766. *Pyrylium Salts Obtained by Diacylation of Olefins. Part IX.*[1] *Formation of Vinylogous Pyrones by Triacylation of Isobutene.*

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Branched olefins, such as isobutene and 2-methylbutene, with an excess of acyl halide and aluminium chloride yield (besides pyrylium salts), triacylation products which are pyrone vinylogues, *e.g.*, 4-acetonylidene-2,6-dimethylpyran (II), and behave like pyrones. The structure of compound (II) is proved by its reactions and spectra. Its formation involves acetylation at each of the carbon atoms bound to the tertiary carbon in the initial olefin.

INVESTIGATION of the pyrylium salts (see refs. 2—4) formed on diacetylation of di-isobutene showed that a 2,4,6-trimethyl-3-t-butylpyrylium salt is the sole product with zinc chloride as catalyst,[5] but that with aluminium chloride di-isobutene is partly depolymerized and then yields also two further products derived from monomeric isobutene, namely, a 2,4,6-trimethylpyrylium salt (I) formed by diacetylation of isobutene[3] and a compound $C_{10}H_{12}O_2$ (II), m. p. 92°, formed by a reaction $Me_2C{:}CH_2 + 3AcX \longrightarrow C_{10}H_{12}O_2 + 3HX + H_2O$. Therefore, triacetylation of isobutene was attempted.

When t-butyl chloride was refluxed with an excess of acetyl chloride and aluminium chloride (conditions more drastic than those required for diacetylation, which proceeds at 20°) all the isobutene was di- or tri-acetylated. The diacetylation product (I) was precipitated by addition of perchloric acid as 2,4,6-trimethylpyrylium perchlorate. The

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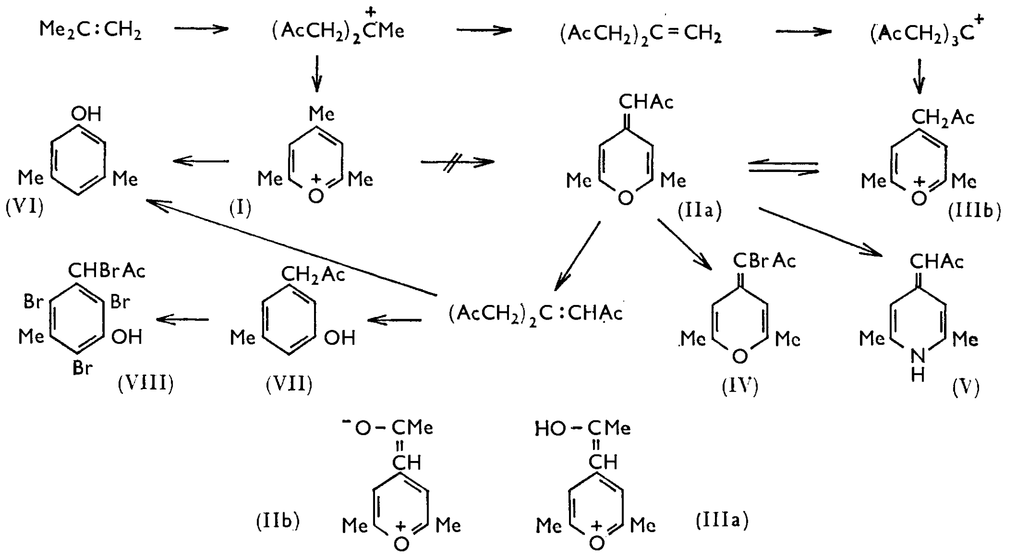
[1] Part VIII, Balaban, Gavat, and Nenitzescu, *Tetrahedron*, in the press.
[2] Katritzky and Lagowski, " Heterocyclic Chemistry," Methuen and Co., Ltd., London, 1960.
[3] Balaban and Nenitzescu, *Studii şi Cercetări Chim.* (*Acad. R.P.R.*), 1961, **9**, 251; *Rev. Chim.* (*Acad. R.P.R.*), 1961, **6**, 269.
[4] Dimroth, *Angew. Chem.*, 1960, **72**, 331.
[5] Balaban, Ghenea, and Nenitzescu, *Izvestia Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 1102.

triacetylation product (II) was obtained on addition of more perchloric acid, as the crystalline perchlorate (III) (32%). Similarly, triacetylation of 2-methylbut-1-ene gave a homologous compound $C_{11}H_{14}O_2$, with similar chemical properties. This confirmed the ability of branched olefins to undergo triacylation.

