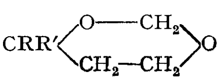
21. *α-Methylenic Reactivity in Olefinic Systems. Part III. The Prins Reaction with Ethylene and α-Methylstyrene.*

By John W. Baker.

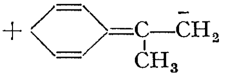
Ethylene reacts very slowly and incompletely with a mixture of 100% acetic–sulphuric acids and trioxymethylene at 80° to give a small yield of the diacetate of trimethylene glycol and a *substance*, b. p. 125°/0·8 mm., of the same empirical composition and acetyl content. α-Methylstyrene reacts readily at 0° with the same mixture to give the *diacetate*, b. p. 142°/0·5 mm., and the cyclic *formal*, m. p. 42°, of 3-*phenylbutane*-1 : 3-*diol* (cf. Part I, *J.*, 1944, 296), together with the isomeric *substances A*, m. p. 202°, and *B*, m. p. 128°, the theoretically possible structures of which it has not been possible to establish experimentally. α-Methylenic activity in the olefin is structurally impossible in ethylene and, as expected, seems to be suppressed in α-methylstyrene. The effect of structural conditions in the olefin on the yield of the 1 : 3-diol in the Prins reaction is briefly discussed.

It was shown in Part I (*J.*, 1944, 296) that propylene reacts with formaldehyde and acetic–sulphuric acids under the conditions of the Prins reaction to give three products : two of these, the cyclic formal (I; R = Me, R′ = H) and the diacetate (II; R = Me, R′ = H) of butane-1 : 3-diol, are produced by acid-catalysed addition to the olefinic double bond, but the third, 4-acetoxytetrahydro-γ-pyran (III; R = H) involves the direct reaction of the α-methylenic hydrogen activated by the hyperconjugation $\mathrm{H{-}\overset{\curvearrowright}{C}{-}C{=}\overset{\curvearrowright}{C}}$.

The investigation has now been extended to include the corresponding reaction with the olefins ethylene and α-methylstyrene. In the former such hyperconjugation is structurally impossible, whilst in the latter it might be expected to be greatly diminished owing to the

(I.) 

CRR'(OAc)·CH_2·CH_2·OAc (II.)

relative importance of structures of the type  in the resonance hybrid of the compound. On the other hand, polarisation of the olefinic double bond, , in the aromatic olefin should be enhanced, and its activity thus increased. With these two olefins the Prins reaction is much less clear cut, and the products less well defined, than with propylene. Under conditions (Part I) in which propylene was rapidly absorbed and the reaction with trioxymethylene proceeded to completion, ethylene is absorbed very slowly, and reaction with the formaldehyde is very incomplete. Raising the reaction temperature to *ca.* 80°, replacement of 100% by 113% sulphuric acid, illumination, addition of mercuric salts, boron trifluoride, platinum black, or benzoyl peroxide, were all without effect in increasing the speed of absorption. A small amount of crude reaction product (23 g.) was obtained by bubbling ethylene, under slight pressure, for several days into the trioxymethylene–100% acetic–sulphuric acid reaction mixture maintained at 60—70°. Repeated fractional distillation of the crude product gave, in addition to a large number of intermediate fractions, three distinct fractions: (1) b. p. 66°/20 mm., (2) b. p. 67°/1 mm. and (3) b. p. 125°/0·8 mm. Fraction (1) is methylene diacetate obtained by simple reaction between the formaldehyde and acetic acid. Fraction (2) is essentially trimethylene glycol diacetate (II; R = R' = H) since it is hydrolysed by 2N-sodium hydroxide to sodium acetate and trimethylene glycol, characterised as its di-*p*-nitrobenzoate, m. p. 119°. The diacetate, although analysing correctly, is, however, contaminated with about 1·8% of formaldehyde, or some product which gives formaldehyde by hydrolysis with a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. Separation from this impurity was not possible with the quantities available. It is possible that the contaminant may be the cyclic formal (I; R = R' = H) since, although no pure fraction of this composition was isolated, analogy with the propylene reaction suggests that it is a likely product. Some support is given to this view by the observation that pure synthetic trimethylene glycol diacetate, deliberately contaminated with dissolved trioxymethylene, could be recovered free from carbonyl activity by fractional distillation.

