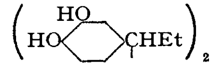
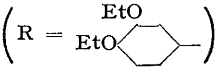
NOTES.

A New Preparation of 3 : 4-*Bis*-(3′ : 4′-*dihydroxyphenyl*)-n-*hexane*. By Gábor Fodor and J. Wein.

The preparation of a derivative of hexoestrol with two hydroxyl groups in the same ring (I), similar to oestriol, was first described by Short (Boots Pure Drug Co. Ltd. and Short, B.P. 525,320/3.12.1938; Short, *Chem. and Ind.*, 1940, **18**, 703), from methyl*iso*eugenol hydrobromide. We had synthesised (I) from 3 : 4-diethoxypropiophenone by the azine route, being unaware that Baker (*J. Amer. Chem. Soc.*, 1943, **65**, 1572) had applied the same method to 3 : 4-dimethoxypropiophenone. As our yields are far better than Baker's, and all the intermediates are different, we briefly record our procedure.


(I.)

(R·CEt:N—)$_2$ (II.) (R·CHEt·N=)$_2$ (III.) (R·CHEt—)$_2$ (IV.)



3 : 4-*Diethoxypropiophenone Azine* (II).—The ketone (Bruckner, Fodor *et al.*, this vol., p. 885) (11·1 g.) was dissolved in anhydrous alcohol (12 c.c.), and hydrazine hydrate (2·5 c.c.) and glacial acetic acid (3 c.c.) were added. The mixture became hot, and after ½ hr.'s heating on a steam-bath it solidified. After ice-cooling, the golden-yellow crystals (11 g.) were filtered off; m. p. 134° (Found : C, 70·8; H, 8·3. $C_{26}H_{36}O_4N_2$ requires C, 70·7; H, 8·2%).

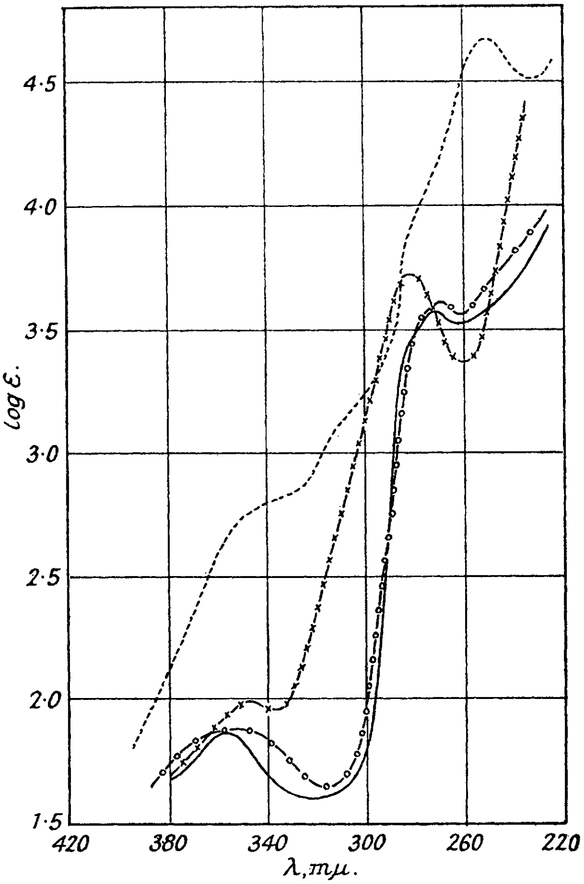
3 : 3′ : 4 : 4′-*Tetraethoxy*-α-*azopropylbenzene* (III).—The foregoing *azine* (4 g.) was added portionwise to 80 c.c. of an alcoholic suspension of palladium–charcoal (0·4 g.) previously saturated with hydrogen, and hydrogenated at 60° until 410 c.c. of gas had been absorbed (Calc. for 2 mols. : 403 c.c.). The catalyst was filtered off, and potassium acetate (2 g.) added to the filtrate; this was cooled to 0° and iodine (1·5 g.) added in small portions until it was present in excess as shown by its colour. The *azo-compound* separated as white crystals (1·5 g.), m. p. 100°, a further 2 g. being obtained on addition of water to the mother-liquor; yield 87·5%. The product can be recrystallised from alcohol (Found : C, 70·8; H, 8·8; N, 6·5. $C_{26}H_{38}O_4N_2$ requires C, 70·9; H, 8·7; N, 6·5%). Like other aryl-aliphatic azo-compounds (see Fodor and Szarvas, *Ber.*, 1943, **76**, 334), (III) has a characteristic ultra-violet absorption band at 350 mμ; in the figure the absorption curve is compared with those of *pp*′-bis-acetamido-α-azopropylbenzene (Fodor and Wein, this vol., p. 684), *pp*′-dimethoxy-α-azopropylbenzene, and *pp*′-dimethoxy-ω-azotoluene (Fodor and Szarvas, *loc. cit.*).