The reactions, spectra, and mechanism of formation of compound (II) may be explained by the vinylogous pyrone structure IIa—b.



Compound (II) is readily soluble in sulphuric or hydrochloric acid and is reprecipitated unchanged by base. Crystalline salts (hydrobromide, perchlorate, picrate, picrolonate, hexachloroplatinate, tetrachloroferrate) $C_{10}H_{13}O_2^+X^-$ were obtained, but some of them are hydrolysed in water. Compound (II) does not yield a normal dinitrophenylhydrazone; with alcoholic 2,4-dinitrophenylhydrazine and perchloric acid it gives a yellow 2,4-dinitrophenylhydrazone perchlorate which is evidence of the presence of a carbonyl group in the salts (III). Alkaline hypobromite yields a substitution product $C_{10}H_{11}BrO_2$ (IV), which gives crystalline salts with acids. Heating compound (II) with ammonia affords a liquid water-soluble pyridone (V). Refluxing aqueous alkali hydroxide gradually dissolves compound (II); acidification then yields two phenols, 3,5-xylenol (VI) and a higher-boiling liquid, isomeric with (II), which is believed to be 3-hydroxy-5-methylphenylacetone (VII) since it gives a phenylcarbamate and a 2,4-dinitrophenylhydrazone and is not identical with 2- or 4-acetyl-3,5-xylenol. This structure is supported by the nuclear magnetic resonance spectrum. The phenol (VII) yields a tetrabromo-derivative, probably (VIII).

The infrared spectrum of compound (II) in carbon disulphide or carbon tetrachloride solution contains several bands in the 1500—1700 cm.$^{-1}$ region. To locate the carbonyl stretching band, the frequencies of these bands for solutions in various solvents (see Table)

Infrared absorption bands of compound (II) in the carbonyl stretching-frequency range (cm.$^{-1}$; ε in parentheses).

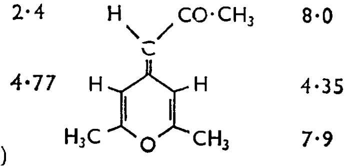
Band	In CCl_4	In MeCN	In $CHCl_3$	In $(CHBr_2)_2$	Slope
1	1687 (410)	1682 (420)	1683 (370)	1682 (550)	+0·41
2	1642 (370)	1630 (370)	1625 (190)	1623 (240)	+1·70
3	1613 (110)	1607 (210)	1616 (140) *	1607 (160) *	
4	1553 (700)	1548 (700)	1551 (500)	—	
5	—	1538 (700)	1538 (500)	1535 (700)	

* Shoulders at 1668 (ε 150) and 1567 cm.$^{-1}$ (ε 360).

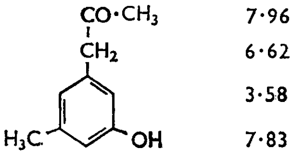
were plotted against the C=O stretching frequencies of acetone (1722, 1716, 1713, and 1709 cm.$^{-1}$, respectively) in the same solvents, and the slopes were found by the method of least squares.[6,7] The highest-frequency band (1682—1687 cm.$^{-1}$) must be due to a C=C vibration mode, and the 1623—1642 cm.$^{-1}$ band with the larger slope (1·7) is the C=O stretching band. This surpassing of a polarized C=O band by a C=C vibration mode was previously encountered for 2,6-dimethyl-4-pyrone[6] (C=O slope +1·94) and tropone[7] (C=O slope +1·66).

Other bands in the spectrum of compound (II) which may be tentatively assigned[8] are: 1680, 1612, 1430, 1420, 1301, 941 (ring vibrations[6]); 1445 and 1381 (asymmetrical and symmetrical methyl CH bending vibrations); 1185, 1167, 1039, and 860 (2,6-dimethyl groups in pyrones); 1556 (band due to the olefinic C=CHAc bond); and the CH stretching modes in the 3000 cm.$^{-1}$ region.

