700. *Pyrylium Salts and Related Compounds. Part I. The Reaction between Olefins and Acylium Perchlorates.*

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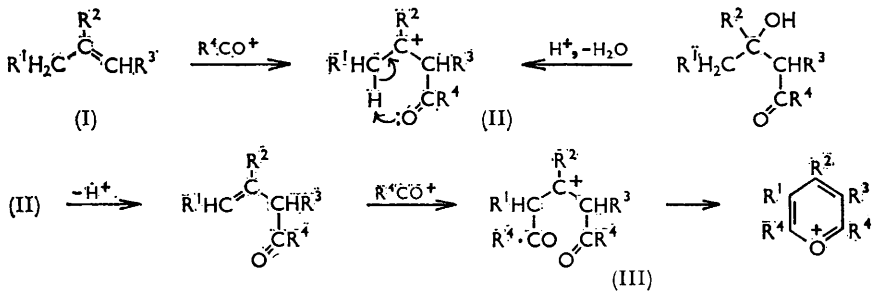
t-Butyl alcohol and t-pentyl alcohol react with acid anhydride–perchloric acid mixtures to give esters, and either olefins or pyrylium perchlorates, depending on the conditions. Evidence is presented that the conversion involves the formation of βγ-unsaturated ketones. The pyrylium salts have been characterised by converting them into the corresponding alkylpyridines.

Some years ago we became interested in reactions between tertiary alcohols and acylium perchlorates,[1] and in the addition of acylium perchlorates to olefins.[2] Recently we published two preliminary notes relating to these reactions.[3,4] Meanwhile, a more detailed investigation of a similar kind has been presented by Balaban and Nenitzescu.[5] A fuller account of our work with the perchlorates is now given.

When perchloric acid is added to an ice-cold mixture of t-butyl alcohol and excess of acetic anhydride, crystals soon separate and the mixture slowly becomes brown. The solid is 2,4,6-trimethylpyrylium perchlorate (75% yield). The salt was previously prepared by Schneider and Sack from the corresponding sulphoacetate,[6] and by Diels and Alder by the action of acetic anhydride and perchloric acid on mesityl oxide.[7] It seemed reasonable to suppose that under our conditions the pyrylium salt arose from mesityl oxide formed *in situ* by the action of acetylium perchlorate on isobutene. Kondakov showed[8] that the acid-catalysed reaction between acetic anhydride and isobutene yields mesityl oxide, and it is known that the reaction of Friedel–Crafts acylating agents with olefins can give unsaturated ketones.[9] Using isobutene in place of t-butyl alcohol we obtained 78% yields of the pyrylium salt. However, under the same conditions, mesityl oxide gave only 46% yields of 2,4,6-trimethylpyrylium perchlorate. Although no other products have been isolated from the last reaction, it is clear from the dark colour of the reaction mixture that the ketone undergoes reactions other than pyrylium salt formation. These results suggest that when t-butyl alcohol is used, a reactive intermediate must be formed that is rapidly converted into the pyrylium salt. Our results can be explained if one supposes the intermediate to be the βγ-unsaturated ketone, and Balaban and Nenitzescu have come to a similar conclusion.[5] High yields (87%) of 2,4,6-trimethylpyrylium



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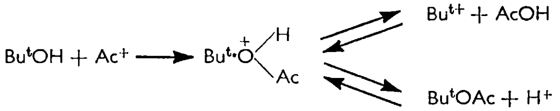
[1] Praill, Ph.D. Thesis, London, 1954.
[2] Burton and Praill, *Chem. and Ind.*, 1954, 75.
[3] Praill, *Chem. and Ind.*, 1959, 1123.
[4] Praill and Whitear, *Proc. Chem. Soc.*, 1959, 312.
[5] Balaban and Nenitzescu, *Annalen*, 1959, **625**, 74.
[6] Schneider and Sack, *Ber.*, 1923, **56**, 1786.
[7] Diels and Alder, *Ber.*, 1927, **60**, 716.
[8] Kondakov, *J. Russ. Phys. Chem. Soc.*, 1894, **26**, 12.
[9] Cf. Baddeley, *Quart. Rev.*, 1954, **8**, 375.

