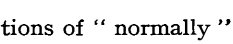
78. α-Methylenic Reactivity in Olefinic Systems. Part I. The Prins Reaction with Propylene.

By John W. Baker.

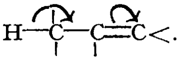
Propylene reacts with paraformaldehyde in the presence of a mixture of 100% acetic and sulphuric acids at 35° to give (1) the diacetate of *n*-butane-1 : 3-diol (63·5%), (2) the cyclic *formal* (14%) of this diol, and (3) 4-*acetoxytetrahydro-γ-pyran* (22·5%). The first two products arise from an acid-catalysed addition to the double bond, but the third, which is not formed by the further reaction of the diol with formaldehyde, involves the direct reaction of the hydrogen of the methyl group of propylene, activated by its conjugation with the olefinic linking. The rate of absorption of each of the reaction ingredients during the course of the reaction has been determined, and mechanisms for the formation of the products are suggested on the basis of these results.

The inclusion of " no-bond " structures of the type $\overset{+}{\mathrm{H}}\ \mathrm{C}{=}\mathrm{C}{-}\overset{-}{\mathrm{C}}$ in the resonance hybrid representing systems, $\mathrm{H}\overset{\curvearrowright}{-}\mathrm{C}{-}\overset{\curvearrowright}{\mathrm{C}{=}}\mathrm{C}$, in which a H–C bond is conjugated with an unsaturated (olefinic) system, was suggested by Baker and Nathan (J., 1935, 1847), and both the polarisability (electromeric) effect (cf. *inter alia*, Baker and Nathan, *ibid*., p. 1844; Baker, *Trans. Faraday Soc*., 1941, **37**, 632; Hughes, Ingold, and Taher, J., 1940, 949) and the polarisation (mesomeric) effect (Baker and Hemming, J., 1942, 191) of alkyl groups arising therefrom, have been experimentally established. The validity of such electron displacement is now generally accepted (cf. Hughes and Ingold, *Trans. Faraday Soc*., 1941, **37**, 674) but the experimental investigations have, hitherto, been restricted mainly to examples in which the H–C bonds are conjugated with an aromatic nucleus. Theoretically, no such restriction is applicable, and it is evident that the postulated " no-bond " resonance structures should give rise to increased reactivity of such α-methylenic hydrogen atoms, possibly smaller in magnitude than, but in no sense different in character from, that which arises from suitable conjugation with other activating unsaturated groups such as carbonyl, $\mathrm{H}\overset{\curvearrowright}{-}\mathrm{C}{-}\overset{\curvearrowright}{\mathrm{C}{=}}\mathrm{O}$, or cyano, $\mathrm{H}\overset{\curvearrowright}{-}\mathrm{C}{-}\overset{\curvearrowright}{\mathrm{C}{\equiv}}\mathrm{N}$. Indeed, evidence for such α-methylenic activity in olefinic and polyolefinic systems is accumulating from the investigations of Farmer and his collaborators in the reactions of such hydrocarbons with maleic anhydride (*Trans. Faraday Soc*., 1942, **38**, 340) and saligenin (Cunneen, Farmer, and Koch, J., 1943, 472), in the mechanism of autoxidation of rubber and drying oils, and in the rearrangement of double bonds during such autoxidations (Farmer, *Trans. Faraday Soc*., 1942, **38**, 348, 356; Farmer, Koch, and Sutton, J., 1943, 541).

A further interesting example is adumbrated in the claim made (B.P. 545,191, 1942) that olefins of the type $\mathrm{R^1R^2C{:}CR^3{\cdot}CH_3}$ ($\mathrm{R^3}$ = alkyl, alicyclic, alphyl or aryl; $\mathrm{R^1}$, $\mathrm{R^2}$ = the same or hydrogen) react at room temperature with trioxymethylene in the presence of catalysts such as stannic chloride, zinc chloride, zinc dichloroacetate, etc., in dry, inert solvents such as ether, chloroform, or saturated hydrocarbons to give unsaturated alcohols of the type $\mathrm{CR^1R^2{:}CR^3{\cdot}CH_2{\cdot}CH_2{\cdot}OH}$. It is specifically stated that the catalyst should be " non-acidic " under the reaction conditions employed, and this is of particular interest in relation to the reaction known to occur between some olefins and trioxymethylene in the presence of acetic–sulphuric acids. Under such conditions Prins (*Chem. Weekblad*, 1919, **16**, 1510) found that the main products are the diacetate $\mathrm{CR_2(OAc){\cdot}CR_2{\cdot}CH_2{\cdot}OAc}$ of the 1 : 3-diol, together with the corresponding cyclic formal  $\mathrm{CR_2}{<}\begin{matrix}\mathrm{CR_2{\cdot}CH_2}\\ \mathrm{O{-}CH_2}\end{matrix}{>}\mathrm{O}$. Thus, whereas under the conditions of the Prins reaction, a normal, acid-catalysed addition to the olefinic linking occurs (see below), the not very dissimilar conditions described in the patent are stated to give rise to reaction at the α-methylenic hydrogen atom.

