free gallic acid after the fermentation with yeast X was completed and the gallotannin had become optically inactive.

To test whether *m*-digallic acid is produced during the fermentation, 10 g. of gallotannin was fermented with yeast X and the ethereal extract methylated with diazomethane. The ethereal solution was investigated for methyl pentamethyl-*m*-digallate as described by Herzig[15] but no trace of this substance was detected.

Ethyl Acetate Solution.—The ethyl acetate solution is evaporated under diminished pressure and the solid left dissolved in a little water, which is removed in a vacuum at room temperature, and this latter process is repeated several times. The solid thus obtained resembles gallotannin in every respect in that it is precipitated by gelatin and quinine and is absorbed by caseinogen and hide powder. On analysis it gives 53.2% of carbon and 3.4% of hydrogen which agree with the values generally obtained for gallotannin. It is optically inactive in water, alcohol, acetone and ethyl acetate and gives no glucose on hydrolysis. The total amount of this gallotannin, when anhydrous, obtained from 129.6 g. of anhydrous gallotannin is 87.2 g., which corresponds to a yield of 65.7%.

In conclusion we wish to thank the Colston Society of the University of Bristol for a grant which has covered the expenses of this investigation.

Summary

A gallotannin is described which is prepared by the action of yeast on purified chinese gallotannin and is optically inactive and free from glucose.

BRISTOL, ENGLAND

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF BRISTOL]

THE ACTION OF DIAZOMETHANE ON SOME AROMATIC ACYL CHLORIDES. III. THE MECHANISM OF THE REACTION

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RECEIVED MARCH 18, 1925 PUBLISHED JUNE 5, 1925

In a series of communications from this[1] and the Zürich[2] Laboratories several ω-chloro-acetophenones have been described, which were prepared by the action of diazomethane on the corresponding acyl chlorides. The yields obtained by Nierenstein and his collaborators varied between 72 and 98% and it seemed therefore remarkable that only 28% of ω-bromoacetophenone is produced by the action of diazomethane on benzoyl bromide.[3]

On repeating this experiment we find that the low yield of ω-bromoacetophenone is due to the formation of 62% (average of 2 preparations) of 3,6-dibromo-3,6-diphenyl-1,4-dioxane[4] (I).

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[15] Herzig, *Ber.*, **56**, 227 (1923).

[1] (a) Clibbens and Nierenstein, *J. Chem. Soc.*, **107**, 1491 (1915). (b) Nierenstein, *ibid.*, **117**, 1153 (1920). (c) Nierenstein, Wang and Warr, THIS JOURNAL, **46**, 2554 (1924). (d) Kahil and Nierenstein, *ibid.*, **46**, 2557 (1924).

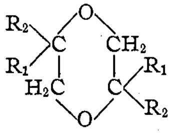
[2] Staudinger and Mächling, *Ber.*, **49**, 1973 (1916).

[3] Clibbens and Nierenstein, *J. Chem. Soc.*, **107**, 1492 (1915).

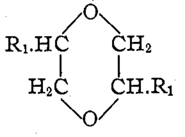
[4] The name and the numbering of this ring are taken from Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Veit and Co., **1920**, vol. I, pt. 3, p. 1149.

The constitution of Substance I is evident from its physical and chemical properties, which agree with those observed by Faworsky[5] in the case of dioxane (diethylene ether) and from the fact that it yields by the method of Grignard and Tissier[6] 3,6-diphenyl-1,4-dioxane (II), from which styrolene alcohol (III) is obtained on hydrolysis.

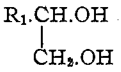
These observations suggest that the high yields obtained in the case of the ω-chloro-acetophenones probably depend on the greater mobility of the chlorine atom as compared with that of the corresponding bromine atom. That this is the case is evident from the fact that triphenyl-acetyl chloride, in which the chlorine atom is known to be remarkably immobile[7] yields 92% (average of three preparations) of 3,6-dichloro-3,6-di-[triphenylmethyl]-1,4-dioxane (IV). This latter substance gives on reduction 3,6-di-[triphenylmethyl]-1,4-dioxane (V), from which α-triphenylmethyl-α,β-dihydroxy-ethane (VI) is produced on hydrolysis.



