with benzylmethyl-acethydroxamic acid; but rearrangement of *d*-benzylmethyl-acetazide was found to give an optically active isocyanate which could be converted into an optically active amine hydrochloride, and into an optically active monosubstituted urea. An explanation of this reaction is suggested.

The velocity of rearrangement of benzylmethyl-acetazide was measured at 35°, and was found to correspond to that of a unimolecular reaction; the value of the constant was $k_{35^\circ} = 0.01178$.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE REARRANGEMENT OF HYDROXAMIC ACIDS ISOMERIC WITH TRIPHENYL-ACETHYDROXAMIC ACID[1]

BY LAUDER W. JONES AND FRANK BRIAN ROOT

RECEIVED JUNE 27, 1925 PUBLISHED JANUARY 8, 1926

Introduction

For some time past the mechanism of reactions which occur during rearrangements of the Lossen-Hofmann-Curtius type has been represented[2] by equations which involve two distinct stages.

$$\text{I. } RCO.N\begin{matrix}-x\\-y\end{matrix} \longrightarrow RCO.N + xy. \quad \text{II. } RCO.N \longrightarrow [R\text{-} + \text{-}CO.N] \longrightarrow OC{=}N{-}R$$

The first leads to the formation of a univalent nitrogen derivative, and the second to the rearrangement of this derivative by the migration of a radical R from the carbon atom to the nitrogen atom.

The conditions which determine the first step have been studied thoroughly by Stieglitz and his co-workers.[3] They varied the groups represented by x and y in many ways and established the factors which promote or inhibit rearrangement in compounds of these classes.

The second step must depend upon the nature of the radical R. Furthermore, since the detachment of this radical from the carbon atom requires the breaking of a bond, it would seem that the radical must exist transiently as a free radical, while it is "wandering" from the carbon atom to the nitrogen atom. This conception of the reaction led Jones and Hurd[4] to study triphenyl-acethydroxamic acid, $(C_6H_5)_3C.CO.NHOH$, in which the radical R is triphenylmethyl, a typical example of a free

---

[1] This article is based upon a thesis submitted by Frank Brian Root to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); **29**, 51 (1903). Jones, *ibid.*, **50**, 440 (1913); THIS JOURNAL, **36**, 1288 (1914).

[3] Slossen, *Am. Chem. J.*, **29**, 289 (1903). Stieglitz and Higbee, *ibid.*, **29**, 52 (1903). Stieglitz and Hesse, *ibid.*, **29**, 56 (1903). Stieglitz and Earle, *ibid.*, **30**, 399, 412 (1903).

[4] Jones and Hurd, THIS JOURNAL, **43**, 2432 (1921).

organic radical. They compared the ease of rearrangement of certain derivatives of this acid with the rearrangement of similar derivatives of monophenyl-acethydroxamic acid, $C_6H_5CH_2CO.NHOH$, and of diphenyl-acethydroxamic acid, $(C_6H_5)_2CHCONHOH$, and found that the compounds related to triphenyl-acethydroxamic acid rearranged with remarkable ease. This fact, in conjunction with other observations, led them to advance the hypothesis that, in reactions of this character, the relative ease of rearrangement "is dependent upon the tendency of the radical R in the univalent nitrogen derivative to exist as a free radical."

Hurd[5] tested this hypothesis further by studying N-diphenyl-N-hydroxyurea, $(C_6H_5)_2N\text{-}CO.NHOH$, which contains the diphenylnitrogen radical, $(C_6H_5)_2N$, shown by Wieland[6] to exist free. He also studied *p*-tolyldiphenyl-acethydroxamic acid,[7] $(C_6H_5)_2(C_6H_4CH_3)C.CO.NHOH$, which contains *p*-tolyldiphenylmethyl, $CH_3C_6H_4(C_6H_5)_2C$, another free radical. In both cases, the potassium salts of the benzoyl esters rearranged readily at comparatively low temperatures.

But, up to the present time, all of the compounds selected for testing this hypothesis have contained radicals of high molecular weight, since all free organic radicals are of relatively large mass. If the ease of rearrangement of these compounds is independent of the fact that their radicals have a decided tendency to exist free, then it is conceivable that it might depend upon the large molecular weights of the radicals concerned.

This assumption could be put to a test by comparing the ease of rearrangement of a compound in which R is a typical free radical with isomeric compounds of the same class whose radicals have not been observed to exist free. With this object in view, the rearrangements of derivatives of triphenyl-acethydroxamic acid were compared with the rearrangements of similar derivatives of hydroxamic acids related to triphenylmethane-carboxylic acids, $(C_6H_5)_2CH.C_6H_4COOH$, both *ortho* and *para*. These two acids may be regarded as derivatives of triphenylmethane or as derivatives of benzoic acid. The radicals, themselves, are substituted phenyl groups and, in many respects, the behavior of the hydroxamic acids derived from these two acids resembles that of benzhydroxamic acid. On this account, and for convenience in nomenclature, they have been named as substitution products of benzoic acid. Thus, the hydroxamic acid obtained from triphenylmethane-*p*-carboxylic acid has been called *p*-benzhydryl-benzhydroxamic acid.

It will be noted that the radicals of the two acids are isomeric with triphenylmethyl and, consequently, have the same molecular weight.

---

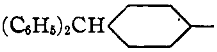
[5] Hurd, THIS JOURNAL, **45**, 1472 (1923).

[6] Wieland, "Die Hydrazine," F. Enke, Stuttgart, **1913**, p. 73.

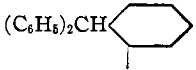
[7] Hurd, THIS JOURNAL, **47**, 174 (1925).

$(C_6H_5)_3C—$

I



II



III

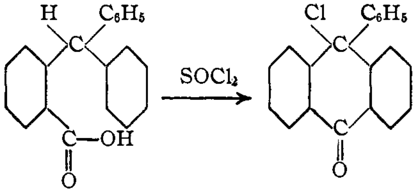
But the tendency for the radicals II and III to exist as free radicals would be decidedly less than for triphenylmethyl, since they are substituted phenyl groups (benzhydrylphenyl) and not triarylmethyl groups.