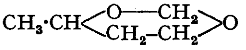
In this series of papers it is proposed to investigate to what extent the typical reactions of " normally " activated hydrogen may be paralleled by similar reactions in which the activation of the hydrogen is dependent solely on its conjugation with an olefinic system. The present communication deals with a further study of the products formed in, and the mechanism of, the Prins reaction.

In his original investigation with styrene, Prins allocated the symmetrical structure $\mathrm{CHPh(CH_2{\cdot}OAc)_2}$ to the diacetate formed, but Fourneau, Benoit, and Firmenich (*Bull. Soc. chim*., 1930, **47**, 860) later proved that the correct structure is $\mathrm{CHPh(OAc){\cdot}CH_2{\cdot}CH_2{\cdot}OAc}$, since cinnamyl alcohol was isolated from the hydrolysis products of Prins's diacetate. Extension of the Prins reaction to certain simple olefins has been briefly described, mainly in the patent literature. Preliminary investigations on the reaction of a number of simple olefins and olefinic compounds with formaldehyde under the conditions of the Prins reaction were carried out by Drs. H. Gudgeon and D. B. Kelly, of Messrs. Imperial Chemical Industries, Ltd. (Dyestuffs Division). The results obtained showed that, of such olefins, propylene is a very suitable compound for further study, since it is rapidly absorbed by a mixture of trioxymethylene in an acetic–sulphuric acid medium at 35° to give good yields of water-insoluble products. These were shown to contain the diacetate of a C_4 diol and the corresponding cyclic formal, but the exact constitutions of the products were not definitely established.

It was decided, therefore, to investigate this reaction more fully, especially since the methyl-group hydrogen atoms are potentially activated by conjugation with the olefinic linking,  $H-\overset{|}{C}-\overset{|}{C}=C<$.

The clean mixture of products obtained by using the conditions described on p. 299 is readily separated by fractional distillation through an effective column. In this manner three pure products were isolated; (I), b. p. 29°/24 mm.; (II), b. p. 47·5°/1 mm.; (III), b. p. 65°/1 mm., the average composition of the total, isolated pure products being 14, 22·5, and 63·5% respectively.

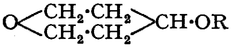
Products (I) and (III) (previously isolated in an impure condition by Gudgeon and Kelly) are the analogues of those obtained by Prins in the corresponding reaction with styrene, and are, respectively, the cyclic *formal* (I) and the diacetate (III) of *n*-butane-1 : 3-diol.

(I.) 
$CH_3\cdot CH<\begin{matrix}O-CH_2\\CH_2-CH_2\end{matrix}>O$

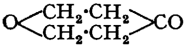
$CH_3\cdot CH(OAc)\cdot CH_2\cdot CH_2\cdot OAc$ (III.)

Evidence for the structures assigned to the products is detailed on p. 300 : (I) is hydrolysed by 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid to give formaldehyde-2 : 4-dinitrophenylhydrazone and *n*-butane-1 3-diol, and (III) is hydrolysed in alkaline solution to the same diol and a metal acetate. In both cases the diol was characterised by conversion into its di-*p*-nitrobenzoate, m. p. 103°, and its *di-α-naphthylurethane*, m. p. 153°, identical with specimens prepared from the genuine diol. Moreover, pyrolysis of (III) at 550° (kindly carried out by Messrs. Imperial Chemical Industries, Ltd.) gave a 50·9% yield of butadiene, closely approximating to that (52·7%) obtained from a genuine synthetic specimen of the diacetate under identical conditions. (I) and (III) thus represent the normal products of the additive reaction at the ethylenic linking.