The nuclear magnetic resonance spectrum of compound (II) shows three sharp bands, each corresponding to one proton, at +2·40, +4·35, and +4·77 p.p.m. (tetramethylsilane as internal standard, = 10 p.p.m.). In the methyl region there are two sharp peaks at +7·90 (two methyl groups) and +8·00 (one methyl). These values can be accommodated to formula (II) in the light of similar studies[9] of 2,6-dimethyl-4-pyrone and its derivatives.



(II)



(VII)

The ultraviolet spectrum of compound (II) shows a marked bathochromic shift from cyclohexane to ethanol. This indicates a polar structure, with a large contribution from (IIb). A further shift towards longer wavelengths in ethanol containing perchloric acid indicates a preference for tautomeric form (IIIa) over (IIIb) in the salts; in (IIIb) the CH$_2$ protons are very acidic owing to the combined effects of the acetyl and the pyrylium group. The infrared spectrum of the perchlorate (III) shows no carbonyl band near 1700 cm.$^{-1}$, supporting its formulation as (IIIa).

The structure of the phenol (VII) follows unambiguously from the infrared and nuclear magnetic resonance evidence. The infrared spectrum of compound (VII) shows the presence of phenolic and methyl groups, and includes a carbonyl band at 1710 cm.$^{-1}$. The formation of this phenol and of 3,5-xylenol (VI) from compound (II) is attributed to acid-fission of a common β-diketonic intermediate. There are only three possibilities for a *C*-acetyl homologue of (VI), namely (VII), (IX), and (X). The last two were synthesized for comparison and proved to be different from our phenol. Their carbonyl bands lie at 1635 (IX; hydrogen-bonded) and 1650 cm.$^{-1}$ (X). Therefore, in phenol (VII), the carbonyl group is not directly attached to the phenolic nucleus.

Mode of Formation.—For the structure of a pyrone or vinylogue $C_{10}H_{12}O_2$ formed by triacetylation of isobutene, four possibilities exist: (II), (XI), (XII), and (XIII). Unstable methylenepyran structures are not considered. Of these, compound (XIII) would not lead to phenol (VII). Structures (XI) and (XII), which might also be reconciled with the chemical and spectral data, are considered less likely than (II) because, in addition to phenol (VII), they could yield other phenols which are not found, and their formation would involve the linking of several acetyl groups head-to-tail. Structure (II), the most symmetrical of all, is the only one that is able to yield only one phenol, and its formation involves the linking of three acetyl groups to each of the primary carbon atoms in isobutene.

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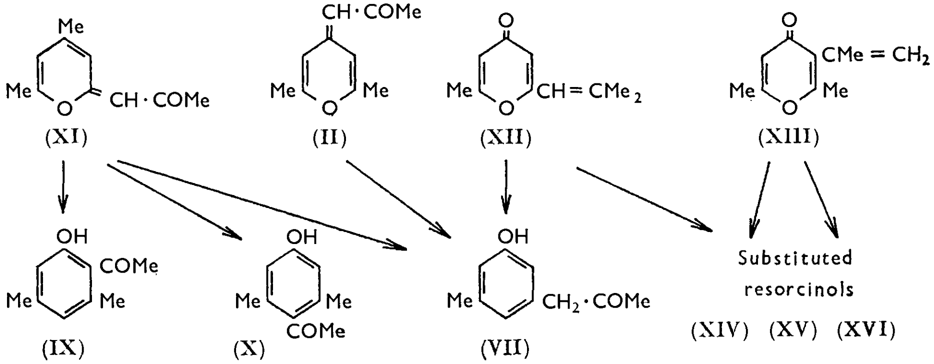
[6] Katritzky and Jones, *Spectrochim. Acta*, 1961, **17**, 64.

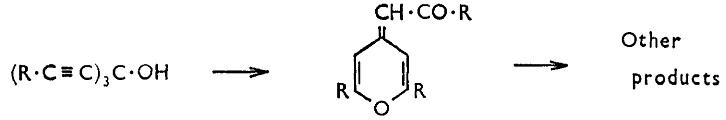
[7] Götz, Heilbronner, Katritzky, and Jones, *Helv. Chim. Acta*, 1961, **34**, 387.

[8] Katritzky, *Quart. Rev.*, 1959, **13**, 353.

[9] Terehara, Obashi, Nakaniski, Yamaguchi, and Hayakawa, *Bull. Chem. Soc. Japan*, 1960, **33**, 1310.

