Fructosemethylphenylhydrazone. By W. J. HEDDLE and E. G. V. PERCIVAL.

PERCIVAL and PERCIVAL (J., 1937, 1320) reported the preparation from fructose of a methylphenylhydrazone, m. p. 170°, $[\alpha]_{D}^{17^{\circ}} - 253^{\circ}$, which yielded a penta-acetate, m. p. 121°, $[\alpha]_{D}^{17^{\circ}} + 86{\cdot}5^{\circ}$. Ofner (*Monatsh.*, 1905, **26**, 1165) had previously described fructose methylphenylhydrazone, m. p. 116—120°. His preparation was repeated and the crystalline methylphenylhydrazone so obtained had m. p. 118—119°, $[\alpha]_{D}^{18^{\circ}} \pm 0^{\circ}$ in (4 : 6)-pyridine–alcohol (*c*, 0·6). Many attempts to prepare a crystalline acetate failed, the pale yellow syrup obtained showing $[\alpha]_{D}^{17^{\circ}} - 75^{\circ}$ in chloroform (*c*, 1·3) (cf. + 86·5° for the acetate of the methylphenylhydrazone, m. p. 170°) (Found : $CH_3{\cdot}CO$, 43·5. $C_{23}H_{30}O_{10}N_2$ requires $CH_3{\cdot}CO$, 43·5%).

These marked differences in rotation obviously exclude any possibility of dimorphism and the occurrence of two fructosemethylphenylhydrazones may be due to different ring structures or the presence of a cyclic structure in one case and not in the other.—KING'S BUILDINGS, UNIVERSITY OF EDINBURGH. [*Received, September 16th*, 1940.]

An Enol-acetate in the Triterpene Series. By E. R. H. JONES and K. J. VERRILL.

THE facility with which the carbonyl group of β-amyranonyl acetate can enolise was demonstrated by Beynon, Sharples, and Spring (J., 1938, 1233), who found that the keto-acetate contained an active hydrogen atom. This observation suggested that bromination of the keto-acetate would proceed easily and some progress had been made in this study when Picard, Sharples, and Spring (J., 1939, 1045) reported successful experiments along these lines. The results obtained by us were in complete agreement with those of the latter authors and in addition it was observed that the bromination could be effected in chloroform solution at room temperature and that the crude bromine-containing product yielded the αβ-unsaturated ketone on crystallisation from acetic acid.

Together with the bromination experiments, the acetylation of the ketone was examined, since in the sterol series a study of the reactions of enol-acetates has yielded results of considerable interest. When the keto-acetate is heated under reflux with acetic anhydride and anhydrous potassium acetate, the *enol-acetate* of *β-amyranonyl acetate*, m. p. 225—227°, can be prepared in good yield, its constitution being proved by hydrolysis to β-amyranonol. The enol-acetate remains unaffected by selenium dioxide oxidation under more drastic conditions than those successfully employed by Ruzicka, Müller, and Schellenberg (*Helv. Chim. Acta*, 1939, **22**, 767) for the conversion of β-amyrin acetate into a dehydro-β-amyrin acetate and is recovered unchanged on heating under reflux with sulphur in benzyl acetate (Simpson, this vol., p. 230).

In the expectation of obtaining results of considerable interest it was intended originally to examine the formation of enol-acetates from various αβ-unsaturated triterpene ketones and it might be pointed out that the preparation of the same or different enol-acetates from the α-amyrenonyl acetate and *epi*(*iso*)-α-amyrenonyl acetate recently described by Ewen and Spring (this vol., p. 1196) would furnish important evidence of their relationship to one another.

Enol-acetate of β-Amyranonyl Acetate.—A solution of β-amyranonyl acetate (1 g.) and freshly fused potassium acetate (0·5 g.) in acetic anhydride (50 c.c.) was heated under reflux for 30 hours. The reaction mixture was treated with water and crystallisation of the solid product from alcohol yielded the *enol-acetate* (750 mg.) in fine needles, m. p. 225—227°, $[\alpha]_D^{20°} + 44°$ ($l = 1$, $c = 1·2$ in chloroform) (Found: C, 77·5; H,10·6. $C_{34}H_{54}O_4$ requires C,77·5; H, 10·3%). Hydrolysis was effected by heating under reflux with methyl-alcoholic potassium hydroxide (10%), yielding β-amyranonol, m. p. 202—203° after crystallisation from aqueous alcohol, undepressed on admixture with an authentic specimen.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7. [*Received, September 19th*, 1940.]