3 : 4-*Bis*-(3′ : 4′-*dimethoxyphenyl*)-n-*hexane* (IV).—The foregoing azo-compound (1·33 g.) was heated in an oil-bath; at 100° it melted and evolution of nitrogen took place, which became vigorous at 135° with a sudden rise of temperature. The mixture was then kept at 170° for 10 mins. to complete the decomposition (loss of weight : 6·8. Calc. : 6·5%). The remaining oil (1·24 g.) was treated with cold light petroleum (10 c.c.) and the resulting crystals of (IV) (0·35 g.) were filtered off; m. p. 100°, raised by recrystallisation from glacial acetic acid or light petroleum to 115° (Found : C, 75·3; H, 9·0. $C_{26}H_{38}O_4$ requires C, 75·3; H, 9·2%). When the solvent was evaporated off from the original mother-liquor, and the residual liquid kept overnight at − 20°, a further crop of (IV) was obtained (0·22 g.; total yield 46%), and distillation of the residue afforded an oil (0·45 g., 36%; b. p. 145—147°/0·02 mm.); this could not be crystallised and was probably a racemic form, (IV) being a *meso*-form.

3 : 4-*Bis*-(3′ : 4′-*dihydroxyphenyl*)-n-*hexane* (I).—(a) *From the crystalline tetraethyl ether.* The above ether (0·3 g.) was dissolved in a mixture of concentrated hydrobromic acid (2·4 c.c.) and glacial acetic acid (2 c.c.), the solution heated under reflux for 4 hrs., and the resulting red solution evaporated in a vacuum to half its volume in a hydrogen atmosphere. On addition of water (10 c.c.) a grey solid (0·2 g.) separated and was washed with water; m. p. 227—228°. After recrystallisation from dilute alcohol, white crystals were obtained, m. p. 232—233° (Short, *loc. cit.*, recorded 231—232°) (Found : C, 71·3; H, 7·05. Calc. for $C_{18}H_{22}O_4$: C, 71·5; H, 7·3%). On standing in air, they became dark violet.

Tetra-acetyl derivative. The crude tetrahydroxy-compound was heated with an excess of acetic anhydride for 3 hrs., the solution evaporated to dryness in a vacuum, and the resulting oily *acetyl* derivative crystallised from benzene–light petroleum; m. p. 164° (Found: C, 66·7; H, 6·7. $C_{26}H_{30}O_8$ requires C, 66·7; H, 6·4%).

(b) *From the liquid tetraethyl ether.* A redistilled sample of this ether (0·3 g.) was treated in a similar manner to the crystalline isomer; the crude product obtained could not be purified by recrystallisation so was distilled in a high vacuum. The distillate melted at 80—90°, and gave the reactions of catechol derivatives. The product was characterised as its *tetrabenzoyl* derivative, made by the pyridine–benzoyl chloride method and twice recrystallised from alcohol; m. p. 63—64° (Found: C, 76·2; H, 5·9. $C_{46}H_{38}O_4$ requires C, 76·8; H, 5·4%).



1. ×—×—×—×— 3 : 3′ : 4 : 4′-*Tetraethoxy-α-azopropylbenzene* (III) *in* 96% *alcohol.*
2. - - - - - - - - - - pp′-*Bisacetamido-α-azopropylbenzene in* n-*butanol.*
3. o—o—o—o—o— pp′-*Dimethoxy-α-azopropylbenzene in* 96% *alcohol.*
4. ———————— pp′-*Dimethoxy-ω-azotoluene in* 96% *alcohol.*

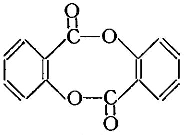
The spectra were observed with a Zeiss " spectrograph for chemists " with tungsten electrodes as light source.

The authors thank Miss Dr. M. Kovács Oskolás for the microanalyses and Dr. L. Láng for the measurements of absorption spectra.—UNIVERSITY, SZEGED, HUNGARY. [*Received, June 2nd,* 1947.]