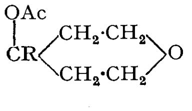
All attempts to identify fraction (3) have failed. It is an acetate and has an empirical composition almost identical with that of trimethylene glycol diacetate. Hydrolysis gives sodium acetate, corresponding to an acetyl content the same as in (2), together with a *product*, m. p. 197° (Found: C, 50·25; H, 9·59%). No structure of molecular complexity consistent with its relatively high boiling point, its analyses, and the composition of its hydrolysis product has yet been devised. Like fraction (2) it is also contaminated with about 1·2% of a formaldehyde product. Such contaminations are not surprising in view of the large excess of trioxymethylene present, owing to the very incomplete nature of the reaction.

Thus, as expected, the reactivity of ethylene is much lower than that of propylene, and the only identified product is that which arises from an acid-catalysed addition to the double bond.

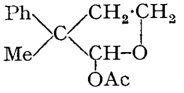
Rapid reaction occurs when α-methylstyrene is added dropwise to a well-stirred mixture of trioxymethylene with 100% acetic–sulphuric acids at 40°, and examination of the products showed that considerable polymerisation of the olefin had occurred. Better results were obtained at 0°, although unreacted α-methylstyrene was then recovered from the products. These were again less well defined and difficult to purify and characterise. After isolation of the 40° reaction products in the usual manner, a small amount of a crystalline *substance* (A), m. p. 202°, of composition $C_{13}H_{16}O_3$, separated out. This product was not isolated from the products of reaction at 0°, repeated fractional distillation of which gave the following fractions: unchanged α-methylstyrene, b. p. 50·5°/18 mm.; a fraction, b. p. 86—88°/0·6 mm., from which the crystalline *formal*, m. p. 42°, of 3-phenylbutane-1 : 3-diol (I, R = Ph; R' = Me) was isolated; a fraction, b. p. 125—132°/0·6 mm., which partly crystallised to yield a *substance* (B), m. p. 128°, isomeric with (A), and a fraction, b. p. 142°/0·5 mm., which is essentially the *diacetate* of 3-phenylbutane-1 : 3-diol (II; R = Ph, R' = Me), contaminated with a small amount of a formaldehyde-containing impurity. A considerable amount of a residual viscous brown gum, probably polymeric products of the original olefin, remained in the distillation flask.

The formal is stable towards alkaline hydrolysis, but readily chars with acid hydrolysing agents. Hydrolysis with 40% sulphuric acid affords formaldehyde, characterised as its 2 : 4-dinitrophenylhydrazone, but no derivative of the corresponding diol could be isolated. The resulting unsaturated viscous gummy products suggest that the diol undergoes dehydration and polymerisation, since similar intractable products were obtained by the action of aqueous alkali on 1-*chloro*-3-*phenylbutan*-3-*ol*, synthesised by the action of methylmagnesium iodide on phenyl 2-chloroethyl ketone (Hale and Britton, *J. Amer. Chem. Soc.*, **1919**, **41**, 845; cf. Kenner and Statham, *J.*, **1935**, 301).