perchlorate were obtained when 4-methylpent-4-en-2-one was used in place of 4-methylpent-3-en-2-one. The tertiary carbonium ion resulting from the attack of acylating agent on the olefin (I), appears to lose a proton preferentially from the terminal position. Loss of a proton from this position might well be assisted by the basic properties of the intramolecular carbonyl-oxygen, as in (II). Supporting evidence for this supposition has been discussed elsewhere.[10]

Normally the βγ-unsaturated ketone would be expected to isomerise to the αβ-compound,[11] but in the presence of excess of acylating agent further reaction could occur to give what is essentially the protonated form (III) of an unsaturated 1,5-diketone. It is well known [12] that under acid conditions such compounds readily lose the elements of water to give pyrylium salts. The formation of a pyrylium salt from mesityl oxide can be interpreted in terms of a relatively slow conversion of the αβ-form into the βγ-form. The experimental conditions allow competing reactions to occur, and a low yield of pyrylium salt results.

It might be expected that dehydration of diacetone alcohol would give rise to the same intermediate carbonium ion (II; $R^1 = R^3 = H$, $R^2 = R^4 = Me$). In conditions similar to those used above, diacetone alcohol gave a 72% yield of 2,4,6-trimethylpyrylium perchlorate.

To gain further information about the initial stages of the reaction we decided to examine how easily olefin could be produced from t-butyl alcohol. Evolution of isobutene from boiling mixtures of the alcohol and acetic anhydride (1 : 1) was slow, although Gutman and Hickinbottom [13] have successfully used acid anhydrides for the dehydration of certain tertiary alcohols. However, when a trace of perchloric acid was added to the cold mixtures, a vigorous reaction occurred after a short induction period. A considerable amount of isobutene was evolved but it was difficult to reproduce the yields. Apart from isobutene, the major products isolated were di-isobutene and t-butyl acetate. By lengthening the reaction time it was found that more di-isobutene was formed at the expense of the t-butyl acetate, but this was a slow reaction. This indicates that under these conditions the esterification is reversible, in agreement with the well-established alkyl-oxygen fission of t-butyl esters [14-16] and their acetolysis.[17] The equilibria established in the reversible addition of carboxylic acids to isobutene have been investigated by Altshul.[18] In our experiments it is clear that equilibrium conditions are not attained owing to the irreversible polymerisation of the olefin. Our results are consistent with the following scheme:



The tertiary carbonium ion may react with acetic acid to give ester,[18-20] or with a molecule of isobutene to give dimeric material. The formation of simple oligomers, rather than high polymers, by the action of acyl perchlorates on isobutene has also been observed by Longworth and Plesch.[21]

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[10] Praill and Saville, *Chem. and Ind.*, 1960, 495.

[11] Stross, Monger, and Finch, *J. Amer. Chem. Soc.*, 1947, **69**, 1627.

[12] Baeyer and Piccard, *Annalen*, 1911, **384**, 208; 1915, **407**, 332; Klages and Trager, *Chem. Ber.*, 1953, **86**, 1327.

[13] Gutman and Hickinbottom, *J.*, 1951, 3344.

[14] Cohen and Schneider, *J. Amer. Chem. Soc.*, 1941, **63**, 3382.

[15] Bunton, Comyns, and Wood, *Research*, 1951, **4**, 383.

[16] Cf. Davies and Kenyon, *Quart. Rev.*, 1955, **9**, 221.

[17] Cohen, *J. Amer. Chem. Soc.*, 1944, **66**, 1395.

[18] Altshul, *J. Amer. Chem. Soc.*, 1946, **68**, 2605.

[19] Knight, Koos, and Swern, *J. Amer. Chem. Soc.*, 1953, **75**, 6212.

[20] Bertram and Walbaum, *J. prakt. Chem.*, 1894, **49**, 1.

