696. *Pyrylium Salts obtained by Diacylation of Olefins. Part II.*[1] *The Two Pyrylium Salts formed in Diacetylation of 2-Methylbut-2-ene.*[2]

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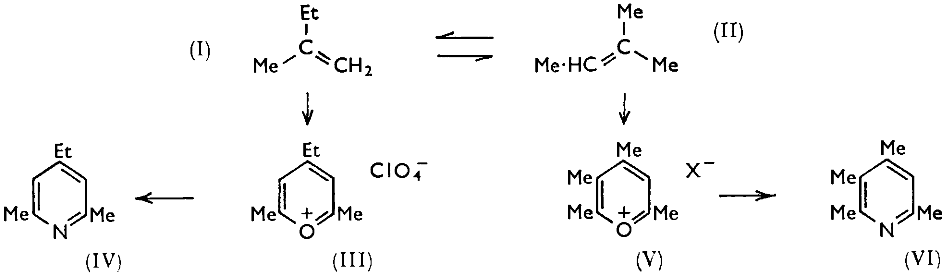
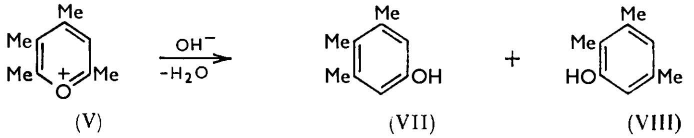
Depending on the catalyst employed, Friedel–Crafts diacetylation of 2-methylbut-2-ene yields 2,3,4,6-tetramethyl- and/or 4-ethyl-2,6-dimethylpyrylium salts. The mechanism and implications of this hitherto unencountered phenomenon are discussed.

IT was reported in Part I [1] that Friedel–Crafts acylation of olefins yields pyrylium salts, besides unsaturated ketones and β-halogeno-ketones. On acylation of methyl and phenyl derivatives of propene with acid chlorides and aluminium, ferric, or stannic chloride, treatment of the aqueous layer formed by hydrolysis of the reaction mixture afforded crystalline pyrylium perchlorates. In extending this reaction to other catalysts it has now been found that suitable conditions for preparing 2,4,6-trimethylpyrylium perchlorate are to treat t-butyl alcohol with a mixture of acetic anhydride and perchloric acid.[3] This compound was previously isolated by Diels and Alder [4] by the action of similar mixtures on mesityl oxide. Mixtures of acetic anhydride and perchloric acid have been extensively studied by Burton and Praill [5] for various acetylations, and Praill and Whitear [5] recently observed the formation of pyrylium salts by the action of such mixtures on olefins or tertiary alcohols.

When this reaction was extended to 2-methylbut-2-ene and aluminium chloride, only one of the two possible pyrylium perchlorates was obtained, namely the 4-ethyl-2,6-dimethylpyrylium salt (III). In the presence of stannic chloride the 2,3,4,6-tetramethyl isomer (V) was formed, but its perchlorate does not crystallise from water.



In order to gather more insight into this interesting dependence of the product on the catalyst employed, we studied the bisacetylation of 2-methylbut-2-ene in the presence of various Friedel–Crafts catalysts, as shown in Table 1.



The products were isolated either as pyrylium salts for qualitative estimation (reineckates, chloroferrates, or chloroantimonates, which are less soluble than the perchlorates), or as pyridines, after treatment of the crude reaction mixture with ammonia.

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[1] The paper by Balaban and Nenitzescu, *Annalen*, 1959, **625**, 74, is considered to be Part I.

[2] Preliminary communication, Balaban and Nenitzescu, *Tetrahedron Letters*, 1960, No. 2, 7.

[3] Nenitzescu and Balaban, *Org. Synth.*, submitted for publication on July 18th, 1959.

[4] Diels and Alder, *Ber.*, 1927, **60**, 716.

[5] Burton and Munday, *J.*, 1957, 1718, 1727, and previous papers in the series; Burton and Praill, *Quart. Rev.*, 1952, **6**, 302; Praill, *Chem. and Ind.*, 1959, 1123; Praill and Whitear, *Proc. Chem. Soc.*, 1959, 312.

The pyridines were subsequently either converted into solid derivatives for qualitative estimation, or quantitatively analysed through infrared spectrophotometry, or gas chromatography.

The structures of the two pyrylium salts formed were proved as follows: 4-ethyl-2,6-dimethylpyrylium salts (*e.g.*, III) were converted by hot alkali into 3-ethyl-5-methylphenol [1] and by ammonia into 4-ethyl-2,6-dimethylpyridine (IV); 2,3,4,6-tetramethylpyrylium salts (V) were converted into a mixture of 3,4,5- (VII) and 2,3,5-trimethylphenol [6] (VIII) and also into 2,3,4,6-tetramethylpyridine (VI).