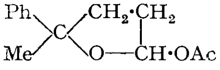
The crystalline isomerides (A) and (B) have not yet been identified. Both compounds are extremely resistant to boiling alkali, but all acid reagents, even hot concentrated hydrochloric acid, cause excessive charring with elimination of formaldehyde and the production of intractable gums. Short treatment of (B) with boiling concentrated hydrochloric acid gave a rose-red solution (suggesting a furan derivative) and a black gummy product from which a small amount of pure crystalline material, m. p. 202°, identical with (A) was isolated. Interconversion of (A) and (B) thus seems to be possible. The analysis figures for these substances agree with those required for the monoacetate (III; R = Ph), analogous to the tetrahydropyran derivative obtained in the reaction with propylene and involving α-methylenic reaction of the olefin, but the existence of *two* isomeric compounds is difficult to reconcile with this view. In an attempt to synthesis such a compound, tetrahydro-γ-pyrone (Part I, p. 300) was converted by phenylmagnesium bromide into 4-hydroxy-4-phenyltetrahydropyran, but all attempts to convert this into its acetate (even with keten) failed, the carbinol being recovered unchanged. Other possibilities for (A) and (B) are the tetrahydrofuran structures (IV)—(VI).



(III.)



(IV.)



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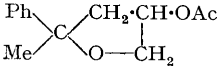
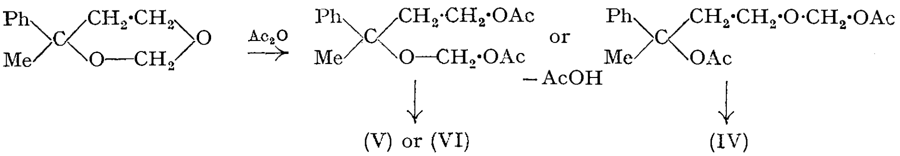
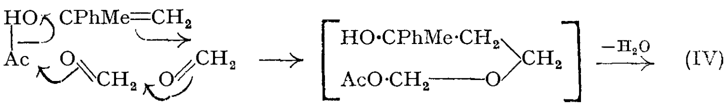


(VI.)

These might arise by ring closure resulting from elimination of acetic acid from various acetoxymethyl ether acetates derived by the action of acetic anhydride–sulphuric acid on the cyclic formal, a reaction established for the formals of aliphatic glycols by Senkus (*J. Amer. Chem. Soc.*, **1946**, **68**, 734), thus :



Alternatively (IV) might be obtained directly from the olefin by the reaction



These views would account for the existence of isomeric compounds, but the action of acetic anhydride and one drop of concentrated sulphuric acid on the pure formal, m. p. 42°, caused a vigorous exothermic reaction, much darkening, and the production of a golden-yellow gum which failed to crystallise even after being seeded with compounds (A) and (B).

In the Prins reaction, α-methylstyrene thus exhibits the expected increased reactivity in reactions which involve addition by electrophilic reagents to the double bond, whilst any reaction involving the methyl group hydrogen is very doubtful.

It is of interest to consider the structural conditions in the olefin which, in the Prins reaction, favour acid-catalysed addition to the double bond. The polarisation $\mathrm{CR'R''}\overset{\curvearrowright}{=}\mathrm{CH_2}$ would be expected to be an important factor. If, owing to the nature of R′ and R″, such activation is too great, the incursion of self-polymerisation side-reactions might restrict the yield of the 1 : 3-diol diacetate.

The following experimental data bear out this conclusion. In consequence of the small polarisation of the double bond, ethylene reacts very slowly and incompletely giving a very small yield of the 1 : 3-diacetate. In propylene the increased polarisation arising from a methyl substituent, by both its inductive and hyperconjugation effects, causes facile reaction and greatly increased yield of the 1 : 3-diacetate, and similar conditions account for the ready reaction of styrene (Prins, *Chem. Weekblad*, **1918**, **16**, 1510; Fourneau and Benoist, *Bull. Soc. chim.*, 1930, **47**, 860) and but-2-ene (private information kindly supplied by Messrs. Imperial Chemical Industries Ltd., Dyestuffs Division, Manchester). The accumulation of strongly electron-releasing groups at one end of the double bond will cause large polarisation, and may so activate the double bond that other condensation or polymerisation reactions may occur very readily under the conditions of the Prins reaction. In such cases, although absorption of the olefin occurs readily, the yields of the 1 : 3-diacetate are poor, and large amounts of complex high-boiling or water-soluble products result. α-Methylstyrene provides an example (this communication), and others have been observed by Messrs. Imperial Chemical Industries Ltd. (private communication), who have also observed that 2-chlorobut-2-ene undergoes the Prins reaction. In the last example the usual deactivating influence of an α-chlorine substituent towards electrophilic addition to the double bond is evidently counterbalanced by the activating polar effect of the methyl substituents. It would seem probable, therefore, that for an olefin to give satisfactory yields of the diacetate of the 1 : 3-diol in the Prins reaction the substituent groups should be of such a polar character as to ensure sufficient but not excessive polarisation of the double bond, *i.e.*, that the olefin should be of the type $CHR'{:}CH_2$ or $CHR'{:}CHR''$, where $R' =$ alkyl or aryl and $R'' =$ alkyl or hydrogen.

