[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Phenyl- and Benzyl-malonohydroxamic Acids and their Rearrangements

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RECEIVED JUNE 27, 1958

Phenyl- and benzyl-malonohydroxamic acids were prepared as sodium salts by reaction of the corresponding ethyl esters with hydroxylamine and sodium ethoxide. Cupric salts were prepared from the sodium salts, but only non-crystalline hydroxamic acids could be obtained from any of the salts. The sodium salts readily were acylated by acetic anhydride or benzoyl chloride. Rearrangement of the sodium salts with toluenesulfonyl chloride led to the formation of 5-phenyl- or 5-benzyl-3-*p*-tolylsulfonoxyhydantoin. Rearrangement of the benzoyl derivative of phenylmalonohydroxamic acid gave rise to a different substance having the properties of a "diphenylhydantil."

Relatively few difunctional hydroxamic acids have ever been studied. Of the malonohydroxamic acids, $RCH(CONHOH)_2$, only the unsubstituted compound ($R = H$) has been studied extensively.[1-5] Considerably more attention has been devoted to the half-hydroxamic derivatives, the N-hydroxymalonamic acids RCH(COOH)CONHOH wherein R = hydrogen,[6] butyl,[6] ethyl,[7] benzyl,[7] allyl[8] and 3-indolylmethyl.[8]

The present study deals with phenylmalonohydroxamic acid (Ia) and benzylmalonohydroxamic acid (Ib). One objective was to learn whether linear polyureas could be prepared by a Lossen rearrangement of derivatives of these acids. It has been reported previously[6] that rearrangement of appropriate derivatives of substituted malonohydroxamic acids of the type HOOC–CHR–CONHOH resulted in linear polypeptides, $(\text{–CHR–CONH–})_n$. It also has been reported[5] that the only isolable product from the rearrangement of benzoylated malonohydroxamic acid was diphenylurea. In the present study we found that rearrangement of the substituted malonohydroxamic acids yielded only cyclic compounds.

Sodium phenylmalonohydroxamate and sodium benzylmalonohydroxamate were prepared from the corresponding malonic esters. The salts were troublesome to handle since they were extremely deliquescent and tended to precipitate as gums. The sodium content of various batches of these salts was lower than the calculated value by as much as 1.8%. The same troubles were reported previously[5,9] for the sodium salts of similar compounds. Prolonged drying of the salts over phosphorus pentoxide at reduced pressure produced analytical results closer to the theoretical. Tests for the presence of hydroxylamine or ethanol in the salt were negative.

$RCH(CONHOH)_2$
Ia, $R = C_6H_5$
b, $R = C_6H_5CH_2$

$RCH(CONHOCOCH_3)_2$
IIa, $R = C_6H_5$
b, $R = C_6H_5CH_2$

$RCH(CONHOCOPh)_2$
IIIa, $R = C_6H_5$
b, $R = C_6H_5CH_2$

No satisfactory way was found for conversion of the sodium salts to pure crystalline forms of the hydroxamic acids themselves (I). Direct acidification and various modes of processing gave rise only to glassy solids. Conversion to the dark green copper salts, followed by treatment with hydrogen sulfide, yielded either gums or glassy solids which could not be made to crystallize. They all gave strong hydroxamic color reactions with ferric chloride. A sample of glassy benzylmalonohydroxamic acid, on boiling with acetonitrile in an attempt to crystallize it, produced a small amount of a white solid, which was insoluble in the common organic solvents, and had a high decomposition point. The behavior of this solid was very similar to that of the rearrangement product of phenylmalono-(benzoylhydroxamic) acid, which is described below.

Another sample of gummy benzylmalonohydroxamic acid was boiled briefly with acetic anhydride. The product analyzed correctly for a tetraacetylated product, presumably benzylmalono-(diacetylhydroxamic) acid.

Acetylation of cold aqueous solutions of the disodium salts of I with acetic anhydride produced phenylmalono-(acetylhydroxamic) acid (IIa), and benzylmalono-(acetylhydroxamic) acid (IIb). The acetyl group in these compounds was quite susceptible to hydrolysis. A sample of pure IIb kept in a screw cap vial became soft and sticky within a few weeks. Eventually it changed to a viscous liquid that had a strong odor of acetic acid and that gave an intense ferric chloride color reaction.