TABLE 1. *Diacetylation of 2-methyl-2-butene (analysis of pyridines was by gas chromatography).*

No.	Olefin	Acyl deriv.	Catalyst	Solvent	Temp.[a]	Time (hr.)	Yield (%)	Rel. props. of pyridines Me$_4$	Et,Me$_2$
1	CMe_2EtCl	AcCl	$AlCl_3$	—[b]	20°	25	46	0	100
2	C_5H_{10}	,,	,,	—[b]	20	25	43	0	100
3	CMe_2EtCl	,,	,,	CS_2[c]	20	25	49	0	100
4	,,	,,	,,	$MeNO_2$[d]	20	25	35	0	100
5	,,	,,	$SbCl_5$	—	15	4	31	0	100
6	,,	,,	,,	—[e]	15	4	26	0	100
7	,,	,,	$FeCl_3$	—[b]	20	25	30	45	55
8	,,	,,	$TiCl_4$	—[b]	30	25	25	50	50
9	,,	,,	$SnCl_4$	—[b]	30	25	36	15	85
10	,,	,,	,,	—[f]	30	25	8	72	28
11	,,	,,	$SnCl_4,H_2O$	—[b,g]	70	5	0	—	—
12	,,	,,	$ZnCl_2$	—[h]	20	25	28	68	32
13	$CMe_2Et{\cdot}OH$	Ac_2O	,,	—[h]	20	25	40	35	65
14	,,	,,	BF_3,Et_2O	—[h]	30	25	40	81	19
15	C_5H_{10}	,,	,,	—[h]	30	25	34	58	42
16	,,	AcCl	$NaClO_4$	Ac_2O[h]	60	20	25	79	21
17	,,	AcCl	,,	Ac_2O–AcOH[h]	60	3	11	85	15
18	$CMe_2Et{\cdot}OH$	Ac_2O	70% $HClO_4$	—[h]	100	5	60	79	21
19	,,	,,	H_2SO_4	—[h]	100	5	33	81	19

[a] The maximum temperature reached during the reaction (during addition of reagents the temperature was usually kept below 10° by cooling). [b] The mixture was treated with water, then with excess of aqueous ammonia, and the pyridines were isolated by steam-distillation. [c] The lower layer was decomposed with ice and hydrochloric acid, treated with excess of ammonia, and steam-distilled. [d] The mixture was hydrolysed with water and hydrochloric acid, and the nitromethane was steam-distilled. Ammonia was then added, and the pyridine was isolated by steam-distillation. [e] The crude crystalline pyrylium chloroantimonate was filtered off, then treated with ammonia and steam-distilled. [f] The mixture was hydrolysed with ice and hydrochloric acid, and ethanol was added. A crystalline chlorostannate was slowly deposited; after 3 days it was filtered off, treated with ammonia, and steam-distilled. [g] As described by Jenny (*Compt. rend.*, 1958, **246**, 3477; 1959, **248**, 3555; cf. Bonnot and Jenny, *ibid.*, 1960, **250**, 1854). [h] The same procedure as for *b*, but with extraction with ether. [i] As described by Mathur, Sharma, Venkataraman, and Krishnamurty (*J. Amer. Chem. Soc.*, 1957, **79**, 3582), 100% acetic acid being used.

It may be seen from Table 1 that most Friedel–Crafts catalysts are effective in bringing about diacylation to pyrylium salts. The complete reaction scheme is outlined in the annexed scheme.

The trisubstituted pyrylium cation (as III) is formed from 2-methylbut-1-ene (I) through the unique sequence shown in the chart, but two routes are open to the tetrasubstituted pyrylium salt (V). The steps (IX ⟶ I), (X ⟶ XIII), and (XI ⟶ XV) involve Hofmann elimination, and the steps (IX ⟶ II), (XI ⟶ XIV), (XI ⟶ XVI), and (X ⟶ XII) involve Saytzeff elimination. Praill and Saville have shown [7,8] that formation of βγ-olefinic ketones (cf. XIII ⟶ XV) is kinetically favoured by a cyclic transition state.

Table 1 shows that, with t-pentyl chloride and acetyl chloride in the presence of the strongest Lewis acids (aluminium chloride and antimony pentachloride), the pathway

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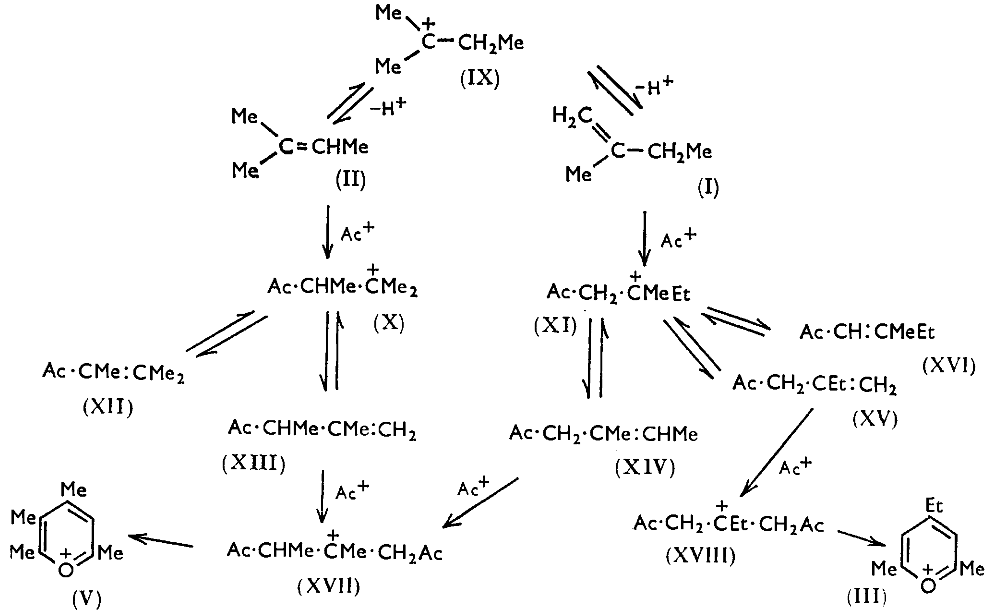
[6] Marshall, Beringer, and Geering, *J. Amer. Chem. Soc.*, 1953, **75**, 2633, and further references therein.
[7] Praill and Saville, *Chem. and Ind.*, 1960, 495.
[8] Deno and Chafetz, *J. Amer. Chem. Soc.*, 1954, **74**, 3940.

