CXXIV.—*Action of Magnesium Phenyl Haloids on Diphenylchloroacetyl Chloride. Constitution of Triphenylvinyl Alcohol.*

By ALEX. MCKENZIE and JOHN SCOTT WALKER BOYLE.

THE chlorine atom in α -chloro- α -phenylpropionic acid undergoes substitution by the hydroxyl group with great readiness, even when the acid is shaken with water at the ordinary temperature (McKenzie and Clough, T., 1910, **97**, 1016), whilst the chlorine in diphenylchloroacetic acid is very easily removed by magnesium phenyl bromide (McKenzie, Drew, and Martin, T., 1915, **107**, 26).

It was accordingly anticipated that diphenylchloroacetyl chloride might display abnormality when acted on by Grignard reagents, and the experiments of which a description is now given show that this expectation was borne out.

In the event of triphenylacetyl chloride being produced by the substitution of the phenyl group for chlorine, thus :

the product should be β -benzopinacolin, since Schmidlin (*Ber.*, 1910, **43**, 1137) has shown that the change,

can be effected. On no occasion, however, did we obtain either β -benzopinacolin or pentaphenylethanol when diphenylchloroacetyl chloride was acted on by magnesium phenyl bromide. On the other hand, when the acid chloride was added to an excess of the Grignard reagent, the main product was triphenylvinyl alcohol, a curious result which is to be attributed to a novel application of the Grignard reagent involving the transient existence of a keten. This explanation is by no means improbable when Schmidlin's observation of the formation of triphenylmethyl by the action of magnesium phenyl iodide on triphenylacetyl chloride is recalled :

Just as in the case investigated by us, the Grignard reagent here splits off halogen from the acid chloride, behaving in the same way as certain metals; molecular silver, for instance, gives triphenylmethyl with triphenylacetyl chloride,

whilst Staudinger obtained diphenylketen from zinc and diphenylchloroacetyl chloride, $\begin{array}{c} \text{Ph} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Ph} \end{array} < \begin{array}{c} \text{Cl} \\ \diagup \\ \text{COCl} \end{array} + \text{Zn} = \begin{array}{c} \text{Ph} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Ph} \end{array} \text{:CO} + \text{ZnCl}_2.$

A parallel action on the splitting off of halogen by the Grignard reagent is also quoted by Schmidlin and v. Escher (*Ber.*, 1910, **43**, 1153), who, in attempting to form hexaphenylethane, found that two chlorine atoms are withdrawn from the molecule of *s*-dichlorotetraphenylethane :

(compare Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2940).

The formation of triphenylvinyl alcohol is probably due to the following changes :

Assuming the intermediate production of diphenylketen, the formation of triphenylvinyl alcohol is readily understood, since Staudinger (*Annalen*, 1907, **356**, 122) obtained the latter compound by acting on diphenylketen with magnesium phenyl bromide, but for valid reasons he does not interpret the action on the basis of equation (b), where the keten is represented to act as if it contained a carbonyl group. Ketens are not ketones, their reactions being explained by the initial addition of reacting material to the ethylenic linking. But Staudinger's formulation,

is nevertheless difficult to accept, since Kohler and others have shown that the Grignard reagent never adds on to an ethylenic linking in the 1:2-position. It may be noted in this connexion that Gilman and Heckert (*J. Amer. Chem. Soc.*, 1920, **42**, 1010) describe the action of benzoyl chloride on the additive compound of diphenylketen with magnesium phenyl bromide. If Staudinger's view were correct, then a 1:3-diketone, namely, diphenyldibenzoylmethane, should be produced :

On the other hand, if the mechanism expressed in (b) be correct, then :

Since the benzoate of triphenylvinyl alcohol was isolated, it was held by the American authors that the Grignard reagent does, after all, add on to the carbonyl group.

The assumption involved in equation (a) receives further support from the following considerations.