The Alleged Reduction of the Phenylurethane of Trichlorolactic Ester and Nitrile by Dilute Aqueous Alkali. By HARRY IRVING and HUGH MARSTON.

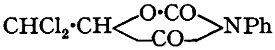
BY shaking with 10% aqueous caustic soda saturated solutions of the phenylurethanes of chloral cyanohydrin or ethyl trichlorolactate (I, X = CN or CO_2Et) in ether–ligroin, Lambling (*Bull. Soc. chim.*, 1898, **19**, 782) obtained crystalline solids which he formulated as reduction products (II, X = CN or CO_2Et), rejecting the structures (IV, X = CN or CO_2Et) on the grounds that the products showed no tendency to add on bromine and that the concomitant formation of phenyl *iso*cyanide could likewise be explained as a reduction of liberated Ph·NCO to Ph·NC. The formation of ωω-dichloroacetanilide, $CHCl_2·CO·NHPh$, together with a lactam formulated as (III) when the urethane (I, X = CN) was boiled with aqueous sodium carbonate was taken as confirming the presence of $CHCl_2$ groups in (II) and (III).

$CCl_3·CHX(O·CO·NHPh)$

(I.)

$CHCl_2·CHX(O·CO·NHPh)$

(II.)



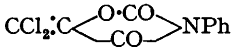
$$CHCl_2·CH\begin{matrix}<\!O·CO\!>\\ \smallsetminus CO \smallsetminus\end{matrix}NPh$$

(III.)

We have repeated and confirmed Lambling's preparations, but there can be no doubt that all the products contain the grouping $CCl_2{:}C{:}$ and are to be formulated as (IV, X = CN or CO_2Et) and (V), since the urethane (IV, X = CN) which Lambling represented as (II) can be obtained from (I, X = CN) by quantitative elimination of hydrogen chloride by means of a cold ethereal solution of triethylamine.

$$\text{(I)} \xrightarrow[(-\,\text{HCl})]{\text{NEt}_3} \text{CCl}_2\text{:CX(O·CO·NHPh)}$$

(IV.)



(V.)

Such facile elimination of hydrogen chloride is, indeed, to be anticipated, since the α-hydrogen atom is activated by CN or CO_2Et (Kötz, *J. pr. Chem.*, **1913**, **88**, 531; **1914**, **90**, 306; Chattaway and Irving, J., **1929**, 1039). That the products (IV) and (V) do not add on bromine is scarcely surprising in view of the well-known deactivating effect of Cl and CN attached to a double bond (cf. Ingold and Ingold, J., **1931**, 2357 and refs. therein; Taylor and Murray, J., **1938**, 2085). The formation of ωω-dichloroacetanilide when the cyanourethane (as I) is boiled with sodium carbonate solution is due to hydrolysis of the primary product (IV, X = CN), isolable when cold dilute alkali or triethylamine is used (see above), followed by the known action of chloral cyanohydrin or dichloroacetonitrile upon aniline resulting from the $Ph·NH·CO_2H$ also formed (Kötz; Chattaway and Irving, *locc. cit.*). This reaction and hydrolysis of the CN group, followed by lactamisation to the oxazolone (V), are independent: on increasing the temperature and strength of alkali, C–C fission of the chloral cyanohydrin to give chloroform takes place to an increasing extent (Hagemann, *Ber.*, 1872, **5**, 152), and the *iso*nitrile observed results from its interaction with aniline in the alkaline medium. The course of these reactions has been followed qualitatively.

It is noteworthy that in agreement with our figures, Lambling's own analyses support formulæ (IV) and (V) rather than those which he himself adopted.

	C, %.	H, %.	N, %.	Cl, %.	*M.*
Calc. for $C_{10}H_8O_2N_2Cl_2$ (II, X = CN)	46·3	3·1	10·8	27·4	259
,, $C_{10}H_6O_2N_2Cl_2$ (IV, X = CN)	46·7	2·3	10·9	27·6	257
Found: Lambling	46·6	2·4	10·8	27·9	240, 253
Irving and Marston	46·7	2·5	10·8	27·7, 27·8	—
Calc. for $C_{10}H_7O_3NCl_2$ (III)	46·15	2·7	5·4	27·3	260
,, $C_{10}H_5O_3NCl_2$ (V)	46·5	1·9	5·4	27·1	258
Found: Lambling	46·3	2·0	5·4	27·0	226, 242
Irving and Marston	46·6	1·85	5·5	27·2, 27·15	—

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