

CXLII.—*Action of Grignard Reagents on Methyl l-Methoxysuccinate, Methyl Maleate, and Maleic Anhydride.*

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It has been shown in the preceding paper that magnesium methyl iodide and magnesium phenyl bromide act on methyl *d*-dimethoxy-succinate in the same manner as on unsubstituted succinic esters. Magnesium methyl iodide gives  $\gamma\delta$ -dimethoxy- $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol, and the phenyl bromide yields 3:4-dimethoxy-2:2:5:5-tetraphenyltetrahydrofuran. The etheric methoxyl groups are not attacked in either case, and the products are therefore optically active.

We find that the action of magnesium methyl iodide on methyl *l*-methoxysuccinate is similar to that of the same reagent on the dimethoxy-ester, the product being optically active  $\gamma$ -methoxy- $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol,  $\text{HO}\cdot\text{CMe}_2\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ . The glycol, however, could not be obtained in the pure state. The product, being a liquid, was isolated by distillation in a vacuum, and this caused partial dehydration. By distillation under atmospheric pressure, complete dehydration was effected, and the final product obtained was the oxide of the glycol (a furan derivative), or possibly an isomeric unsaturated alcohol. In acetone solution, the compound gave  $[\alpha]_D + 44.9^\circ$ . Calculating the rotatory power of the glycol in acetone solution from that of a mixture with the anhydride, the approximate composition of which was determined by the results of analysis, the value should be about  $[\alpha]_D + 35^\circ$ . The initial ester being levorotatory, the conversion of ester into glycol results in a change of sign of rotation. This is also the case in the production of the corresponding dimethoxy-glycol from the dimethoxy-ester (see the preceding paper). But whilst the conversion of the latter glycol into its oxide brings about a second reversal of the sign, in the dehydration of the mono-methoxy-glycol the sign remains the same. This difference is not in agreement with the usual optical effect of ring formation, and suggests that the dehydration referred to above proceeds on different lines, giving possibly an unsaturated alcohol.

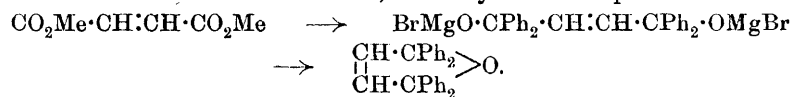
The action of magnesium phenyl bromide on methyl *l*-methoxy succinate proved to be more complex than that of magnesium methyl iodide. Two crystalline compounds were isolated from the product of the reaction, having respectively the composition  $\text{C}_{23}\text{H}_{22}\text{O}$  (m. p.  $190\text{--}191^\circ$ ) and  $\text{C}_{22}\text{H}_{18}\text{O}_2$  (m. p.  $160\text{--}161^\circ$ ), but

neither contained methoxyl, and both were optically inactive. The former substance was found to be 2:2:5:5-tetraphenyl-2:5-dihydrofuran,  $\begin{array}{c} \text{CH}\cdot\text{CPh}_2 \\ | \\ \text{CH}\cdot\text{CPh}_2 \end{array} > \text{O}$ , and the latter a triphenylbutyrolactone.

The unsaturated character of the dihydrofuran derivative was exhibited in its behaviour towards bromine, with which it readily combined, and by its rapidly decolorising cold alkaline permanganate solution. The constitution was deduced from the following observations. Oxidation by boiling dilute alkaline permanganate solutions gave benzophenone. Distillation with zinc dust, according to Baeyer's process, gave a hydrocarbon,  $\text{C}_{28}\text{H}_{20}$  (m. p. 157—158°), and reduction of this with sodium and amyl alcohol gave the  $\alpha\alpha\delta\delta$ -tetraphenylbutane,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHPh}_2$ , which Valeur (*Bull. Soc. chim.*, 1903, [iii], **29**, 683) obtained similarly from tetraphenylbutadiene,  $\text{CPh}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CPh}_2$ . The hydrocarbon  $\text{C}_{28}\text{H}_{20}$  agrees in melting point and composition with a hydrocarbon obtained by Buttenberg (*Annalen*, 1894, **279**, 329) from the action of concentrated sulphuric acid on  $\beta\beta$ -diphenylvinyl ether,  $\text{CPh}_2\cdot\text{CH}\cdot\text{OEt}$ , and the substances are presumably identical. The only formula for the hydrocarbon, consistent with the result of its reduction, as given above, with the molecular weight found by us, and with Buttenberg's method of preparation, appears to be  $\text{CPh}_2\cdot\text{C}\cdot\text{C}\cdot\text{CPh}_2$ .