(IX) $\longrightarrow$ (I), etc., $\longrightarrow$ (III) involving only Hofmann eliminations is exclusively followed, while in the presence of the weaker Lewis acids (ferric chloride, titanium tetrachloride, zinc chloride, stannic chloride) one or both of the other two sequences are also involved. With t-pentyl alcohol and acetic anhydride, water is formed in the reaction medium and according to the Zucker–Hammett hypothesis [9] this complicates the picture. Also, if, in order to avoid water formation, the olefin (II) is directly acetylated, the situation is complicated by the kinetic relationships (II) $\rightleftharpoons$ (I). It may be seen from Table 1 that the results do not differ much if the olefin is used instead of the chloride (Nos. 1 and 2), but the difference is considerable between the olefin and the alcohol (Nos. 14 and 15). Anyhow, it may be concluded that weaker Lewis acids and proton acids favour Saytzeff eliminations: the higher the water concentration, the more the Saytzeff elimination prevails (compare also Nos. 16 and 17). The behaviour of stannic chloride (Nos. 9—11) and zinc chloride (Nos. 12 and 13) is rather difficult to interpret.



It seems that minute factors considerably affect the product composition, and thus pyrylium salt formation through diacylation of amylene can be a sensitive method of comparing Friedel–Crafts acylating agents. A further factor is the nature of the acid chloride employed: with t-pentyl chloride and acetyl chloride, in the presence of aluminium chloride, only the trisubstituted pyrylium salt (as III) results. The pyrylium salts formed in the same conditions with propionyl chloride and benzoyl chloride were attributed [1] trisubstituted structures by analogy. Subsequent analysis revealed that they had tetrasubstituted structures, analogous to (V): the former through conversion into phenol (see the Experimental section), and the latter through its ultraviolet absorption spectrum.

Separate experiments have shown that the two pyrylium salts (III) and (V) are not interconvertible under the usual reaction conditions; so the difference does not arise from kinetic or thermodynamic control of the reaction. Gas chromatography of the ketonic mixtures (Table 1, Nos. 1, 14, and 18) has shown the presence of several ketonic peaks. However, fractional distillation and isolation as semicarbazones and 2,4-dinitrophenylhydrazones afforded only 3,4-dimethylpent-3-en-2-one (XII) in acetylations catalysed

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[9] Taft, jun., *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 53, 72; 1953, **75**, 1253, 3955; 1955, **77**, 1584, 837; *Ann. Rev. Phys. Chem.*, 1958, **9**, 287; Long and Paul, *Chem. Rev.*, 1957, **57**, 1, 935.

by boron trifluoride of perchloric acid, and a β-chloro-ketone in the reaction catalysed by aluminium chloride, whose dehydrochlorination with diethylaniline yielded the same αβ-unsaturated ketone (XII). For the various acetylations of 2-methylbut-2-ene reported in the literature,* only Kondakoff[10] mentioned the formation of 4-methylhex-3-en-2-one (XVI) in the presence of zinc chloride, but his experimental details are not convincing. From reactions in the presence of stannic chloride, Colonge,* Stevens,* and later workers[11] found only the ketones formed in sequence (XII) and (XIII). The same results were obtained with sulphoacetic acid.[12] Of the stronger Lewis acids, only aluminium chloride has been applied by Krapiwin * and subsequent workers[13] to the acetylation of 2-methylbut-2-ene; the β-chloro-ketone yielded, by dehydrochlorination, the same ketone (XII). No definite conclusion can yet be drawn from the study of the ketones formed by monoacetylation. Since the equilibria between αβ- and βγ-olefinic forms are very labile and easily modified by the usual isolation procedure (cf., *e.g.*, refs. 8, 12, 14) or by the basic agents employed for dehydrochlorination of the intermediate chloro-ketones, finer techniques must be applied to the reaction mixture in order to separate and identify the five possible unsaturated ketones (XII—XVI) and the two possible chloro-ketones.

Of the factors which could possibly be responsible for the preferential formation of one or the other pyrylium salt in amylene diacetylation, various electronic effects or differences between Lewis and proton acids cannot explain the results; the presence or absence of water or other hydroxylic species in the reaction medium does not much influence the nature of the products; a difference between thermodynamic and kinetic control has been experimentally ruled out; the only remaining factors are the steric requirements of the base accepting the proton, and the acid strength of the catalyst. Brown has shown[15] that Saytzeff elimination is affected by steric hindrance, while Hofmann elimination is not; in the reaction now under discussion, bases with a large volume, such as the complex metallic anions MX_n^-, favour Hofmann elimination more than do bases with a smaller volume, such as water, acetic acid, BF_4^-, and ClO_4^-. However, with metallic halides the results vary so much that other factors, namely, acid strength and formation of unsaturated ketone–metal halide complexes † must be taken into account.