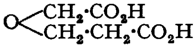
The greatest interest from the point of view of the main object of this series of investigations attaches to the new *product* (II). This is a fragrant liquid of composition $C_7H_{12}O_3$ (II, R = Ac). Hydrolysis with cold alkali shows that it contains one acetoxy-group per molecule and converts it into a secondary *alcohol* $C_5H_{10}O_2$ (II, R = H). Oxidation of this with potassium dichromate and sulphuric acid gives a ketone $C_5H_8O_2$, identical with tetrahydro-γ-pyrone (IV) obtained by Borsche (*Ber.*, 1915, **48**, 683; 1923, **56**, 2012). Oxidation of either (II) or (IV) with nitric acid affords β-carboxymethoxypropionic acid (V), m. p. 97°, identical with the acid, m. p. 93—94°, obtained by Borsche by oxidation of tetrahydro-γ-pyrone with potassium permanganate. This acid was shown by direct comparison not to be identical with either β-hydroxyglutaric acid, m. p. 95°, or α-carboxymethoxypropionic acid, m. p. 69° (Jungfleisch and Godchot, *Compt. rend.*, 1907, **145**, 71, give m. p. *ca.* 30°) which would be obtained from other possible structures for (II). Moreover, the structure of (V) was confirmed by its conversion into β-iodopropionic acid by hydrolysis with hydriodic acid; it has been characterised by conversion into its *diamide*, m. p. 174°, its *methyl ester monoamide*, m. p. 77°, and its *dimethyl* ester, b. p. 138°/24 mm.


$O<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot OR$

(II.)


$O<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CO$

(IV.)


$O<\begin{matrix}CH_2\cdot CO_2H\\CH_2\cdot CH_2\cdot CO_2H\end{matrix}$

(V.)

Before discussing the mechanism of the formation of (II), reference must be made to the results of a kinetic study of the course of the reaction. By methods described on p. 299 the reaction between propylene and paraformaldehyde in homogeneous solution in acetic–sulphuric acid medium was followed ; determination of (1) total acidity, by titration, and (2) sulphuric acid, by gravimetric determination as barium sulphate, together gave the rate of absorption of acetic acid; (3) absorption of formaldehyde was followed by gravimetric determination as its 2 : 4-dinitrophenylhydrazone; (4) propylene absorption was found by direct measurement from a graduated gasometer. The results, summarised in Table I, are shown in the figure.

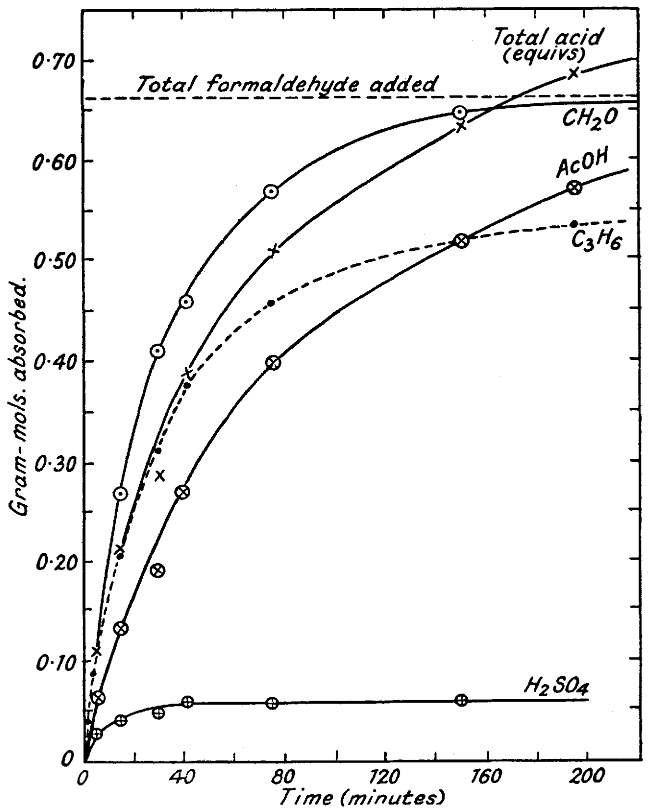
TABLE I.

	Time (mins.).	C_3H_6 absorbed (g.-mol.).	CH_2O absorbed (g.-mol.).	AcOH absorbed (equiv.).	H_2SO_4 absorbed.		Total acid absorbed (equiv.).
					Equiv.	G.-mol.	
Original	0	0	0·663	2·659	0·572	0·286	3·231
	5	0·116	—	0·063	0·058	0·029	0·121
	15	0·205	0·267	0·133	0·082	0·041	0·215
	30	0·310	0·407	0·190	0·096	0·048	0·286
	41	0·376	0·456	0·269	0·114	0·057	0·383
	75	0·457	0·567	0·397	0·110	0·055	0·507
	150	0·517	0·645	0·517	0·115	0·057	0·632
	195	0·533	—	0·569	—	—	0·684
Unused	—	—	0·018	2·090	0·457	0·229	2·547

All figures refer to a 200 c.c. sample.