I, IV



II, V



$$\begin{array}{l} R_1.\text{CH.OH} \\ \quad | \\ \text{CH}_2.\text{OH} \end{array}$$

III, VI

I, II, III: $R_1 = C_6H_5$; $R_2 = Br$.
IV, V, VI: $R_1 = C.(C_6H_5)_3$; $R_2 = Cl$.

The production of 92% of the dioxane IV from triphenyl-acetyl chloride is of particular interest, since phenyl- and diphenyl-acetyl chloride give 87% (average of two preparations) of α-chloro-γ-phenyl-acetone, $C_6H_5.CH_2.CO.CH_2.Cl$ and 82% (average of three preparations) α-chloro-γ,γ-diphenyl-acetone, $(C_6H_5)_2.CH_2.CO.CH_2.Cl$. These differences are in agreement with the relative immobility of the chlorine atom in triphenyl-acetyl chloride and the mobility of the chlorine atom in phenyl-acetyl chloride and diphenyl-acetyl chloride. Thus, Schmidlin and Hodgson[7] have found that 0.3068 g. of triphenyl-acetyl chloride gives 0.12 g. of unchanged chloride when heated for two hours with 10% potassium hydroxide solution. This observation was used by us as a comparative measure of the mobility of the chlorine atoms in these three acetyl chlorides. One g. of each of these three substances was heated for 30 minutes with 50 cc. of 5% potassium hydroxide solution, during which time both phenyl- and diphenyl-acetyl chloride were completely converted into the corresponding acids. Triphenyl-acetyl chloride, however, gave 0.62 g. of unchanged chloride.

Our results permit a decision between the two interpretations which have been given to this reaction by Staudinger[8] and Oliveri-Mandalà,[9]

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[5] Faworsky, *J. Russ. Phys. Chem. Soc.*, **38**, 741 (1906).

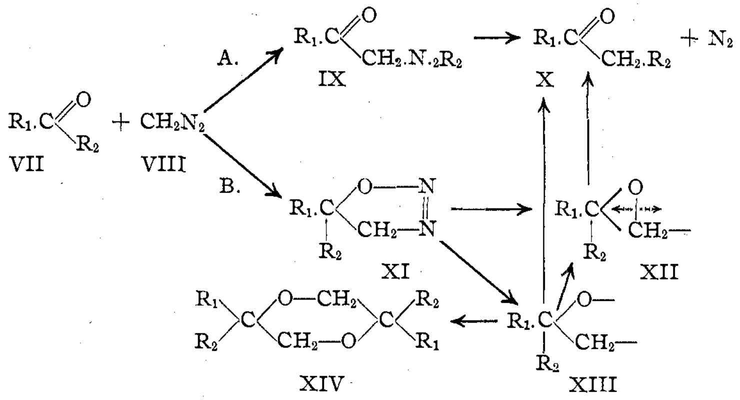
[6] Grignard and Tissier, *Compt. rend.*, **132**, 835 (1901).

[7] Compare Schmidlin and Hodgson, *Ber.*, 41, 443 (1908).

[8] Staudinger, *Helvetica chim. Acta*, **5**, 92 (1922).

[9] Oliveri-Mandalà, *Gazz. chim. ital.*, **52**, ii, 104 (1922).

respectively. These interpretations are shown in the two equations A (Staudinger) and B (Oliveri-Mandalà), in which R_2 = Cl, Br and H, so as to include the Schlotterbeck[10] reaction.



As will be seen, Equation A (Staudinger) requires the migration of R_2 before VII and VIII are joined to give IX, which is obviously not in agreement with our results. Our observations support to a great extent Equation B (Oliveri-Mandalà) which assumes the formation of XI, from which XII is produced by the loss of nitrogen, yielding X on fission and rearrangement. We are inclined towards the assumption that XIII is produced from XI through the loss of nitrogen, yielding either X or XIV, which does not, however, exclude the formation of X through the intermediary substance XII as suggested by Oliveri-Mandalà.