Thus monoacylation of olefins to give unsaturated ketones (the Kondakov reaction [10]) involves electrophilic attack on one carbon atom in ethylene derivatives; formation of a pyrylium salt by diacylation [3] involves the two terminal carbon atoms in propene derivatives; and the reaction here described, formation of pyrone vinylogues, involves the three terminal carbon atoms in isobutene derivatives. As shown in the formulæ, pyrylium salts are not intermediates in the triacylation, since 2,4,6-trimethylpyrylium perchlorate and tetrachloroferrate were not converted into compound (II) by refluxing acetyl chloride–aluminium chloride (a substantial amount of the iron complex of acetylacetone was isolated in the reaction with the tetrachloroferrate). Such triacylations have not previously been reported (allylbenzene may be triacetylated to a 3-*p*-acetylphenyl-2,6-dimethylpyrylium salt,[11] but here one of three acetylations involves an aromatic ring). However, compounds similar to (II) are thought to arise in the acid-catalysed hydration of triethynylcarbinols.[12]





Other, more complex, vinylogous pyrones have been prepared [13] by condensation of dimethyl-4-pyrones with compounds containing active methylene groups.

EXPERIMENTAL

Preparation of Compound (II) *by Triacetylation of Isobutene.*—(*a*) *From di-isobutene or tri-isobutene.*[5] To acetyl chloride (55 c.c.), aluminium chloride (40 g.) was added at 0—5°, followed by di-isobutene (32 c.c.) during 1 hr. with cooling and stirring. Hydrogen chloride was evolved. After 12 hr., the mixture was hydrolysed with ice (200 g.) and concentrated hydrochloric acid (20 c.c.). Water-insoluble products were removed in ether, and the aqueous solution treated with 60% perchloric acid (50 c.c.). After 2 hours' cooling, 2,4,6-trimethylpyrylium perchlorate (7·5 g.) was collected. The filtrate was shaken with a little ether to help separation of the oily perchlorate, which was then treated in the cold with aqueous ammonia. The basic product was extracted in ether and the extracts were fractionated, yielding 2,4,6-trimethyl-3-t-butylpyridine (6 g.), b. p. 135—150°/60 mm. From the crystalline residue the vinylogous pyrone (II) (3·5 g.) was obtained by pressing on porous plate, followed by recrystallization from aqueous ethanol or light petroleum, or by steam-distillation.

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[10] Gowan and Wheeler, "Name Index of Organic Reactions," Longmans, London, 1960, p. 138.

[11] Balaban, Gavăt, Mateescu, and Nenitzescu, *J.*, 1961, 3564.

[12] Siemiatycki, *Ann. Chim.* (*France*), 1957, **13**, 189, and references therein.

[13] Kato, Ogawa, and Ohta, *Bull. Chem. Soc. Japan*, 1960, **33**, 1468; Dimroth and Wolf, *Angew. Chem.*, 1960, **72**, 777.

(*b*) *From t-butyl chloride.* To acetyl chloride (450 ml.), aluminium chloride (280 g.) was gradually added, followed by t-butyl chloride (110 c.c.), all at 0—10°. The mixture was stirred without cooling for 2 hr., then refluxed until no more hydrogen chloride was evolved (2 hr.). The syrupy mixture was poured on ice (1 kg.) and hydrochloric acid (70 c.c.). The clear solution was treated with 65% perchloric acid (200 c.c.). 2,4,6-Trimethylpyrylium perchlorate separated. It was filtered off after ¼ hr. (88 g., 40%). In the filtrate needles of the *perchlorate* of compound (II) appeared gradually and were filtered off next day (88 g., 32%). This compound, crystallized from acetic acid–ether, had m. p. 85° (Found: C, 45·0; H, 5·3. $C_{10}H_{13}ClO_6$ requires C, 45·4; H, 4·95%).

The perchlorate is hydrolysed by water, becoming green. For conversion into compound (II) it was dissolved in 5% warm hydrochloric acid and poured into aqueous ammonia and ice. If this perchlorate did not crystallize (the perchloric acid concentration is critical) more perchloric acid (200 c.c. of 60%) and ether (*ca.* 1 l.) were added. The ether dissolved appreciably in the acid solution, and an upper layer was formed containing ether, water, and the perchlorate. This layer was diluted with water (freely miscible) and made alkaline in the cold with ammonia. Compound (II) crystallized.

