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we could only isolate o-hydroxydiphenylacetic acid lactone IV whereas in the case of p-nitrothiophenol this lactone and p,p'-dinitrodiphenyldisulfide were obtained.

EXPERIMENTAL

The benzene used was dried over sodium. The CO_2 stream was produced by the action of hydrochloric acid on marble and then dried with concd. H₂SO₄.

Action of thiophenol on hexaphenylethane. A solution of hexaphenylethane was prepared by refluxing for 45 min. a solution of 3 g. (0.0108 mole) of triphenylchloromethane in 20 ml. of benzene, after addition of 8 g. of copper bronze. After filtration an orange solution of hexaphenylethane (triphenylmethyl) was obtained. Its color was discharged very rapidly after the addition of 0.6 g. (0.0054 mole) thiophenol in 5 ml. of benzene. After refluxing for 3 hr., benzene was driven off under reduced pressure leaving residue A. All these manipulations were carried out in a stream of dry CO_2 .

Residue A was extracted with 50 ml. of petroleum ether $(60-80^{\circ})$ which yielded a residue after evaporation. The residue was fractionally crystallized from alcohol. The first fraction yielded 0.9 g. triphenylphenylmercaptomethane (0.0025 mole) and on concentration 0.5 g. (0.002 mole) of triphenylmethane. These two substances were identified by melting point and mixed melting point 104° and 92° respectively, with authentic samples. The phenylmercapto derivative³ was also identified by its color reaction with concd. H₂SO₄; the substance dissolved in acetic acid gave no color reaction with sodium nitrite crystals which proved that no thiol group was present. The substance was also prepared from phenylmercury mercaptide and triphenylchloromethane.

Triphenylphenylmercaptomethane. To 0.25 g. (0.0006 mole) of bis(phenylmercapto)mercury⁴ in 25 ml. hot benzene was added 0.75 g. of (0.0027 mole) triphenylchloromethane. After heating for 90 min. in a bath (60°) followed by refluxing for 1 hr., the benzene was removed by distillation and the residue was extracted with hot benzine (60-80°). After evaporation of the benzine the residue was twice crystallized from alcohol. Triphenylphenylmercaptomethane was obtained in colorless crystals m.p. 104°, no depression with an authentic sample.³

Anal. Calcd. for $C_{25}H_{20}S$: C, 85.2; H, 5.7; S, 9.1. Found: C, 85.4; H, 5.6; S, 8.8.

Action of 9,9'-diphenyl-9,9'-bifluorenyl (I) on (a) Thiophenol. Four-tenths of a gram (0.00083 mole) of I^s and 0.2 g. (0.0018 mole) of thiophenol in 40 ml. of dry benzene were refluxed for three hours in a stream of carbon dioxide. The solvent was removed by distillation in a stream of carbon dioxide and the residue treated with 15 ml. of boiling alcohol (96%). The solution was quickly cooled in ice and then allowed to stand for 30 minutes at room temperature. The deposit (0.15 g. 0.00062 mole; m.p. $136-140^{\circ}$) yielded after crystallization from alcohol 9-phenylfluorene, melting point and mixed melting point with an authentic sample 148°. The crystals gave no color reaction with concd. sulfuric acid.

Anal. Calcd. for C₁₉H₁₄: C, 94.2; H, 5.8. Found: C, 94.0; H, 5.8.

The alcoholic filtrate was concentrated to 5 ml. whereupon crystals $(0.1 \text{ g.; m.p. 110-114}^\circ)$ were obtained which after crystallization from benzine $(60-80^\circ)$ yielded 9-phenyl9-phenylmercaptofluorene of m.p. 118°, no depression with a sample prepared according to the method described below.

(b) *Thioacetic acid*. Similarly from 0.6 g. (0.00125 mole) of I and 0.2 g. (0.0026 mole) of thioacetic acid in 50 ml. benzene

after 3 hr. of refluxing, 0.25 g. of 9-phenylfluorene were obtained, identified (after crystallization from ethyl alcohol) by melting point and mixed melting point (142°) .

9-Phenyl-9-phenylmercaptofluorene. The substance was obtained from 0.25 g. (0.00006 mole) of bis(phenylmercapto)mercury and 0.7 g. (0.0025 mole) of 9-chloro-9-phenylfluorene in 25 ml. benzene as described in the case of phenylmercaptotriphenylmethane. Pale yellow crystals, m.p. 118°, were formed, which dissolved in concd. sulfuric acid with an orange color.

Anal. Calcd. for $C_{25}H_{18}S$: C, 85.7; H, 5.1; S, 9.1. Found: C, 85.3; H, 5.1; S, 8.6.

Action of 2,2'-diketo-3,3'-diphenyl-3,3'-dicoumarinyl (II) on: (a) Thiophenol. To 0.8 g. (0.0019 mole) of (II) in 20 ml. dry chlorobenzene was added 0.2 g. (0.0019 mole) of thiophenol. After refluxing for 30 min. in stream of carbon dioxide the blue color of the hot solution was almost completely discharged. The solvent was removed in a vacuum and the residue pressed on a porous plate. A solid was obtained which after recrystallization from petroleum ether (60-80°) yielded colorless crystals 0.15 g. (0.00071 mole) which proved to be the lactone of o-hydroxyliphenylacetic acid (IV); m.p. and mixed m.p. 110-112°.