The constitution of the dihydrofuran derivative suggested that the disappearance of the methoxyl group was due to the abstraction of a molecule of methyl alcohol from the monomethoxysuccinate with the production of a maleic or fumaric ester or other derivative, which was then further acted on by the Grignard reagent. We accordingly examined the action of magnesium phenyl bromide on methyl fumarate and maleate and on maleic anhydride.

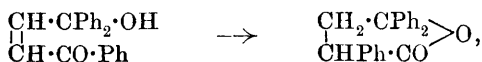
Methyl fumarate gave an uncrystallisable syrup, the examination of which yielded no definite result. Methyl maleate, however, gave the same tetraphenyldihydrofuran which has been already described. The reaction is of a normal kind, and may be thus represented:



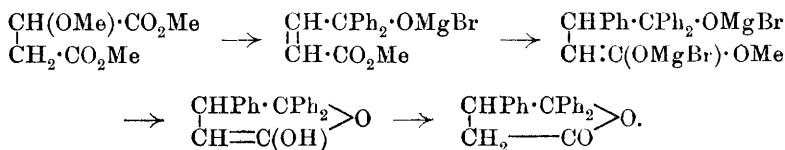
It appears therefore that in the case of methyl methoxysuccinate, methyl alcohol is split off from the ester at the outset, or at an early stage, of the Grignard reaction, which otherwise follows the normal course. The second product of the action of magnesium phenyl bromide on methyl methoxysuccinate has been already referred to as triphenylbutyrolactone (m. p. 160—161°); we assign a lactonic structure to the compound on the following grounds.

The substance showed neither alcoholic nor ketonic properties, and it behaved as a saturated compound. It dissolved sparingly, and only on prolonged boiling, in aqueous potassium hydroxide and ammonia solutions. It was, however, converted by boiling alcoholic potash into a potassium salt, which, after removal of the alcohol, dissolved completely in water. The aqueous solution of the salt gave with mineral acids a white, flocculent precipitate, which was soluble with effervescence in cold sodium carbonate solution, and was doubtless hydroxytriphenylbutyric acid. The precipitated acid, after being dried at 90°, melted at 140—145°, and still decomposed warm sodium carbonate solution, but after being heated for an hour at 130°, it was no longer soluble in sodium carbonate, and then showed the melting point of the original substance, 160°.

With respect to the position of the three phenyl groups, we regard the compound provisionally as  $\beta\gamma\gamma$ -triphenylbutyrolactone, for the following reasons. As the substance gives benzophenone on oxidation, two of the phenyl groups must be attached to the same carbon atom, and without assumption of improbable transposition, this can only be the  $\gamma$ -carbon atom. The phenyl groups must therefore be in the  $\alpha\gamma\gamma$ - or  $\beta\gamma\gamma$ -positions. The former constitution implies a transposition of the following kind:



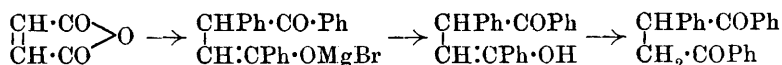
which is certainly not improbable. A  $\beta\gamma\gamma$ -lactone, however, might result normally from the Grignard reaction according to the following scheme:



The addition of the Grignard reagent is here supposed to take effect in the 1: 4-position, which Kohler has found to be a common mode of action with unsaturated ketones and esters (*Amer. Chem. J.*, 1904, **31**, 642, etc.).\* We failed to obtain evidence of this mode of addition in the case of methyl maleate, but we find, on the other hand, that maleic anhydride reacts with magnesium phenyl bromide, probably in the manner in question, the product being A. Smith's

\* If direct addition of the Grignard reagent to the two unsaturated carbon atoms occurs, then either an  $\alpha\gamma\gamma$ - or  $\beta\gamma\gamma$ -lactone might be formed. The action is, in other respects, like that described by Shibata in the case of the phthalic esters (*Trans.*, 1909, **95**, 1449).

desylacetophenone (Trans., 1890, **57**, 643). The action may be formulated thus:



The triphenylbutyrolactone (m. p. 160—161°) sublimes unchanged when heated alone under diminished pressure, but when heated with mineral acids it is converted nearly quantitatively into an isomeric lactone, melting at 197°. The latter substance resembled the former in giving benzophenone on oxidation, in its behaviour as a saturated compound, and in its insolubility in cold alkali hydroxide solutions. It dissolved, however, much more readily than the former lactone in boiling aqueous potassium hydroxide and ammonia solutions, and the acid which was precipitated on acidification—presumably a triphenylhydroxybutyric acid—lost its solubility in sodium carbonate, and regained the original melting point, 197°, on being simply dried in a vacuum without heating. The solution of the potassium salt coagulated to a jelly on cooling, which redissolved on sufficient water being added. A silver salt of the corresponding hydroxy-acid was precipitated on adding silver nitrate to an ammonia solution of the lactone after the excess of ammonia had been boiled off. After being dried at 100°, it gave  $\text{Ag} = 24.87$ ;  $\text{C}_{22}\text{H}_{19}\text{O}_3\text{Ag}$  requires  $\text{Ag} = 24.59$  per cent. The production of the lactone just described might be accounted for by the migration of a phenyl group, but we refrain from discussing the nature of the isomeric change until the two lactones and the acids derivable from them have been further examined.

#### EXPERIMENTAL.

The methyl *l*-methoxysuccinate used in the following experiments was obtained by methylating methyl malate by means of dry silver oxide and methyl iodide.

The boiling point of the liquid ester was 135°/42 mm., and it gave  $[\alpha]_{\text{D}}^{15} - 54.2^\circ$ .

#### *Action of Magnesium Methyl Iodide on Methyl l-Methoxysuccinate.*

Preliminary experiments showed that the product of the action was an uncrystallisable oil. Using four molecular proportions of the Grignard reagent to one of the ester, the carbon content of the distilled product indicated that the action was incomplete, but with excess of the reagent, a liquid of lower boiling point was obtained having approximately the composition of an anhydride of the ditertiary glycol, which was expected to result from the

reaction. In the following experiment, therefore, an excess of the Grignard reagent was employed.

Ten grams of the ester (1 mol.), dissolved in ether, were added slowly to an ethereal solution of magnesium methyl iodide, prepared from 10 grams (7.4 atoms) of magnesium. After the brisk reaction which ensued had subsided, the mixture was heated for three hours on a water-bath, and thereafter decomposed in the usual way with dilute sulphuric acid. The product was then thoroughly extracted with ether. The dried ethereal solution gave, on evaporation, a brownish oil, which was distilled under diminished pressure. Some water was produced during the distillation, presumably from decomposition of the glycol, and 10 grams of a colourless, mobile liquid, with a camphoraceous odour, were collected at 60—90°/90 mm. After distilling this twice, a fraction (b. p. 63—64°/33 mm.), weighing 4.5 grams, was obtained, which gave, in acetone solution,  $[\alpha]_D^{20} + 42.5^\circ$  ( $c = 2.2336$ ), and on analysis C = 66.75, H = 11.36, OMe = 19.3. The expected ditertiary glycol,  $C_8H_{17}O_2(OMe)$ , requires C = 61.36, H = 11.36, OMe = 17.61 per cent.; its anhydride,  $C_{18}H_{15}O(OMe)$ , requires C = 68.35, H = 11.39, OMe = 19.62 per cent.