After filtration and washing with cold water, the *compound* (II) was freed from aluminium hydroxide by recrystallization from dilute ethanol; it forms white (by steam-distillation) or pale yellow needles (by recrystallization), m. p. 92—93° [Found: C, 73·2; H, 7·4%; *M* (Rast), 183. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%; *M*, 164]. It is soluble in ethanol, acetone, chloroform, or benzene, moderately soluble in ether, and can be recrystallized from light petroleum, water, or 50% ethanol. It has $\lambda_{\text{max.}}$ (log ε in parentheses) in cyclohexane 335 (4·40), 234 (3·81), in EtOH 358 (4·42), 243 (3·86), and in $HClO_4$–EtOH 371 (4·60), 287 mμ (3·97); it had $\nu_{\text{max.}}$ [in CS_2 (670—1300 cm.$^{-1}$) and CCl_4 (1330—3800 cm.$^{-1}$); UR10 Jena spectrometer] 691w, 790w, 860m, 880w, 906m, 941s, 960w, 985w, 1016w, 1039m, 1065w, 1167s, 1187vs, 1258s, 1301m, 1348s, 1358vs, 1381w, 1420m, 1430vw, 1445w, 1556vs, 1612m, 1643vs, 1690vs, 2848w, 2875m, 2925s, 2960s, 3002m, 3025m, 3060w, 3098m.

The nuclear magnetic resonance spectrum was run on a Varian apparatus with an internal standard ($SiMe_4 = 10$).

The infrared spectrum of the perchlorate (III) was run on a Perkin–Elmer model 21 apparatus: 3140w, 3090vw, 1666mw, 1648w, 1604vs, 1580s, 1540s, 1480m, 1436m, 1386m, 1324s, 1262mw, 1201mw, 1162m, 1123vs, 1056vs, 965m, 929m, 921m, 886s, 812mw.

The *picrate* had m. p. 134° (from aqueous ethanol) (Found: C, 49·1; H, 3·9; N, 10·9. $C_{16}H_{15}N_3O_9$ requires C, 48·9; H, 3·8; N, 10·7%). An alternative method of separation of the pyrone (II) consists in the addition of concentrated aqueous picric acid at 70° to the aqueous solution resulting after hydrolysis of the original reaction mixture. The greenish-brown picrate crystallized on cooling and scratching and was filtered off and washed with warm water; the compound (II) was set free by basification. The much more soluble 2,4,6-trimethylpyrylium picrate [4] crystallized from the filtrate as yellow plates, m. p. 129°.[14]

The *picrolonate* had m. p. 158° (from ethanol) (Found: C, 56·6; H, 4·6. $C_{20}H_{20}N_4O_7$ requires C, 56·1; H, 4·7%). The *hexachloroplatinate*, prepared in concentrated hydrochloric acid, had m. p. 182° (Found: C, 31·1; H, 4·0; Pt, 25·3. $C_{10}H_{13}Cl_3O_2Pt_{1/2},H_2O$ requires C, 31·0; H, 3·9; Pt, 25·2%. Found, after heating at 105° for 4 hr.: C, 32·75; H, 3·5; Pt, 26·6. $C_{10}H_{13}Cl_3O_2Pt_{1/2}$ requires C, 32·5; H, 3·55; Pt, 26·4%). The *hydrobromide*, prepared in carbon tetrachloride by means of gaseous hydrogen bromide, or bromine, had m. p. 205°; it slowly darkens and is immediately hydrolysed by water (Found: Br, 32·8. $C_{10}H_{13}BrO_2$ requires Br, 32·6%).

With small amounts of concentrated acids, the compound (II) gives a greenish colour; on melting, the picrate and picrolonate also become green. With ferric chloride in concentrated hydrochloric acid, it gives a yellow precipitate which melts (becoming green) at 136° after crystallization from acetic acid–ether (Found: C, 42·35; H, 4·6; Cl, 30·1, corresponding to a formula $C_{10}H_{13}O_2Fe_{0\cdot6}Cl_{2\cdot4}$).

The compound (II) is oxidized by potassium permanganate, and is hydrogenated in ethanol over Pd–$CaCO_3$ at normal pressure to an oily tetrahydro-derivative b. p. 215°/760 mm., 133°/55 mm., showing ketonic properties. With bromine in carbon tetrachloride it yields an oily bromo-derivative.