EXPERIMENTAL.

Reaction with Ethylene.—Ethylene, stored in a gasometer over water, was dried by passage through phosphoric oxide and was passed under slight pressure into a mixture of 100% acetic acid (105 g.), 100% sulphuric acid (15·5 g.), and trioxymethylene (16·5 g.) maintained at 35° and shaken mechanically, using the technique previously described for propylene (Part I, *loc. cit.*). Absorption of ethylene was very slow, and neither raising the temperature to *ca.* 100° nor the other devices described in the introduction increased the absorption. The small amount of product (23 g.) investigated was obtained by slowly bubbling ethylene (14—15 l.) through a similar mixture in a flask fitted with a mechanical stirrer and heated to 65—70° for 24—30 hours, and working up the combined products of several runs in the manner described in Part I. Air was passed through the isolated crude product at room temperature to remove as much as possible of the remaining quantity of free formaldehyde. Repeated fractional distillation of the product (using the column described in Part I during the earlier stages of the distillation) gave a large number of intermediate fractions and three fractions which seemed to have constant boiling points : (1) b. p. 66°/20 mm.; (2) b. p. 67°/1 mm.; and (3) b. p. 125°/0·8 mm.

Fraction (1). The boiling point and analytical data (Found : C, 45·96; H, 6·1. Calc. for $C_5H_8O_4$: C, 45·5; H, 6·0%) show that this fraction is essentially methylene diacetate. Apart from confirmation that sodium acetate (usual tests) was produced by alkaline hydrolysis, it was not examined further.

Fraction (2). This consists essentially of trimethylene glycol diacetate (Found : C, 52·3; H, 7·7. Calc. for $C_7H_{12}O_4$: C, 52·5; H, 7·5%). The ester (2 g.) was hydrolysed with excess (15 c.c.) of 1·9N-sodium hydroxide at 40° for 15 minutes, and the homogeneous solution so obtained was exactly neutralised with dilute sulphuric acid and evaporated to dryness first on the steam-bath and then in a vacuum desiccator. The residue was extracted with boiling, dry acetone, the extract dried (K_2CO_3), and the solvent removed. The syrupy residue (0·6 g.) was converted into a di-*p*-nitrobenzoate which, after crystallisation from ether, had m. p. 119°, either alone or mixed with a genuine specimen of trimethylene glycol di-*p*-nitrobenzoate (Found : C, 54·6; H, 3·8. Calc. for $C_{17}H_{14}O_8N_2$: C, 54·6; H, 3·7%). The solid hydrolysis residue was sodium acetate (usual tests). Quantitative hydrolysis of 0·2777 g. of fraction (2) gave acetic acid equivalent to 5·84 c.c. of 0·501N-sulphuric acid, corresponding to only 1·69 acetyl groups per molecule. Corrected for the formaldehyde-containing impurity (see below), this was raised to 1·78. Hydrolysis of 0·2346 g. of fraction (2) with 20 c.c. of water and 50 c.c. of a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid gave only 0·0297 g. of a 2 : 4-dinitrophenylhydrazone corresponding to a formaldehyde content of only 1·8%.