Our results prove conclusively that the large molecular weight of the radicals does not determine the ease of the rearrangement. The alkali salts of the acyl esters of triphenyl-acethydroxamic acid, for example, $(C_6H_5)_3C\text{-}CONNa(OCOR)$, showed so great a tendency to rearrange that they could not be prepared in a pure state. Even at low temperatures, aqueous solutions of the salts became turbid at once and triphenylmethylisocyanate, the product of rearrangement, formed rapidly. On the other hand, the corresponding derivatives of *o*- and *p*-benzhydryl-benzhydroxamic acid were unusually resistant to rearrangement. It was necessary to heat a water solution of the potassium salt of benzoyl *p*-benzhydrylbenzhydroxamate to boiling before any rearrangement was observed, and a solution of the corresponding derivative of the *ortho* acid showed even greater resistance to change.

Discussion of Results

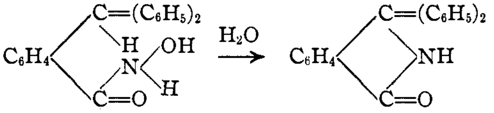
***p*-Benzhydryl-benzhydroxamic acid** was easily made by treating an ether solution of *p*-benzhydrylbenzoyl chloride with hydroxylamine. It formed colorless leaflets, m. p. 157°, and showed the usual qualitative reactions of a hydroxamic acid. From this acid the benzoyl and acetyl esters as well as their sodium, potassium and silver salts were prepared. The salts rearranged when their aqueous solutions were heated to boiling and *sym.*-di-*p*-benzhydrylphenyl-urea, $[(C_6H_5)_2CH.C_6H_4NH]_2CO$, was formed. Rearrangement also took place in alcohol when the solution was heated to 100° in a sealed tube; *p*-benzhydrylphenyl-urethan, $[(C_6H_5)_2CH]C_6H_4NH.CO_2C_2H_5$, was the main product in this case. Both the urea and the urethan were synthesized for comparison with the rearrangement products.

In the *ortho* series, greater difficulties were encountered than in the *para* series. A very singular reaction was noticed when *o*-benzhydrylbenzoic acid was treated with thionyl chloride. The compound formed was 9-phenyl-9-chloro-anthrone, not the acid chloride. Thionyl chloride apparently acted both as a chlorinating and as a condensing agent. Finally,

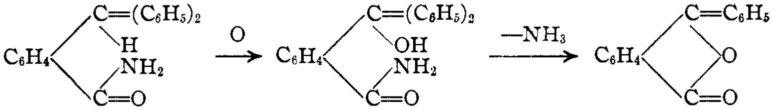


the acid chloride (m. p., 85°) was prepared successfully by treating a solution of the acid in chloroform or in carbon disulfide with thionyl chloride. Thionyl chloride reacted upon the acid chloride as it reacted with the carboxylic acid; 9-phenyl-9-chloro-anthrone was produced.

o-**Benzhydryl-benzhydroxamic acid** was prepared in a manner similar to that by which the *para* acid was obtained. This compound melted at 178° with decomposition. From the residue that remained after decomposition was complete, there was isolated a compound (m. p., 196°) and the same compound was formed when the benzoyl ester was heated with a dilute solution of potassium hydroxide. Although the compound later proved to be *sym.*-di-*o*-benzhydrylphenyl-urea [*o*-$(C_6H_5)_2CH.C_6H_4$-$NH]_2CO$, it was thought at first that it might be a ring compound, diphenyl-phthalimidine, the formation of which might be expected because structural conditions were favorable for the formation of a five-member ring and because the hydroxamic acid showed considerable resistance to rearrangement.



Several attempts were made to prepare diphenyl-phthalimidine from diphenylphthalide by methods analogous to those by which phthalimide is prepared from phthalic anhydride, but none was successful. In another set of experiments the amide of *o*-benzhydrylbenzoic acid was oxidized to the corresponding triphenylcarbinol derivative. It was expected that diphenyl-phthalimidine would result from the carbinol by the loss of water. However, the product was diphenylphthalide, formed by the loss of ammonia, instead of water.



Benzoyl *o*-benzhydryl-benzhydroxamate was made by dissolving the hydroxamic acid in dil. alcohol containing a slight excess of potassium hydroxide and treating this solution with benzoyl chloride. When the benzoyl ester was dissolved in a dilute solution of potassium hydroxide, or when its potassium or silver salt was dissolved in water, rearrangement occurred after the solutions had been boiled for a short time. *sym.*-Di-*o*-benzhydrylphenyl-urea (m. p., 196°) was the rearrangement product. The urea, synthesized by the action of *o*-benzhydrylaniline upon phosgene, was found to be identical with this rearrangement product.

m-**Benzhydrylbenzoic Acid.**—In the *meta* series, only the carboxylic acid was prepared. *m*-Benzhydrylaniline was diazotized and treated with a potassium cuprous cyanide solution to give the nitrile of *m*-benzhydrylbenzoic acid, which was then hydrolyzed to the acid. The yield of carboxylic acid was very small.

Experimental Part

Hydroxamic Acids Derived from *p*-Benzhydrylbenzoic Acid

The Preparation of *p*-Benzhydrylbenzoic Acid.—METHOD I. Benzilic acid was condensed with toluene in the presence of stannic chloride to form *p*-tolyldiphenylacetic acid,[8] which was oxidized by means of an alkaline solution of potassium permanganate to form *p*-carboxyphenyl-diphenylacetic acid.[9] This acid, heated above its melting point (246°), lost carbon dioxide and gave the desired acid; m. p., 160–161°.

METHOD II. The starting material was methyl *p*-toluate. This ester, treated with phenylmagnesium bromide, gave *p*-tolyldiphenyl-carbinol,[10] and oxidation of the methyl group of the latter by means of nitric acid gave *p*-carboxy-triphenylcarbinol. Red phosphorus and iodine in glacial acetic acid reduced the carbinol to *p*-carboxy-triphenylmethane.[11] The acid was purified readily through its sodium salt which is only slightly soluble in cold water.

Although both methods of preparation are lengthy, the first is the easier; both give good yields. The acid has also been prepared by the hydrolysis of the nitrile.[12]

The acid chloride[13] was obtained by heating the acid with an excess of thionyl chloride. The mixture was poured upon ice and the yellow solid which separated was collected, dried and crystallized from ligroin; m. p., 88–90°.