In view of the complicated nature of the reaction (it is probable that the three products are formed in separate, concurrent reactions), a detailed kinetic analysis is not possible, but several features are worthy of note.

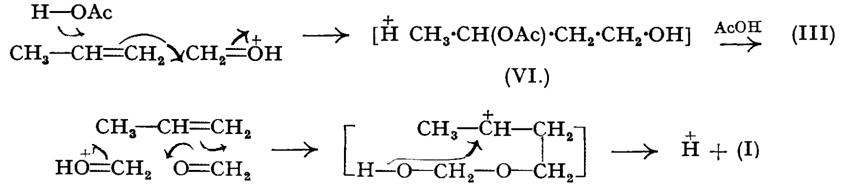
At an early stage (*ca.* 30 mins.) the quantity of sulphuric acid absorbed attains a value which then remains constant throughout the remainder of the reaction. This suggests the formation of an intermediate which subsequently remains in equilibrium with free sulphuric acid. The difficulty inherent in such a suggestion is that any intermediate must be of a character such that it cannot be precipitated as barium sulphate after dilution of the reaction medium. Alternatively, the early absorption may depend on a side reaction such as the formation of a hydroxy-sulphonate, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}SO_3H$, at an initial rate comparable to that of the olefin–formaldehyde reaction, but which is rapidly suppressed as the latter reaction becomes of preponderating importance. The subsequent, constant concentration of the sulphuric suggests that, in the main reactions, it functions purely as an acid catalyst for the additive reactions to the carbonyl group in formaldehyde, *e.g.*, $CH_2{:}O + H_2SO_4 \rightleftharpoons CH_2{:}\overset{+}{O}H + H\overset{-}{S}O_4$. The molecular ratio, formaldehyde absorbed/olefin absorbed, rapidly attains a value > 1, in harmony with the fact that two out of the three products formed require a molecular ratio $2CH_2O/1C_3H_6$.



(*Note : Values for the acids absorbed at* 30 *mins. are known to be slightly low.*)

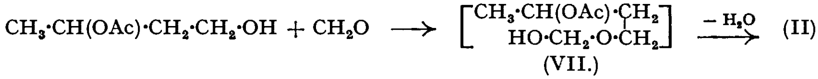
The lag in the absorption of acetic acid in the earlier stages is explained partly by the formation of the formal (in the production of which acetic acid plays no part) and partly by the slower acetylation of the hydroxy-monoacetate (VI) which is, presumably, the initial product in the ultimate production of (III). The following scheme for the formation of (I) and (III) is in harmony with the experimental data :

$$CH_2{:}O + H_2SO_4 \rightleftharpoons CH_2{:}\overset{+}{O}H + H\overset{-}{S}O_4$$



The formation of the tetrahydro-γ-pyran derivative (II) must involve, at some stage, reaction of a hydrogen of the methyl group in propylene. Further addition of 0·65 g.-mol. of formaldehyde, at the stage when the absorption of the original formaldehyde is practically complete, causes a sudden increase in the rate of propylene absorption, which increase, however, is not long maintained. The composition of the resulting product, *viz.*, (I) 28, (II) 28, (III) 43%, shows an increase in the relative proportions of (I) and (II) formed at the expense of (III), together with a much larger proportion of water-soluble products.

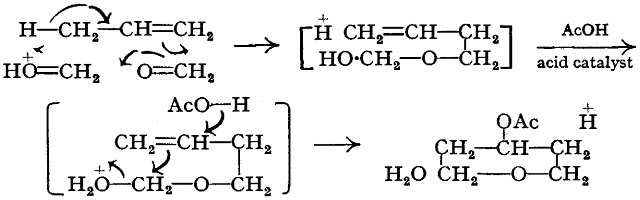
It was at first thought that (II) might be formed by elimination of water from an intermediate (VII) obtained by further condensation, of a hemiacetal type, between (VI) and another molecule of formaldehyde :



$$CH_3\cdot CH(OAc)\cdot CH_2\cdot CH_2\cdot OH + CH_2O \longrightarrow \begin{bmatrix} CH_3\cdot CH(OAc)\cdot CH_2 \\ HO\cdot CH_2\cdot O\cdot CH_2 \end{bmatrix} \xrightarrow{-H_2O} (II)$$

(VII.)