(1) Diphenyl is always formed in the preparation of magnesium phenyl bromide, but the amount of it can be lessened if an excess of magnesium is employed in preparing the reagent. Although this device was adopted throughout the present work, the amount of diphenyl isolated from the products of the reactions was greater than would have been expected had it been formed in the making of the reagent alone. On this ground equation (a), which involves the production of diphenyl, is preferred to the alternative scheme :

(2) When the experimental conditions were altered so that the Grignard reagent was added very slowly to an ice-cold ethereal solution of the chloro-chloride, the course of the reaction was quite different from that followed when the materials were added in the reverse order. The ethereal solution, after decomposition with ice and mineral acid, assumed an orange-red tint, and this is the appearance of diphenylketen. The main product of the action was in this case not triphenylvinyl alcohol but a plastic, brown, amorphous product, which gradually solidified to a hard mass resembling aldehyde-resin and doubtless consisted of polymerised diphenylketen. Staudinger mentions that diphenylketen resinifies completely at 250°, but although we did not at any point have the temperature so high as this, it is nevertheless likely that polymerisation may have been induced by catalytic influences, more especially since during the preparation of ketens by means of zinc it is occasionally found that the zinc haloid behaves as a polymerising agent. Since the conditions were such that in the early stages of the action there was a large excess of the acid chloride, the liberated keten, instead of combining with the Grignard reagent, may have undergone rapid polymerisation by the acid chloride itself, Staudinger having shown that acid chlorides, such as benzoyl chloride, polymerise diphenylketen. Staudinger and his pupils (*Ber.*, 1911, **44**, 530; *Annalen*, 1911, **384**, 109; *Ber.*, 1914, **47**, 41) have isolated three polymerides of diphenylketen melting respectively at 244–245°, 176°, and 188°, and of these three the constitution only of the first, diketotetraphenylcyclobutane, has been determined. As a rule, however, diphenylketen gives resins when heated with condensing agents such as zinc chloride or sodium acetate. We extracted the small quantity of triphenylvinyl alcohol contained in our resin by means of petroleum, but no definite compound was obtained from the residue left after the extraction.

(3) Under the experimental conditions of (2), a product sparingly soluble in ether was obtained in relatively small amount. It melted at 256.5–257.5°, and its analysis suggested that it was an additive compound of diphenylketen and triphenylvinyl alcohol. It is well known that ketens have the property of adding on to unsaturated compounds with the formation of tetramethylene derivatives (although this conception of their structure is not accepted by Schröter), and Staudinger and Suter (*Ber.*, 1920, **53**, 1092) have shown that certain ethylenic compounds combine with diphenylketen to form what are regarded as cyclobutanone derivatives, styrene, for instance, giving the substance, $\begin{array}{c} \text{CHPh} \cdot \text{CH}_2 \\ \text{CO} - \text{CPh}_2 \end{array}$. Possibly, therefore, the compound isolated from the action of magnesium

phenyl bromide on diphenylchloroacetyl chloride has the formula $\text{CPh}_2\cdot\text{CPh}\cdot\text{OH}$, but further work would be necessary before this $\text{CO}-\text{CPh}_2$ point could be established definitely.

Constitution of Triphenylvinyl Alcohol.

Triphenylvinyl alcohol presents many interesting features from the point of view of desmotropism. Delacre (*Bull. Soc. chim.*, 1895, [iii], **13**, 857) and Gardeur (*Bull. Acad. roy. Belg.*, 1897, [iii], **34**, 67) formulated the compound obtained by the action of aluminium chloride on trichloroacetyl chloride and benzene as triphenylethanone (I).

Doubt was thrown on the validity of this formula by Biltz (*Ber.*, 1899, **32**, 650; *Annalen*, 1897, **296**, 242), whose arguments in favour of the structure (II) were so cogent that the designation triphenylvinyl alcohol has been almost universally adopted until quite recently. Biltz's grounds were briefly as follows. The compound is not triphenylacetaldehyde (III), since it forms neither an oxime nor a phenylhydrazone, and it does not undergo oxidation to triphenylacetic acid. The occurrence of benzophenone and benzoic acid as products of the oxidation pointed rather to (II) being correct; moreover, the addition of the elements of water effected by boiling with alcoholic sodium hydroxide gave diphenylmethane and benzoic acid. The analogy with diphenylvinyl alcohol (Breuer and Zincke, *Annalen*, 1879, **198**, 182; Claisen, *Ber.*, 1892, **25**, 1781) was close, since this substance on oxidation also gave benzophenone, whilst diphenylmethane was also formed by boiling with alcoholic potassium hydroxide. Moreover, if the replacement of two hydrogen atoms in vinyl alcohol by two phenyl groups directly attached to a carbon atom leads to the hydroxymethylene type, it is all the more likely that the introduction of a third phenyl group would impart still greater stability, and triphenylvinyl alcohol should not only be capable of a separate existence, but should be stable. The fourth possibility (IV) of triphenylethylene oxide is excluded by Biltz on the ground that the compound in question forms both an acetyl and a benzoyl derivative. The fact that triphenylvinyl alcohol does not give a urethane falls into line with the observation of Knoevenagel that many alcohols, for example, triphenylcarbinol, do not react with