The *p*-toluidide was prepared by treating an ether solution of the acid chloride with *p*-toluidine. It formed long, colorless needles when crystallized from alcohol; m. p., 164°.

p-Benzhydryl-benzhydroxamic Acid

$p\text{-}[(C_6H_5)_2CH]C_6H_4.CO.NHOH$

Free hydroxylamine was made according to the method of Lecher and Hofmann.[14] A solution of 5 g. of the acid chloride in 100 cc. of dry benzene was treated with an excess (4 g.) of free hydroxylamine and the mixture was shaken frequently. The next day the precipitate which formed was collected on a filter, washed with water and dried. Concentration of the benzene mother liquor gave additional crystals. The entire product was dissolved in boiling ethyl acetate, and ligroin (b. p., 60–70°) was added

---

[8] Bistrzycki and Wehrbein, *Ber.*, **34**, 3080 (1901).

[9] Bistrzycki and Gyr, *Ber.*, **37**, 662 (1904).

[10] Ref. 9, p. 663.

[11] Staudinger and Clar, *Ber.*, **44**, 1628 (1911).

[12] Fischer and Albert, *Ber.*, **26**, 3080 (1893).

[13] Ref. 11, p. 1623.

[14] Lecher and Hofmann, *Ber.*, **55**, 912 (1922).

until the solution became turbid. Thus, colorless leaflets of the acid, melting at 156–157°, were obtained; yield, 3 g.

Anal. Subs., 0.2703: N, 10.8 cc. (23°, 767 mm.). Calcd. for $C_{20}H_{17}O_2N$: N, 4.62. Found: 4.54.

This acid showed the ordinary qualitative reactions of a hydroxamic acid; it gave a red coloration with ferric chloride and a light green copper salt with copper acetate. The reaction with ferric chloride must be carried out in the presence of alcohol or a similar solvent, since the acid is insoluble in water. It was insoluble in ligroin, moderately soluble in ether, in benzene and in alcohol and very soluble in ethyl acetate and in acetone.

Benzoyl *p*-Benzhydryl-benzhydroxamate

p-$[(C_6H_5)_2CH]C_6H_4CO.NHOCOC_6H_5$

Fourteen g. of the hydroxamic acid was heated with twice this weight of benzoic anhydride until a sample failed to show the presence of the monohydroxamic acid when tested with ferric chloride (about one minute). The mixture, when cool, solidified; it was broken up, placed in a Soxhlet extractor and extracted with ligroin until it was free from benzoic anhydride and benzoic acid. The product, recrystallized from dil. alcohol, gave 16.1 g. of ester. The ester was also prepared by the Schotten-Baumann reaction.

This compound was quite insoluble in warm alkalies and, on this account, it was thought to be the dibenzoyl ester instead of the monobenzoyl ester. A complete analysis failed to indicate the correct formula, since the percentage composition of the two are so nearly alike. However, a molecular-weight determination (made by measuring the lowering of the melting point of camphor)[15] showed that it was the monobenzoyl ester.

Anal. Subs., 0.4290: N_2, 13.4 cc. (28°, 753 mm.). Subs., 0.2885: CO_2, 0.8419; H_2O, 0.1467.

Calcd. for $C_{27}H_{21}NO_3$: C, 79.61; H, 5.16; N, 3.44. Calcd. for $C_{34}H_{25}NO_4$: C, 79.84; H, 4.89; N, 2.74. Found: N, 3.37; C, 79.59; H, 5.64.

Mol. Wt. Subs., 0.1421, 0.0499: 2.1025, 1.0535 g. of camphor: Δt 7°, 4.5°. Calcd. for $C_{27}H_{21}NO_3$: mol. wt., 407; for $C_{34}H_{25}NO_4$: 511. Found: 386, 420.

POTASSIUM SALT, $[(C_6H_5)_2CH]C_6H_4.CONKO.COC_6H_5$.—Five g. of the benzoyl ester was treated with warm absolute alcohol until not quite all of it had dissolved. A concentrated solution of potassium ethylate (containing 0.48 g. of potassium) was then added, whereupon the remaining benzoyl ester dissolved. This showed that the salt was much more soluble in alcohol than the acid. It required 500 cc. of dry ether to precipitate the salt completely. It was a white powder that "puffed" at 91° when it was heated slowly in a melting-point tube.

Anal. Subs., 0.5750: K_2SO_4, 0.0514. Calcd. for $C_{27}H_{20}O_3NK$: K, 8.78. Found: 8.94.

REARRANGEMENT OF THE POTASSIUM SALT IN WATER.—The potassium salt was apparently almost insoluble in cold water, but dissolved slightly in boiling water. The solution when boiled became turbid in a few seconds.

One g. of the potassium salt was suspended in 50 cc. of water and the water was heated to boiling for half an hour. Carbon dioxide was evolved. The white solid was collected and crystallized from acetone. This gave long, shining needles, m. p. 262–263°, of *sym.*-di-*p*-benzhydrylphenyl-urea, $[(C_6H_5)_2CH.C_6H_4NH]_2CO$ (see below).

---

[15] Rast, *Ber.*, **55**, 1053 (1922).

The yield was almost quantitative. No hydrolysis to form the monohydroxamic acid took place since no test with ferric chloride could be obtained at any time during the reaction.

REARRANGEMENT OF THE POTASSIUM SALT IN ALCOHOL.—The rearrangement in alcohol was carried out most successfully by heating the potassium salt with alcohol in a sealed tube at 100°. If the salt was heated with alcohol in a flask attached to a reflux condenser, it was decomposed almost completely to give the monohydroxamic acid, and little if any rearrangement occurred.

Four-tenths g. of the potassium salt and 20 cc. of absolute alcohol were heated at 100° in a sealed tube for four hours. When the solution cooled, a white solid deposited which, when separated and recrystallized, proved to be the urea; m. p., 161°; yield, 0.08 g. The filtrate from the urea was boiled to concentrate it and then allowed to cool. A precipitate weighing 0.28 g. was collected which, after crystallization from dil. alcohol, melted at 102–103°. This was *p*-benzhydrylphenyl-urethan, $p\text{-}(C_6H_5)_2CH\cdot C_6H_4NH.CO.OC_2H_5$ (see below).