[21] Longworth and Plesch, *Proc. Chem. Soc.* ,1958, 117.

Bourne, Stacey, Tatlow, and Worrall [22] have shown that t-butyl trifluoroacetate is readily formed from t-butyl acetate and trifluoroacetic acid, or from the alcohol and acetyl trifluoroacetate. By analogy, we should expect to obtain t-butyl perchlorate, but since perchloric acid is stronger than trifluoroacetic acid, t-butyl perchlorate is less stable than the trifluoroacetate, and only products to be expected from tertiary carbonium ions can be isolated.[23]

The initial, rapid formation of isobutene in our experiments indicates that an alternative path to the olefin might be operating. This could be protonation of the alcohol followed by the loss of water. Ciapetta and Kilpatrick [24] have shown that the equilibrium $Bu^tOH + H^+ \rightleftharpoons Bu^{t+} + H_2O$ lies to the left. Under the conditions we have used, this reaction would be forced to the right, both by loss of isobutene, and by loss of water through the rapid acid-catalysed reaction with acetic anhydride.[25] At present, the information available does not distinguish between the above pathways to the olefin.

When similar reactions were carried out with t-pentyl alcohol the system was complicated by the formation of a mixture of olefins. Here, with equimolecular amounts of acetic anhydride and the alcohol, the amount of monomeric olefin obtained was about 50% of the theoretical. The mixture contained 93—97% of 2-methylbut-2-ene, the remainder being 2-methylbut-1-ene. This result is consistent with the proposals of Ingold, Hughes, *et al.*[26,27] and of Brown and Moritani [28] on eliminations following the Saytzeff rule, and offers further support for carbonium-ion intermediates. Here too, with excess of acetic anhydride, high yields of mixtures of 2,3,4,6-tetramethylpyrylium perchlorate with some 4-ethyl-2,6-dimethylpyrylium perchlorate were obtained. Balaban and Nenitzescu [5] observed that from t-pentyl chloride, acetyl chloride, and aluminium chloride only the 4-ethyl-2,6-dimethyl salt could be isolated. To substantiate these observations we carried out experiments with pure 2-methylbut-1- and -2-ene. The latter with acetic anhydride gave a product that contained 82% of the tetramethylpyrylium perchlorate, but 2-methylbut-1-ene yielded only 67% of this isomer, indicating that some isomerisation of the olefins took place, contrary to observations on acid-catalysed additions in aqueous media.[29] The yields of the various products will depend on the relative rates of isomerisation and acylation of the olefin which we may expect to be markedly affected by the composition of the medium, *e.g.*, the ratio of acid to acid anhydride. We confirm Balaban and Nenitzescu's observation regarding the 4-ethyl-2,6-dimethylpyrylium salt under their conditions, and this also suggests that the extent and direction of the reaction alter with the conditions.

Balaban and Nenitzescu suggested that pyrylium salts are formed when the initial attack of acylium ion on the olefin gives a tertiary carbonium ion. We have shown that the reaction can be extended to cases where tertiary carbonium ions cannot be formed. Pent-1-ene gave small amounts of 3-ethyl-2,6-dimethylpyrylium perchlorate; pent-2-ene gave the 2,3,5,6-tetramethyl compound in 30% yield.

Since many of the pyrylium perchlorates were not easy to crystallise, especially when impure, the compounds were best characterised by conversion into pyridines with aqueous ammonia or with ammonium acetate in acetic acid. The reaction was extended to the preparation of 5,6,7,8-tetrahydro-1,3-dimethylisoquinoline by starting with 1-methylcyclohexene. Nenitzescu and his colleagues have obtained the same compound from the isomeric methylenecyclohexane.[30]

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[22] Bourne, Stacey, Tatlow, and Worrall, *J.*, 1958, 3268.
[23] Burton, Munday, and Praill, *J.*, 1956, 3933.
[24] Ciapetta and Kilpatrick, *J. Amer. Chem. Soc.*, 1948, **70**, 639.
[25] Yvernault, *Compt. rend.*, 1955, **241**, 485.
[26] Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *J.*, 1948, 2093.
[27] Hughes, Ingold, and Shiner, *J.*, 1953, 3837.
[28] Brown and Moritani, *J. Amer. Chem. Soc.*, 1955, **77**, 3607.
[29] Levy, Taft, and Hammett, *J. Amer. Chem. Soc.*, 1953, **75**, 1253.
[30] Personal communication, cf. also, *Tetrahedron Letters*, 1960, No. 2, 7.