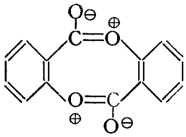
Stereochemistry of the Disalicylides. By ALEXANDER SCHÖNBERG.

Two disalicylides are known, α- and β- isomers (m. p. 213° and 199—200° respectively), the former being more reactive than the latter; each on being heated furnishes a mixture of the two. For both, formula (I) is established, in agreement with the lack of colour, the synthesis, molecular weight, chemical reactions, and Raman spectra (Einhorn and Pfeiffer, *Ber.*, 1901, **34**, 2591; R. Anschütz, *Ber.*, 1919, **52**, 1880; L. Anschütz and Neher, *J. pr. Chem.*, 1941, **159**, 264; L. Anschütz and Mayer, *ibid.*, 1942, **159**, 343; Kohlrausch, *ibid.*, 1941, **159**, 268; Kahovec and Kohlrausch, *Monatsh.*, 1943, **74**, 333; L. Anschütz and Neher, *Ber.*, 1944, **77**, 634; L. Anschütz and Gross, *ibid.*, p. 644).

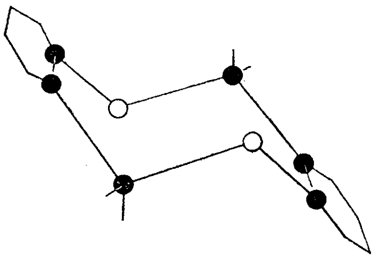
It has been suggested by Höhn (see Richter–Anschütz, "Chemie der Kohlenstoffverbindungen," 12th edtn., Vol. II, Part 2, p. 392) that (I) represents two stereoisomers, namely, the " chair " form (II)



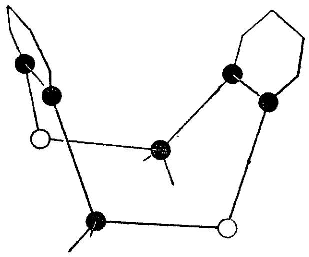
(I.)



(IV.)



(II.)

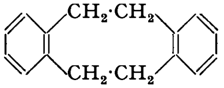


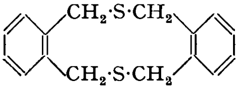
(III.)

and the " boat " form (III) (cf. " Beilstein," 4th edtn., Vol. 19, p. 172), but this hypothesis has not been generally accepted; for instance, Meerwein (*Ber.*, 1941, **74**, 52) stated that the remarkable isomerism had not found a satisfactory explanation, and Anschütz and Mayer (*loc. cit.*) regard Höhn's explanation as unusual and state that no analogous cases of isomerism are known.

It is true that it is doubtful if " chair " and " boat " isomers of *cyclo*hexane will ever be *isolated*, at least under normal conditions of temperature; and only one form of *s*-dibenz*cyclo*octadiene (V) has been isolated although several Sachse–Mohr isomers are theoretically possible (Baker, Banks, Lyon, and Mann, *J.*, 1945, 28). There are theoretically several stereochemical forms possible of *cyclo*octatetraene which have been described by Kaufman, Fankuchen, and Mark as " tub," " chair," and " crown " forms (XIth Int. Congr. Pure and Appl. Chem., Abstract No. 221/3), but only one form has been isolated.

(V.)





(VI.)

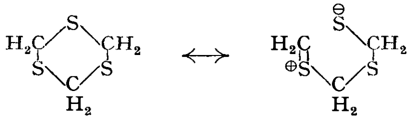
The critics of Höhn's theory have failed to advance any alternative explanation, and his theory would be more readily acceptable if it afforded an explanation for the fact that the " boat " and the " chair " isomer of the disalicylides may be isolated, but that this is not possible with the hydrocarbons previously mentioned. Such an explanation is now offered.

There is a fundamental difference between the disalicylides and these three hydrocarbons; in the former, the actual state of the molecules cannot be correctly described without taking into consideration contributions of intrapolar forms [cf. *inter alia* (IV)], but these contributions are negligible in the case of the hydrocarbons : (IV) represents an intrapolar form of (II), as well as of (III).

