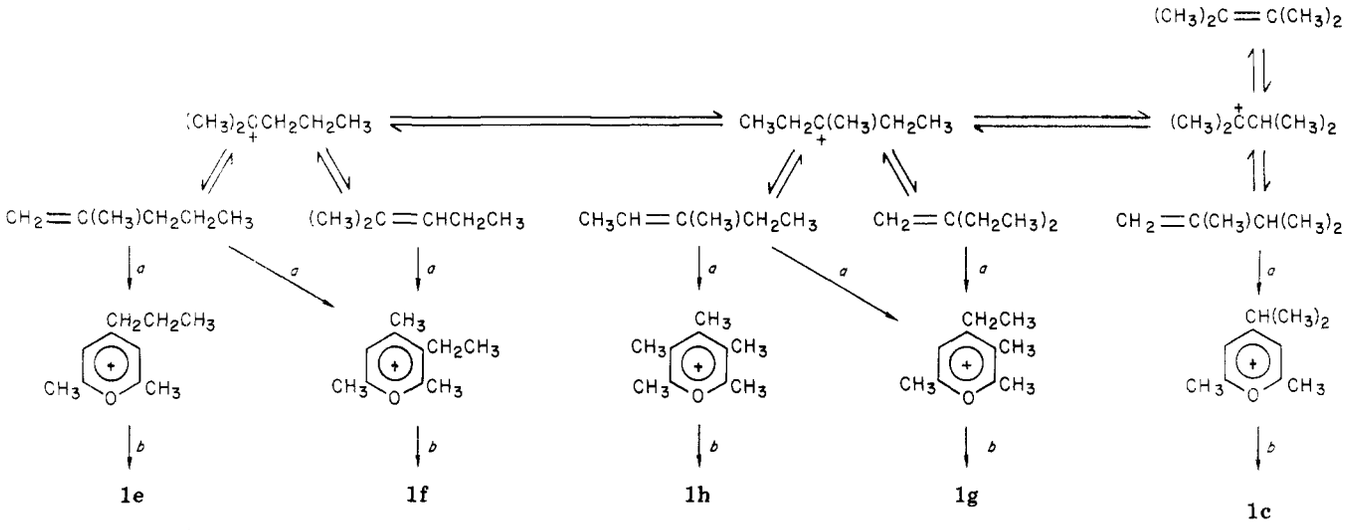
(14) CH_3CH_2Cl was trapped in small amounts in run 2; the occurrence of this product could indicate that ethanol was formed from acetylium ion in the medium.

Table III. ^{13}C NMR Chemical Shifts of Pyridines 2a-h in $CDCl_3$



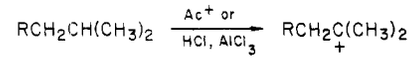
	δ (carbon)														
	2	3	4	5	6	2'	3'	4'	5'	6'	7	8	α	α'	β'
2a	157.9	121.4	143.6	121.4	157.9	24.2		49.8		24.2	204.3	29.6			
2b	158.4	119.6	149.9	119.6	158.4	24.3		52.9		24.3	207.1	28.5		16.8	
2c	158.3	117.7	153.7	117.7	158.3	24.6		52.2		24.6	209.5	25.6		24.6	
2d	158.4	120.1	148.5	120.1	158.4	24.3		60.9		24.3	206.8	29.3		24.8	12.0
2e	156.7	127.1	141.8	122.7	154.4	23.1	14.5	48.6		23.7	204.5	29.5			
2f	157.1	126.1	148.0	119.2	155.0	23.5	14.3	49.7		24.0	207.2	28.4		16.3	
2g	156.6	133.0	141.4	123.1	154.8	22.4	21.8	47.9		23.9	205.0	29.6	13.7		
2h	153.1	127.4	140.6	127.4	153.1	23.2	15.4	44.9	15.4	23.2	204.4	29.6			

Scheme III



[a] $CH_3C^+=O$. [b] NH_4OH.

Scheme IV



and on a Varian CFT 20 in deuteriochloroform. IR spectra were run on a Perkin-Elmer IR 397 by using a capillary layer of the substance between NaCl windows.