EXPERIMENTAL

Materials.—Wherever possible "AnalaR" materials were used; other reagents were redistilled before use. The olefins were examined for purity by vapour-phase chromatography through a column of Celite 545 (60—80 mesh) containing 30% of Silicone E/301.

Reactions with t-Butyl Alcohol and Acetic Anhydride.—(i) A mixture of t-butyl alcohol (0·3 mole) and acetic anhydride (0·3 mole) was cooled in ice-salt, and 70% perchloric acid (0·2 ml., 0·003 mole) was added. A vigorous reaction occurred after a few minutes with the evolution of isobutene (3·9 g.) which was collected in a trap cooled by carbon dioxide. After 2 hr. the mixture was poured into water and extracted thrice with ether. The ethereal solution was washed with sodium carbonate solution, dried (Na_2SO_4), and evaporated. Distillation of the residue gave material boiling mainly at 94—98° (19·5 g.). The ester content (90·3%) was determined by saponification; unsaturated material (5·1% as di-isobutene) was determined iodometrically. There was a higher-boiling residue (3·3 g.).

A similar mixture that had been left for 3 days gave material, b. p. 95—100° (13·4 g.), that contained 82·8% of t-butyl acetate and 10% of di-isobutene.

(ii) t-Butyl acetate, b. p. 97·5—98·5° (30 g.), was dissolved in 0·2N-perchloric acid in glacial acetic acid (20 ml.) and left at room temperature for 5 days. Vapour-phase chromatography of the recovered material showed that it contained traces of isobutene, more di-isobutene, and unchanged ester.

(iii) When experiment (i) was repeated with acetic anhydride (0·91 mole) a few crystals of 2,4,6-trimethylpyrylium perchlorate separated. The following fractions were obtained: b. p. 80—100° (4·5 g.), mainly t-butyl acetate; b. p. 100—104° (7·9 g.), mainly di-isobutene; b. p. 104—106° (2·8 g.); b. p. 172—176° (1·1 g.), tri-isobutene; residue (1·7 g.).

(iv) t-Butyl alcohol (0·5 mole) and acetic anhydride (0·5 mole) were refluxed together for 5½ hr. There was a slow evolution of isobutene and, when the mixture was worked up, t-butyl acetate (22·2 g.) containing a little unchanged alcohol was obtained.

(v) 72% Perchloric acid (0·12 mole) was slowly added, with stirring, to an ice-cooled mixture of t-butyl alcohol (0·6 mole) and acetic anhydride (3·0 moles). Solid soon began to be formed, but to ensure complete separation the mixture was left overnight. The pyrylium salt (0·09 mole), when recrystallised from acetic acid, gave colourless needles, m. p. 250° (decomp.) (Balaban and Nenitzescu [5] give m. p. 245—246°), $\lambda_{max.}$ 234 (ε 5340), 284 (ε 9020 in H_2O) [Balaban, Sahina, and Keplinger [31] give $\lambda_{max.}$ 233 (ε 5450), 284 mμ (ε 7900 in H_2O), and noted a reduction of intensity on irradiation]. When an equivalent amount of sodium hydroxide was added to the aqueous solution a new peak appeared, with $\lambda_{max.}$ 242 mμ (ε 9600). Woodward [32] has shown that disubstituted $\alpha\beta$-unsaturated ketones have similar absorption characteristics.