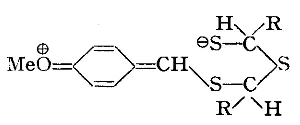
Stereoisomers of the Sache–Mohr type can only be isolated if a high energy barrier hinders their interconversion. In the disalicylides such a barrier may be due to the fact that interconversion cannot be brought about without overcoming either the attraction of electric forces (in the case of positive and negative " poles ") and/or the repulsion of " poles " of the same sign, but such a stabilising effect is lacking in the " chair " and the " boat " form of *cyclo*hexane, of (V), and of *cyclo*octatetraene.

Relationship between the Stereochemistry of the Disalicylides and that of Ring Systems containing Sulphur Atoms.—Autenrieth has synthesised a number of compounds containing rings with two sulphur atoms and at least six carbon atoms. For these substances [e.g. (VI); see Autenrieth and Hennings, *Ber.*, 1902, **35**, 1390] stereoisomers of the Sachse–Mohr type should be possible, but they have not yet been isolated as far as the author is aware. In these sulphur compounds, the true state of the heterocyclic ring system can be described without taking into consideration intrapolar structures, as their influence is negligible, and therefore the fact that the theoretically possible Sachse–Mohr isomers have not been isolated may be explained as it has been for *cyclo*hexane.

Stereochemistry of Trithians.—For trithian (VII) and its derivatives the theory demands the existence of stereoisomers of the Sachse–Mohr type. In a number of cases isomers have been isolated (*e.g.*, two isomeric trithiobenzaldehydes, m. p. 167° and 225°, are known) and these isomers are now believed to be of the Sachse–Mohr type (see Schönberg and Barakat, *J.*, 1947, 693; *Nature*, 1948, in the press). With regard to these substances, the true state of the molecules (this applies to molecules both of the " chair " and of the " boat " form) can only be represented by taking into consideration intrapolar forms [cf. *inter alia* (VII*a*) and also (VIII, R = C_6H_4·OMe)], and the theory advanced to explain the high energy barrier between the two stereoisomeric disalicylides should also be applied to the trithioaldehydes. The term " intrapolar stabilisation " is now proposed to describe the stability of stereoisomers of this type, in place of the term " resonance stabilisation " previously used (Schönberg and Barakat, *J.*, 1947, 693); the latter term was used in view of the fact that (VII) and (VII*a*) are resonance forms.



(VII.) (VII*a*.)



(VIII.)

It is impossible to decide by means of chemical methods whether the stereoisomers of the isomeric thioaldehydes and disalicylides represent " chair " and " boat " configurations (in the classical sense) or forms which lie between these two extremes. The classical models, which do not take into consideration the influence of electrostatic forces, are somewhat misleading.

Physical methods used in the investigation of stereoisomers of the Sachse–Mohr type have led to contradictory results; for instance, for *cyclo*octatetraene, Fankuchen, Kaufman, and Mark (*X*-ray diffraction) and Thompson (infra-red data) favour the " tub " form, but Hassel (electron diffraction) is in favour of the " crown " form (see Kaufman, Fankuchen, and Mark, *Nature*, 1948, **161**, 165).—FOUAD I UNIVERSITY, FACULTY OF SCIENCE, ABBASSIA-CAIRO, EGYPT. [*Received, June 4th*, 1947.]

The Preparation of 4-Hydroxyquinoline Derivatives from Aromatic Amines and Ethyl Ethoxymethylenemalonate.

By G. F. DUFFIN and J. D. KENDALL.

IN a series of papers which have appeared recently (Price and Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 1204; Riegel *et al.*, *ibid.*, p. 1264; Lauer *et al.*, *ibid.*, p. 1268) the preparation of a number of 4-hydroxyquinoline derivatives has been discussed. These compounds were prepared following the method originally suggested by Gould and Jacobs (*ibid.*, 1939, **61**, 2809) for 4-hydroxyquinoline-3-carboxylic acids by the ring-closure of ethyl anilinomethylene- or nuclear-substituted anilinomethylenemalonates, the resultant ethyl 4-hydroxyquinoline-3-carboxylates giving, on hydrolysis and decarboxylation, the corresponding 4-hydroxyquinolines. Schofield and Simpson (*J.*, 1946, 1033), using the same method, have reported difficulties in the preparation of ethyl ethoxymethylenemalonate and ethyl anilinomethylenemalonate, and the formation of by-products in the cyclisation of the latter.