Synthesis Procedures. A double-jacketed glass reactor (500 mL) equipped with a bottom outlet valve, a vibromixer, an efficient ice-cooled condenser, and a dropping funnel is used in all runs. The desired temperature is obtained by circulating water. The reactor is charged with the desired amount of $AlCl_3$ and acetyl chloride and the paraffin is added rapidly at 0 °C (10 min). The reaction temperature is maintained by circulating water. When chloroform is used, the same procedure is followed and chloroform is charged first. An abundant evolution of HCl is observed. At the end of the chosen reaction time, the crude brown reaction mixture is poured, after cooling, into 500 mL of concentrated NH_4OH (34% NH_3, d = 0.89 g/cm^3) and the temperature kept below 20 °C. The aqueous solution is extracted continuously with 500 mL of $CHCl_3$ during 18 h. The chloroform phase is treated three times with 150 mL of 5% HCl. The aqueous phase which contains the pyridinium chlorides is washed with chloroform and treated, with cooling, with 8 g of NaOH pellets. The aqueous phase is extracted continuously by 250 mL of dichloromethane during 10 h. The CH_2Cl_2 is evaporated under reduced pressure. The crude pyridine mixture is put in a drybox with NaOH pellets for 12 h and then weighed (weight loss 3–5%). A control on 2,4,6-trimethylpyridine indicated that 10% of the material was lost during the whole procedure. The GLC analysis is performed on the dichloromethane phase before evaporation. The alkylpyridines **1a–h** can be separated from the acetylated pyridines **2a–h** by careful steam distillation.

Product Analysis. Pyridines **1a–h** have already been described.[4,15] Mass spectral and ^1H NMR data are given. The structures of compounds **2a–h** have been established on the basis of their mass and NMR spectra. The general features of the ^1H NMR spectra are 1.94–2.20 (CH_3CO), 2.43–2.54 (2- (and 6-) methyl group, 3.40–3.90 (CH_3COCH(R)-pyr), 6.70–6.85 (3- (and 5-) pyridine ring protons) ppm. The integration shows that in the given solvent the possible tautomeric equilibria largely favor the given structure.[16] ^{13}C NMR chemical shifts are given in Table III: the typical chemical shifts for pyridines and acetyl compounds are observed.[17]

Mass spectra of pyridines **2a–h** show in all cases the molecular ion (M). The M - 1 peak which is generally observed in alkylpyridines is of low intensity if present. Together with the peaks of alkylpyridines (m/e 79, 93),[18] the identification of the compounds is supported by the observed McLafferty rearrangement with hydrogen transfer to the carbon in position 3 or 5 of the pyridine ring and loss of CH_2=C=O (Scheme V). The M - 42 peak is in all cases strong and is the base peak for **2a,b,e,h**. The rearrangement is in competition with fission a (Scheme V) which

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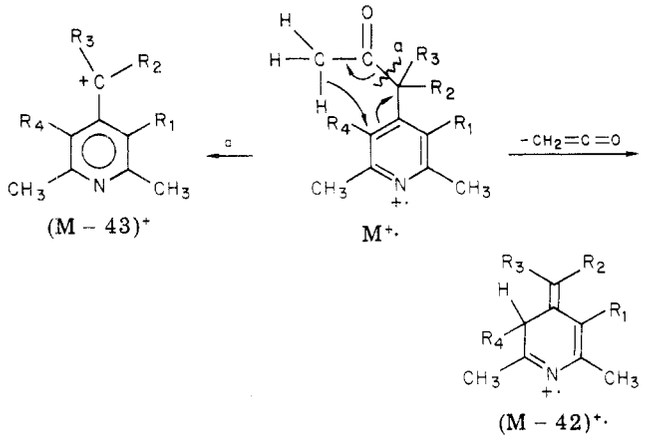
(17) G. C. Levy and G. L. Nelson in "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 98.
(18) Q. N. Porter and J. Baldas in "Mass Spectra of Heterocyclic Compounds", A. Weissberger and E. C. Taylor, Eds., Wiley-Interscience, New York, N.Y., 1971, p 378.

Scheme V



gives an abundant M - 43 peak and the base peak for **2c,f,g**. The relative abundance of the M - 42 and M - 43 peaks should be related in a more detailed analysis to the conformational state of the acyl group in relation with the steric requirements of the R_1, R_2, R_3, and R_4 substituents. In all compounds, the intense peak m/e 43 is unambiguously associated with the acetylium group.