In order to capture some of the $\beta\gamma$-unsaturated ketone, mixtures similar to the above were rapidly quenched with an excess of 2,4-dinitrophenylhydrazine in acetic acid. A little mesityl oxide 2,4-dinitrophenylhydrazone was obtained (m. p. and mixed m. p.) but even after ½—1 min. an 11% yield of 2,4,6-trimethylpyrylium perchlorate was isolated.

The pyrylium salt with *p*-toluidine in ethanol gave 2,4,6-*trimethyl*-p-*tolylpyridinium perchlorate*, pale yellow plates (from ethanol), m. p. 145—146° (Found: C, 58·1; H, 6·2; N, 4·4; Cl, 11·2. $C_{15}H_{18}ClNO_4$ requires C, 57·8; H, 5·8; N, 4·5; Cl, 11·4%) (Baeyer and Piccard [33] give m. p. 141—142°).

Treating the pyrylium salt with ammonia (*d* 0·880) gave 2,4,6-trimethylpyridine (57%). This and its picrate, m. p. 157° (Found: N, 15·9. Calc. for $C_{14}H_{14}O_7N_4$: N, 16·0%), had properties identical with those of commercial 2,4,6-trimethylpyridine and its picrate.

A cleaner product was obtained, in 76% yield, if the conversion was brought about by dissolving the salt in 10% acetic acid (8 vols.), adding ammonia (*d* 0·88; 14 vols.), and refluxing the whole for 90 min.[34] All other pyridines were prepared by this method.

Reactions with t-Pentyl Alcohol and Acetic Anhydride.—(i) 72% Perchloric acid (0·005 mole) was added to a mixture of t-pentyl alcohol (0·51 mole) and acetic anhydride (0·51 mole). After 20 hr. the mixture was worked up as above, but without the ether-extraction; distillation gave fractions: b. p. 38·5—39·5° (18·2 g.); b. p. 39—110° (1·7 g.); b. p. 116—124° (9 g.); residue (5·2 g.). Vapour-phase chromatography of samples taken from similar mixtures at intervals

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[31] Personal communication.

[32] Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 76.

[33] Baeyer and Piccard, *Annalen*, 1911, **384**, 219.

[34] Cf. Frank and Meikle, *J. Amer. Chem. Soc.*, 1950, **72**, 4184.

showed that the olefin contained 93—97% of 2-methylbut-2-ene and 3—7% of 2-methylbut-1-ene, by comparison with known mixtures. Analysis of the olefin mixtures by means of their refractive indices tended to indicate too high a proportion of 2-methylbut-2-ene. Gas chromatography gave good agreement with mixtures of known composition.

(ii) When a mixture of t-pentyl alcohol (0·11 mole) and acetic anhydride (1·5 mole) was treated with perchloric acid (0·06 mole) no solid separated. The mixture was poured into ether (300 ml.), and the precipitated pyrylium salt (0·04 mole) was collected. Quantitative separation of the mixed pyrylium perchlorates was unsuccessful.

Acylation of Olefins.—General procedure. The olefin (0·06 mole) in the acid anhydride (20 ml.) was slowly added during about 15 min. to an ice-cold solution of perchloric acid (0·05 mole) in the acid anhydride (50 ml.). After ½ hr. (or several hours in the case of less reactive olefins), the mixture was poured into ether (300 ml.) and left at 0° overnight. Next day the ethereal solution was decanted from the precipitate which was often dark and gummy. On treatment with a little fresh ether the residue usually solidified. The perchlorate could then be recrystallised from a suitable solvent or converted into the pyridine.

Isobutene. This was freshly prepared from t-butyl alcohol and 50% sulphuric acid. Reaction with acetic anhydride gave 2,4,6-trimethylpyrylium perchlorate in 78% yield.