A survey of the literature concerning olefin acylations in the presence of various catalysts disclosed the probable formation of pyrylium salts, not recognised as such, in other instances besides those listed in footnote 3 of Part I. Thus, Byrns and Doumani's studies[16] of the acetylation of di-isobutylene in the presence of zinc chloride yielded a " zinc chloride complex of a 1,3-diketone " which was converted by ammonia into a nitrogen-containing base; all attempts to set the " diketone " free from the complex failed. We proved[6b] that the " complex " is a pyrylium salt. Also, in the presence of sulphoacetic acid there are indications of the formation of pyrylium salts from olefins[17] or from unsaturated ketones.[18]

EXPERIMENTAL

Preparation of 2,4,6-*Trimethylpyrylium Salts*.—(a) *With aluminium chloride in carbon disulphide*. Acetyl chloride (250 g., 3·2 moles) is added at 0—10° to a stirred suspension of powdered aluminium chloride (270 g., 2 moles) in carbon disulphide (500 ml.), then 138 g.

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* See footnote 3 in ref. 1; the first two references in that footnote must be inverted (Krapiwin with Kondakoff).

† Suggested by a referee.

[10] Kondakoff, *Bull. Soc. chim. France*, 1892, **7**, 576.

[11] Favre and Schinz, *Helv. Chim. Acta*, 1952, **35**, 2388.

[12] Heilmann, de Gaudemaris, and Noack, *Bull. Soc. chim. France*, 1954, 990, 992.

[13] Petrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1955, 639.

[14] Arnaud, *Compt. rend.*, 1957, **244**, 1785.

[15] Brown and Moritani, *J. Amer. Chem. Soc.*, 1956, **78**, 2203, and previous papers in the series.

[16] (*a*) Byrns and Doumani, *Ind. Eng. Chem.*, 1943, **35**, 349; Byrns, U.S.P. 2,315,046, 2,355,703, and 2,453,619; (*b*) Balaban, Ghenea, and Nenitzescu, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 1102.

[17] Doumani and Cuneo, U.S.P. 2,411,823, 2,438,334, Byrns, U.S.P. 2,463,742.

[18] Morel and Verkade, *Rec. Trav. chim.*, 1948, **67**, 539; 1949, **68**, 619; 1951, **70**, 35.

(1·5 moles) of t-butyl chloride (138 g., 1·5 moles) are added during 3 hr., the temperature being kept at 10°. Stirring is continued for 4—6 hr. The next day, the lower layer is decomposed with ice (1·2 kg.) and hydrochloric acid (50 ml.), and water-insoluble by-products are removed by extraction with ether. The aqueous solution contains 2,4,6-trimethylpyrylium chloroaluminate (47—53% yield) from which various salts may be prepared (cf. Part I).

On addition of picric acid in equivalent amount, in water, an unidentified greenish-yellow precipitate is first deposited (m. p. 130°; from 20% ethanol) (Found: C: 48·6; H, 3·9; N, 10·8%). Filtration of the solution and cooling affords the more soluble trimethylpyrylium picrate,[1] m. p. 129° (from water). The mixed m. p. between these two compounds shows depression. Only the latter compound yields other pyrylium salts on treatment with the appropriate reagent.

(b) *With perchloric acid.*[3] A mixture of anhydrous t-butyl alcohol (2 moles) and acetic anhydride (10 moles), cooled at $-10°$, is cautiously treated with 70% perchloric acid (1·75 moles). The temperature is kept between 90° and 100° by controlling the rate of addition and by cooling. The mixture is then heated at 100° for 2 hr. After cooling, the crystalline 2,4,6-trimethylpyrylium perchlorate is filtered off, and washed with a mixture of acetic acid and ether, then with ether (yield, 205—215 g., 53—57%). Recrystallisation from water (1500 ml.) acidified with 70% perchloric acid (5 ml.) (carbon) gives white crystals (200—205 g.), m. p. 244°. If the last reagent added to the mixture of the other two is the alcohol or the anhydride, yields of pyrylium perchlorate are small, and appreciable amounts of tri-isobutene separate as a colourless upper layer (b. p. 172° over sodium) (Found: C, 85·65; H, 14·15. Calc. for $C_{12}H_{24}$: C, 85·6; H, 14·4%).

(c) *With antimony pentachloride.* If t-butyl chloride (0·1 mole) is slowly added at 5—10° to the complex from antimony pentachloride (0·1 mole) and acetyl chloride (1·0 mole) hydrogen chloride is evolved and a clear red solution is obtained, which soon crystallizes. The 2,4,6-*trimethylpyrylium chloroantimonate* is filtered off and washed with ether (yield, 21 g., 46%). Recrystallized from acetic acid containing hydrogen chloride, it has m. p. 174° (decomp.) (Found: C, 21·3; H, 2·3. $[C_8H_{11}O]^+SbCl_6^-$ requires C, 21·0; H, 2·4%). It may also be prepared from trimethylpyrylium perchlorate and old, yellow antimony pentachloride in acetic acid.

(d) *With zinc chloride.* t-Butyl alcohol (7·5 g., 0·1 mole) is added without cooling to a solution of anhydrous zinc chloride (40 g.) and acetic anhydride (100 ml.). The mixture is stirred for 2 hr. at 90°, then cooled and treated with water (50 ml.). An hour later an excess of perchloric acid is added. The perchlorate is filtered off and washed with ether (yield, 10 g., 45%).