(b) $p-\tilde{N}itrothiophenol$. To 0.7 g. (0.0016 mole) of II in 20 ml. dry chlorobenzene was added 0.35 g. (0.0023 mole) of p-nitrothiophenol⁶ and the mixture was heated as above for 60 min. The yellowish green solution was evaporated to dryness in a vacuum and the residue was extracted with 20 ml. of ether. The insoluble material (0.2 g.) (0.00066 mole) was crystallized from benzene and proved by melting point (181°) and mixed melting point to be p,p-dinitrophenyl-disulfide. Evaporation of the ether yielded an oil from which 0.15 g. (0.00071 mole) of the lactone of o-hydroxydiphenyl-acetic acid was obtained; m.p. and mixed m.p. 110-112° after crystallization from petroleum ether (60-80°).

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Photochemical Reactions in Sunlight. XX. Photoreaction between Benzaldehyde and Khellinquinone

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The photochemical addition of aldehydes to p-quinones leading to the formation of ketones is known in a number of cases¹. Thus, p-benzoquinone and benzaldehyde give 1,4-dihydroxybenzophenone. A photoreaction leading to the formation of an ester seems, however, to have been observed only in the case of chloranil and benzaldehyde (ultraviolet light);² the monobenzoate of tetrachloroquinol being formed. We should like to report a second example of this type, namely, the reaction in sunlight between benzaldehyde and khellinquinone

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(2-methylfuro-4',5'-6,7-chromone-5,8-quinone) (I).³ For the structure of the reaction product, which is phenolic in character (ferric chloride reaction), the choice lies between IIa and IIb. That formula IIa is correct could be seen from the fact that methylation with ethereal diazomethane (in the absence of methyl alcohol) could be effected with the formation of IIe. Chromones with hydroxyl groups in position 5 are very resistant toward ethereal diazomethane solutions,⁴ this is believed to be due to chelation.⁵ The photo-product is soluble in aqueous alkali, while the mono-hydroxy chromones with the hydroxyl group in position 5 are not.^{4,6}



IIe could also be obtained by the treatment of 5-hydroxy-8-methoxy-2-methylfour-4',5,'6,6-chromone (IId)⁴ with benzoyl chloride in pyridine. A facile hydrolysis of IIa to IIc⁷ using dilute hydrochloric acid was observed. The photoaddition of benzaldehyde to anthraquinone was tried without success.

EXPERIMENTAL

General remarks. The photoexperiments were carried out in Schlenk tubes⁸ of Pyrex glass. The tubes were sealed while a stream of carbon dioxide was passing through. The benzene used was thiophene-free and dried over sodium. The ferric chloride tests were carried out by dissolving the substance in ethyl alcohol and adding ferric chloride in water.

Photochemical reaction between benzaldehyde and khellinquinone. Khellinquinone (I) (1.1 g., 1 mole) and freshly distilled benzaldehyde (1.5 g., 3 mole), in 30 ml. benzene, were exposed to sunlight for 60 days (Jan.-Feb.). At the end of the experiment, a yellow deposit (I is orange) was formed, filtered off, washed with benzene, and crystallized from ethyl alcohol. IIa forms almost colorless crystals m.p. 220° with decomposition, (yield, 0.7 g.). IIa is soluble in aqueous 10% sodium hydroxide, dissolves in concd. sulfuric acid with a yellow orange color, and gives a blue-green ferric chloride color reaction.

Anal. Caled. for $C_{19}H_{12}O_6$: C, 67.8; H, 3.6. Found: C, 67.6; H, 3.5.

Action of diazomethane on IIa. To 1 g. of IIa was added an ethereal solution of diazomethane (from 6 g. of nitrosomethylurea). The reaction vessel was kept in the ice chest for 24 hr. The solid phase was filtered off and crystallized from ethyl alcohol as colorless crystals of IIe, m.p. 210° . Admixture with the product obtained as described below gave no depression, but on admixing with IIa, there was a depression in the m.p. to 190° . IIe is insoluble in 10% aqueous sodium hydroxide solution, soluble in concd. sulfuric acid with a yellow-orange color, and gives no color reaction with ferric chloride.

Anal. Calcd. for $C_{20}H_{14}O_6$: C, 68.6; H, 4.0. Found: C, 68.5; H, 3.9.

Benzoylation of IId. To 0.6 g. of IId in 10 ml. of pyridine (dried over potassium hydroxide and then distilled) was added about 1 g. of benzoyl chloride and the mixture was heated with shaking on a boiling water bath for 15 min. The mixture was left to cool and then acidified with 10% ice cold acetic acid. The deposit was filtered off, washed with water, and crystallized from ethyl alcohol as colorless crystals of IIe, m.p. 210°. It is insoluble in 10% aqueous sodium hydroxide and gives no color reaction with ferric chloride.

Anal. Calcd. for $C_{20}H_{14}O_6$: C, 68.6; H, 4.0. Found: C, 68.8; H, 4.1.

Hydrolysis of IIa. To 0.5 g. of IIa in 20 ml. of dioxane was added 15 ml. of hydrochloric acid (7.5 ml. of concd. hydrochloric acid of sp. gr. 1.18, mixed with 7.5 ml. water) and the solution was refluxed for 1 hr. The solution was allowed to cool and the product obtained was filtered off and crystallized from acetic acid as yellow crystals of IIc, m.p., 276° ; admixture with an authentic sample⁷ gave no depression.

Photochemical reaction between benzaldehyde and anthraquinone. A similar experiment was carried out as in the case of benzaldehyde and khellinquinone. Anthraquinone was recovered unchanged as proved by melting point, and mixed melting point.

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Stereochemistry of the Tropane Alkaloids. XI.¹ Oxidation of Four Epimeric Ecgoninols by Silver Oxide

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A recent paper of this series² dealt with the preparation and configurations³ of 2β -hydroxymethyl-tropan- 3α -ol and 2α -hydroxymethyltropan- 3α -ol,

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