Elimination of acetic acid from (VII) would also provide an alternative route for the production of the formal (I). This hypothesis cannot be maintained since, when the Prins reaction is repeated under identical conditions but with half the original molecular proportion of formaldehyde and *n*-butane-1 : 3-diol in place of propylene, no trace of (II) can be detected in the product, which consists almost entirely of the diacetate (III) together with a little formal (I). It must therefore be concluded that (II) is formed directly from propylene by a route essentially of the following type :



It thus involves the direct reaction of the α-methylenic hydrogen activated by the adjacent olefinic linking.

In the olefin–formaldehyde reaction under the conditions prescribed by the British patent (*loc. cit.*), a cyclic formal [as (I)] is formed together with the unsaturated alcohol. Hence, both in this and in the Prins reaction, the unsaturated linking and the α-methylenic hydrogen are *both* reactive, and the problem of the different course of the reaction, in the two cases, is thus narrowed to the differential functions of the various catalytic conditions on the two possible centres of reactivity. It is hoped that future investigations may throw further light on this aspect.

Finally, an attempt was made to use boron trifluoride as a catalyst for the Prins reaction. The preliminary results in Table II show that this compound in solution (as its complex) in 100% acetic acid is not, in itself, an effective catalyst for the Prins reaction, but it increases the catalytic efficiency of *small* concentrations of sulphuric acid.

TABLE II.

Volume (c.c.) of C_3H_6 absorbed by 10 c.c. of AcOH–BF_3 solution in time, *t*, in the presence of 1 g. of CH_2O + *x* g. of 100% H_2SO_4.*

t (mins.).	*x* = 0·14	0·3	0·42	0·42 (*without* BF_3)
10	18	34	50	32
20	26	51	81	47
30	36	71	108	64
40	44	91	131	79

* Under the conditions of the kinetic experiment 124 c.c. of C_3H_6 were absorbed in 5 mins.

The reaction mixture remains water-white if BF_3–H_2SO_4 is used as a catalyst, whereas it becomes deep brown when high concentrations of sulphuric acid alone are employed.

EXPERMENTAL.

(All micro-analyses were carried out by Drs. Weiler and Strauss, Oxford.)

The propylene used was kindly supplied by Messrs. Imperial Chemical Industries Limited (Dyestuffs Division) and had been prepared by catalytic vapour-phase dehydration of *iso*propyl alcohol over activated alumina at *ca.* 300°. The gas was condensed in a Drikold–ethanol-cooled coil and collected in a cylinder. It was transferred to a graduated 10-l. gas holder, whence it was passed by hydrostatic pressure through calcium chloride drying tubes into the closed glass reaction vessel, contained in a water-tight bath through which water at 35° from a thermostat was circulated. The reaction vessel and bath were suitably mounted on a mechanical shaker. Preliminary experiments showed that the rate of absorption of the propylene by the paraformaldehyde (33 g.)–acetic acid (210 g.)–sulphuric acid (32 g.) mixture, is greatly increased by replacement of ordinary concentrated sulphuric acid by 100% sulphuric acid and, to a smaller extent, by the use of 100% acetic acid in place of ordinary " glacial " acetic acid ; the 100% acids were therefore used throughout the investigation. Since the purely preparative runs were carried out essentially in the same manner as the quantitative examination, only the latter is described.

