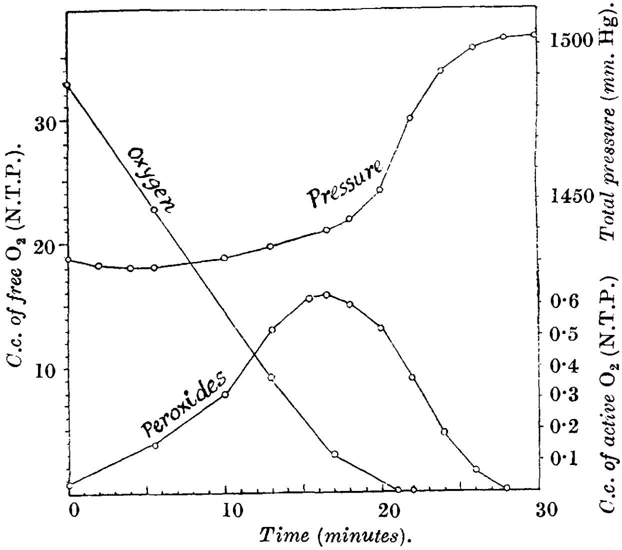
NOTES.

The Oxidation of n-*Hexane.* By MAX BRUNNER and ERIC KEIGHTLEY RIDEAL.

IN a previous communication (this vol., p. 1162), it was shown that *n*-hexane–air mixtures in a closed bulb maintained at temperatures well below the so-called critical inflexion temperature or temperature of initial combustion actually underwent reaction at appreciable velocities. The pressure–time curves all exhibited well-marked characteristics, a period of no or small pressure change followed by a short and final period of rapidly rising pressure. It was assumed that these two periods were characterised in their rates of reaction, it being thought that the " induction " period was a period of slow combustion, which was followed by a period of rapid combustion, this being initiated by a rising content of peroxide molecules. Further investigation on the rate of oxygen consumption, whilst confirming the view that the period of rapid pressure increase is associated with an oxidation process by means of peroxide molecules formed prior to the observed pressure increase, has shown that the rate of oxygen uptake during the initial period of no pressure change, previously called the induction period, is in reality quite rapid. This is made clear from a consideration of the curves representing the analyses, conducted as previously described, after various periods of time of a 42% (by volume) hexane–58% oxygen mixture maintained in a bulb of 57·9 c.c. capacity at 210°. It is evident that the rapid increase in pressure occurs when the oxygen has almost disappeared and is to be attributed to reactions involving decomposition or reaction of peroxide molecules. It is significant that the rate of oxygen uptake appears to be a zero-order reaction over a wide range of pressure.

The results of a detailed examination of the varied compositions of the reaction products during this period of isopiestic combustion have been described by one of us (M. B., *Helv. Chim. Acta*, Oct., 1928), but it is clear that observations on the rate of change of pressure or volume or on the content of substances giving peroxide reactions, two methods frequently adopted, are not safe criteria for determination of reaction velocities in the slow combustion of hydrocarbons. The reactions which appear to predominate in the initial stages of combustion in glass vessels at low temperatures may be summarised by the equations

FIG. 1.



$$C_6H_{14} + O_2 \longrightarrow C_6H_{14}O_2 \text{ (active moloxide)}$$
$$C_6H_{14} + C_6H_{14}O_2 \longrightarrow 2C_6H_{12} + 2H_2O$$
$$C_6H_{12} + O_2 \longrightarrow C_6H_{12}O_2 \longrightarrow \text{decomposition.}$$

Although, at low temperatures, surfaces appear to play an important part in the formation of peroxides, consideration of the great reaction velocity during the period of no pressure change leads us to suspect that the peroxides themselves cannot be the reaction centres for the propagation of the chemical action through the homogeneous bulk phase.—THE UNIVERSITIES OF ZÜRICH AND CAMBRIDGE.

[*Received, August* 10*th*, 1928.]

The Preparation of Cholestenone. By WILFRED ARCHIBALD SEXTON.

A MIXTURE of pure cholesterol (20 g.) and copper bronze (15 g.) was heated gently at 2—3 mm. pressure in a 200 c.c. Jena glass distillation flask (see Heilbron and Sexton, this vol., p. 347). As soon as the sterol was molten a violent reaction commenced with evolution of a thick white vapour. This condensed as a white powder in a second distillation flask serving as receiver; glass wool in a **U**-tube placed between the side arm and the pump effectually prevented the escape of solid particles. After a few minutes the violence of the reaction abated and the catalyst became caked together in a porous mass. The sublimate (0·2 g.) proved to be unchanged cholesterol. The temperature was then gradually raised until distillation commenced. The distillate (280—290°/3—4 mm.) (17 g.) was golden-yellow and of high viscosity. It crystallised from methyl alcohol at 0° in white needles (6 g.), m. p. 72—76°, which was raised to 80° by repeated crystallisation from methyl alcohol: no depression of m. p. occurred on heating a mixture with cholestenone prepared by heating the sterol with copper oxide. It gave the characteristic semicarbazone, m. p. 234°. By evaporation of the filtrate in a desiccator over calcium chloride a further crop (10 g.) of crude cholestenone was obtained (total yield, 80%).—THE UNIVERSITY, LIVERPOOL. [*Received, August 25th*, 1928.]