phenylcarbimide. Moreover, the hydroxylic structure of triphenylvinyl alcohol is supported by its absorption in the molten state of electric waves of high frequency.

The structure (II) was accepted by Staudinger (*loc. cit.*), Anschütz and Förster (*Annalen*, 1909, **368**, 89), Tiffeneau (*Compt. rend.*, 1908, **146**, 31), and by McKenzie and Wren (*T.*, 1910, **97**, 474). On the other hand, Kohler (*Amer. Chem. J.*, 1906, **36**, 177) reverts to formula (I) on two grounds; the formation of acyl derivatives, on which the argument for (II) is largely based, is invalidated by the fact that ketones can be acylated (Lees, *T.*, 1903, **83**, 152), whilst the behaviour towards magnesium ethyl bromide shows that the compound acts as a ketone, giving the corresponding tertiary alcohol. Orékhoff (*Bull. Soc. chim.*, 1919, [iv], **25**, 9, 186) examined the action of magnesium phenyl bromide and of magnesium benzyl chloride, and drew the same conclusion as Kohler.

Lately Meyer and Gottlieb-Billroth (*Ber.*, 1921, **54**, [B], 575) describe the conversion of phenyldiphenylene-ethanone into the isomeric phenyldiphenylenevinyl alcohol. Since the latter compound behaves as a normal enol, inasmuch as when freshly prepared it dissolves in cold dilute alkali, whilst its alcoholic solution decolorises bromine immediately, the conclusion is drawn that (I) is correct. The tendency for triphenylethanone to undergo enolisation is extremely slight, no enolisation being caused by alcoholic potassium hydroxide.

The chief grounds for reverting to (I) appear to be the insolubility in alkali and the behaviour towards Grignard reagents. An allelotropic mixture such as ethyl acetoacetate reacts towards Grignard reagents as if it were entirely enolic (Grignard, *Ann. Chim. Phys.*, 1902, [vii], **27**, 548; McKenzie, *T.*, 1906, **89**, 365). Now triphenylvinyl alcohol, reacting according to (II), would give an additive compound when acted on by magnesium phenyl bromide, and the original substance would be regenerated on treatment of the additive compound with water. If the original substance were triphenylethanone, and if it had any tendency at all to undergo isomeric change into triphenylvinyl alcohol, the result would be the same, if triphenylethanone and triphenylvinyl alcohol were to behave like other isomerides that have been investigated from this point of view.

We accordingly repeated the action of magnesium phenyl bromide on triphenylvinyl alcohol, since the yield of *s*-tetraphenylethanol quoted by Orékhoff is smaller than would have been expected if one had to deal with triphenylethanone only, and since no details of the yield of tetraphenylpropan- β -ol are given by Orékhoff. We first employed magnesium phenyl bromide (3 mols.) for triphenyl-

ethanone (1 mol.), three times the calculated quantity; nevertheless, much of the original material was recovered. The action was more complete, however, when six molecular proportions of the Grignard reagent were employed. These results would point to the conclusion that if (I) is the correct formula, the reactivity of the carbonyl group is impaired just as it is in β -benzopinacolin. That we have to deal with a hydroxylic compound which under the influence of the Grignard reagent is slowly converted into a ketone which then reacts normally, is extremely improbable.

The balance of the evidence is certainly strongly in favour of the representation as triphenylethanone, but until further proof is given that the objections raised by Biltz are invalid, we do not go so far as Orékhoff and Meyer, who advocate that the term triphenylvinyl alcohol should now be deleted from the literature.

EXPERIMENTAL.