Benzoylation of the disodium salts of I with benzoyl chloride in cold buffered aqueous solution produced phenylmalono-(benzoylhydroxamic) acid (IIIa) and benzylmalono-(benzoylhydroxamic) acid (IIIb); IIIb was obtained in higher yield than IIIa.

The benzene washings of crude IIIa contained benzoic acid and dibenzohydroxamic acid. The formation of dibenzohydroxamic acid points to a reaction of the benzoyl chloride with free hydroxylamine that originated from phenylmalonohydroxamic acid by hydrolysis.

It is interesting to note in this connection that Botteron[10] was unable to obtain malono-(benzoylhydroxamic) acid by reaction of disodium malonohydroxamate with benzoyl chloride in aqueous solution, but that he did obtain it by working in anhydrous ether. Old samples of the sodium salt of Ia, although stored in tightly closed bottles over a

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(1) A. Hantzsch, Schatzmann and Urbahn, *Ber.*, **27**, 803 (1894).

(2) H. Schiff, *Ann.*, **321**, 363 (1902).

(3) R. H. Pickard, C. A. Allen, W. A. Bowdler and W. Carter, *J. Chem. Soc.*, **81**, 1572 (1902).

(4) C. D. Hurd and F. D. Pilgrim, THIS JOURNAL, **55**, 757 (1933).

(5) C. D. Hurd and D. G. Botteron, *J. Org. Chem.*, **11**, 207 (1946).

(6) C. D. Hurd and C. M. Buess, THIS JOURNAL, **73**, 2409 (1951).

(7) C. D. Hurd and L. Bauer, *ibid.*, **73**, 4387 (1951).

(8) C. D. Hurd and L. Bauer, *J. Org. Chem.*, **18**, 1440 (1953).

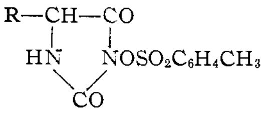
(9) C. D. Hurd, C. M. Buess and L. Bauer, *ibid.*, **19**, 1140 (1954).

(10) D. G. Botteron, Doctoral Dissertation, Northwestern University, 1942, p. 24.

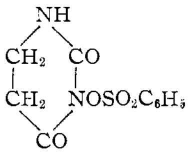
desiccant, developed yellow to red colors and an odor resembling benzaldehyde.

It also was found necessary to rinse the sodium salts completely from the crude products before recrystallization. Failure to do so resulted in extensive rearrangement, particularly with IIa and IIb. When this happened, a red oil and a white solid were produced. Red oils were produced also in attempts to benzoylate old, colored samples of disodium phenylmalonohydroxamate; but attempts to isolate the oils from the sodium salts were not successful. The oils were soluble in water, and treatment with organic solvents caused the separation of white insoluble solids which decomposed at about 340°. The white solids showed all the characteristics of the insoluble product obtained when IIIa was subjected to the Lossen rearrangement, as described later.

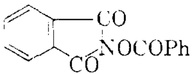
Disodium phenylmalonohydroxamate, treated with *p*-toluenesulfonyl chloride, gave rise to 3-*p*-tolylsulfonoxy-5-phenylhydantoin (IVa). The result of this rearrangement is exactly analogous to the formation of 3-phenylsulfonoxy-5,6-dihydrouracil (V) from disodium succinohydroxamate and benzenesulfonyl chloride, as described by Hurd and Bauer.[11] The formation of IVa from the rearrangement of Ia, and the findings of Hurd, Buess and Bauer[9] that benzoylation of old, colored samples of disodium phthalohydroxamate produced only "benzoylphthaloxime" (VI) suggest that the red oils obtained from Ia contained 3-hydroxy-5-phenylhydantoin (VII), but none of this material was separated in the pure state.