The so-called Bisthiohydantoins of Frerichs, Förster, and Höller.

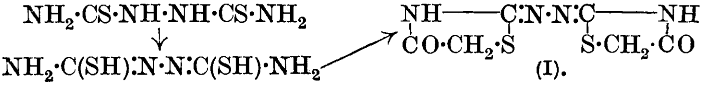
By HERBERT WILLIAM STEPHEN and FORSYTH JAMES WILSON.

BY the interaction of hydrazodithiodicarbonamide and chloroacetic acid in boiling aqueous solution, Frerichs and Förster (*Annalen*, 1909, **371**, 257) obtained a compound which they regarded as 3 : 3-bisthiohydantoin (or, according to present nomenclature, 3 : 3-bis-ψ-thiohydantoin); and in a similar manner, from α-bromopropionic and -*n*-butyric acids Frerichs and Höller (*ibid.*, 1913, **398**, 256) obtained compounds considered to be substituted 3 : 3-bis-ψ-thiohydantoins (R = Me or Et):

$NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2 + 2CHRBr{\cdot}CO_2H =$

$$\begin{array}{l} NH{:}C\text{———}N\text{——}N\text{———}C{:}NH \\ \quad S{\cdot}CHR{\cdot}CO \quad CO{\cdot}CHR{\cdot}S \end{array} + 2H_2O + 2HBr.$$

In a recent communication (this vol., p. 1415) we showed from the products of hydrolysis that the so-called 3 : 3-bis-ψ-thiohydantoin is really 2 : 4-diketotetrahydrothiazole-2-ketazine (I), and its formation would therefore be represented thus:



$$\begin{array}{l} NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2 \\ \qquad\downarrow \\ NH_2{\cdot}C(SH){:}N{\cdot}N{:}C(SH){\cdot}NH_2 \end{array} \nearrow \begin{array}{l} NH\text{——}C{:}N{\cdot}N{:}C\text{——}NH \\ CO{\cdot}CH_2{\cdot}S \quad S{\cdot}CH_2{\cdot}CO \end{array}$$

(I).

We have now shown that the two compounds described by Frerichs and Höller give on hydrolysis hydrazine hydrochloride together with the corresponding 5-alkyl derivative of 2 : 4-diketotetrahydrothiazole; and we therefore regard these compounds as 2 : 4-diketo-5-alkyltetrahydrothiazole-2-ketazines.

Frerichs and Höller, in noting that the alleged 3 : 3-bis-ψ-thiohydantoins are more acidic than basic, remark that this is somewhat surprising, since ψ-thiohydantoin is more basic than acidic; but the acidity of these compounds is to be expected from the structures now assigned, since the 2 : 4-diketotetrahydrothiazoles are acidic.

2 : 4-*Diketo-5-methyltetrahydrothiazole-2-ketazine*, prepared by the method of Frerichs and Höller from hydrazodithiodicarbonamide and α-bromopropionic acid, melted sharply at 289° and possessed the properties ascribed to it by these authors, who give the m. p. as above 280°. It was boiled for ½ hour with concentrated hydrochloric acid, and the solution evaporated on the water-bath and finally in a vacuum over soda–lime and concentrated sulphuric acid. Extraction with hot benzene left a residue of hydrazine hydrochloride (identified by conversion into benzalazine), and the extract on evaporation left a viscous oil which solidified after distillation (166—168°/20 mm.); the solid was crystallised from benzene–light petroleum and then had m. p. 46—47°. From its properties this was evidently 2 : 4-diketo-5-methyltetrahydrothiazole (Wheeler and Barnes, *Amer. Chem. J.*, 1900, **24**, 60; Wilson and Burns, J., 1923, **123**, 799).

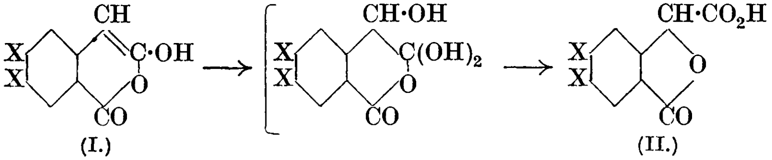
2 : 4-*Diketo-5-ethyltetrahydrothiazole-2-ketazine*, similarly prepared from α-bromo-*n*-butyric acid, crystallised from glacial acetic acid in slightly rose-coloured plates and, when freed from solvent of crystallisation by washing with ether, had m. p. 233° (Frerichs and Förster give 225—226°) (Found: N, 19·6. Calc.: N, 19·6%). Hydrolysis as in the preceding case yielded hydrazine hydrochloride, and evaporation of the benzene extract left a colourless oil which solidified on cooling; crystallisation of the solid from benzene–light petroleum gave prisms, m. p. 64—65°, identical with 2 : 4-diketo-5-ethyltetrahydrothiazole (Wheeler and Barnes; Wilson and Burns, *locc. cit.*).