Kinetic Examination.—For a kinetic examination a homogeneous solution (not attained in the initial stages of the preparative experiments) is essential. A mixture of 210 g. of 100% acetic acid, 32 g. of 100% sulphuric acid, and 32 g. of paraformaldehyde was warmed on a steam-bath with constant shaking until an almost homogeneous solution was obtained. This was freed from a trace of undissolved paraformaldehyde by filtering through glass wool under suction, cooled to 35°, and 200 c.c. of the clear solution were pipetted into the reaction vessel. The latter consisted of a 750-c.c. Pyrex flask fitted with a cork through which passed a lead-in tube for the propylene and a sampling tube fitted with a tap just below a standard glass socket into which was fitted a 2-c.c. pipette with a ground tip. By suitable manipulation of the tap, the reaction mixture could be forced into the pipette by the slight pressure of propylene in the reaction vessel, so a 2-c.c. sample of the reaction mixture could be obtained at any stage in the reaction. The principle of the sampling method was identical with that used by Baker and Hemming (*loc. cit.*) in their examination of the aldehyde–cyanohydrin reaction. All lead-in tubes and the reaction vessel were filled with propylene before the initial gasometer reading was noted, and the absorption was started by setting the shaker in motion. The 2-c.c. sample was diluted to 250 c.c. with distilled water. In 100 c.c. of this diluted solution, *total* acid was determined by titration with 1·915N-sodium hydroxide solution. In another 50 c.c., sulphuric acid was determined gravimetrically as barium sulphate, and thus the acetic acid present was determined by difference. A further 10 c.c. of the diluted solution was pipetted into 50 c.c. of a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid and, after standing overnight in the refrigerator, the separated formaldehyde-2 : 4-dinitrophenylhydrazone was filtered off on a weighed, sintered-glass crucible, washed, and dried over sulphuric acid in a vacuum to constant weight. The composition of the original reaction mixture was initially determined in the same manner. The volume of propylene absorbed was noted by direct reading from the graduated gas-holder, suitable corrections for temperature and pressure being applied. The results obtained have been given in Table I.

Isolation of the Products.—The reaction mixture was neutralised with sodium carbonate decahydrate, the minimum quantity of water being added to prevent the mixture becoming too thick. The resulting mush was extracted once with ether, and the aqueous layer filtered under suction. The separated sodium salts were repeatedly washed, on the Büchner funnel, with ether, and these washings were used to extract the aqueous filtrate. The combined ethereal extracts were washed with water, dried over sodium sulphate, and the ether was removed through a Widmer column. The pale yellow residue was fractionally distilled first through a Widmer column and then refractionated under reduced pressure by means of a 30-cm. complete-reflux, vacuum-jacketed column heated electrically to the appropriate temperature by means of a Sunvic current regulator. The column, packed with 3·5-mm. glass helices (75% single-turn and 25% double-turn spirals) of efficiency equivalent to 6 theoretical plates, was designed and constructed by Dr. I. Dostrovsky (University College) at the Edward Davies Chemical Laboratory, Aberystwyth. The composition of the product was determined by direct weighing of the isolated pure products. The yields thus represent minimum values. Those obtained in the kinetic run are typical and are given below, based on the olefin absorbed :

Propylene absorbed, 0·533 g.-mol.

$$\text{Products isolated: }\left.\begin{array}{llll}\text{(I)} & \text{Formal} & 0{\cdot}059\text{ g.-mol.} & = 11\% \\ \text{(II)} & \text{Monoacetate} & 0{\cdot}08\quad ,, & = 15\% \\ \text{(III)} & \text{Diacetate} & 0{\cdot}187\quad ,, & = 35\%\end{array}\right\}\text{Total 61\% of the theoretical.}$$

The molecular ratios of the three reactants required for the formation of the three products are theoretically :

Product	(I).	(II).	(III).	Product	(I).	(II).	(III).	Product	(I).	(II).	(III).
C_6H_6	1	1	1	AcOH	0	1	2	CH_2O	2	2	1

On the basis of the product composition, the molecular ratios of acetic acid and formaldehyde absorbed in the actual reaction per molecule of olefin should be 1 : 1·46 : 1·38, the average values observed being 1 : 1·3 : 1·5. In view of the approximate estimate of the composition possible by actual separation and the neglect of small high-boiling residues and water-soluble products, the agreement is satisfactory.

Characterisation of Products.—*4-Methyl-*1 : 3-*dioxan* (I). This is the most volatile product, b. p. 25°/22 mm. (Found : C, 58·6; H, 9·85. $C_5H_{10}O_2$ requires C, 58·2; H, 9·85%. The *formal* was warmed on a steam-bath with a slight excess of a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid, and then kept at room temperature for several days to complete the precipitation of the formaldehyde-2 : 4-dinitrophenylhydrazone. This, after crystallisation from alcohol, had m. p. 166° either alone or mixed with a genuine specimen. The filtrate was made just alkaline with sodium hydroxide, and excess of 2 : 4-dinitrophenylhydrazine was removed by extraction with ether. The residual aqueous liquor was evaporated to dryness on a steam-bath, and the diol extracted with dry acetone. The residue from the acetone solution after evaporation of the solvent was treated with *p*-nitrobenzoyl chloride and aqueous sodium hydroxide. The di-*p*-nitrobenzoate of *n*-butane-1 : 3-diol, after crystallisation from alcohol, had m. p. 103° either alone or mixed with a specimen prepared from a genuine sample of the diol.