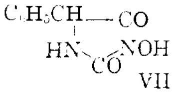
IVa, R = C_6H_5
b, R = $C_6H_5CH_2$



V

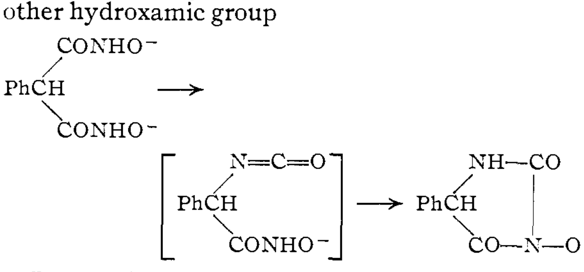


VI



VII

The formation of IVa from the anion of I may be explained by the rearrangement of one hydroxamic group to an isocyanate, which then reacts with the other hydroxamic group



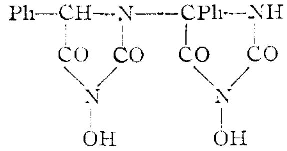
Removal of the solvent from the filtrate of a rearrangement reaction (using toluenesulfonyl chloride) left a residue, which was soluble in water and gave a strong hydroxamic color test with ferric chloride. Boiling the aqueous solution produced benzaldehyde and an ammonium salt, results which can be explained by the rearrangement of both hydroxamic groups of I. The diisocyanate, thus formed, is then hydrolyzed to a diamine, which in turn changes into an aldehyde and ammonia.

$$PhCH(CONHOH)_2 \longrightarrow [PhCH(NCO)_2] \longrightarrow [PhCH(NH_2)_2] \longrightarrow PhCHO + 2NH_3$$

Reaction of disodium benzylmalonohydroxamate with *p*-toluenesulfonyl chloride, either in refluxing toluene or in chloroform at room temperature, produced 3-*p*-tolylsulfonoxy-5-benzylhydantoin (IVb), analogous to IVa. In contrast to the results from the rearrangement of Ia and Ib with *p*-toluenesulfonyl chloride, a different result was obtained by attempting a conventional Lossen rearrangement of the sodium salt of the benzoyl derivative IIIa. When an aqueous solution of this salt was heated to 100°, a white solid precipitated.

Characterization of this solid proved to be extremely difficult. Because of its insolubility in all common organic solvents it was not possible to purify it by recrystallization, but it did dissolve in alkali and it reprecipitated on acidification. Even so, it was not possible to tell whether any purification had actually taken place because the solid had no definite melting point. It pyrolyzed without melting in the vicinity of 335-340°. The reprecipitated material decomposed at about 320°, and the unwashed original precipitate at about 285°. In addition to the purification difficulties, there were genuine analytical difficulties. None of the analytical results of any sample was reproducible. The range of results obtained suggested compositions varying from $C_{17}H_{14}N_4O_5$ to $C_{21}H_{16}N_4O_5$. Of the possible simple urea or urethan structures, which could be conceived as a product from the rearrangement of either one or both hydroxamic groups of phenylmalonohydroxamic acid, none fitted the suggested formulas.

Finally, degradation of the product by heating with concentrated hydrochloric acid at 165° in a sealed tube gave some information on its probable composition. Carbon dioxide, ammonium chloride, benzoic acid, phenylglyoxylic acid and phenylglycine were all identified as products. This result pointed to a "diphenylhydantil" type structure (VIII). The molecular formula for this compound is $C_{18}H_{14}N_4O_6$, which is within the range of results of the elemental analyses. The formation of VIII in the rearrangement of IIIa in alkaline solution could be explained by the rearrangement of one hydroxamic group to an isocyanate, followed by reaction of this with the other hydroxamic group to give rise to VII. Two such molecules then combine, in the hot alkaline solution, to produce VIII. A comparable reaction actually has been carried out by Pinner[12] who obtained "diphenylhydantil" (IX) by heating 5-phenylhydantoin (X) in alcoholic potassium hydroxide solution. Compound IX also was obtained by



VIII

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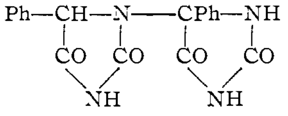
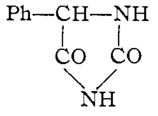
[11] C. D. Hurd and L. Bauer, THIS JOURNAL, **76**, 2791 (1954); L. Bauer, *ibid.*, **78**, 1945 (1956).

[12] A. Pinner, *Ann.*, **350**, 135 (1906).