SODIUM SALT.—This salt was prepared in the same way as was the potassium salt. It was a white powder which decomposed at 109°. The aqueous solution of this salt became turbid when it was boiled.

SILVER SALT.—One g. of the benzoyl ester was dissolved in alcohol and a little less than the calculated amount of solid silver nitrate was added; when the solution was warmed slightly the silver nitrate dissolved. A large amount of ether was necessary to precipitate the heavy white salt which was collected and washed with water. When dry it decomposed at about 190° and turned black. It darkened slowly in the light.

Anal. Subs., 0.0699: Ag, 0.0147. Calcd. for $C_{27}H_{20}O_3NAg$: Ag, 21.01. Found: 21.03.

Acetyl *p*-Benzhydryl-benzhydroxamate

$p\text{-}[(C_6H_5)_2CH]C_6H_4CO.NHO.COCH_3$

Five g. of the hydroxamic acid was heated with 15 cc. of acetic anhydride until the reaction was complete (as determined by the ferric chloride test). As the mixture cooled, a solid mass of crystals formed; washed with water and dried, the product weighed 5.7 g. (quantitative yield). The ester could be recrystallized from a mixture of benzene and ligroin, but dil. methyl alcohol was better. From the latter it was deposited in clusters of long, silky needles; m. p., 157–158°.

Anal. Subs., 0.3987: N_2, 15.4 cc. (26°, 758 mm.). Calcd. for $C_{22}H_{19}O_3N$: N, 4.06. Found: 4.20.

POTASSIUM SALT.—This salt was prepared in the same way as was the potassium salt of the benzoyl derivative. It was a fine, white powder that decomposed when heated to 130°. Its rearrangement was similar to that of the potassium salt of the benzoyl ester.

Anal. Subs., 0.3428: K_2SO_4, 0.0799. Calcd. for $C_{22}H_{18}NO_3K$: K, 10.20. Found: 10.19.

SODIUM SALT.—Methyl alcohol was better than ethyl alcohol for the preparation of this salt. A relatively small amount of ether was required to precipitate it from the alcoholic solution. It was a white solid that decomposed at 140°, and gave the urea when heated with water.

Anal. Subs., 0.4856: Na_2SO_4, 0.0873. Calcd. for $C_{22}H_{18}NO_3Na$: Na, 6.26. Found: 5.96.

SILVER SALT.—One g. of the acetyl ester was dissolved in methyl alcohol, and a concentrated aqueous solution containing not quite the calculated amount of silver nitrate was added. When the solution was concentrated by evaporation in an open dish, the silver salt was obtained as a heavy, white powder. It began to darken at 150° and decomposed at 200°.

Anal. Subs., 0.2002: Ag, 0.0483. Calcd. for $C_{22}H_{18}NO_3Ag$: Ag, 24.4. Found: 24.1.

In order to establish more completely the identity of the rearrangement products, which are new compounds, *sym.*-di-*p*-benzhydrylphenyl-urea and *p*-benzhydrylphenyl-urethan were prepared in another way.

p-Benzhydrylbenzamide

p-$[(C_6H_5)_2CH]C_6H_4CONH_2$

This compound was formed by the action of ammonia on *p*-benzhydrylbenzoyl chloride dissolved in benzene or in ether. When benzene was used, the amide precipitated along with ammonium chloride, from which it was separated by extracting the ammonium chloride with water. With ether, the ammonium chloride was removed by filtration and the ether solution of the amide evaporated. Recrystallized from benzene or from dilute alcohol it formed long, colorless needles; m. p., 149°; yield, almost quantitative.

Anal. Subs., 0.6748: N_2, 30.8 cc. (28°, 748 mm.). Calcd. for $C_{20}H_{17}ON$: N, 4.88. Found: 4.91.

p-Benzhydrylphenyl-urethan

p-$[(C_6H_5)_2CH]C_6H_4NHCO_2C_2H_5$

Ten g. of the acid amide was suspended in an alcoholic solution of sodium ethylate made from 2.7 g. of sodium and to this solution 9.2 g. of bromine was added, that is, an amount equivalent to the sodium used. An excess of sodium ethylate and bromine was necessary to secure a satisfactory yield of urethan. Thus, about 3.3 equivalents were employed while the reaction calls for only 2. The mixture was refluxed for 15 minutes after which sodium bromide was removed by filtration and the alcohol by evaporation. The residue was dissolved in hot benzene and, as the solution cooled, 3 g. of unchanged amide separated. This was removed and the benzene distilled; the residue was the desired urethan. It crystallized from dil. alcohol in the form of very fine, colorless prisms; m. p., 103°; yield, 6 g., or 53%.

Anal. Subs., 0.6218: N_2, 25.2 cc. (22°, 757 mm.). Calcd. for $C_{22}H_{21}O_2N$: N, 4.23. Found: 4.43.

The melting point was unchanged when this compound was mixed with the compound formed by the rearrangement of the hydroxamic acid in alcohol.

p-Benzhydrylphenyl-isocyanate

p-$[(C_6H_5)_2CH]C_6H_4NCO$

The method used was adopted from Folin.[16] Three g. of the urethan in 10 cc. of chloroform was treated with 1.9 g. (1 molecular equivalent) of phosphorus pentachloride. The mixture was warmed a short time; then most of the phosphorus oxychloride was expelled in a stream of hydrogen chloride. During this operation chloroform was added from time to time to replace that lost by evaporation. Finally, 50 cc. of benzene was added and this solution, which contained the urea chloride, was treated with lime. On the next day the solution of the isocyanate was filtered from the lime. No attempt

---

[16] Folin, *Am. Chem. J.*, **19**, 324 (1897).

was made to isolate the isocyanate; the solution was treated directly with the amine to form the urea.