Action of Magnesium Phenyl Bromide on Diphenylchloroacetyl Chloride.

The following details, which are of importance for the successful preparation of diphenylchloroacetyl chloride, may be added to the descriptions of Bickel (*Ber.*, 1889, **22**, 1539) and of Staudinger (*Annalen*, 1907, **356**, 72). The oil resulting from the action of phosphorus pentachloride on benzilic acid is poured on to ice contained in a flat dish of such size that a thin layer of the acid chloride is exposed to the action of water. When, after frequent stirring, the oil has solidified, it is powdered under ice-cold water, and the whole allowed to remain overnight in the ice-chest. The solid is then separated, washed with water and with light petroleum, and dried over paraffin wax under diminished pressure. In a typical preparation, using 50 grams of phosphorus pentachloride (2 mols.) and 27.5 grams of benzilic acid (1 mol.), the yield of crude product was 30 grams. This was crystallised from 150 c.c. of light petroleum (b. p. 40–50°). The crystals melted at 48.5–49.5°, whereas Bickel gives 50°. The yield was 21 grams, 68 per cent. of the theoretical.

A solution of 40 grams of diphenylchloroacetyl chloride (1 mol.) in 100 c.c. of ether was gradually added within an interval of thirty-five minutes to the Grignard reagent prepared from 144 grams of bromobenzene (6 mols.), 400 c.c. of ether, and 48 grams of magnesium. The vigorous reaction was attended by the appearance of a green coloration in the solution. After boiling briskly for half-an-hour, the product was treated with ice and sulphuric acid in the usual manner. Overnight the colourless, crystalline solid

in suspension between the two layers was separated and washed with a little ether, in which it is sparingly soluble. It amounted to 22 grams and melted at $134-135.5^{\circ}$. The ethereal layer was extracted with sodium hydroxide to remove the phenol and free acid present, the ether removed, and the residue distilled in a current of steam, when 13.3 grams of diphenyl were obtained. The residue, after removal of the diphenyl, was extracted with petroleum (b. p. $80-90^{\circ}$), and from the petroleum extract 7 grams of a product melting at $126-130^{\circ}$ were obtained. The 29 grams of crude crystalline material were crystallised from petroleum (b. p. $80-105^{\circ}$), when colourless needles melting at $135-136^{\circ}$ separated. They contained no halogen, and gave the brilliant emerald-green coloration with concentrated sulphuric acid which is characteristic of triphenylvinyl alcohol. The molecular weight determined in benzene solution by the boiling point method gave the value 267 (calc. 272) (Found: C=88.1; H=6.0. Calc., C=88.2; H=5.9 per cent.). The yield of pure product was 58 per cent. of the theoretical.

The action takes a different course when the Grignard reagent is added to the chloro-chloride under the following conditions. An ethereal solution of magnesium phenyl bromide prepared from 84 grams of bromobenzene ($3\frac{1}{2}$ mols.), 250 c.c. of ether, and 28 grams of magnesium, was gradually siphoned within an interval of four and a half hours into a solution of 40 grams of diphenylchloroacetyl chloride (1 mol.) in 100 c.c. of ether. The flask was immersed in ice-cold water during the addition of the chloro-chloride, when two layers gradually separated, the upper layer being pale brown in tint and the lower layer dark brown. After forty hours, the decomposition was conducted as before, and in this case the ethereal layer assumed a bright orange tint, and a yellow, oily layer separated between the ethereal and aqueous layers. After five days, this oily layer solidified. It amounted to 4.5 grams and apparently contained no triphenylvinyl alcohol, since it gave only a pale brown coloration with concentrated sulphuric acid. It was crystallised several times from benzene, from which it separated sluggishly in tiny prisms, and melted at $256.5-257.5^{\circ}$. It was free from halogen, and was sparingly soluble in ethyl alcohol, ether, or light petroleum (Found: C=88.0; H=5.8. $C_{34}H_{26}O_2$ requires C=87.6; H=5.6 per cent.).

The quantity of diphenyl obtained from the ethereal layer was 12.8 grams. The main product of the action amounted to 37 grams, and on cooling after the removal of the diphenyl it was plastic, but gradually set to a brown, hard, amorphous mass with the appearance of aldehyde-resin. All attempts to isolate a definite

product from it failed. With concentrated sulphuric acid at the ordinary temperature a trace of the substance first became dark red, and on gently warming green. Apparently a trace of triphenylvinyl alcohol was present, but after extraction with boiling petroleum the residue still gave no definite compound.