IX


X

Gabriel[13] on heating with 5-hydroxy-5-phenylhydantoin in aqueous solution, and in a variety of other ways from X. He favored structure IX, and he degraded it to the same products that we found from the degradation of our compound. Compound IX is a white solid decomposing at 336°, insoluble in the usual organic solvents, but soluble in alkali. It has been obtained also by oxidation of X with hydrogen peroxide in alkaline solution, or with potassium permanganate in dilute sulfuric acid.[14]

Compounds with a "diphenylhydantil" type of structure may have been involved in other experiments involving X, though they have not been characterized. Thus, a mixture of phenylglyoxal hydrate, $PhCOCH(OH)_2$, and urea, after being refluxed in glacial acetic acid, yielded[15] a solid that was insoluble in the usual organic solvents, soluble in base, and infusible below 340°. It was assigned the formula $(C_9H_8N_2O_2)_n$, and it was regarded[16] as a polymer of X.

The above-mentioned formation of benzaldehyde and VIII from Ia by means of toluenesulfonyl chloride has its parallel in the apparent production of benzaldehyde from the anion of IIIa on heating, and the isolation of a solid resembling VIII during crystallization of crude IIb.

Experimental

Disodium Phenylmalonohydroxamate.—A filtered, ethanolic solution of hydroxylamine was prepared by liberation of the base from 0.6 mole of hydroxylammonium chloride in 200 ml. of absolute ethanol using sodium ethoxide. This solution, cooled to −2°, was mixed with 47.2 g. (0.2 mole) of ethyl phenylmalonate. A solution of sodium ethoxide (0.4 mole) in 200 ml. of absolute ethanol was added to it slowly with stirring. The temperature rose to 12°. The solution was then left at room temperature. A precipitate started, forming within a few minutes. The solids, collected by suction on a filter after 24 hours, weighed 28 g. Addition of 3 liters of pentane to the filtrate caused precipitation of a gum which, after drying over phosphorus pentoxide at low pressure for 24 hours, reverted to a powder (22.5 g.). Total weight of salt obtained was 50.5 g. or 99.4% yield based on $C_9H_8N_2Na_2O_4$. Analytical samples of the salt were dried over phosphorus pentoxide at low pressure.

Anal. Calcd. for $C_9H_8N_2Na_2O_4$: Na, 18.1. Found: Na, 17.4, 17.1, 18.7 (different samples).

The salt was a very hygroscopic solid, and it gave the hydroxamic acid color reaction, but not the free hydroxylamine test with a 5% aqueous potassium permanganate solution. To test for the presence of ethanol of crystallization in the salt, an aqueous solution of it was treated with an iodine solution in potassium iodide added dropwise until its color persisted. An exothermic reaction took place and a gas was evolved, but no iodoform was produced. A very small amount of a dark yellow solid which was formed had no odor and melted at 86–96° to a dark red liquid.

Copper Phenylmalonohydroxamate.—A filtered cold solution of 2.54 g. of disodium phenylmalonohydroxamate in 20 ml. of water was added with stirring to a solution of 3.00 g. of cupric acetate in 50 ml. of water. The green copper salt precipitated in colloidal form. After 23 hours at 30° it was filtered; weight, 2.44 g.

Phenylmalonohydroxamic Acid (Ia).—The phenylmalonohydroxamic acid was obtained as a glassy solid by treatment of a suspension of copper phenylmalonohydroxamate with a saturated solution of hydrogen sulfide in ethanol. It was insoluble in ether, but soluble in water and ethyl formate. It gave an intense dark red color with aqueous ferric chloride. On heating, it started decomposing at about 50°, and it melted completely with continuing decomposition at 125°.

Phenylmalono-(acetylhydroxamic) Acid (IIa).—A solution of 7.62 g. of disodium phenylmalonohydroxamate in 30 cc. of water at 3° was treated with 3.6 g. (one equivalent part) of 97% acetic anhydride, added in small portions. The mixture was shaken vigorously after each addition. A gummy solid precipitated that was collected, washed with benzene and dried in the air; yield 1.6 g. After two recrystallizations from ethyl acetate, it melted at 156.5–157° dec. A better yield of IIa would have resulted if 2 equiv. of acetic anhydride had been used.

Anal. Calcd. for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.80; N, 9.52. Found: C, 53.13; H, 4.76; N, 9.64.