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[14] Balaban and Nenitzescu, *Annalen*, 1959, **625**, 74.

With Brady's reagent, the compound (II) gives a colour but no precipitate. By adding perchloric acid and diluting the solution with ether, a yellow precipitate is obtained, which recrystallizes from ethanol–ether in the presence of small amounts of perchloric acid. The yellow 2,4-*dinitrophenylhydrazone perchlorate*, m. p. 174°, becomes violet-brown in neutral or alkaline solution (Found: C, 43·2; H, 4·2; N, 12·5. $C_{16}H_{17}N_4O_5{}^+ClO_4{}^-$ requires C, 43·2; H, 3·85; N, 12·6%), and has $\lambda_{max.}$ (in 1,2-dichloroethane) 270 (4·14), 328 (4·01) and 405vs (4·50) (solution lemon-yellow) or (in NaOH–EtOH) 231 (4·18), 272 (4·16), 331 (4·13), and 437 mμ (4·27) (log ε in parentheses).

Refluxing compound (II) for 2 hr. with 2 equiv. of 10% aqueous sodium hydroxide gives a clear solution. Acidification, ether-extraction, and fractionation of the extracts under reduced pressure yields 3,5-xylenol (30%) (VI), b. p. 140°/55 mm., m. p. 67° (phenylcarbamate, m. p. 154°; tribromo-derivative, m. p. 167°; identified by mixed m. p.s., and another 3-*hydroxy*-5-*methylphenylacetone* (60%) (VII), b. p. 215°/55 mm. (Found: C, 72·0; H, 7·5. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%).

The ultraviolet absorption spectrum of (VII) shows two non-resolved maxima at 283 and 276 mμ (log ε 3·18 in cyclohexane and 3·24 in 1,2-dichloroethane for both maxima). In NaOH–EtOH a band at 302 mμ (log ε 3·48) and a shoulder at 243 mμ (log ε 3·84) are found. Infrared absorption maxima (liquid film and solution in CCl_4) are at 685w, 714m, 802m, 850m, 969w, 1001w, 1032m, 1160s, 1230m, 1272m, 1305s, 1325s, 1360s, 1435w, 1468m, 1500m, 1601vs, 1620s, 1716vs, 2855w, 2920m, 2956w, 3000vw, 3030w, 3115w, 2290s (broad) 3688m (apparent only in solution, not in liquid film).

The phenol (VII) gives a violet colour with ferric chloride and slowly forms a *phenylcarbamate*, m. p. 69—70° (from aqueous ethanol) (Found: C, 72·3; H, 5·8. $C_{17}H_{17}NO_3$ requires C, 72·1; H, 6·05%), and a red 2,4-*dinitrophenylhydrazone* m. p. 160° (from aqueous ethanol) (Found: C, 55·8; H, 4·8; N, 16·2. $C_{16}H_{16}N_4O_5$ requires C, 55·8; H, 4·7; N, 16·3%), $\lambda_{max.}$ (in 1,2-dichloroethane) 267 (4·06), 366 mμ (4·33), and a shoulder at *ca.* 445 mμ (3·60).

The phenol consumes 4 mol. of bromine in carbon tetrachloride, yielding a *tetrabromo-derivative* (VIII), m. p. 165° (from aqueous ethanol) (Found: C, 25·2; H, 1·8; Br, 66·7. $C_{10}H_8Br_4O_2$ requires C, 25·0; H, 1·7; Br, 66·6%). Diazomethane converts the phenol (VII) into its methyl ether, $\nu_{max.}$ (in CCl_4) 710m, 855m, 931w, 960w, 1000w, 1078s, 1159vs, 1171vs, 1200s, 1230m, 1300s, 1333vs, 1360s, 1380w, 1442m, 1470vs, 1610vs, 1720vs, 1730w, 2838m, 2854w, 2930s, 2959s, 3000m.