(e) *With stannic or titanic tetrachloride.* Acetyl chloride (1 mole) and stannic or titanic chloride (0·2 mole) are mixed, stirred, and treated during 1 hr. with t-butyl chloride (0·2 mole). The next day the trimethylpyrylium chlorostannate[1] is filtered off, and the filtrate (or the whole reaction mixture with titanic chloride, which yields no crystalline pyrylium salt) is hydrolysed with ice and hydrochloric acid, and then treated with perchloric acid (0·2 mole). Yields were 43% ($SnCl_4$) or 30% ($TiCl_4$).

(f) *With aluminium or ferric chloride.* With careful exclusion of moisture the anhydrous metallic halide (0·4 mole) is gradually introduced into acetyl chloride (1 mole), with efficient cooling and stirring, the temperature being kept below 10°. Then t-butyl chloride (0·3 mole) is slowly introduced at 0—5°; after 3—4 hr. evolution of hydrogen chloride has subsided, and the mixture is allowed to reach room temperature and is stirred for 6—8 hr. longer. Next day the mixture is poured on ice and hydrochloric acid (20 ml.), water-insoluble material is extracted with ether, and the perchlorate is precipitated by addition of perchloric acid; yields are 40—45% ($AlCl_3$) and 30—35% ($FeCl_3$).

(g) *Mercury dichloride and boron fluoride–ether complex.* With t-butyl chloride and acetyl chloride, no reaction could be observed by refluxing in the presence of these substances.

2,4,6-*Trimethylpyrylium reineckate* was prepared from the perchlorate and Reinecke salt in 80% ethanol solution; it had m. p. 165° (from ethanol) (Found: C, 32·9; H, 3·9; N, 18·9. $C_{12}H_{17}CrN_6OS_4$ requires C, 32·6; H, 3·9; N, 19·0%).

2,4,6-*Trimethylpyrylium chloroferrate* (yellow) was obtained from the perchlorate and ferric chloride in concentrated hydrochloric acid; it had m. p. 53° (from 30% hydrochloric acid) (Found: C, 29·9; H, 3·4. $[C_8H_{11}O]^+FeCl_4^-$ requires C, 29·95; H, 3·5%).

2,4,6-*Trimethylpyrylium periodide* was obtained from the perchlorate with a warm aqueous solution of iodine in sodium iodide, as a dark-brown heavy oil which crystallized on cooling and after recrystallization from acetic acid had m. p. 72° (Found: C, 19·3; H, 2·3; I, 75·2. $[C_8H_{11}O]^+I_3^-$ requires C, 19·1; H, 2·2; I, 75·6%).

Diacetylation of 2-Methylbut-2-ene.—General. The olefin was prepared by catalytic dehydration of isopentyl alcohol over kieselguhr at 400°, followed by careful fractionation. The fraction of b. p. 38° was used. t-Pentyl chloride was prepared from t-pentyl alcohol (b. p. 101·5—102·5°) by a procedure similar to that given for t-butyl chloride.[19] The acetylation was carried out as described for trimethylpyrylium salts.

At the end of the reaction and before hydrolysis the mixture was treated with a solution of old, yellow antimony pentachloride in acetic acid, alternatively after hydrolysis with an ethanolic solution of Reinecke salt or a solution of ferric chloride in concentrated hydrochloric acid. The m. p. of the pyrylium salts (see Table 2) indicated whether salt (III) or (V) was predominantly formed.

TABLE 2. *Pyrylium salts formed in the diacetylation of 2-methylbut-2-ene.*

					2,3,4,6-Me$_4$			2,6-Me$_2$-4-Et		
	Recryst.		Required (%)			Found (%)			Found (%)	
Anion	from	Formula	C	H	M. p.	C	H	M. p.	C	H
Perchlorate	EtOH	$C_9H_{13}ClO_5$	45·7	5·5	95° [a]	45·5	5·4	189° [b]	45·5	5·5
Chloroantimonate	AcOH	$C_9H_{13}Cl_6OSb$	22·9	2·8	191 [b]	23·0	2·9	140 [a]	22·9	2·7
Reineckate [c]	EtOH	$C_{13}H_{19}CrN_6OS_4$	34·3	4·2	187 [b]	34·5	4·2	155 [b]	34·3	4·2
Chloroferrate	25% HCl	$C_9H_{13}Cl_4FeO$	32·3	3·9	155 [b]	32·5	3·7	45 [b]	32·3	3·8

[a] Directly from the reaction mixture. [b] By treatment of the reaction mixture with the appropriate reagent. [c] Found: (tetramethyl) N, 18·2; (ethyldimethyl) N, 18·2. Required: N, 18·45%.