n-*Butane*-1 : 3-*diol diacetate* (III). This had b. p. 65°/1 mm. (Found : C, 55·5; H, 8·4. Calc. for $C_8H_{14}O_4$: C, 55·2; H, 8·1%); 0·1587 g. required baryta equivalent to 3·54 c.c. of 0·501N-sulphuric acid for hydrolysis, whence the number of acetyl groups per molecule = 1·95 (calc. : 2·0). A little of the ester was shaken with 50% aqueous sodium hydroxide until a homogeneous solution was formed. This was then shaken with *p*-nitrobenzoyl chloride, and the separated di-*p*-nitrobenzoate was collected and crystallised from alcohol. It had m. p. 103° either alone or mixed with a genuine specimen of *n*-butane-1 : 3-diol di-*p*-nitrobenzoate. The presence of sodium acetate in the original hydrolysis product was established by the usual tests.

The *di-α-naphthyl urethane*, m. p. 153°, after crystallisation from acetone (Found : C, 73·2; H, 5·6. $C_{26}H_{24}O_4N_2$ requires C, 72·9; H, 5·65%), of the diol was prepared in the usual manner from α-naphthyl *iso*cyanate.

4-*Acetoxytetrahydro-γ-pyran* (II, R = Ac). This had b. p. 47·5°/1 mm. (Found : C, 58·3; H, 8·55; OAc, 40·90. $C_7H_{12}O_3$ requires C, 58·3; H, 8·3; OAc, 40·97%). The *ester* (14 g.) was hydrolysed by keeping at room temperature with 250 c.c. of saturated baryta for 2 hrs., a homogeneous solution resulting. The excess baryta was just neutralised with ½N-sulphuric acid and evaporated to " dryness " on a steam-bath. Anhydrous potassium carbonate was added to the residue, which was then extracted with dry acetone. The acetone solution was dried over anhydrous potassium carbonate. Distillation of the residue from the acetone solution gave 4-*hydroxytetrahydro-γ-pyran*, b. p. 60·5/0·7 mm., as a colourless viscous liquid (Found : C, 59·4; H, 9·7. $C_5H_{10}O_2$ requires C, 58·8; H, 9·8%). Its p-*nitrobenzoate* had m. p. 69° after crystallisation from ligroin (b. p. 40—60°) containing a little ether (Found : N, 5·8. $C_{12}H_{13}O_5N$ requires N, 5·6%.

To a mixture of 5 g. of the secondary alcohol, 20 c.c. of water, and 5 g. of concentrated sulphuric acid, 5 g. of sodium dichromate (= 1 atom of oxygen) were added in small successive portions without cooling. The mixture was gently warmed until the colour of the dichromate was destroyed. The cooled mixture was neutralised with anhydrous sodium carbonate, and the product extracted with ether. Distillation of the residue from the dried ethereal solution gave tetrahydro-γ-pyrone, b. p. 73°/20 mm. (Borsche, *loc. cit.*, gives b. p. 67—68°/18 mm.), as a liquid with a pleasant evergreen odour (Found : C, 59·5; H, 8·4. Calc. for $C_5H_8O_2$: C, 60·0; H, 8·0%). It was characterised and identified as its 2 : 4-*dinitrophenylhydrazone*, m. p. 186—187°, after crystallisation from alcohol (Found : C, 47·1; H, 4·3; N, 19·6.

$C_{11}H_{12}O_5N_4$ requires C, 47·1; H, 4·3; N, 20·0%), its 4-phenylsemicarbazone, m. p. 171·5° (Borsche, *loc. cit.*, gives m. p. 169°), and its 2 : 6-dibenzylidene derivative, m. p. 186° (Borsche, *loc. cit.*, gives m. p. 185°).