Reaction of Compound (II) *with Ammonia.*—The compound (5 g.) was heated in a sealed tube with 28% aqueous ammonia (80 c.c.) at 100° for 4 hr. The clear solution was distilled under reduced pressure, yielding as sole product 4-*acetonylidene*-1,4-*dihydro*-2,6-*dimethylpyridine* (V), b. p. 172°/80 mm. (Found: C, 73·45; H, 8·4; N, 8·8. $C_{10}H_{13}NO$ requires C, 73·6; H, 8·0; N, 8·6%); this gives a *hexachloroplatinate*, decomp. 202° (from 1% hydrochloric acid) (Found: C, 33·1; H, 4·1; Cl, 28·4; N, 3·9; Pt, 25·7. $C_{10}H_{14}Cl_3NOPt_{1/2}$ requires C, 33·6; H, 3·8; Cl, 28·9; N, 3·8; Pt, 26·5%), *picrolonate*, m. p. 222° (from ethanol) (Found: C, 56·3; H, 5·0; N, 16·4. $C_{20}H_{21}N_5O_6$ requires C, 56·2; H, 4·95; N, 16·4%), and *picrate*, m. p. 101—102° (from aqueous ethanol) (Found: N, 14·3. $C_{16}H_{16}N_4O_8$ requires N, 14·4%).

Reaction of Compound (II) *with Sodium Hypobromite.*—To an aqueous solution (prepared at 15° from 5 g. of sodium hydroxide and 1·6 ml. of bromine), was added compound (II) (1·5 g.), and the solution was stirred in the cold. After a few minutes a vigorous reaction took place, yielding a *monobromo-derivative* which was filtered off and washed with water and sodium hydrogen sulphite solution; it had m. p. 102° (from 70% ethanol) and was light yellow and soluble in acids (Found: C, 49·3; H, 4·7; Br, 32·9. $C_{10}H_{11}BrO_2$ requires C, 49·0; H, 5·3; Br, 32·6%). The *picrolonate* had m. p. 122° (from aqueous ethanol) (Found: C, 47·1; H, 3·85. $C_{20}H_{19}BrN_4O_7$ requires C, 47·3; H, 3·8%), and the *hexachloroplatinate*, m. p. 183° (Found: Br + Cl, 41·3. $C_{10}H_{12}BrCl_3O_2Pt_{1/2}$ requires Br + Cl, 41·6%).

Preparation of the Phenols (IX) *and* (X).—3,5-Xylyl acetate [15] was rearranged to 2-hydroxy-4,6-dimethylacetophenone (IX) by Baddeley's method; [16] this had m. p. 58°, ν (CO) 1635 cm.$^{-1}$ [*phenylcarbamate*, m. p. 109° (Found: C, 72·9; H, 6·0; N, 5·3. $C_{17}H_{17}NO_3$ requires C, 72·1; H, 6·05; N, 4·95%); 2,4-*dinitrophenylhydrazone*, m. p. 164° (from ethanol) (Found: C, 55·7; H, 4·8; N, 16·25. $C_{16}H_{16}N_4O_5$ requires C, 55·8; H, 4·7; N, 16·3%)].

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[15] von Braun and Haensel, *Ber.*, 1926, **59**, 1999.
[16] Baddeley, *J.*, 1943, 273.

Isomerization of this product with an excess of aluminium chloride (cf. Baddeley [16]) yielded 4-hydroxy-2,6-dimethylacetophenone (X), m. p. 68°, ν (CO) 1650 cm.$^{-1}$ [2,4-*dinitrophenylhydrazone*, m. p. *ca.* 280° (Found: C, 55·8; H, 4·9; N, 16·2%)].

Triacetylation of 2-*Methylbut*-1-*ene*.—Reaction by method (*b*) above, but with t-pentyl in place of t-butyl chloride, gave 4-ethyl-2,6-dimethylpyrylium perchlorate as diacetylation product, and a *homologue* of compound (II) as triacetylation product [its perchlorate does not crystallize, so that the solution has to be made strongly acid with perchloric acid and then shaken with ether, in order to obtain an upper (ethereal) layer containing the perchlorate]; this substance has m. p. 83°, is yellowish (from light petroleum) (Found: C, 73·9; H, 8·15. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%), gives a large m. p. depression with (II) but shows similar properties and affords a *picrolonate*, m. p. 170° (Found: N, 12·7. $C_{21}H_{22}N_4O_7$ requires N, 12·7%), and *picrate*, m. p. 122° (from aqueous ethanol) (Found: N, 10·2. $C_{16}H_{17}N_3O_9$ requires N, 10·3%).

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