Experimental Part

General Procedure.—An excess of diazomethane, prepared according to the method of Staudinger and Kupfer,[11] is allowed to react on the corresponding acyl halides, dissolved in anhydrous ether (Grignard). The solid left on evaporation of the ether is powdered, mixed with dry sand (purified by washing with hydrochloric acid) and extracted in a Soxhlet apparatus with ligroin (b. p., 50–60°) and then with benzene dried over sodium. The first extraction, which dissolves only the ω-halogeno-acetophenones formed, is concluded when no solid is left on evaporation of a little of the overflowing liquid. The benzene, which is dried in the same manner, dissolves the dioxanes formed.

3,6-Dibromo-3,6-diphenyl-1,4-dioxane (I).—This substance is soluble in alcohol, benzene and chloroform and crystallizes in long needles from benzene; m. p., 159°. The alcoholic solution mixed with picric acid dissolved in alcohol gives a well-crystallizing picrate; m. p., 217°. Molecular-weight estimations carried out according to the method of Rast[12] gave 372 and 386, respectively, whereas the formula $C_{16}H_{14}O_2Br_2$ requires 398.

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[10] Schlotterbeck, *Ber.*, **40**, 479 (1907).

[11] Staudinger and Kupfer, *Ber.*, **45**, 501 (1912).

[12] Rast, *Ber.*, **55**, 1051 (1922).

Anal. Subs., 0.1625, 0.1118, 0.1987: AgBr, 0.1618, 0.1172, 0.1552. Calcd. for $C_{16}H_{14}O_2Br_2$: Br, 40.2. Found: 42.4, 40.8, 40.3.

3,6-Diphenyl-1,4-dioxane (II).—Two g. of the bromo product I dissolved in 100 cc. of dry ether (Grignard) and 0.5 g. of "activated" magnesium are heated on a water-bath, when the solution becomes deep-red in about 20 minutes; thereafter the solution is heated for another two hours. The solid left on evaporation of the ether is treated with ice and hydrochloric acid. It is then dissolved in alcohol and precipitated with water. The carefully dried substance crystallizes from benzene in colorless, pointed needles; m. p., 103°; yield, 76%. In this connection it is interesting to note that styrol oxide is a liquid that boils at 191–192° at ordinary pressure.[13] The product is soluble in the usual organic solvents and when dissolved in glacial acetic acid yields a deep yellow solution. The colorless alcoholic solution turns deep-red on the addition of a few drops of concd. hydrochloric acid. A molecular weight estimation by Rast's method gave 217, whereas the formula $C_{16}H_{16}O_2$ requires 240.

Anal. Subs., 0.1116: CO_2, 0.3269; H_2O, 0.0703. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 79.9; H, 7.0.

The *picrate* crystallizes from alcohol in strawberry-colored plates; m. p., 227°.

Anal. Subs., 0.2536: N_2 (moist.), 18.7 cc. (18°, 748 mm.). Calcd. for $C_{16}H_{16}O_2.C_6H_3O_7N_3$: N, 8.9. Found: 8.7.

The hydrolysis of Substance II to styrolene alcohol (III) is carried out as follows. A solution of 1 g. of the product in 50 cc. of benzene is refluxed on a boiling water-bath for three hours with 50 cc. of 10% potassium hydroxide solution. The aqueous layer, which is carefully extracted with ether and freed from ether and benzene by steam distillation, is acidified with dil. sulfuric acid and exhaustively extracted with ether. The solid left on evaporation of the ether crystallizes from chloroform in small needles; m. p., 67–68°. This melting point, which is in agreement with the one given in the literature for styrolene alcohol,[14] is not depressed on admixture with authentic material; yield, 62%.

3,6-Di-[triphenylmethyl]-3,6-dichloro-1,4-dioxane (IV).—This product[15] crystallizes from alcohol in faintly yellow needles; m. p., 167°. The faintly yellow alcoholic solution gives a picrate (m. p., 249–251°) on the addition of picric acid and turns deep red on the addition of a few drops of hydrochloric acid.

Anal. Subs., 0.1585: AgCl, 0.0684. Calcd. for $C_{42}H_{34}O_2Cl_2$: Cl, 11.1. Found: 10.7.