Oxidation of this ketone, the secondary alcohol, or its acetate with nitric acid (1 : 1) and evaporation of the solution to dryness affords β-carboxymethoxypropionic acid, m. p. 97°, after crystallisation from ether–ligroin (b. p. 40—60°) (Borsche, *loc. cit.*, gives m. p. 93—94°) (Found : C, 40·7; H, 5·40; equiv., by titration, 77·5. Calc. for $C_5H_8O_5$: C, 40·5; H, 5·4%; equiv., 74). The *amide*, prepared through the acid chloride, crystallised from dry alcohol, m. p. 174°, but was difficult to separate from the ammonium chloride (Found : C, 41·6; H, 7·6. $C_5H_{10}O_3N_2$ requires C, 41·1; H, 6·9%). Esterification with methyl alcohol and dry hydrogen chloride gave the *dimethyl* ester, b. p. 138°/24 mm. (Found : C, 48·1; H, 6·9. $C_7H_{12}O_5$ requires C, 47·7; H, 6·8%), converted by methyl-alcoholic ammonia into the above amide, m. p. 174°, and, from the mother-liquor (probably) the *methyl ester amide*, m. p. 73°, after crystallisation from ether (Found : C, 45·6; H, 6·75; N, 8·5. $C_6H_{11}O_4N$ requires C, 44·7; H, 6·8; N, 8·7%).

A small quantity of the acid was warmed with a few c.c. of hydriodic acid (*d* 1·7) for 36 hours on a steam-bath. Evaporation of the liquor gave a residue which crystallised in a vacuum desiccator. Crystallisation from light petroleum (b. p. 40—60°) gave β-iodopropionic acid, m. p. 85° either alone or mixed with a genuine sample.

In agreement with its structure, the $C_5H_8O_5$ acid distilled unchanged without anhydride formation. The m. p. (95°) of β-hydroxyglutaric acid was depressed to 65—85° by admixture with (VI). The isomeric α-carboxymethoxypropionic acid was prepared by the method of Jungfleisch and Godchot (*loc. cit.*), who describe it as having m. p. *ca.* 30°. This acid is exceedingly hygroscopic, but a specimen carefully dried over phosphoric oxide readily crystallised from dry benzene, the m. p. thus being raised to 69°.

Repeated attempts to synthesise β-carboxymethoxypropionic acid by the action of methyl iodoacetate on the sodium derivative of methyl hydracrylate failed, probably because the action of sodium on methyl hydracrylate is more complex than simple substitution at the hydroxyl group. Condensation of ethyl β-iodopropionate with the product of the action of sodium on methyl glycollate afforded ethyl acrylate as the sole product.

Although no specimen of tetrahydro-γ-pyrone was available for direct mixed m. p. comparisons with the derivatives of the ketone $C_5H_8O_2$, the identity of the physical constants with those given by Borsche place its structure beyond reasonable doubt.

Condensation of n-*Butane*-1 : 3-*diol with Formaldehyde in Acetic–Sulphuric Acid Medium.*—The diol (20 g.) was added dropwise with mechanical stirring to a mixture of 88 g. of 100% acetic acid, 11·8 g. of 100% sulphuric acid, and 4·4 g. of paraformaldehyde maintained at 35°. Stirring was continued for 2 hrs., and the product was then neutralised and worked up as in the case of the reaction with propylene. Fractional distillation of the product by means of the column described on p. 300 gave *ca.* 1 g. of the cyclic formal, b. p. 21°/16 mm., and then a sharp rise to the diacetate, b. p. 72—73°/0·8 mm. (12 g.). A further 2·5 g., b. p. 105°/18 mm., were obtained by distillation of the residue and column hold-up from a fractionating Claisen flask. The two diacetate fractions both had Ac, 48·0% (Calc. : 49·4%), and the presence of an acetate in the hydrolysis products was confirmed in the usual manner.

No trace of the monoacetate, b. p. 47·5°/1 mm., was obtained.

Use of Boron Trifluoride as a Catalyst.—Boron trifluoride, prepared by heating a mixture of 69 g. of potassium borofluoride, 10 g. of boric anhydride, and 60 c.c. of concentrated sulphuric acid, was washed with concentrated sulphuric acid saturated with boric anhydride and absorbed in 100% acetic acid. No attempt was made to determine the concentration of boron trifluoride in the fuming liquid thus obtained, but the same solution was used in all the comparative experiments. Propylene was passed from a graduated gas-holder into a solution of 1 g. of paraform in 10 c.c. of this solution to which had been added the appropriate quantity of 100% sulphuric acid. The reaction vessel was shaken in a small, water-tight bath through which water from a thermostat at 35° was circulated. The results are in Table II. The volumes of olefin were not corrected for temperature and pressure in this trial series of experiments.

The author thanks Messrs. Imperial Chemical Industries Ltd. (Dyestuffs Division) for assistance in the prosecution of this work.

THE UNIVERSITY, LEEDS.

[*Received, March* 21*st*, 1944.]