The liquid was presumably a mixture of the ditertiary glycol and its oxide, the latter having been produced by the elimination of water in the course of the distillation. As it was found that but little increase of the carbon content was brought about by further distillation under diminished pressure, the liquid was now distilled under the atmospheric pressure. A fraction collected after two distillations (b. p. 150—151°) gave C = 67.88, H = 11.39, OMe = 19.17.

The substance is therefore a dehydration product of the glycol,  $\gamma$ -methoxy- $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol. A cryoscopic determination of the molecular weight in benzene solution gave 152;  $C_8H_{15}O(OMe)$  requires 158. The specific rotation in acetone solution was  $[\alpha]_D^{20} 44.9^\circ$ ,  $c = 3.9185$ ,  $l = 2$ .

*Action of Magnesium Phenyl Bromide on Methyl l-Methoxy-succinate.*

The conditions observed in the following experiment were found to be the most advantageous in respect of the yield of crystalline product. Thirty grams of the ester (1 mol.) in ethereal solution were added slowly to an ethereal solution of the Grignard reagent prepared from 33 grams of magnesium (8 atoms) and 215 grams of bromobenzene (8 mols.) A vigorous reaction occurred. After remaining twelve hours at the ordinary temperature, the mixture was treated with ice-cold dilute sulphuric acid in the usual manner. On evaporating the ethereal layer, successive crops of crystals were deposited, in all 44 grams, which were found to consist of two

substances melting at 190—191° and 160—161° respectively. The separation of these was effected by dissolving each of the crops in benzene and adding one and a-half times as much ether to each solution. This treatment precipitated the much less soluble compound of higher melting point, and, on concentrating the mother liquors, the compound melting at the lower temperature was deposited. By systematic repetition of the process, 7.5 grams of each substance were obtained nearly pure; the remaining material consisted mostly of the compound (m. p. 160—161°), which was the main crystalline product of the reaction.

As already stated, the compound melting at 190—191° is 2:2:5:5-tetraphenyl-2:5-dihydrofuran, and the compound melting at 160—161° a triphenylbutyrolactone.

2:2:5:5-Tetraphenyl-2:5-dihydrofuran crystallises from a mixture of benzene and ether in fine needles. It is moderately soluble in cold benzene, sparingly so in cold alcohol, acetone, or petroleum of high boiling point, but fairly soluble in the hot solvents, and almost insoluble in boiling ether. It crystallises unchanged from hot glacial acetic acid:

Found, C=89.56; H=6.00.

$C_{28}H_{22}O$  requires C=89.84; H=5.88 per cent.

The following observations are in accord with the constitution assigned to the compound. A 6 per cent. solution in benzene at 40° was optically inactive. On applying Zeisel's process for estimating methoxyl to a solution of the substance in acetic anhydride, no silver iodide was formed, even when the temperature was raised to 130°. An alcoholic solution of the compound reduced alkaline permanganate instantly in the cold. On adding bromine (2 atoms) in carbon disulphide solution to the compound (1 mol.) in the same solvent, an additive compound was evidently formed, as the colour of the bromine disappeared quickly in the dark, and a crop of yellow, acicular crystals was deposited. On attempting to recrystallise the substance, however, decomposition occurred with liberation of hydrogen bromide, and estimation of bromine in different preparations gave varying figures approximating to those required for a monobromo-derivative.

Oxidation of the furan derivative with a boiling dilute alkaline solution of potassium permanganate gave benzophenone. The product was isolated by distillation in a current of steam, and was identified by its melting point (48°), and by that of the phenyl-hydrazone prepared from it (136°).