Preparation of *p*-Benzhydrylaniline

p-$[(C_6H_5)_2CH]C_6H_4NH_2$

The amine was prepared according to the method described by Baeyer and Löhr.[17] *p*-Nitrobenzaldehyde, made by the action of chromyl chloride[18] on *p*-nitrotoluene, was condensed with benzene in the presence of concd. sulfuric acid, to form *p*-nitro-triphenylmethane. Reduction of this nitro compound by means of tin and hydrochloric acid in alcoholic solution, gave the amine; m. p., 83°.

sym.-Di-*p*-Benzhydrylphenyl-urea

$[(C_6H_5)_2CH.C_6H_4NH]_2CO$

The solution of the isocyanate prepared as described above was treated with 3 g. of *p*-benzhydrylaniline. After a few hours, a voluminous white precipitate deposited. This was collected and digested with warm, dil. hydrochloric acid to free it from the amine hydrochloride which might be present if any urea chloride remained undecomposed after the treatment with lime. Recrystallization of this solid from acetone produced long, silky needles; m. p., 262°; yield, 4 g.

Anal. Subs., 0.6063: N_2, 28.4 cc. (22°, 757 mm.). Calcd. for $C_{39}H_{32}ON_2$: N, 5.16. Found: 5.23.

The melting point of a mixture of this substance and that obtained by the rearrangement of the hydroxamic acid in water was 262°; so no change in melting point occurred.

Hydroxamic Acids Derived from *o*-Benzhydrylbenzoic Acid

The Preparation of *o*-Benzhydrylbenzoic Acid, *o*-$[(C_6H_5)C_2H]C_6H_4.COOH$.—This substance was prepared according to the method of Baeyer.[19] Phthalyl chloride was treated with benzene and aluminum chloride and gave diphenylphthalide. The latter was reduced by zinc dust in an alkaline solution to form the acid; m. p., 161°.

o-Benzhydryl-benzhydroxamic Acid

o-$[(C_6H_5)_2CH]C_6H_4.CO.NHOH$

The Decomposition of Hydroxylammonium *o*-Benzhydrylbenzoate.—An attempt was made to prepare the hydroxamic acid of *o*-benzhydrylbenzoic acid by heating its hydroxylammonium salt, a method found by Jones and Oesper[20] to be applicable in the case of a few of the aliphatic acids.

PREPARATION OF HYDROXYLAMMONIUM *o*-BENZHYDRYLBENZOATE, *o*-$[(C_6H_5)_2CH]$-$C_6H_4COONH_3OH$.—An alcoholic solution of *o*-benzhydrylbenzoic acid was treated with an equivalent amount of free hydroxylamine and concentrated in a vacuum. The salt was obtained as a fine, white powder which, when recrystallized from alcohol, melted at 146–148° (with decomposition).

Anal. Subs., 0.4276: N_2, 16.8 cc. (23°, 757 mm.). Calcd. for $C_{20}H_{19}O_3N$: N, 4.36. Found: 4.42.

---

[17] Baeyer and Löhr, *Ber.*, **23**, 1623 (1890).

[18] v. Richter, *Ber.*, **19**, 1060 (1886).

[19] Baeyer, *Ann.*, **202**, 50 (1880).

[20] Jones and Oesper, *Am. Chem. J.*, **42**, 315 (1909).

DECOMPOSITION OF THE HYDROXYLAMMONIUM SALT.—When the salt was heated in an oil-bath to 150°, it melted and decomposed. A gas escaped which contained ammonia. When gas evolution had ceased, the melted mass solidified slowly and did not melt again until the temperature was raised to 161°, the melting point of the free acid. Under no conditions could a test for the hydroxamic acid be obtained during the decomposition. The reaction consisted of dissociation into the carboxylic acid and hydroxylamine, which decomposed.

The Action of Hydroxylamine upon Methyl *o*-Benzhydrylbenzoate. PREPARATION OF METHYL *o*-BENZHYDRYLBENZOATE, *o*-$[(C_6H_5)_2CH]C_6H_4CO.OCH_3$.—Ten g. of *o*-benzhydrylbenzoic acid was dissolved in 50 cc. of a 3% solution of hydrogen chloride in methyl alcohol and the solution was heated under a reflux condenser for four hours. The solution was then neutralized with sodium carbonate and concentrated. The solid which separated when the solution cooled was crystallized from ethyl acetate; yield, 9.5 g.; m. p., 98°. This compound has also been prepared by Haller and Guyot[21] by the action of methyl sulfate upon the acid in alkaline solution.

THE ACTION OF HYDROXYLAMINE UPON THE ESTER.—When the methyl ester was dissolved in methyl alcohol, and treated with hydroxylamine and an equivalent amount of sodium methylate, it gave a slight test for the hydroxamic acid after a day. However, the amount of the copper salt of the hydroxamic acid that was precipitated by the addition of a solution of copper acetate was very small even after several days.

The Action of Hydroxylamine upon *o*-Benzhydrylbenzoyl Chloride. THE ACTION OF THIONYL CHLORIDE UPON *o*-BENZHYDRYLBENZOIC ACID.—In an attempt to prepare the acid chloride, *o*-benzhydrylbenzoic acid was treated with an excess of pure, redistilled thionyl chloride and warmed under a reflux condenser until evolution of hydrogen chloride ceased. When the excess of thionyl chloride was distilled, a yellow crystalline residue remained; recrystallized from a mixture of benzene and ligroin, it melted at 164°.

This was not the acid chloride since it could not be hydrolyzed to the carboxylic acid. In concd. sulfuric acid it gave a brilliant red coloration which is characteristic of hydroxy-anthrone[19] derivatives. When it was dissolved in hot absolute alcohol, light yellow leaflets melting at 158° separated as the solution cooled. 9-Phenyl-9-ethoxy-anthrone[22] melts at 158°. Also, when it was shaken in ether with a small amount of an aqueous solution of sodium carbonate, it was hydrolyzed to give a compound which, when crystallized from toluene, formed long, shining needles melting at 208°; 9-phenyl-9-hydroxyanthrone[19] has the same melting point. Therefore, the compound obtained by the action of thionyl chloride on *o*-benzhydrylbenzoic acid was 9-phenyl-9-chloro-anthrone[23] (m. p., 164°). This was checked by a chlorine determination.

Anal. Subs., 0.5093: AgCl, 0.2386 (Carius). Calcd. for $C_{20}H_{13}OCl$: Cl, 11.66. Found: 11.58.