The IR spectra show an intense carbonyl absorption at 1710–1720 cm^{-1}.

2,4,6-Trimethylpyridine[4a] (**1a**): NMR (CCl_4) 2.2 (3 H, s), 2.4 (6 H, s), 6.6 (2 H, s) ppm; MS (80 eV) m/e 121 (100), 120 (31.6), 106 (20.4), 79 (30.6), 77 (16.3), 39 (12.2).

2,6-Dimethyl-4-ethylpyridine[4b] (**1b**): NMR (CCl_4) 1.22 (3 H, t), 2.4 (6 H, s), 2.46 (2 H, q), 6.66 (2 H, s) ppm; MS (80 eV) m/e 135 (100), 120 (31.7), 107 (7.5), 91 (14.6), 79 (20.7), 77 (14.3), 39 (22.1).

2,6-Dimethyl-4-isopropylpyridine[4a] (**1c**): NMR (CCl_4) 1.22 (6 H, d), 2.43 (6 H, s), 3.72 (1 H, sept), 6.48 (2 H, s) ppm; MS (80 eV) m/e 149 (88.6), 135 (12.4), 134 (100), 91 (12.7), 77 (13.9), 65 (8.8), 39 (10.8).

2,3,4,6-Tetramethylpyridine[4b] (**1d**): NMR (CCl_4) 2.1 (3 H, s), 2.16 (3 H, s), 2.32 (3 H, s), 2.37 (3 H, s), 6.74 (1 H, s) ppm; MS m/e (80 eV) 135 (100), 134 (52.9), 120 (23.5), 106 (3.6), 93 (7.3), 91 (12.3), 79 (25), 77 (9.6), 39 (6.1).

2,6-Dimethyl-4-propylpyridine[4a] (**1e**): NMR ($CDCl_3$) 0.89 (3 H, t), 1.57 (2 H, m), 2.45 (6 H, s and 2 H, t), 6.74 (2 H, s) ppm; MS m/e (80 eV) 149 (82), 148 (6), 134 (30.8), 121 (100), 120 (30.8), 106 (7.4), 93 (7.4), 91 (8.7), 79 (12), 77 (25.6), 39 (14.1).

3-Ethyl-2,4,6-trimethylpyridine[4a] (**1f**): NMR ($CDCl_3$) 1.1 (3 H, t), 2.23 (3 H, s), 2.4 (3 H, s), 2.5 (3 H, s), 2.6 (2 H, q), 6.76 (1 H, s) ppm; MS (80 eV) m/e 149 (56.7), 148 (10.4), 134 (100), 121 (8.9), 93 (14.9), 91 (14.9), 79 (5.9), 77 (14.9), 39 (8.9).

4-Ethyl-2,3,6-trimethylpyridine[4a] (**1g**): NMR ($CDCl_3$) 1.16 (3 H, t), 2.16 (3 H, s), 2.48 (6 H, s), 2.56 (2 H, q), 6.67 (1 H, s) ppm; MS (80 eV) m/e 149 (100), 148 (73.6), 134 (27.8), 121 (27.8), 120 (18), 93 (16.7), 91 (15.3), 79 (6.9), 77 (16.7), 39 (9.7).

2,3,4,5,6-Pentamethylpyridine[4a] (**1h**): NMR ($CDCl_3$) 2.2 (9 H, s), 2.5 (6 H, s) ppm; MS (80 eV) m/e 149 (100), 148 (39.5), 134 (30.2), 121 (11.6), 120 (7.0), 93 (26.7), 91 (15.1), 79 (5.8), 77 (8.1), 39 (8.1).

1-(2,6-Dimethylpyridyl)-2-propanone (**2a**): NMR (CCl_4) 2.02 (3 H, s), 2.38 (6 H, s), 3.43 (2 H, s), 6.85 (2 H, s) ppm; MS (80 eV) m/e 163 (20), 121 (100), 106 (4), 73 (5.5), 77 (16), 43 (62), 39 (6.7); IR 1715 (C=O), 1605, 1565 (pyridine) cm^{-1}; colorless oil.