Propionic anhydride in place of acetic anhydride gave a 55% yield of 2,6-diethyl-4-methylpyrylium perchlorate, plates (from acetic acid), m. p. 192° (Found: C, 47·6; H, 5·9; Cl, 14·9. Calc. for $C_{10}H_{15}O,ClO_4$: C, 47·9; H, 6·0; Cl, 14·2%) (Balaban and Nenitzescu [5] give m. p. 189°). The salt was converted into 2,6-diethyl-4-methylpyridine, b. p. 180—182°/765 mm., $n_D^{20\cdot5}$ 1·4922 [picrate, needles (from water), m. p. 140° (Found: C, 51·1; H, 4·9; N, 14·6. Calc. for $C_{16}H_{18}N_4O_7$: C, 50·9; H, 4·8; N, 14·8%) (Balaban and Nenitzescu [5] give b. p. 195° and m. p. 139°)]. 1-p-*Tolylpyridinium perchlorate* crystallised in plates (from water), m. p. 144° (Found: C, 60·5; H, 6·9; N, 4·1. $C_{17}H_{22}N,ClO_4$ requires C, 60·1; H, 6·5; N, 4·1%).

2-*Methylbut*-1-*ene.* A redistilled commercial sample, b. p. 31—32°, n_D^{20} 1·3887, on reaction with acetic anhydride gave a 70% yield of the mixed 2,3,4,6-tetramethyl- and 4-ethyl-2,6-dimethyl-pyrylium salts. Attempts to separate the salts were not successful; only small amounts of the less soluble 4-ethyl-2,6-dimethyl compound were obtained by recrystallisation from water. The aqueous solutions were thermochromic, being blue when hot and pink when cold. The pyridines obtained from them had a boiling range of 192—199°. Vapour-phase chromatography showed the composition to be 4-ethyl-2,6-dimethylpyridine 33% and 2,3,4,6-tetramethylpyridine 67%.

2-*Methylbut*-2-*ene.* A redistilled commercial sample, b. p. 38·4—38·7°, n_D^{20} 1·3874, with acetic anhydride gave a mixture of pyrylium salts; repeated crystallisation from ethyl acetate–acetic acid (4 : 1) gave needles, m. p. 189° (Found: C, 45·6; H, 5·5. Calc. for $C_9H_{13}ClO_5$: C, 45·7; H, 5·5%) (Balaban and Nenitzescu [5] give m. p. 189—190° for the 4-ethyl-2,6-dimethylpyrylium perchlorate). A mixed m. p. with material obtained by the method of Balaban and Nenitzescu gave no depression; the composition of this compound has been established by these workers (personal communication).

The mixture of pyrylium salts was converted into the pyridines (61·4% yield), b. p. 199—201°, n_D^{25} 1·5068 (Tsuda *et al.*[35] give b. p. 203—204° for 2,3,4,6-tetramethylpyridine). Vapour-phase chromatography showed our material to contain 2,3,4,6-tetramethyl- (retention time 7·6 min.) 85% and 4-ethyl-2,6-dimethyl-pyridine (retention time 5·8 min.) 15%. The derived picrates, on crystallisation from ethanol, gave needles, m. p. 107° (Found: C, 49·7; H, 4·6; N, 15·2. Calc. for $C_{15}H_{16}N_4O_7$: C, 49·5; H, 4·4; N, 15·4%) (lit., 2,3,4,6-tetramethylpyridine picrate 107°,[36,37] 123° [35,38]; Balaban and Nenitzescu [30] have established this as a case of dimorphism). The pyridine liberated from this picrate showed, on vapour-phase chromatography, a single peak with a retention time of 7·6 min.

The 4-ethyl-2,6-dimethylpyrylium perchlorate isolated as above was converted into the pyridine (vapour-phase chromatography gave a single peak with retention time of 5·8 min.), and its picrate, needles (from ethanol), m. p. 121—122° (Found: N, 15·2. Calc. for $C_{15}H_{16}N_4O_7$: N, 15·4%) (Balaban and Nenitzescu [5] give m. p. 119—120°).

[35] Tsuda, Ikekawa, Mishima, Iino, and Morishige, *Pharm. Bull.* (*Japan*), 1953, **1**, 122.

[36] Eguchi, *Bull. Chem. Soc., Japan*, 1928, **3**, 237.