Free thionyl chloride not only caused condensation of the acid to form an anthrone derivative but also chlorinated the anthrone.

PREPARATION OF SODIUM *o*-BENZHYDRYLBENZOATE, *o*-$[(C_6H_5)_2CH]C_6H_4COONa$.—The acid, dissolved in hot alcohol, was treated with an equivalent amount of sodium ethylate in alcoholic solution. When the solution was cool the salt precipitated in the form of long, fine needles and an additional amount of the salt was obtained by adding ether to the filtrate. It was dried at 200°.

Anal. Subs., 0.4194: Na_2SO_4, 0.0961. Calcd. for $C_{20}H_{15}O_2Na$: Na, 7.42. Found: 7.41.

---

[21] Guyot, *Compt. rend.*, **139**, 9 (1904).

[22] Liebermann and Lindenbaum, *Ber.*, **38**, 1802 (1905).

[23] Haller and Guyot, *Bull. soc. chim.*, [3] **17**, 876 (1897).

THE ACTION OF PHOSPHORUS OXYCHLORIDE UPON THE SODIUM SALT.—The sodium salt, suspended in ether or in benzene, was heated with the calculated amount of phosphorus oxychloride for several hours. The formation of a small amount of acid chloride could be shown by diluting a few drops of the reaction mixture with ether and adding a little hydroxylammonium chloride, sodium carbonate and a drop of water. After the solution had been shaken for a minute it was tested for the hydroxamic acid by means of ferric chloride. The presence of the hydroxamic acid showed that the original solution contained acid chloride, but in very small amount. The products isolated were mainly unchanged acid together with some phenylanthrone[24] (formed by internal condensation), and a small amount of a compound which crystallized from toluene in long, silky needles and melted at 276°. It is probable that this was the acid anhydride, but the amount obtained was too small for identification.

THE PREPARATION OF *o*-BENZHYDRYLBENZOYL CHLORIDE, *o*-$[(C_6H_5)_2CH]C_6H_4$-COCl.—A large number of experiments were carried out in which the free acid was dissolved in solvents such as ether, benzene, ligroin, chloroform and carbon disulfide and heated for varying periods of time with phosphorus pentachloride, phosphorus oxychloride or thionyl chloride. When the acid was dissolved in chloroform, or in carbon disulfide (or a mixture of the two) and the solution was refluxed with a slight excess of thionyl chloride until hydrogen chloride ceased to be evolved, the acid chloride was produced without the simultaneous formation of the by-products mentioned above. The following method was adopted.

Ten g. of *o*-benzhydrylbenzoic acid was dissolved in a mixture of 50 cc. of chloroform and 50 cc. of carbon disulfide and treated with an excess (8 g.) of thionyl chloride. After the mixture had been heated under a reflux condenser for four hours, the liquids were distilled in a stream of dry air. More solvent was added from time to time to make sure that all unused thionyl chloride was displaced. Finally, all of the solvent was distilled and the yellow, viscous residue was crystallized from ligroin. It formed large, slightly yellow needles; m. p., 85°.

Anal. Subs., 0.2418: AgCl, 0.1128 (Carius). Calcd. for $C_{20}H_{15}OCl$: Cl, 11.57. Found: 11.54.

The acid chloride gave a dark brown color to concd. sulfuric acid, which changed rapidly through green to violet; the color change was hastened by heat.

THE PREPARATION OF *o*-BENZHYDRYL-BENZHYDROXAMIC ACID, *o*-$[(C_6H_5)_2CH]$-$C_6H_4CONHOH$.—The acid chloride obtained from 10 g. of the carboxylic acid was dissolved in 200 cc. of ether, and a slight excess of hydroxylammonium chloride (3.7 g.) together with sodium carbonate (5.8 g.) was added to this solution. Five cc. of water was introduced and the mixture was stirred mechanically for an hour, after which it was filtered and the ether distilled. The residue was purified by dissolving it in hot amyl acetate and adding ligroin to the solution until it became turbid. The acid was deposited in the form of small, thick needles melting at 177–178° with decomposition; yield, 7 g. It was soluble in most organic solvents, insoluble in water and in ligroin, and only slightly soluble in dil. alkalies.

Anal. Subs., 0.9216: N_2, 35.4 cc. (28°, 757 mm.). Calcd. for $C_{20}H_{17}O_2N$: N, 4.62. Found: 4.3.

The Decomposition of *o*-Benzhydryl-benzhydroxamic Acid when Heated.—One g. of the hydroxamic acid was heated in a test-tube placed in an oil-bath. At 180° decomposition took place. When the decomposition was complete the solid residue was dissolved in hot acetone from which, as the solution cooled, small, shining needles (0.6 g.) deposited; m. p., 196°.

---

[24] Lossen, *Ann.*, **175**, 320 (1875).

Ring compounds are very readily formed from *ortho* disubstituted benzene derivatives of this kind. A monohydroxamic acid when heated[24] usually undergoes the Beckmann rearrangement, but if the radical had very little tendency to migrate as in this case, dehydration of the hydroxamic acid with the formation of a ring compound might take place in preference to rearrangement. If this occurred in the case of *o*-benzhydrylbenzhydroxamic acid it would give diphenyl-phthalimidine.

Attempts to Prepare Diphenyl-phthalimidine, $(C_6H_5)_2\overline{C.C_6H_4.CO.N}H$.—Diphenylphthalide was heated in an atmosphere of ammonia and also with a saturated alcoholic solution of ammonia in a sealed tube for several hours at 140°, but diphenylphthalide was recovered unchanged. Diphenylphthalide was also heated to 200° with urea but the product was the unchanged phthalide together with cyanuric acid.

The next method chosen consisted in the oxidation of *o*-benzhydryl-benzamide to the triphenylcarbinol derivative. The latter might lose water to give diphenyl-phthalimidine.

The Preparation of *o*-Benzhydrylbenzamide, *o*-$[(C_6H_5)_2CH]C_6H_4CONH_2$.—Ammonia was passed into an ether solution of the acid chloride formed from 5 g. of the carboxylic acid. The solution of the acid amide was filtered from the precipitate of ammonium chloride and the ether distilled. The residue was crystallized from a mixture of benzene and ligroin; this gave a felt-like mass of colorless needles; yield, 3.7 g.; m. p., 129–130°.