The reduction of the compound was effected by distilling 9.5 grams with zinc dust in a current of hydrogen at a temperature considerably below a red heat. The distillate solidified, on cooling, to

an amber-coloured glass, which was deposited in a crystalline state from a solution in a mixture of ethyl alcohol and ether. After three crystallisations from this medium, 2.4 grams of colourless, rectangular plates were obtained, melting at 157—158°. The substance was sparingly soluble in alcohol, readily so in ether, benzene, or chloroform, and decolorised cold alkaline permanganate instantly:

Found, (I) C=93.85; H=5.80. (II) C=94.17; H=5.94.

$C_{28}H_{20}$  requires C=94.38; H=5.62 per cent.

The molecular weight in chloroform solution, determined by the ebullioscopic method, was 364.  $C_{28}H_{20}$  requires 356.

One gram of the hydrocarbon was dissolved in 50 c.c. of boiling amyl alcohol, and 10 grams of sodium were added in small pieces. The hot solution was then poured into a mixture of 400 c.c. of water and 7 grams of glacial acetic acid. The alcoholic layer, evaporated under diminished pressure to half its bulk, gave 0.4 gram of crystalline, rectangular plates, which, after being recrystallised from ethyl alcohol, melted at 121°. The substance resembled stilbene, but it was found that admixture with pure stilbene caused a considerable lowering of the melting point, and, moreover, it decolorised cold dilute alkaline permanganate only after some time. (Found, C=92.47; H=6.93. Calc., C=92.82; H=7.18 per cent.) This hydrocarbon, as already stated, is  $\alpha\alpha\delta\delta$ -tetraphenylbutane.

*Triphenylbutyrolactone* (m. p. 160—161°), which was isolated, as already described, from the crude product of the action of the Grignard reagent, crystallises in microscopic needles. It is readily soluble in cold acetone or chloroform, moderately so in cold ether, sparingly so in cold alcohol and benzene, but fairly soluble in the latter solvents when hot. At 200°/20 mm. it sublimes unchanged in beautiful prisms:

Found, (I) C=83.85; H=6.01. (II) C=83.91; H=5.98.

$C_{22}H_{18}O_2$  requires C=84.08; H=5.73 per cent.

The molecular weight in chloroform solution, determined by the ebullioscopic method, was 337.  $C_{22}H_{18}O_2$  requires 314.

The compound was optically inactive. Only a trace of silver iodide was formed when 2 grams of it were heated with hydriodic acid for one and a-half hours according to Zeisel's process. It was not affected by heating with an alcoholic solution of hydroxylamine for nine hours at 160°, by boiling for three hours with acetyl chloride, or by shaking with benzoyl chloride and sodium hydroxide solution. In each case, the substance was recovered unchanged after the treatment. It decolorised an alkaline solution of potassium permanganate in the cold only slowly, and it was recovered unaltered after being twelve hours in contact with bromine in carbon disulphide solution. Oxidation with boiling dilute alkaline per-



manganate solution gave benzophenone, which was identified by conversion into the oxime. The lactonic behaviour of the compound has been already described.

*Action of Mineral Acids on Triphenylbutyrolactone*  
(m. p. 160—161°).

In testing for methoxyl by Zeisel's method in an impure fraction obtained by crystallising the crude product of the Grignard reagent, 2 grams of the material, melting about 140°, were boiled with hydriodic acid (D 1·7) for one and a-half hours. The residual solid from this treatment, after being washed with water and a little alcohol, and recrystallised from benzene, weighed 1·6 grams, and now melted at 192—196°. Similar treatment of the pure triphenyl-lactone (m. p. 160—161°) showed that the change of melting point was due to the apparently quantitative conversion of this compound into an isomeric lactone, melting at 197°. The same change occurred when the lactone of lower melting point was heated with concentrated hydrochloric acid in a sealed tube, or with sulphuric acid (70 per cent. by volume) for two hours at 140°.

*Triphenylbutyrolactone* (m. p. 197°) crystallises from chloroform or benzene in well-defined, prismatic needles. It is insoluble in water, moderately soluble in cold ether and acetone and in hot benzene, readily so in hot chloroform, but sparingly soluble in the two latter solvents or alcohol when cold. The compound proved to be optically inactive:

Found, (I) C=84·22; H=5·89. (II) C=84·10; H=5·81.