During an investigation into the synthesis of 4-hydroxyquinolines commenced in October 1944, a number of the compounds described by the aforementioned workers were prepared, using an analogous method. No difficulties were experienced in the preparation of ethyl ethoxymethylenemalonate or ethyl anilinomethylenemalonate, and cyclisation was effected easily without the formation of by-products. The ethyl ethoxymethylenemalonate was prepared by the method of Claisen (*Annalen*, 1897, **297**, 75), and it was found that, provided the operations were carried through rapidly, yields higher than that claimed by Claisen were obtained. Ethyl anilinomethylenemalonate was prepared, as stated by Claisen, simply by heating molecular equivalents of aniline and ethyl ethoxymethylenemalonate on the steam-bath for a short period, the anilino-ester readily crystallising on cooling in ice. Other nuclear-substituted anilinomethylenemalonates were obtained similarly by heating the appropriate intermediates on the steam-bath for periods varying from 20 minutes for *o*-toluidine to 16 hours for *p*-nitroaniline. All the anilino-esters crystallised either on cooling or, if of high m. p., immediately on removal from the steam-bath. Ring closure of the anilino-esters was effected by heating them in liquid paraffin, B.P., at 260—290° for periods varying from 15 minutes to 1 hour. With recrystallised anilino-esters the closure went smoothly and in one sense only, but attempts at cyclisation before purification gave low yields of dark products. Hydrolysis of the ring esters with aqueous sodium hydroxide followed by acidification with acetic acid gave the free acids in almost quantitative yield. These acids were characterised by high m. p.s and low solubility in all solvents. The acids were decarboxylated by heating them with liquid paraffin (B.P.) at 270—310° for 5—30 minutes, the course of decarboxylation being followed by measurement of the carbon dioxide evolved. Only with 6-nitro- and 6-acetamido-4-hydroxyquinoline-3-carboxylic acid did the method fail to give the corresponding 4-hydroxyquinoline (cf. Riegel *et al.*, *loc. cit.*; Baker, *ibid.*, 1946, **68**, 1267).

It would appear, therefore, that the difficulties experienced by Schofield and Simpson were due to impurities in their starting materials, particularly the ethyl ethoxymethylenemalonate. This would account for the formation, in the ring closure of their impure anilinomethylenemalonates, of by-products derived from more than one mol. of primary amine.

Among the compounds prepared by the authors the following have not been described previously: *ethyl* o-*toluidinomethylenemalonate*, *ethyl* p-*toluidinomethylenemalonate*, *ethyl* p-*acetamidoanilinomethylenemalonate*, and their corresponding *quinoline* derivatives.

Ethyl Ethoxymethylenemalonate.—A mixture of redistilled ethyl malonate 160 g.; 1 g.-mol.), ethyl orthoformate (148 g.; 1 g.-mol.), acetic anhydride (204 g.; 2 g.-mols.) and freshly fused anhydrous zinc chloride (2—3 g.) was boiled under reflux for 45 minutes. The initial heating was gentle as otherwise the vigorous boiling which began with the formation of ethyl acetate sometimes caused the reaction to become uncontrollable. The mixture was then distilled at ordinary pressures until the temperature in the boiling liquid was 190°. The residue was cooled, filtered as rapidly as possible, and distilled under reduced pressure, the fraction, b. p. 140—160°/10 mm., being collected. If these operations were

Ethyl Anilinomethylenemalonates.

Amine used.	Time of heating.	M. p.	Yield (purified, %).	Formula.	Found, %.		Reqd., %.	
					C.	H.	C.	H.
Aniline	20 mins.*	50°	76	$C_{14}H_{17}O_4N$		(2)		
o-Toluidine	20 mins.	63	73	$C_{15}H_{19}O_4N$	65·2	6·55	65·0	6·85
p-Toluidine	30 mins.	48	41	$C_{15}H_{19}O_4N$	65·2	6·30	65·0	6·85
m-Chloroaniline	1 hour	57	74	$C_{14}H_{16}O_4NCl$		(1)		
p-Chloroaniline	1½ hours	82	79	$C_{14}H_{16}O_4NCl$		(2)		
p-Nitroaniline	16 hours **	142	79	$C_{14}H_{16}O_6N_2$		(2)		
α-Naphthylamine ...	2 hours	88	65	$C_{18}H_{19}O_4N$	69·2	5·85	69·0	6·07
p-Acetamidoaniline	30 mins.***	178	77	$C_{16}H_{20}O_5N_2$	60·2	6·50	60·0	6·25

* Product recrystallised from light petroleum (b. p. 40—60°)–ether; ** from ethyl acetate; *** from ethanol; all others from light petroleum (b. p. 40—60°).