Anal. Subs., 014682: N_2, 21 cc. (23°, 746 mm.). Calcd. for $C_{20}H_{17}ON$: N, 4.89. Found: 4.93.

The anilide was prepared in a similar way with aniline instead of ammonia. It formed long needles; m. p., 152–153°.

The Oxidation of *o*-Benzhydrylbenzamide.—One g. of the amide was dissolved in 25 cc. of glacial acetic acid, the solution was treated with a slight excess of chromic anhydride, warmed on a water-bath for two hours and poured into water. This precipitated a white solid which was collected and washed. Recrystallized from alcohol, it melted at 114° and proved to be diphenylphthalide. It was formed by the loss of ammonia instead of water from the carbinol derivative.

It was subsequently shown that the compound formed by heating the hydroxamic acid could not be diphenyl-phthalimidine. When it was hydrolyzed by heating it in a sealed tube at 140° with concd. hydrochloric acid it gave *o*-benzhydrylaniline (*o*-aminotriphenylmethane)[25] which was identified by its melting point (128°) and by conversion into the acetyl derivative (m. p., 154°). Diphenyl-phthalimidine when hydrolyzed would give diphenylphthalide. The compound (m. p., 196°) was *sym.*-di-*o*-benzhydrylphenyl-urea, (*o*-$[(C_6H_5)_2CH]C_6H_4NH)_2CO$, (see below).

Benzoyl *o*-Benzhydryl-benzhydroxamate

o-$[(C_6H_5)_2CH]C_6H_4.CO.NHO.COC_6H_5$

Difficulty was encountered in preparing the benzoyl ester of the hydroxamic acid. When the hydroxamic acid was heated with benzoic anhydride a very impure compound and a small yield resulted. The slight solubility of the hydroxamic acid in dil. alkali made it difficult to employ the Schotten-Baumann reaction. However, this reaction, modified as follows, gave satisfactory results.

Six g. of *o*-benzhydryl-benzhydroxamic was dissolved in 100 cc. of 60% alcohol containing a slight excess of potassium hydroxide. The solution was benzoylated by treating it gradually with benzoyl chloride. After each addition of the chloride the

---

[25] Baeyer and Bassett, *Ber.*, **37**, 3199 (1904).

mixture was shaken. This was continued until a test portion of the solution gave no coloration when treated with ferric chloride. Slightly more than the calculated amount of benzoyl chloride was required; some ethyl benzoate was formed. The benzoyl ester which precipitated during the reaction was collected and washed with water. Crystallized from alcohol it gave small, colorless needles; m. p., 118–120°.

Anal. Subs., 0.3083: N_2, 9.8 cc. (28°, 750 mm.). Calcd. for $C_{27}H_{21}O_3N$: N, 3.44. Found: 3.42.

It was soluble in most of the organic solvents but insoluble in water. It was insoluble in cold, dilute solutions of the alkalies, but dissolved slightly when the solution was heated.

Rearrangement of the Benzoyl Ester.—Two g. of the benzoyl ester was suspended in a normal solution of potassium hydroxide and heated to boiling for two hours. The white solid was then collected; yield, 1.5 g. Recrystallized from alcohol, it melted at 196°. This was the urea (see below).

POTASSIUM SALT.—One g. of the benzoyl ester was dissolved in as little methyl alcohol as possible (5 cc.) and treated with the calculated amount of a concentrated solution of potassium methylate. When 300 cc. of dry ether was added, a cloudiness appeared in the solution and, after some time, a tardy precipitation of 0.4 g. of the potassium salt. The dry salt was very stable when heated; it darkened slightly at about 200°. In boiling water it rearranged slowly to give the urea.

SILVER SALT.—An aqueous solution of silver nitrate was added to a methyl alcoholic solution of the potassium salt. A voluminous white precipitate appeared which was collected and washed. The dry salt darkened when heated above 210°.

Anal. Subs., 0.1976: AgCl, 0.0416. Calcd. for $C_{27}H_{20}O_3NAg$: Ag, 21.01. Found: 21.04.

sym.-Di-*o*-Benzhydrylphenyl-urea

$(o\text{-}[(C_6H_5)_2CH]C_6H_4.NH)_2CO$

In order to prove that the compound (m. p., 196°) formed when the hydroxamic acid rearranged was *sym.*-di-*o*-benzhydrylphenyl-urea, the latter was synthesized for comparison.

Preparation of *o*-Benzhydrylaniline, $o\text{-}[(C_6H_5)_2CH]C_6H_4NH_2$.—The amine was made according to the method described by Baeyer and Bassett.[26] *o*-Amino-triphenylcarbinol, formed by the action of phenylmagnesium bromide upon methyl anthranilate, was reduced in glacial acetic acid by means of zinc dust to form the acetyl derivative of *o*-benzhydrylaniline. Hydrolysis of the latter compound by means of alcoholic hydrochloric acid gave the amine hydrochloride from which the free amine was obtained by the action of alkali; m. p., 128°.

Preparation of *sym.*-di-*o*-Benzhydrylphenyl-urea, $(o\text{-}[(C_6H_5)_2CH]C_6H_4.NH)_2CO$.—Five g. of the amine was dissolved in 100 cc. of benzene and treated with an excess of phosgene. The solution was allowed to stand for a day after which the benzene was distilled. The residue was then boiled with a dilute solution of sodium hydroxide. This caused hydrolysis of the urea chloride (*o*-benzhydrylphenyl-carbamyl chloride) formed by the action of the excess of phosgene and gave a yield of the urea which was almost quantitative. Recrystallized from alcohol, the urea melted at 196°; the melting point remained unchanged when some of the product formed in the rearrangements described above was mixed with the synthesized urea.

Anal. Subs., 0.4011: N_2, 19.6 cc. (25°, 753 mm.). Calcd. for $C_{39}H_{32}ON_2$: N, 5.15. Found: 5.21.

---

[26] Ref. 25, p. 3192.

m-Benzhydrylbenzoic Acid

Preparation of *m*-Nitro-triphenylmethane, *m*-$O_2N.C_6H_4.CH(C_6H_5)_2$.—This nitro compound was made by Tschacher.[27] He condensed *m*-nitrobenzaldehyde with benzene in the presence of concd. sulfuric acid. The following procedure was adopted.