Phenylmalono-(benzoylhydroxamic) Acid (IIIa).—A solution of 7.62 g. of disodium phenylmalonohydroxamate in 30 ml. of water at 3° was treated with 8.7 g. (2 equivalent parts) of benzoyl chloride, added in small portions. The precipitated solid was collected, washed twice with 30 ml. of water, twice with 15 ml. of benzene, and air-dried; yield 6 g. It was crystallized from absolute alcohol, giving material melting at 164–165° dec. A material prepared similarly by Ludwig Bauer melted at 161° with decomposition (private communication).

Anal. Calcd. for $C_{23}H_{18}N_2O_6$: C, 66.01; H, 4.34; N, 6.70; neut. equiv., 209. Found: C, 65.92; H, 4.41; N, 6.74; neut. equiv., 208.

The solid obtained by evaporation of the benzene washings was a mixture of dibenzohydroxamic acid (m.p. 160°, neut. equiv. 241.2) and benzoic acid (m.p. 120–121°). The two acids were separated by fractional precipitation from a concentrated ethanolic solution with water.

3-*p*-Tolylsulfonoxy-5-phenylhydantoin (IVa).—(A) A solution of 4.2 g. of *p*-toluenesulfonyl chloride in 10 ml. of dry toluene was added to a vigorously stirred suspension of 2.54 g. of disodium phenylmalonohydroxamate in 30 ml. of toluene at 29°. The mixture warmed up slightly. It was refluxed for one hour, cooled to room temperature, and filtered. Then, in the course of several hours, a white solid (IVa) gradually separated from the filtrate. This was collected and was crystallized twice from benzene–ligroin, m.p. 152.5–153.5° dec., weight 0.5 g. It gave no test with ferric chloride in ethanolic or warm aqueous solution.

Anal. Calcd. for $C_{16}H_{14}N_2O_5S$: C, 55.48; H, 4.07. Found: C, 55.08; H, 4.09.

(B) A rapidly stirred suspension of 2.5 g. of disodium phenylmalonohydroxamate in chloroform was treated with 4 g. of crude *p*-toluenesulfonyl chloride (containing about 30% of *p*-toluenesulfonic acid), partly dissolved in 20 ml. of chloroform. After stirring for one hour, the precipitated solid was filtered off and was treated with boiling ether twice. The IVa melted at 152.5–154° dec. and weighed 0.6 g. The residue from the chloroform filtrate, dissolved in water, gave a strong test with ferric chloride solution. The aqueous solution was refluxed for one hour and then distilled. The cloudy distillate was extracted with ether, and the ether solution was dried with anhydrous sodium sulfate, and evaporated to dryness. The residue was an oil (0.75 g.) with a strong odor of benzaldehyde. A sample of it, treated with 2,4-dinitrophenylhydrazine, gave benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 236–237° (lit. m.p. 237°). Addition of 20% sodium hydroxide solution to the residue in the distillation flask caused the evolution of ammonia which was detected by its odor and by reaction with moistened indicator paper.

Formation of VIII by Rearrangement of IIIa.—A solution of 4.18 g. (0.01 mole) of IIIa and 0.80 g. (0.02 mole) of sodium hydroxide in 25 ml. of water was refluxed for 8 minutes. Within the first three minutes of refluxing a white solid separated. The cooled reaction mixture was filtered, giving a weakly alkaline filtrate with a strong odor of benzaldehyde. The precipitate was boiled in succession with

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[13] S. Gabriel, *Ann.*, **350**, 125 (1906).

[14] G. A. Holmberg, *Acta Chem. Scand.*, **4**, 821 (1950).

[15] H. J. Fisher, J. B. Ekeley and A. R. Ronzio, THIS JOURNAL, **64**, 1434 (1942).

[16] Reference 15 lists this as $(C_9H_8N_2O_3)_n$ through typographical error. Also it names X as 4-phenylhydantoin.

water, dilute acetic acid, dilute sulfuric acid, ethanol and ether. The vacuum-dried solid weighed 1 g., and it decomposed at 335–340°. It was insoluble in water, ethanol, acetic acid, chloroform, ethyl acetate, toluene, 2-propanol, formic acid, Cellosolve, dioxane and dimethylformamide. It was readily soluble in cold dilute alkali. On acidification, a solid decomposing at 320° was precipitated. These compounds were very difficult to burn, and analyses gave scattered results (C, 57.8–62.2; H, 4.0; N, 15.6–14.1).