Ethyl 4-*Hydroxyquinoline*-3-*carboxylates.*

Substituent.	Ring closure. Temp.	Ring closure. Time.	M. p.	Yield (purified, %).	Formula.	Found, %. C.	Found, %. H.	Reqd., %. C.	Reqd., %. H.
None	250°	1 hr.*	270°	90	$C_{12}H_{11}O_3N$		(2)		
8-Methyl-	250—260	1 hr.**	259	77	$C_{13}H_{13}O_3N$	67·9	5·83	67·5	5·63
6-Methyl-	290	15 mins.**	268	55	$C_{13}H_{13}O_3N$	67·35	5·47	67·5	5·63
7-Chloro-	280	15 mins.	297	59	$C_{12}H_{10}O_3NCl$		(1)		
6-Chloro-	260	1 hr.	293	60	$C_{12}H_{10}O_3NCl$		(2)		
6-Nitro-	250—270	1 hr.	>300	76	$C_{12}H_{10}O_5N_2$		(2)		
7 : 8-Benz-	250	1 hr.	256	88	$C_{16}H_{13}O_3N$	71·8	5·15	71·7	4·90
6-Acetamido-	290	15 mins.	290 (decomp.)	61	$C_{14}H_{14}O_4N_2$	61·7	4·99	61·3	5·14

* Product recrystallised from acetic acid; ** from benzene; all others from nitrobenzene.

4-*Hydroxyquinoline*-3-*carboxylic Acids.*

Substituent.	Recryst. from	M. p.*	Formula.	Found, %. C.	Found, %. H.	Reqd., %. C.	Reqd., %. H.
None	nitrobenzene	270°	$C_{10}H_7O_3N$		(2)		
8-Methyl-	,,	265	$C_{11}H_9O_3N$	65·1	4·72	65·1	4·43
6-Methyl-	,,	266	$C_{11}H_9O_3N$	65·2	4·22	65·1	4·43
7-Chloro-	,,	269	$C_{10}H_6O_3NCl$		(1)		
6-Chloro-	,,	261	$C_{10}H_6O_3NCl$		(2)		
6-Nitro-	acetic acid	273	$C_{10}H_6O_5N_2$		(2)		
7 : 8-Benz-	acid could not be crystallised	278	$C_{14}H_9O_3N$	—	—	—	—
6-Acetamido-		265	$C_{12}H_{10}O_4N_2$	—	—	—	—

* All with decomposition.

4-*Hydroxyquinolines.*

Substituent.	Decarboxylation. Temp.	Decarboxylation. Time.	M. p.	Yield (purified, %).	Formula.	Found, %. C.	Found, %. H.	Reqd., %. C.	Reqd., %. H.
None	270—280°	30 mins.*	201°	85	C_9H_7ON		(2)		
8-Methyl-	280	20 mins.	211	81	$C_{10}H_9ON$	75·5	5·76	75·4	5·67
6-Methyl-	280	20 mins.	230	90	$C_{10}H_9ON$	75·15	5·35	75·4	5·67
7-Chloro-	260	20 mins.**	274	51	C_9H_6ONCl		(2)		
6-Chloro-	280	20 mins.**	271	57	C_9H_6ONCl		(2)		
7 : 8-Benz-	310	5 mins.	243	95	$C_{13}H_9ON + \frac{1}{2}H_2O$	76·5 76·3	5·09 5·21	76·4	4·92

* Product recrystallised from ethanol; ** from water–ethanol; all others from water.

(1) Cf. Price and Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 1204.
(2) Cf. Riegel *et al.*, *ibid.*, p. 1264.

performed over a period of 2½—3 hours, the residue after distillation was extremely small. The product on redistillation boiled almost completely at 156—160°/14 mm., and this fraction (80—100 g.) was pure enough for all subsequent reactions.

Details of all other experimental work are summarised in the Tables.—RODENSIDE ORGANIC LABORATORY, ILFORD LIMITED, and SOUTH-EAST ESSEX TECHNICAL COLLEGE, DAGENHAM. [*Received, June* 10*th*, 1947.]

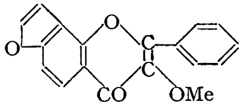
Experiments on the Synthesis of Karanjin. By A. SEETHARAMIAH.