[37] Van Meter, Bailey, Smith, Moore, Allbright, Jacobson, Hylton, and Ball, *Analyt. Chem.*, 1952, **24**, 1758.

[38] Nisbet and Pryde, *Nature* ,1951, **168**, 832.

With propionic anhydride in place of acetic anhydride a mixture of 2,4,6-triethyl- and 2,6-diethyl-3,4-dimethyl-pyrylium perchlorate (74% yield) was obtained. Little success was had in the separation of these or the corresponding pyridines. Vapour-phase chromatography indicated that approximately equal amounts of each isomer were present.

Pent-1-*ene*. We were unable to isolate a pure specimen of a pyrylium salt from this olefin. The pyridine was obtained in 14% yield, based on olefin, as a slightly yellow liquid, b. p. 91—93°/17 mm., 188°/763 mm., n_D^{25} 1·5002, and gave a picrate, needles (from ethanol), m. p. 122° (Found: C, 49·6; H, 4·6; N, 15·1. Calc. for $C_{15}H_{16}N_4O_7$: C, 49·5; H, 4·4; N, 15·3%) (Dornow and Machens [39] give b. p. 75°/13 mm.; picrate, m. p. 122°, for 3-ethyl-2,6-dimethylpyridine).

Pent-2-*ene*. The dark product obtained on reaction with acetic anhydride was recrystallised several times from butan-1-ol, to give pink needles, m. p. 82·5—83·5°. The crude pyrylium salt could be converted into the pyridine (21% yield based on olefin), b. p. 94—96°/17 mm., flakes (from ether), m. p. 76—77° (Found: C, 79·6; H, 9·9; N, 10·3. Calc. for $C_9H_{13}N$: C, 80·0; H, 9·6; N, 10·4%) [picrate, rhombohedra (from ethanol), m. p. 177·5° (Found: C, 50·1; H, 4·7; N, 15·2. Calc. for $C_{15}H_{16}N_4O_7$: C, 49·5; H, 4·4; N, 15·4%) (Tsuda *et al.*[35] give b. p. 198° and m. p. 76° for 2,3,5,6-tetramethylpyridine, and m. p. 173·5° for its picrate)].

4-*Methylpent*-1-*ene*. No crystalline pyrylium salt was isolated on reaction of this olefin with acetic anhydride. However, a 17% yield of the 3-isopropyl-2,6-dimethylpyridine was obtained as a colourless liquid, b. p. 90—93°/13 mm., 196°/751 mm., n_D^{25} 1·4975. The *picrate* crystallised as amber-coloured plates, m. p. 168°, from ethanol–water (1 : 10) (Found: C, 50·6; H, 4·8; N, 14·8. $C_{16}H_{18}N_4O_7$ requires C, 50·8; H, 4·8; N, 14·8%).

3-*Ethylpent*-2-*ene*. This material, made by the dehydration of 3-ethylpentan-3-ol, had b. p. 95·2—96·2°/759 mm. Reaction with acetic anhydride gave the pyrylium salt (69%), which on recrystallisation from ethyl acetate–acetic acid (4 : 1) gave needles, m. p. 108° (Found: C, 49·6; H, 6·6. $C_{11}H_{17}O,ClO_4$ requires C, 49·9; H, 6·4%).

The pyrylium salt gave a 75% yield of 4-*ethyl*-2,3,5,6-*tetramethylpyridine*, b. p. 130·5—131°/17 mm., n_D^{25} 1·5167, m. p. 20—21° [*picrate*, needles (from ethanol), m. p. 168° (Found: C, 52·4; H, 5·3; N, 14·4. $C_{17}H_{20}N_4O_7$ requires C, 52·0; H, 5·1; N, 14·3%)].