3,6-Di-[triphenylmethyl]-1,4-dioxane (V).—Two g. of Substance IV is treated in the same manner as described in the case of Substance I. The product crystallizes in small, colorless needles; m. p., 133° (decomp.); yield, 79%. It is soluble in the usual organic solvents. It yields a pink solution when dissolved in glacial acetic acid and the colorless alcoholic solution turns deep red on the addition of a few drops of concd. hydrochloric acid.

Anal. Subs., 0.1062: CO_2, 0.3415; H_2O, 0.0623. Calcd. for $C_{42}H_{36}O_2$: C, 88.0; H, 6.3. Found: C, 87.7; H, 6.6.

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[13] Tiffeneau and Fourneau, *Compt. rend.*, **146**, 697 (1908).

[14] Zincke, *Ann.*, **216**, 294 (1883). Evans and Morgan, THIS JOURNAL, **35**, 58 (1913).

[15] The triphenyl-acetic acid was prepared by the method of Schmidlin and Hodgson [*Ber.*, **41**, 438 (1908)] but it was found that only by lowering the temperature from the boiling point of the water as recommended by Schmidlin and Hodgson to about 50–60° could a good yield (79–80%) be obtained. This is in agreement with the recent observations of Gilman and Parker [THIS JOURNAL, **46**, 2817 (1924)].

The *picrate* crystallizes from alcohol in brick-colored needles that decompose at 259–263° without melting.

Anal. Subs., 0.2159: N_2 (moist.), 10.4 cc. (18°, 762 mm.). Calcd. for $C_{42}H_{36}O_2.C_6H_3O_7N_3$: N, 5.2. Found: 5.6.

α-Triphenylmethyl-α,β-dihydroxyethane (VI).—The hydrolysis of Substance V is carried out in the same manner as that described in the case of Substance II. Substance VI crystallizes from alcohol in small needles; m. p., 116°; yield, 71%.

Anal. Subs., 0.1855: CO_2, 0.5646; H_2O, 0.1046. Calcd. for $C_{21}H_{20}O_2$: C, 82.9; H, 6.6. Found: C, 83.0; H, 6.4.

The *di-p-nitrobenzoyl*-derivative crystallizes from alcohol in faintly yellow needles; m. p., 192–194° (decomp.).

Anal. Subs., 0.1141: N_2 (moist), 5.1 cc. (24°, 713 mm.). Calcd. for $C_{35}H_{26}O_8N_2$: N, 4.6 Found: 4.7.

α-Chloro-γ-phenylacetone, $C_6H_5.CH_2.CO.CH_2.Cl$, crystallizes from chloroform in star-shaped needles that melt at 72–73°, as previously found by Clibbens and Nierenstein.[16]

The *acetate* crystallizes from alcohol in thick needles; m. p., 131°.

Anal. Subs., 0.1426: CO_2, 0.3587; H_2O, 0.0808. Calcd. for $C_{11}H_{12}O_3$: C, 68.8; H, 6.2. Found: C, 68.6; H, 6.3.

α-Chloro-γ,γ-diphenylacetone, $(C_6H_5)_2.CH.CO.CH_2.Cl$, crystallizes from chloroform in small needles; m. p., 91–92°.

Anal. Subs., 0.2247: AgCl, 0.1290. Calcd. for $C_{15}H_{13}OCl$: Cl, 14.2. Found: 14.2.

The *acetate* crystallizes from alcohol in long needles; m. p., 147°.

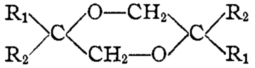
Anal. Subs., 0.1216: CO_2, 0.3389; H_2O, 0.0678. Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 76.0; H, 6.2.

In conclusion we wish to generalize as follows: All ω-chloro-acetophenones examined by us during the last ten years have the characteristic odor common to ω-chloro- and ω-bromo-acetophenones, by which they are easily differentiated from the dioxanes which are odorless. To the latter, however, are peculiar the color changes produced by the addition of acids, as already observed by Faworsky in the case of dioxane itself. Each of these factors serves as a useful preliminary guide to an understanding of the mechanism of the reaction.

Summary

It is shown that the reaction $R_1.CO.R_2 + CH_2.N_2$ may proceed in two directions giving rise to the formation of

$R_1.CO.CH_2.R_2$ or



which depends on the mobility of R_2.

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[16] Ref. 1 a, p. 1492.