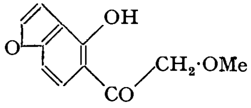
WHILE experiments were in progress on the total synthesis of karanjin (I), Seshadri and Venkateswarlu (*Proc. Indian Acad. Sci*, 1941, **13**, *A*, 404: 1943, **17**, *A*, 16) synthesised the keto-phenolic compound (II), which had been previously converted into karanjin by Manjunath *et al.* (*Ber.*, 1939, **72**, 96). In the present note the results of experiments carried out in this field are placed on record.

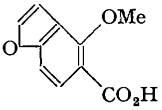
Since only resinous products were obtained when the Hoesch reaction (with methoxymethyl cyanide or methyl cyanide) and the Friedel–Crafts reaction (with methoxyacetic anhydride) were carried out with 4-hydroxybenzfuran, the former reaction was carried out with 4-*hydroxy*-2 : 3-*dihydrobenzfuran* and methoxymethyl cyanide. The *product* (m. p. 174°), was found to be different from that obtained (m. p. 72°) on reducing the furan ring in (II). It is assumed that the side chain has entered the position 7.

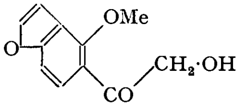
Attempts were made to synthesise (II) from 4-methoxybenzfuran-5-carboxylic acid (III), which was converted into the *diazo-ketone via* the acid chloride. Hydrolysis of the diazo-ketone was expected to yield (IV). But the only product that could be isolated in a pure state had the formula $C_{10}H_6O_3$, did not contain any methoxyl group, and is regarded as a *coumaronone* of structure (V) (cf. Clibbens and Nierenstein, *J.*, 1915, **107**, 1491). It must be added that it was not possible to obtain it by treating demethylated keto-phenolic compound (II) with 50% formic acid or boiling it in benzene solution with phosphoric oxide.

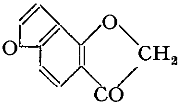
4-*Hydroxy*-2 : 3-*dihydrobenzfuran.*—4-Hydroxycoumarone (1 g.) dissolved in glacial acetic acid (10 c.c.) was catalytically reduced with hydrogen using 25% palladium–charcoal (0·5 g.) prepared according to Ott and Eichler (*Ber.*, 1922, **55**, 2661), until 215 c.c. of hydrogen (30°, 686 mm.) had been absorbed. The solution was diluted with ether and filtered, and the solvent removed under reduced pressure. The residue was distilled at 2 mm. from an air bath (bath temp. 120—135°). The *compound* (0·9 g.) crystallised from light petroleum (b. p. 60—70°) in needles, m. p. 75° (Found: C, 70·8; H, 6·2. $C_8H_8O_2$ requires C, 70·6; H, 5·9%).


(I.)


(II.)


(III.)

(IV.)



(V.)

4-*Hydroxy*-7-*methoxyacetyl*-2 : 3-*dihydrobenzfuran.*—A solution of 4-hydroxy-2 : 3-dihydrobenzfuran (0·35 g.) and methoxymethyl cyanide (0·19 g.) in absolute ether (12 c.c.) was cooled in a mixture of ice and salt and saturated by passing a slow current of dry hydrogen chloride through it. The mixture was left in an ice-chest for 35 hours and the crystalline hydrochloride separated by decantation. It was decomposed by the addition of warm water and the solution heated on the water-bath for ½ hour. On cooling, a white *compound* separated in needles, m. p. 174° (yield, 0·15 g.) (Found: C, 63·4; H, 6·0. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%). The compound did not give any coloration with ferric chloride solution and is regarded as being isomeric with the dihydro-derivative of the keto-phenolic compound (II).

4-*Hydroxy*-5-*methoxyacetyl*-2 : 3-*dihydrobenzfuran.*—The keto-phenolic compound (II) (0·52 g.) dissolved in ethyl acetate (15 c.c.) was catalytically reduced with hydrogen, using platinum black (0·1 g.) (*Org. Synth.*, Vol. VIII, 1928, pp. 92—99), until it had absorbed 75 c.c. of hydrogen (27°, 687 mm.). The solution was filtered and the solvent removed. The residue on crystallisation from water separated in white flakes (yield, 0·15 g.), m. p. 72° (Found: C, 63·4; H, 5·9. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%). The *compound* gave a reddish-blue colour with ferric chloride solution, and gave a pale yellow *semicarbazone* which separated in plates from dilute alcohol; m. p. 250—251° (decomp.) (Found: N, 16·3. $C_{12}H_{15}O_4N_3$ requires N, 15·9%).