Action of Magnesium Phenyl Iodide on Diphenylchloroacetyl Chloride.

Since Schmidlin has shown that the behaviour of magnesium phenyl bromide and magnesium phenyl iodide on triphenylacetyl chloride is different, and since Gomberg obtained pentaphenylethanol from β -benzopinacolin by using magnesium phenyl iodide in place of the bromide, the following experiments were carried out.

A solution of 13 grams of diphenylchloroacetyl chloride (1 mol.) in 50 c.c. of ether was acted on as before with magnesium phenyl iodide, prepared from 60 grams of phenyl iodide (6 mols.), the chloro-chloride being added to the Grignard reagent. After decomposition with ice and sulphuric acid, the solid in suspension was removed and found to consist of pure triphenylvinyl alcohol (4.1 grams). The ethereal layer contained dissolved iodine, which was removed with sodium hydrogen sulphite, and the free acids were removed as well as the diphenyl. The residue from the ether was a brown, plastic mass (7.2 grams), from which 4 grams of crude triphenylvinyl alcohol were extracted by boiling petroleum.

A solution of 13 grams of diphenylchloroacetyl chloride (1 mol.) in 50 c.c. of ether was siphoned within an interval of four hours into a solution of magnesium phenyl iodide prepared from 35 grams of phenyl iodide ($3\frac{1}{2}$ mols.). When the addition was complete, the upper layer was orange-red and the lower layer reddish-brown. On remaining at the ordinary temperature, iodine was gradually liberated. After ninety hours, the manipulation was conducted as before. The resin produced in this case amounted to 13 grams, and contained very little triphenylvinyl alcohol.

Action of Magnesium Phenyl Bromide on Triphenylvinyl Alcohol.

Assuming that triphenylvinyl alcohol reacts in its desmotropic form, triphenylethanone, only one molecular proportion of magnesium phenyl bromide would be required to form the additive compound, $\text{Ph}_2\text{CH}\cdot\text{CPh}_2(\text{OMgBr})$. Although in the following experiment an excess (3 mols.) of Grignard reagent was employed, a considerable quantity of the triphenylvinyl alcohol was recovered.

Powdered triphenylvinyl alcohol (24 grams, 1 mol.), prepared by the dehydration of triphenylethylene glycol, was gradually

added within an interval of twenty minutes to the Grignard reagent prepared from 42 grams of bromobenzene (3 mols.). Heating was then carried out for four hours, and the product decomposed as usual. The solid in suspension amounted to 26 grams and consisted largely of triphenylvinyl alcohol, of which 9 grams of the pure product were isolated by extraction with petroleum (b. p. 80—90°). The residue after extraction with petroleum was crystallised from benzene, when 3 grams of $\alpha\alpha\beta\beta$ -tetraphenylethyl alcohol separated in colourless needles which melted at 232.5—233°, whereas Orékhoff (*loc. cit.*) gives 235—236° (Found: C=88.9; H=6.5. Calc., C=89.1; H=6.3 per cent.).

An additional 2 grams were also isolated, whilst from the ethereal solution in which the solid had been suspended a small quantity of triphenylvinyl alcohol was also obtained.

When a larger excess of magnesium phenyl bromide was employed and when the heating after the addition of the reagent was prolonged for seven hours, the proportion of triphenylvinyl alcohol in the product was much smaller than was the case in the experiment just quoted. Twenty grams of triphenylvinyl alcohol (1 mol.) were heated for seven hours with a solution of magnesium phenyl bromide prepared from 70 grams of bromobenzene (6 mols.). The amount of solid which remained undissolved after the addition of ice and sulphuric acid was in this case only 8.7 grams, and the proportion of $\alpha\alpha\beta\beta$ -tetraphenylethyl alcohol in this solid product was much greater than before. The product from the ethereal solution contained very little triphenylvinyl alcohol.

The authors desire to express their thanks to the Carnegie Trust for a grant in aid of this research.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

[Received, June 1st, 1921.]