Alternatively, the reaction mixture was heated with enough water to hydrolyse the acyl derivative and then an excess of ammonia was added, without cooling. When metallic hydroxides were precipitated, the mixture was steam-distilled and the distillate was extracted with ether. When no metallic hydroxide was precipitated, or when it was soluble in an excess of ammonia, the mixture was extracted with ether. The ethereal extract was shaken with 10% hydrochloric acid. Distillation of the ethereal layer after neutralisation with aqueous sodium hydrogen carbonate and drying (Na_2SO_4) afforded the ketone. The acid layer, made alkaline, extracted with ether, and dried (NaOH), yielded the pyridine. This was converted into solid derivatives (chloroplatinate, methiodide, picrolonate, or, as in most cases, picrate) whose m. p. and mixed m. p. with standard samples indicated the approximate composition of the product. Alternatively the base was analysed as follows:

(i) Infrared spectra: [20] for the products obtained in reactions with aluminium chloride or sulphuric or perchloric acid; the results were in good agreement with those obtained by gas chromatography. (ii) Gas chromatography: this was on a 2-m. column of 0·5 cm. diameter, filled with dodecyl phthalate on chamotte, with hydrogen as eluent at 22 ml./min., at 150°. The results in Table 1 are calculated from approximate area integration. 4-Ethyl-2,6-dimethylpyridine has a retention time of 21 min., and 2,3,4,6-tetramethylpyridine of 30 min. (samples 0·05—0·1 ml.). If traces of β-chloro-ketone exist in the sample, hydrogen chloride is removed and the chromatographic results become unreliable.

(a) *With boron fluoride–ether complex* (Table 1, Nos. 14 and 15). Acetic anhydride (1 mole) was mixed with boron fluoride–ether complex (0·5 mole) and then t-pentyl alcohol or 2-methylbut-2-ene (0·5 mole) was slowly added with moderate cooling. The next day water (30 ml.) was added with cooling [occasionally boric acid crystallised; m. p. 159° (decomp.)], and after 1 hr. an excess of ammonia was added and the pyridine was isolated as indicated above.

(b) *With sodium perchlorate* (Table 1, Nos. 16 and 17). (i) 2-Methylbut-2-ene (0·2 mole) was gradually added during 2 hr. to a stirred mixture of anhydrous sodium perchlorate (0·2 mole), 100% acetic acid (1·6 moles), acetyl chloride (0·2 mole), and acetic anhydride (0·6 mole). The yellow solution was heated for 3 hr. at 60°, and then the dark-brown mixture was poured into cooled 20% aqueous ammonia (400 ml.), ether was added, and the pyridine was isolated as above.

(ii) The same procedure was used but without acetic acid. The sodium chloride did not dissolve as previously. The mixture was left overnight and then worked up as described in (i).

[19] Norris and Olmsted, *Org. Synth.*, Coll. Vol. I, 1941, p. 144.
[20] Cook and Church, *Analyt. Chem.*, 1956, **28**, **993**.

(c) *With zinc chloride* (Table 1, No. 12). t-Pentyl chloride (40 ml.) was added with cooling and efficient stirring to acetyl chloride (80 ml.) and powdered anhydrous zinc chloride (85 g.). Next day the viscous oil was poured into water, extracted with ether, treated with an excess of ammonia, and worked up as above.

(d) *With stannic chloride* (Table 1, Nos. 9—11). (i) Stannic chloride (0·25 mole) was mixed with acetyl chloride (1 mole), then t-pentyl chloride (0·25 mole) was added as follows: about 7 g. without cooling, but with stirring for 0·5 hr. until the reaction began. The rest of the t-pentyl chloride was added at 10—20° (bath), then the mixture was stirred at 20—30° for 5—6 hr. longer and left overnight. Next day it was poured into stirred, cooled aqueous ammonia (300 ml.), then steam-distilled and worked up as above.

(ii) In a second experiment the reaction mixture was poured into ice and hydrochloric acid. The solution was diluted with an equal volume of ethanol and kept in the refrigerator overnight. White crystals were formed, which were filtered off, and the solution was again cooled, etc. Several crops were thus obtained. The m. p. of the crude 2,3,4,6-*tetramethylpyrylium chlorostannate* was 260—265° (decomp.) and by recrystallisation from acetic acid containing hydrogen chloride was raised to 280° (Found: C, 35·6; H, 4·4. $C_{38}H_{26}Cl_6O_2Sn$ requires C, 35·7; H, 4·3%). If the aqueous-ethanolic hydrolysis solution was further diluted with ether, the chlorostannate was more rapidly precipitated (15—60 min.) but it had a lower m. p. (240—250°). The crude chlorostannate afforded on treatment with ammonia a pyridine mixture containing 90% of 2,3,4,6-tetramethylpyridine. The recrystallised chlorostannate yielded pure tetramethylpyridine.

(iii) Water (9 ml., 0·5 mole) was added to stannic chloride (26 g., 0·1 mole), then acetic anhydride (30 g., 0·3 mole) was cautiously introduced. The temperature was kept under 20° by cooling in ice–salt. t-Pentyl chloride (11 g., 0·1 mole) was introduced and the mixture refluxed for 5 hr. with stirring on a water-bath at 70°. No reaction took place, only dimerisation of 2-methylbut-2-ene. With a reaction mixture prepared from stannic chloride, hydrochloric acid, and 2-methylbut-2-ene, immiscible t-pentyl chloride was immediately formed.