4-*Methoxy*-5-*diazoacetylbenzfuran.*—The acid chloride (1·5 g.), m. p. 71°, prepared according to Manjunath and Seetharamiah (*J. Mysore University*, 1941, *B*, Vol. II, Pt. III, pp. 20—21) from 4-methoxybenzfuran-5-carboxylic acid (III), was dissolved in benzene (20 c.c.) and added slowly with shaking to a solution of diazomethane (2·5 mols.) in dry ether cooled in ice during 20 minutes. A mild and persistent evolution of gas was noticed. After 24 hours, when the solution was still yellow, ether was removed by a current of cold air. To the benzene solution light petroleum (b. p. 50—60°) was added to precipitate the compound which was collected at the pump. It was recrystallised several times from benzene–light petroleum, and was obtained in the form of yellow needles, m. p. 105—106° (decomp.) (yield, 0·8 g.) (Found: N, 13·1. $C_{11}H_8O_3N_2$ requires N, 12·95%).

Furano(2′ : 3′ : 6 : 7)*dihydrobenzfuran*-3-*one.*—The above diazo-ketone (2·5 g.) was added in small quantities with shaking to 50% formic acid. A vigorous reaction took place with evolution of gas. The mixture was heated on the water-bath for 15 minutes to complete the reaction, filtered hot, and allowed to cool. A light yellow solid (0·8 g.) separated. This was collected at the pump and refluxed with 50% ethyl alcohol for 4 hours. It was crystallised twice from the same solvent, and a yellow crystalline material, m. p. 91—94°, was obtained. This was found to be a mixture which could not be resolved.

The filtrate (from above) on dilution with water deposited a yellow crystalline compound (1·5 g.). It was refluxed for 4 hours with just the amount of 50% ethyl alcohol necessary to keep the compound in solution. On cooling, a crystalline compound separated; it was twice crystallised from the same solvent; light yellow needles, m. p. 103—104° (yield, 0·7 g.) [Found: C, 68·9; H, 3·6; *M*(Rast), 180. $C_{10}H_6O_3$ requires C, 69·0; H, 3·4%; *M*, 174].

When the diazo-ketone was hydrolysed with 100% formic acid there was very considerable resinification and a very poor yield of the compound, m. p. 103—104°. The diazo-ketone on hydrolysis with dilute alcoholic sulphuric acid yielded the same compound, m. p. 103—104°, in fairly good yields.

The *coumaranone* (V) gave a *semicarbazone* which on two crystallisations from absolute alcohol (charcoal), in which it is sparingly soluble, separated in white crystals, m. p. 242—244° (decomp.) [Found (Analysis by Drs. Weiler and Strauss, Oxford): C, 57·3; H, 4·0; N, 17·9. $C_{11}H_9O_3N_3$ requires C, 57·1; H, 3·9; N, 18·2%].

4-*Hydroxy*-5-*hydroxyacetylbenzfuran.*—Compound (II), m. p. 96° (3 g.), was dissolved in glacial acetic acid (25 c.c.), and 3 c.c. of hydriodic acid (*d* 1·7) was added. The mixture was heated on a water-bath for 2 hours, cooled, and diluted with water (250 c.c.). A tarry material which solidified on cooling was obtained. This was dissolved in dilute sodium hydroxide solution. On passage of carbon dioxide through this solution about 1 g. of material, m. p. 85—94°, was obtained; it was removed by filtration. Carbon dioxide was again passed through the filtrate, and the solid material (0·7 g.) collected at the pump. It was repeatedly crystallised from water; white needles (0·4 g.), m. p. 139° (Found: C, 62·5; H, 4·4. $C_{10}H_8O_4$ requires C, 62·5; H, 4·2%). The compound reduced Fehling's solution very readily, and gave a blue colour with ferric chloride solution. It did not undergo cyclisation on being heated in 50% formic acid or refluxed with phosphoric oxide in benzene solution.

The author wishes to record his grateful thanks to Dr. B. L. Manjunath for his useful suggestions and interest in the investigation, which was carried out in the laboratories of the Central College, the University of Mysore, Bangalore.—THE DEPARTMENT OF LEATHER INDUSTRIES, THE UNIVERSITY, LEEDS. [*Received, June, 26th,* 1947.]