C<sub>22</sub>H<sub>18</sub>O<sub>2</sub> requires C=84·08; H=5·73 per cent.

By oxidation with boiling dilute alkaline permanganate solution, 1 gram of the substance gave 0·4 gram, nearly the calculated yield, of benzophenone (m. p. 47—49°). Baeyer's permanganate test showed that the compound was saturated, and this was confirmed by its resistance to a cold solution of bromine in carbon disulphide. After being in the bromine solution for twelve hours, the compound was recovered unchanged. The lactonic properties of the substance have been already described in the introduction.

*Action of Magnesium Phenyl Bromide on Methyl Maleate.*

Methyl maleate was prepared by the interaction of methyl iodide and silver maleate, the latter being obtained from maleic anhydride. Twenty grams of the anhydride gave 23 grams of the ester (b. p. 201—205°).

Ten grams of methyl maleate (1 mol.) were treated with magnesium phenyl bromide obtained from 6·7 grams of magnesium



(4 atoms) and 44 grams of bromobenzene (4 mols.). The procedure was the same as in the previous cases. After the spontaneous vigorous action had subsided, the mixture was heated for an hour on the water-bath, and then treated in the usual manner. The ethereal layer, on evaporation, left a syrup which deposited crystalline matter after some time. The syrup having been removed by stirring the product with a little ether, 2 grams of residual solid were collected and recrystallised by dissolving it in benzene and adding ether. By repeating the process, 1.2 grams of pure substance were obtained in fine, colourless needles, which melted sharply at  $190^{\circ}$ . The solubilities of the compound, the melting point, and the results of analysis showed it to be the same 2:2:5:5-tetra-phenyl-2:5-dihydrofuran already described as one of the products of the action of the Grignard reagent on methyl methoxysuccinate. (Found, C=89.41; H=6.14. Calc., C=89.84; H=5.88 per cent.)

The syrup which constituted the main product of the reaction was distilled under diminished pressure, but diphenyl was the only crystalline substance found in it. The syrup was boiled with hydriodic acid in the hope that the lactone (m. p.  $197^{\circ}$ ) might be produced, but without result.

#### *Action of Magnesium Phenyl Bromide on Maleic Anhydride.*

The method pursued was the same as in the action with methyl maleate. The materials were 10 grams of maleic anhydride (1 mol.) and magnesium phenyl bromide prepared from 11 grams of magnesium (4.5 atoms) and 72 grams of bromobenzene (4.5 molecules). The reaction was vigorous, and was moderated by cooling in ice. The mixture was heated for an hour after spontaneous action had ceased, and was then treated in the usual manner. The oil, left on evaporating the ethereal extract, soon deposited crystalline matter, which was collected and washed with a little alcohol. The total isolated product consisted of 10 grams of nearly pure crystalline substance, and about an equal weight of uncrystallisable oil. The crystals, after being once recrystallised from alcohol containing a few drops of acetic acid and once from absolute alcohol, melted sharply at  $126-127^{\circ}$ . (Found, C=84.16; H=5.93.  $C_{22}H_{18}O_2$  requires C=84.08; H=5.73 per cent.)

The substance was therefore isomeric with the two lactones previously described, but its insolubility in potassium hydroxide solution on long boiling showed that its character was neither acidic nor lactonic. It proved to be identical with A. Smith's desylaceto-phenone (Trans., 1890, 57, 643) ( $\alpha\delta$ -diketo- $\alpha\beta\delta$ -triphenylbutane), which he found to be converted into 2:4:5-triphenylfuran (m. p.  $92^{\circ}$ ) by cold concentrated sulphuric acid. On following Smith's

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directions, we obtained from our product by the action of sulphuric acid a crop of acicular crystals which melted at  $92^{\circ}$ , and otherwise resembled the furan derivative referred to. The identity was confirmed by analysis. (Found, C=88.85; H=5.62. Calc., C=89.19; H=5.41 per cent.)

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