We wish to thank the Governors of this College for a Research Assistantship awarded to one of us (H. W. S.).—THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, July 26th*, 1928.]

The Enolisation of Homophthalic Anhydrides. By THOMAS STEVENS STEVENS and JAMES LEGGAT WILSON.

4 : 5-*Methylenedioxyhomophthalic anhydride* (enolic form as I, $XX = CH_2O_2$) not only resembles the unsubstituted homophthalic anhydride in forming yellow alkali salts (compare Dieckmann,

Ber., 1914, **47**, 1428), but is itself deep yellow in the solid state, unlike homophthalic anhydride on the one hand and methylenedioxyhomophthalic acid on the other. A general investigation of the behaviour of analogous substances was planned, but as a paper bearing on this subject has recently appeared (Davies and Poole, this vol., p. 1616), it was deemed advisable to publish the results so far obtained.



(I.) (II.)

4 : 5-Methylenedioxyhomophthalic anhydride is obtained by boiling the parent acid with excess of acetyl chloride for several hours, until the original white powder has been replaced by yellow crystals. It separates from benzene in yellow needles, m. p. 178—180° [Found : equiv. in ice-cold acetone, 199·8; in boiling water, 102·1. $C_{10}H_6O_5$ requires equiv. 206 (monobasic), 103 (dibasic)]. The anhydride is not readily affected by bromine, but gives a dark brown precipitate with ferric chloride under the conditions specified by Davies and Poole (*loc. cit.*) for homophthalic anhydride.

Preliminary experiments on the methylation of homophthalic anhydride led to no definite result. An estimation by Hieber's method (*Ber.*, 1921, **54**, 902) indicated a small percentage of enol, but no great reliance is to be placed on the observation, as the formation of a stable chelate ring-system (on which the whole method presumably depends) is improbable in the present case. On the other hand, Dieckmann's general criticism (*Ber.*, 1921, **54**, 2251) of the Hieber reaction may not apply here, as the anhydride is a well-defined acid.

When the calculated amount of aqueous permanganate was added to an ice-cold alkaline solution of homophthalic anhydride, phthalidecarboxylic acid (II, X = H), m. p. 151°, was produced, which gave phthalide, m. p. 73°, on heating. Methylenedioxyhomophthalic anhydride similarly yielded methylenedioxyphthalidecarboxylic acid, m. p. 213—215° (decomp.) (Ruhemann, J., 1912, **101**, 783, gives 216° decomp.), and methylenedioxyphthalide, m. p. and mixed m. p. 188—189° (Stevens and Robertson, J., 1927, 2790).—THE UNIVERSITY, GLASGOW. [*Received, September* 21*st*, 1928.]

Preparation of 4-*Bromophthalic Acid.* By LESLIE CHARLES BAKER.

PHTHALIC anhydride was converted into ethyl 4-nitrophthalate by Miller's method (*Annalen*, 1881, **208**, 224; compare also Cohen, Woodroffe, and Anderson, J., 1916, **109**, 226), and this compound reduced to the amino-ester by Baeyer's method (*Ber.*, 1877, **10**, 1079). (This reduction is best effected at 30—40°, since at lower temperatures the ester tends to solidify when liberated from its alcoholic solution by the addition of acid.) From the precipitate obtained by neutralising the solution with sodium carbonate, after drying, hot absolute alcohol extracted ethyl 4-aminophthalate in 71% yield. This ester (12 g.) was diazotised at 0° (concentrated hydrochloric acid 36 c.c., water 95 c.c.; sodium nitrite 8 g.), and the resulting mixture poured into an ice-cold solution of cuprous bromide (8 g.) in hydrobromic acid (20 c.c.); after $\frac{1}{2}$ hour, the whole was boiled. An ethereal extract of the cold solution, after being washed with dilute acid, sodium carbonate, and water and dried, yielded 10 g. of ethyl 4-bromophthalate (66%) as a pale yellow oil, b. p. 194—195°/16 mm. Von Braun (*Ber.*, 1923, **56**, 2332) gives the b. p. as 190—191°/16 mm.

A mixture of ethyl 4-bromophthalate (7 g.) and baryta (9 g.) in water (140 c.c.) and alcohol (100 c.c.) was heated for 2—3 hours with shaking, the solution was then acidified with concentrated hydrochloric acid, and the alcohol boiled off. Hot *N*-sulphuric acid (65 c.c.) was added slowly with stirring, the precipitated barium sulphate removed when cold, and the filtrate concentrated; 4-bromophthalic acid (5 g.; 88% yield) then separated, m. p. 173—175° after recrystallisation from water.—UNIVERSITY COLLEGE, LONDON. [*Received, October* 1*st*, 1928.]