Twenty-five g. of *m*-nitrobenzaldehyde was dissolved in 150 cc. of dry benzene, and 75 cc. of concd. sulfuric acid was added. The mixture was shaken for 12 hours in a shaking machine, after which the benzene layer was removed and washed with sodium hydroxide, followed by a solution of sodium hydrogen carbonate and finally by water. The benzene solution, dried over calcium chloride, was distilled; an oily residue remained which solidified later; yield, 30 to 40 g.

Preparation of *m*-Amino-triphenylmethane, *m*-$H_2N.C_6H_4.CH(C_6H_5)_2$.—The nitro compound can be reduced to the amine by means of zinc dust in glacial acetic acid,[26] but reduction in alcoholic solution with tin and hydrochloric acid is better.

Forty g. of the nitro compound was dissolved in 150 cc. of alcohol, and 20 g. of granulated tin was added. The boiling solution was then gradually treated under a reflux condenser with 30 cc. of concd. hydrochloric acid. After all of the acid had been added the mixture was refluxed for half an hour to complete the reduction. The excess of tin was collected and a part of the alcohol distilled. When the remaining solution was poured into a large amount of ice and water the amine hydrochloride separated. This was collected and crystallized from hot water from which it came down as a felt-like mass of fine needles; yield, 90%. The free base melted at 120°, as recorded by Tschacher.

***m*-Carboxy-triphenylmethane,** *m*-$HOOC.C_6H_4.CH(C_6H_5)$.—The amine was converted into the carboxylic acid by means of the Sandmeyer reaction as modified by Clarke.[28] On account of its insolubility in cold water, the amine hydrochloride could not be diazotized in aqueous solution. The method adopted was as follows.

Ten g. of the amine hydrochloride was suspended in 20 cc. of alcohol and 3 cc. of concd. hydrochloric acid was added. Nitrous fumes from arsenious oxide and nitric acid were then passed in until the hydrochloride had completely dissolved. The resulting alcoholic solution of the diazonium chloride (cooled to 0°) was then neutralized by means of a solution of sodium carbonate.

A solution of sodium cuprocyanide was made according to the directions of Clarke.[28] This was covered with 200 cc. of benzene and cooled. The neutral diazonium solution prepared above was added slowly while the mixture was stirred. This caused a brown precipitate to form which gradually disappeared as the temperature of the solution approached 50°. The benzene layer was separated and washed with water. When the benzene was distilled, a thick, brown residue containing much tar remained. By extraction with hot alcohol most of the tar was left behind.

The alcoholic extract which contained the nitrile was treated with a strong solution of potassium hydroxide and heated under a reflux condenser until ammonia ceased to be evolved. Part of the alcohol was then distilled and the remaining solution, diluted with water and filtered, was acidified with hydrochloric acid. This caused the precipitation of the carboxylic acid as a flocculent, brown solid.

To purify the acid it was dissolved in the least possible amount of a hot solution of sodium carbonate. When the solution cooled, the sodium salt, which is only slightly soluble in cold water, precipitated and was collected. By dissolving the salt in warm water and adding dil. hydrochloric acid to the solution the free acid was precipitated as a white powder. Recrystallized from dilute alcohol, it formed clusters of colorless needles; m. p., 179°; yield, 0.5 g.

---

[27] Tschacher, *Ber.*, **21**, 188 (1888).

[28] Clarke, THIS JOURNAL, **46**, 1001 (1924).

Anal. Subs., 0.2462: CO_2, 0.7531; H_2O, 0.1451. Calcd. for $C_{20}H_{16}O_2$: C, 83.33; H, 5.55. Found: C, 83.45; H, 5.45.

Summary

1. The hydroxamic acids derived from *o*- and *p*-benzhydrylbenzoic acids were prepared and their ease of rearrangement was studied.

2. These hydroxamic acids undergo rearrangement with great difficulty, which is in marked contrast to the ease of rearrangement of triphenylacethydroxamic acid. Since they contain a radical (benzhydrylphenyl) which is isomeric with triphenylmethyl, the radical found in triphenylacethydroxamic acid, it is conclusively shown that the mass of the radical is not the factor that determines the ease of rearrangement in reactions of the Lossen-Hofmann-Curtius type. Therefore, the ease of rearrangement seems to be related in some way to the "tendency of the radical to exist as a free radical."

3. *o*- and *p*-Benzhydrylphenyl-urea, the products obtained when these hydroxamic acids rearrange in water, were synthesized and found to be identical with the rearrangement products. *p*-Benzhydrylphenyl-urethan, the rearrangement product of *p*-benzhydryl-benzhydroxamic acid in alcohol, was also synthesized.

4. 9-Phenyl-9-chloro-anthrone was formed when *o*-benzhydrylbenzoic acid was treated with thionyl chloride. In chloroform or in carbon disulfide solution, *o*-benzhydrylbenzoyl chloride was formed when the acid was treated with thionyl chloride.

5. Unsuccessful attempts were made to prepare diphenyl-phthalimidine.

6. *m*-Benzhydrylbenzoic acid was prepared.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

THE OXIDATION OF *d*-GLUCOSE BY AIR IN CALCIUM HYDROXIDE SOLUTION

BY M. H. POWER AND FRED W. UPSON[1,2]

RECEIVED JULY 23, 1925 PUBLISHED JANUARY 8, 1926

The conversion of an aldose into another aldose and several ketoses by weak alkalies or certain salts, first observed by Lobry de Bruyn[3] and later investigated by Nef,[4] was interpreted by the latter as depending on the presence of several "enols," similar to the enol common to glucose, mannose and fructose suggested by Wohl.[5] In a series of studies by Nef

---

[1] Abstracted from a thesis submitted by M. H. Power in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Nebraska.

[2] The junior author acknowledges the aid of the du Pont Scholarship in Chemistry during the year 1920–21.

[3] de Bruyn, *Rec. trav. chim.*, **14**, 204 (1895).

[4] Nef, *Ann.*, **403**, 206, 338 (1914).

[5] Wohl, *Ber.*, **33**, 3095 (1900).