Degradation of VIII, the Product of Rearrangement.—A sample of VIII weighing 1.5 g. was heated with 20 ml. of concentrated hydrochloric acid in a sealed tube at 165–170° for 4.5 hours. When the cooled tube was opened, carbon dioxide gas escaped from it under slight pressure. It was identified by the formation of barium carbonate. Undissolved benzoic acid, m.p. 122°, weight 0.75 g., was in the residue. The solution, after filtration, was evaporated to dryness, and the residue was extracted with boiling ether. Evaporation of the ether left an oil. It was characterized as phenylglyoxylic acid by the formation of its yellow phenylhydrazone from acid solution (m.p. 163° dec., lit.[17] m.p. 163°, weight 130 mg.) and by the characteristic red to blue-violet color reaction with concentrated sulfuric acid and benzene that contained a trace of thiophene. The residue, unextracted by ether, was dissolved in water. A small portion of the solution gave evidence of containing ammonium chloride, since on treatment with 20% sodium hydroxide solution it evolved ammonia which was detected by its strong odor and by moistened indicator paper. The rest of the solution was treated with a boiling sodium acetate solution. The white solid which precipitated (120 mg.) was 2-phenylglycine, characterized as N-phthalyl-2-phenylglycine, m.p. 168–170° (lit.[18] m.p. 168°).

Disodium Benzylmalonohydroxamate.—(A) A solution of sodium ethoxide in absolute ethanol (prepared from 3.9 g. of sodium) was added to a vigorously stirred suspension of 10.4 g. of hydroxylammonium chloride in 50 ml. of absolute ethanol to the phenolphthalein end-point. The resulting 125 ml. of hydroxylamine solution was filtered, cooled to −4° and mixed with 12.5 g. of ethyl benzylmalonate at −4°. A sodium ethoxide solution, made from 2.3 g. of sodium, was added to the mixture with stirring and the mixture was left at 30° for 12 hours. The white solid which precipitated was filtered off and dried at reduced pressure. It weighed 11.0 g. An additional 1.5 g. of solid was recovered from the filtrate by dilution with hexane and ether.

(B) In a preparation of a larger amount of material, a total amount of 47.5 g. of product was obtained from 50 g. (0.2 mole) of ethyl benzylmalonate.

Anal. Calcd. for $C_{10}H_{10}N_2Na_2O_4$: Na, 17.2. Found: Na, 15.8.

Copper Benzylmalonohydroxamate.—A solution of 1.5 g. of copper acetate monohydrate in 25 ml. of water was added to a solution of 1.34 g. of disodium benzylmalonohydroxamate in 15 ml. of water. The green salt which precipitated weighed 1.7 g. when dry.

Benzylmalonohydroxamic Acid (Ib).—The air-dried copper benzylmalonohydroxamate was ground to a fine powder. It was suspended in a small amount of dry methanol and the suspension was saturated with hydrogen sulfide, filtered to remove copper sulfide, and the filtrate was evaporated at reduced pressure. Benzylmalonohydroxamic acid appeared as a slimy material, which reverted to a glassy solid on prolonged drying over phosphorus pentoxide at reduced pressure. A very dilute aqueous solution of it gave an intense color reaction with ferric chloride solution. Attempts to obtain a crystalline material by treatment of the glassy solid with warm ethyl acetate or ethyl propionate were not successful, but when the glassy solid was treated with boiling acetonitrile a small amount (0.1 g.) of a white solid was obtained. This solid was insoluble in the common organic solvents, and it decomposed at 330–335° without melting.

Tetraacetyl Derivative of Benzylmalonohydroxamic Acid.—A sample of the glassy benzylmalonohydroxamic acid was boiled for two minutes with an excess of acetic anhydride. Much water then was added and the solid which precipitated was filtered off, after the excess of anhydride had decomposed. The tetraacetylated benzylmalonohydroxamic acid was recrystallized thrice from dry methanol; m.p. 141–142°.