(e) *With perchloric acid* (Table 1, No. 18). The reaction was carried out by adding 70% perchloric acid (1 mol.) to a mixture of acetic anhydride (5 mol.) and t-pentyl alcohol (1 mol.), as described for trimethylpyrylium perchlorate. No pyrylium perchlorate crystallised on cooling, but, on addition of water, then ethanol and ether, the homogeneous solution deposited brown crystals (alternatively, the reaction mixture was treated with ether, and the lower, dark, fuming layer was diluted with ethanol, but this procedure is more hazardous [21] and less satisfactory). The product was filtered off and washed with ether, and had m. p. *ca.* 90°. It consisted of a mixture of 2,3,4,6-tetramethyl- with some 4-ethyl-2,6-dimethyl-pyrylium perchlorate and could not be recrystallised from water. The latter salt was obtained pure by repeated recrystallizations from ethanol, because although present in minor amounts in the mixture, it is less soluble. The m. p.s and analyses of the two perchlorates are shown in Table 2.

If the above mixture of perchlorates was converted into chloroferrates, by treatment with ferric chloride in concentrated hydrochloric acid, 2,3,4,6-tetramethylpyrylium chloroferrate was obtained pure after recrystallisation from 30% hydrochloric acid. By dissolving this chloroferrate in warm 70% perchloric acid, cooling, filtering off, washing thoroughly with ether, repeating the procedure once more, and finally recrystallising the product from isopropyl alcohol, pure 2,3,4,6-tetramethylpyrylium perchlorate was obtained. The test for purity of 2,3,4,6-tetramethylpyrylium salts was the gas chromatogram of the respective pyridine rather than the m. p.

(f) *With sulphuric acid* (Table 1, Nos. 10, 19). The procedure of Schneider and Sack [22] was followed.

Attempted Interconversion of the Pyrylium Salts (III) *and* (V).—No change could be detected in the pyridines from 4-ethyl-2,6-dimethyl- or 2,3,4,6-tetramethyl-pyrylium perchlorate that had been treated under a variety of conditions with sulphuric acid or 20% oleum, antimony pentachloride, or aluminium chloride.

Pyridines (IV) *and* (VI).—2,3,4,6-Tetramethylpyridine (VI) was obtained pure (Table 1, Nos. 14, 18, 19) by recrystallisation of the picrate and regeneration of the base with ammonia or alkali. It gave a picrate, m. p. 107° or 123° (from ethanol) (Found: C, 49·8; H, 4·8;

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[21] Kahane, *Compt. rend.*, 1948, **227**, 841.

[22] Schneider and Sack, *Ber.*, **1923**, **56**, 1786.

N, 15·2. Calc. for $C_{15}H_{16}N_4O_7$: C, 49·45; H, 4·4; N, 15·4%). The m. p. of this picrate is variously reported as 107° (ref. 23) or 123° (ref. 24). Initially, we obtained the lower-melting form, but after Professor H. B. Nisbet had kindly supplied us with a sample of the picrate of m. p. 123° we were able to obtain either form, by seeding either the melt on the Kofler hot stage or the saturated alcoholic solution. *X*-Ray diffraction patterns of the two forms of the picrate were photographically registered with a copper anticathode during 15 hr. with 38 kv accelerating voltage and 10 mA current; a 114 mm. diam. chamber and a 12μ nickel filter were used. The most intense group of six lines led in both cases to the same *d*-values: 4·16, 3·91, 3·81, 3·63, 3·44 (most intense), and 3·27 Å. The intensities were however different.

This base gave a methiodide, m. p. and mixed m. p. 188° (from absolute ethanol) (lit.,[24] m. p. 192—193°), picrolonate, m. p. and mixed m. p. 224—225° (from ethanol (lit.,[24] 225·5°), *chloroplatinate*, m. p. 288° (from dilute hydrochloric acid) (Found: C, 31·8; H, 4·45; N, 4·2; Pt, 28·6. $C_{18}H_{28}Cl_6N_2Pt$ requires C, 31·8; H, 4·45; N, 4·1; Pt, 28·7%).

4-Ethyl-2,6-dimethylpyridine (IV), its picrate, m. p. 119—120°, and chloroplatinate, m. p. 213°, have been described.[1] It gives a *picrolonate*, m. p. 215° (from methanol) (Found: N, 17·4. $C_{19}H_{21}N_5O_5$ requires N, 17·5%), and *methiodide*, m. p. 205° (from absolute ethanol) (Found: C, 43·4; H, 6·0; N, 5·0. $C_{10}H_{16}IN$ requires C, 43·4; H, 5·8; N, 5·05%).

Ketones Formed in Acetylation of 2-*Methylbut*-2-*ene*.—The ketone obtained by use of boron trifluoride–ether or perchloric acid boiled at 135—155° (mostly at 148°) and yielded a semicarbazone, m. p. 201° (from 50% ethanol) (Found: C, 57·1; H, 9·0; N, 24·8. Calc. for $C_8H_{15}N_3O$: C, 56·8; H, 8·9; N, 24·8%), and a 2,4-dinitrophenylhydrazone, m. p. 129° (from ethanol) (Found: C, 53·3; H, 5·5; N, 25·1. Calc. for $C_8H_{15}N_3O$: C, 53·4; H, 5·5; N, 24·85%). The m. p. agree with those recorded for 3,4-dimethylpent-3-en-2-one derivatives (semicarbazone, from 176—180° to 199—200°; 2,4-dinitrophenylhydrazone, 127·5° [12] and 132—133 [11]).