3-(2,6-Dimethylpyridyl)-2-butanone (**2b**): NMR ($CDCl_3$) 1.48 (3 H, d), 2.08 (3 H, s), 2.52 (6 H, s), 3.66 (1 H, q), 6.84 (2 H, s) ppm; MS (80 eV) m/e 177 (35.9), 135 (100), 134 (97.4), 121 (10.6), 107 (17.9), 91 (21.2), 43 (61.5), 39 (29.5); IR 1710 (C=O), 1600, 1560 (pyridine) cm^{-1}; colorless oil.

3-(2,6-Dimethylpyridyl)-3-methyl-2-butanone (**2c**): NMR ($CDCl_3$) 1.45 (6 H, s), 1.94 (3 H, s), 2.53 (6 H, s), 6.85 (2 H, s) ppm; MS (80 eV) m/e 191 (24.7), 149 (89), 148 (100), 134 (45.2), 121 (7.7), 120 (24.7), 43 (21.9), 39 (9.5); IR 1705 (C=O), 1660, 1555 (pyridine) cm^{-1}; colorless oil.

3-(2,6-Dimethylpyridyl)-2-pentanone (**2d**): NMR ($CDCl_3$) 0.83 (3 H, t), 1.1 (2 H, m), 2.15 (3 H, s), 2.46 (6 H, s), 6.82 (2 H, s) ppm; MS (80 eV) m/e 191 (18), 149 (36.1), 148 (18), 134 (100), 120 (14.7), 106 (3.3), 91 (8.4), 79 (4.8), 77 (9.1), 43 (31.1), 39 (7.1); IR 1710 (C=O), 1600, 1562 (pyridine) cm^{-1}; colorless oil.

1-(2,3,6-Trimethylpyridyl)-2-propanone (**2e**): NMR ($CDCl_3$) 2.12 (3 H, s), 2.17 (3 H, s), 2.45 (3 H, s), 2.49 (3 H, s), 3.68 (2 H, s), 6.76 (1 H, s) ppm; MS (80 eV) m/e 177 (28.6), 135 (100), 134 (20.8), 121 (3), 120 (10.4), 106 (2.4), 93 (8.9), 91 (2.5), 79 (6.8), 77 (12.5), 43 (46.7), 39 (12.5); IR 1710 (C=O), 1590, 1560 (pyridine) cm^{-1}; mp 61 °C.

3-(2,3,6-Trimethylpyridyl)-2-butanone (**2f**): NMR ($CDCl_3$) 1.3 (3 H, d), 2.0 (3 H, s), 2.2 (3 H, s), 2.43 (3 H, s), 2.48 (3 H, s), 3.9 (1 H, q), 6.7 (1 H, s) ppm; MS (80 eV) m/e 191 (37.8), 149 (81.0), 148 (100), 121 (21.6), 91 (12.2), 79 (8.6), 77 (13.7), 43 (43.2), 39 (7.2); IR 1710 (C=O), 1590, 1558 (pyridine) cm^{-1}; colorless oil.

1-(2,6-Dimethyl-3-ethylpyridyl)-2-propanone (**2g**): NMR ($CDCl_3$) 1.08 (3 H, t), 2.16 (3 H, s), 2.46 (3 H, s), 2.54 (3 H, s), 2.56 (2 H, q), 3.64 (2 H, s) 6.77 (1 H, s) ppm; MS (80 eV) m/e 191 (46), 149 (72.0), 148 (100), 134 (28.0), 121 (40), 91 (16.0), 79 (6.6), 77 (14.3), 43 (66.0), 39 (15.4); IR 1720 (C=O) 1595, 1560 (pyridine) cm^{-1}; mp 66 °C.

1-(2,3,5,6-Tetramethylpyridyl)-2-propanone (**2h**): NMR ($CDCl_3$) 2.14 (3 H, s), 2.22 (6 H, s), 2.5 (6 H, s), 3.82 (2 H, s) ppm; MS (80 eV) m/e 191 (46.1), 149 (100), 148 (38.5), 134 (13.4), 93 (3.5), 91 (13.9), 79 (7.2), 77 (5.5), 43 (44.2), 39 (8.2); IR 1710 (C=O) 1565 (pyridine) cm^{-1}; mp 93 °C.

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