α-*Methylstyrene*. When this material reacted with acetic anhydride, the pyrylium salt separated from the reaction mixture. The bright red solid was filtered off and washed with benzene to remove any polymeric material, and then recrystallised from water as pale orange laths (28%), m. p. 220° (decomp.). The corresponding picrate crystallised from water as needles, m. p. 190° (decomp.). (Baeyer and Piccard [33] give m. p. 210—212° (decomp.) for the perchlorate and 193° for the picrate of 2,6-dimethyl-4-phenylpyran-2-ol.)

The perchlorate was converted into 2,6-dimethyl-4-phenylpyridine, prisms (from ether), m. p. 58·5—59·5°. The picrate crystallised as needles (from ethanol), m. p. 234° (decomp.). Baeyer and Piccard [33] give m. p. 58—59° and *ca.* 230° respectively.

1-*Methylcyclohexene*. This material [40] with acetic anhydride gave a 30% yield of 5,6,7,8-*tetrahydro*-1,3-*dimethyl*-2-*benzopyrylium perchlorate*, prisms (from butan-1-ol), m. p. 81° (Found: C, 50·5; H, 5·9. $C_{11}H_{15}O,ClO_4$ requires C, 50·3; H, 5·7%).

5,6,7,8-Tetrahydro-1,3-dimethylisoquinoline (84% yield) had b. p. 129°/12 mm., n_D^{25} 1·5350. It gave a picrate, needles (from ethanol), m. p. 124—125° alone or mixed with a specimen obtained from Professor Nenitzescu (Found: C, 52·5; H, 4·5; N, 14·4. Calc. for $C_{17}H_{18}N_4O_7$: C, 52·3; H, 4·6; N, 14·4%).

Acylation of 4-*Methylpent*-4-*en*-2-*one*.—This ketone had b. p. 120·4°, $\lambda_{max.}$ 290 mμ (ε 79·0 in cyclohexane) with negligible absorption at 329 mμ [Gray, Rassmussen, and Tunnicliff [41] give $\lambda_{max.}$ 290 mμ (ε *ca.* 77 in "iso-octane")]; it contained approximately 1% of 4-methylpent-3-en-2-one.

The ketone (0·05 mole) in acetic anhydride (50 ml.) was added to an ice-cold solution of perchloric acid (0·05 mole) in acetic anhydride (50 ml.). 2,4,6-Trimethylpyrylium perchlorate (0·043 mole) was filtered off after 1½ hr.

Use of propionic anhydride led to 6-*ethyl*-2,4-*dimethylpyrylium perchlorate* (0·037 mole), m. p. 201—202° (Found: C, 45·8; H, 5·6. $C_9H_{13}O,ClO_4$ requires C, 45·6; H, 5·5%), and thence 6-*ethyl*-2,4-*dimethylpyridine* b. p. 181·5—182°/744 mm., n_D^{25} 1·4944 [picrate, needles (from

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[39] Dornow and Machens, *Ber.*, 1940, **73**, 357.
[40] Signaigo and Cramer, *J. Amer. Chem. Soc.*, 1933, **55**, 3326.
[41] Gray, Rasmussen, and Tunnicliff, *J. Amer. Chem. Soc.*, 1947, **69**, 1630.

ethanol), m. p. 114° (Found: C, 49·9; H, 4·4; N, 15·4. Calc. for $C_{15}H_{16}N_4O_7$: C, 49·5; H, 4·4; N, 15·3%)]. Balaban and Nenitzescu[5] give b. p. 181° and m. p. 112—113°, respectively.

Under the same experimental conditions mesityl oxide [b. p. 130°; $\lambda_{max.}$ 329 mμ (ε 40·6 in cyclohexane)] [Gray *et al.*[41] give $\lambda_{max.}$ 329 mμ (ε 40·5 in " iso-octane ")] gave 2,4,6-trimethylpyrylium perchlorate (0·022 mole). An additional 0·001 mole was obtained after 3 days.

Similarly, propionic anhydride gave 6-ethyl-2,4-dimethylpyrylium perchlorate (0·015 mole).

2,4,6-Trimethylpyrylium perchlorate (0·036 mole) was also obtained by using diacetone alcohol instead of isomesityl oxide.

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