The ketone obtained by use of aluminium chloride boiled over a wider range. Fractionation at 40 mm. yielded a forerun, b. p. 30—55°/40 mm. (which gave a semicarbazone, m. p. 190°, and a 2,4-dinitrophenylhydrazone, m. p. 98°; these were not investigated further), and a major faction, b. p. 65—75°/40 mm., that gave a 2,4-*dinitrophenylhydrazone*, m. p. 134° (from ethanol) (Found: C, 47·9; H, 5·5; N, 16·95. $C_{13}H_{17}ClN_4O_4$ requires C, 47·5; H, 5·2; N, 17·0%). In the preparation of the semicarbazone, hydrogen chloride is split off, and a chlorine-free semicarbazone, m. p. 185—190° (m. p. 195° after repeated recrystallizations), was obtained, which gave no depression with the previous semicarbazone, m. p. 201°. When this fraction was refluxed with diethylaniline, it was completely dehydrochlorinated, yielding 3,4-dimethylpent-3-en-2-one, whose semicarbazone, m. p. 199°, and 2,4-dinitrophenylhydrazone, m. p. 126°, gave no depression with the corresponding derivatives prepared from the ketone obtained as above. The formation of 4-methylhex-3-en-2-one mentioned by Kondakov,[10] as formed in the zinc chloride acetylation of 2-methylbut-2-ene, was not observed in reactions with boron trifluoride or aluminium chloride.

Conversion into Phenols.—(a) *Tetramethylpyrylium salts*. The mixture produced from acetic anhydride (100 ml.), t-pentyl alcohol (25 ml.) and 70% perchloric acid (30 ml.) was hydrolysed with water (500 ml.) and then gradually treated, with cooling, with a concentrated solution of sodium hydroxide. At pH ~4 the upper ketonic layer was separated, and the solution was then made strongly alkaline and boiled under reflux for 1 hr. After cooling, non-acid products were removed in ether, and the aqueous solution was acidified with hydrochloric acid. A phenolic mixture separated as a yellow oil, which soon crystallised. It was filtered off and after being washed with ligroin had m. p. 70—80°; after two recrystallisations from 60% methanol, the m. p. was 95° and remained constant on further recrystallisation. This phenol was identified as 2,3,5-trimethylphenol by conversion into a dibromo-derivative, m. p. 150° (from 50% methanol) (Found: C, 36·9; H, 3·6; Br, 54·1. Calc. for $C_9H_{10}Br_2O$: C, 36·8; H, 3·4; Br, 54·4%), and into a phenylurethane, m. p. 178° (from 50% methanol) (Found: N, 5·4. Calc. for $C_{16}H_{17}NO_2$: N, 5·7%). The literature [25] reports the following m. p.s: phenol 93° to 96°, dibromo-derivative 150—151°, and urethane 173—174°. Evaporation of

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[23] Eguchi, *Bull. Chem. Soc. Japan*, 1928, **3**, 227; van Meter, Bailey, Smith, Moore, Allbright, Jacobson, Hylton, and Ball, *Analyt. Chem.*, 1954, **24**, 1758.

[24] Nisbet and Pryde, *J. Inst. Fuel*, 1954, **27**, 58; *Nature*, 1951, **168**, 832; Benzie, Milne, and Nisbet, " Oil Shale and Cannel Coal," Inst. Petroleum, London, 1951, Vol. II, p.784; Tsuda, Ikekawa, Mishima, Iino, and Morishige, *Bull. Chem. Soc. Japan*, 1953, **1**, 122.

[25] Auwers and Saurwein, *Ber.*, 1922, **55**, 2372; Baddeley, *J.*, 1944, 330; Kruber and Schmitt, *Ber.*, 1931, **64**, 2270.

the mother-liquors gave a phenolic mixture, m. p. 65—70° after washing with light petroleum. 3,4,5-Trimethylphenol was obtained by fractional sublimation;[6] the residue after recrystallisation from light petroleum had m. p. 105—106° (lit., m. p. 107°,[25] 109·5° [6,26]).

(b) 2,6-*Diethyl*-3,4-*dimethylpyrylium salts.* The pyrylium perchlorate (7 g.), m. p. 109° (from water or dilute ethanol), obtained by propionylation [1] of 2-methylbut-2-ene, was added gradually to a hot solution of sodium hydroxide (5 g.) in water (30 ml.) and refluxed for 20 min. After dilution with water (20 ml.) and extraction with ether, the aqueous solution was acidified with hydrochloric acid and kept in the refrigerator for 2 days. The product, after recrystallisation from light petroleum, had m. p. 49—50°. This phenol gave a *monobromo-derivative*, m. p. 78° (from 50% ethanol) (Found: C, 54·0; H, 6·3; Br, 32·5. $C_{11}H_{15}BrO$ requires C, 54·3; H, 6·2; Br, 32·9%); therefore the perchlorate was not 2,4,6-triethylpyrylium as initially supposed [1] but 2,6-diethyl-3,4-dimethylpyrylium perchlorate. The phenol formed therefrom was 3-ethyl-2,4,5- or 3-ethyl-2,5,6-trimethylphenol, or a mixture thereof.

Analyses were by Miss Elvira Sliam and Miss Violeta Săndulescu. Infrared absorption spectra were recorded with an automatic UR10 spectrophotometer by Mrs. Colomba Lupu. *X*-Ray powder diffraction patterns were determined by Rodica Gheorghiu, Ludmila Benes, and Dr. Dorel Bally. Gas chromatograms were recorded by Mr. I. Pogany and F. Badea.

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[26] Kruber and Marx, *Ber.*, 1940, **73**, 1175.