Fraction (3). The fraction, b. p. 123—126°/0·8 mm. (Found : C, 52·5; H, 7·13%), gave the same analysis figures as did fraction (3), b. p. 125°/0·8 mm., obtained by refractionation of this run [Found : C, 52·6; H, 7·16. $(C_7H_{12}O_4)_x$ requires C, 52·5; H, 7·5%]. Quantitative alkaline hydrolysis of 0·3548 g. gave acetic acid equivalent to 7·30 c.c. of 0·501N-sulphuric acid, corresponding to an acetyl content identical with that in fraction (2). Similarly, 0·2966 g. gave only 0·0250 g. of formaldehyde 2 : 4-dinitrophenylhydrazone, representing only 1·2% of formaldehyde impurity. Hydrolysis of 0·65 g. of fraction (3) with warm 1·9N-sodium hydroxide until a homogeneous solution was obtained, and isolation of the alcohol as described above, gave a syrup which crystallised. After crystallisation from acetone-benzene this *substance* had m. p. 192° (Found : C, 50·25; H, 9·59. Calc. for $C_{15}H_{34}O_9$: C, 50·25; H, 9·57%). The presence of acetate in the hydrolysate was proved by the usual tests. No structure could be assigned to either the acetate or its hydrolysis product.

Reaction with α-Methylstyrene.—Crude α-methylstyrene (kindly supplied by courtesy of Messrs. Imperial Chemical Industries Ltd. from British Resin Products) was fractionated, using an efficient column, and the fraction, b. p. 65·5—67°/28 mm., was used. Experiments at 40° and 0° were carried out in a similar manner, and only the latter will be described. α-Methylstyrene (32·5 g.) was added dropwise over a period of 0·5 hour to a mechanically-stirred mixture of 100% acetic acid (105 g.), 100% sulphuric acid (16·5 g.), and trioxymethylene (16·5 g.), cooled at 0°. After stirring had been continued for 0·5 hour the product was neutralised with hydrated sodium carbonate and worked up in the usual manner; yield, 53 g. of a pale yellow liquid. At a reaction temperature of 40° the product (50 g.) slowly deposited 0·5 g. of crystalline material. This, after crystallisation from methyl alcohol gave *substance* (A), m. p. 202° (decomp.) (Found: C, 70·75; H, 7·3. $C_{13}H_{16}O_3$ requires C, 71·0; H, 7·3%).

Repeated fractional distillation of the combined products gave the following fractions: (1) b. p. 50·5°/18 mm.; (2) b. p. 86—88°/0·6 mm.; (3) b. p. 125—132°/0·6 mm.; and (4) b. p. 142°/0·5 mm.

Fraction (1). The b. p., odour, and degree of unsaturation of this fraction showed that it was mainly unchanged olefin, although analysis proved it to be impure (Found: C, 87·2; H, 10·1. Calc. for C_9H_{10}: C, 91·5; H, 8·5%).

Fraction (2). This fraction partly crystallised. Crystallisation of the solid portion from ligroin (b. p. 40—60°) at 0° gave the *formal*, m. p. 42°, of 3-phenylbutane-1 : 3-diol (Found: C, 74·4; H, 7·9. $C_{11}H_{10}O_2$ requires C, 74·1; H, 7·9%).

All attempts to hydrolyse this formal with alkaline reagents (*e.g.*, boiling 4N-sodium hydroxide for 8 hours) gave only unchanged material. Acid reagents charred the formal. Hydrolysis with warm 40% sulphuric acid for a few minutes gave an odour of formaldehyde. The hydrolysate was diluted with water and extracted with ether. The aqueous liquors were partly neutralised with ammonia, buffered with sodium acetate, and treated with 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. The precipitated 2 : 4-dinitrophenylhydrazone, after crystallisation from alcohol, had m. p. 166° either alone or mixed with a genuine specimen of formaldehyde 2 : 4-dinitrophenylhydrazone. The ether extract contained mainly unchanged material. Longer hydrolysis with 40% sulphuric acid gave only a golden-yellow gum from which no crystalline derivative of 3-phenylbutane-1 : 3-diol could be prepared.

Attempted Synthesis of 3-*Phenylbutane*-1 : 3-*diol*.—Phenyl 2-chloroethyl ketone (8·4 g.) (Hale and Britton, *J. Amer. Chem. Soc.*, 1919, **41**, 845; cf. Kenner and Statham, *J.*, 1935, 301), cooled to 0°, was treated dropwise with the Grignard solution obtained from 1·2 g. of magnesium and 7·1 g. of methyl iodide in dry ether. The product was decomposed with ice and ammonium chloride, extracted with ether, washed, and dried (Na_2SO_4). Distillation of the residue from the dried ether extract gave 1-*chloro*-3-*phenylbutan*-3-*ol*, b. p. 96°/0·5 mm. (Found: C, 65·5; H, 7·1; Cl, 20·1. $C_{10}H_{13}OCl$ requires C, 65·0; H, 7·0; Cl, 19·2%). Attempts to hydrolyse this chloride with aqueous potassium hydroxide in the cold gave similar intractable material from which no di-*p*-nitrobenzoate could be prepared. An attempt to prepare the hydroxy-ester direct from the chloride with sodium *p*-nitrobenzoate and potassium iodide at 150° (cf. Fourneau and Ramart-Lucas, *Bull. Soc. chim.*, 1920, **27**, 550) was also unsuccessful.

Fraction (3). This fraction also crystallised. After draining on porous procelain the clean solid was crystallised from ether to give *substance* (B), m. p. 128° (Found: C, 70·7; H, 7·4. $C_{13}H_{16}O_3$ requires C, 71·0; H, 7·3%). It is thus isomeric with substance (A). Substance (B) is also stable to boiling aqueous alkali, but readily chars with all acid reagents. Warming with 50% sulphuric acid gave intense charring and a pungent odour of formaldehyde. Substance (B) (0·8 g.) was boiled with 8 c.c. of concentrated hydrochloric acid under reflux for 10 minutes. The solution went pink, and black gummy material separated. The cooled solution was extracted with ether (purple aqueous layer which became turbid on dilution). The ether extracts were washed successively with sodium carbonate and water, and dried (Na_2SO_4). The black oily residue (*ca.* 0·7 g.) from the dried ether extract partly crystallised. After draining on porous porcelain the crystalline material was crystallised twice from methyl alcohol, with addition of animal charcoal, and gave substance (A), m. p. 202° (decomp.) either alone or mixed with a genuine specimen.

Fraction (4). This is essentially 3-*phenylbutane*-1 : 3-*diacetate* (Found: C, 68·3; H, 7·4. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%), but it is contaminated with a little impurity which yields an odour of formaldehyde when warmed with 50% sulphuric acid. The diacetate (1—2 g.) was refluxed with alcoholic potassium hydroxide for 4—5 hours. The mixture was evaporated to dryness on the steam-bath and extracted with dry acetone. The brown viscous gum from the acetone extract was converted into a *p*-nitrobenzoate with *p*-nitrobenzoyl chloride and aqueous sodium hydroxide, warmed in the alkaline solution to dissolve any *p*-nitrobenzoic anhydride, and extracted with ether. Crystallisation from ether–ligroin (b. p. 40—60°) of the product from the ether extract gave a small quantity of material, m. p. 104°, which seemed to be an impure specimen of the *di*-p-*nitrobenzoate* of the 1 : 3-diol (Found: C, 63·1; H, 5·6; N, 5·6. $C_{24}H_{20}O_8N_2$ requires C, 62·1; H, 4·3; N, 6·0%). The presence of potassium acetate in the hydrolysate was proved by the usual tests.

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