Anal. Calcd. for $C_{18}H_{20}N_2O_8$: C, 55.10; H, 5.14; N, 7.14. Found: C, 54.64; H, 5.22; N, 7.48.

Benzylmalono-(acetylhydroxamic) Acid (IIb).—A solution of 5.36 g. of disodium benzylmalonohydroxamate in 20 ml. of ice-cold water was treated with 4.20 g. (2 equiv. parts) of 97% acetic anhydride, added in small portions with gentle shaking of the flask. (Vigorous shaking caused decomposition with evolution of gas.) The precipitated solid was collected on a filter, washed well with water and dried over phosphorus pentoxide; yield 4.25 g. It was recrystallized from methanol and ethyl acetate, m.p. 169–170° (sample inserted in m.p. bath at 155° and heated up fairly fast).

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: C, 54.54; H, 5.23; N, 9.02; equiv. wt., 154. Found: C, 54.32; H, 5.16; N, 9.21; equiv. wt., 157.

The crude product was washed free of sodium salt before it was recrystallized. Recrystallization of unwashed samples of crude benzylmalono-(acetylhydroxamic) acid from methanol or ethyl acetate produced only about one-half the amount of pure product and a red oil. Prolonged treatment of the red oil with boiling ethyl acetate converted it to a white solid, insoluble in all the common organic solvents, and decomposing at 320–330°.

Storage of the crystalline benzylmalono-(acetylhydroxamic) acid in a tightly closed screw cap vial did not prevent it from becoming soft and sticky after a few weeks at 25°. Its m.p. was about 20° lower, and diffuse. An alcoholic solution of it gave a faint color test with ferric chloride, whereas the original material gave no coloration. After a few more weeks at room temperature the contents of the vial had changed to a viscous liquid. A strong odor of acetic acid was readily detectable and an aqueous solution of the sample gave a very intense color with ferric chloride solution.

Benzylmalono-(benzoylhydroxamic) Acid (IIIb).—A solution of 5.1 g. of disodium benzylmalonohydroxamate in 20 ml. of water at 0° was treated in succession with 6 ml. of benzoyl chloride, 5.4 g. of sodium acetate trihydrate and a trace of saponin. The mixture was shaken vigorously and was kept in an ice-bath for 10 minutes. After addition of 2 ml. more of benzoyl chloride, the solution was left at 0° for 15 more minutes. It was then stirred with a mixture of 50 ml. of benzene and 50 ml. of hexane, and the aqueous layer was separated and acidified (concentrated HCl). The solid product which precipitated weighed 9 g. It was slightly soluble in boiling absolute ethanol (about 0.2 g. per 100 ml.), and practically insoluble in boiling ethyl acetate, butyl acetate, butanol, or acetone. It was purified by repeated washing with water, and with boiling ethanol; m.p. 184–185° dec.

Anal. Calcd. for $C_{24}H_{20}N_2O_6$: C, 66.65; H, 4.66; N, 6.48. Found: C, 66.50; H, 4.80; N, 6.48.

3-*p*-Tolylsulfonoxy-5-benzylhydantoin (IVb).—(A) A solution of 8.0 g. of *p*-toluenesulfonyl chloride in 20 ml. of dry toluene was added to a vigorously stirred suspension of 5.4 g. of powdered disodium benzylmalonohydroxamate in 30 ml. of dry toluene. The mixture was refluxed for 0.5 hour, and filtered while hot. Addition of pentane to the filtrate, prolonged chilling of the mixture in an ice-bath, caused precipitation of 0.95 g. of IVb, m.p. 155–155.5° after three recrystallizations from methanol.

Anal. Calcd. for $C_{17}H_{16}N_2O_5S$: C, 56.66; H, 4.47. Found: C, 56.80; H, 4.23.

(B) Half quantities of reactants used in experiment A were mixed in dry chloroform. The mixture warmed up slightly, and was kept at 31° for 1.5 hours under vigorous stirring. The suspension was filtered and the chloroform was evaporated from the filtrate at room temperature. The residue, after washing with pentane, weighed 0.65 g. It was crude IVb, m.p. 150–152° dec.

Evaporation of the pentane washings left unreacted *p*-toluenesulfonyl chloride. It was dissolved in chloroform, and mixed with the residue from the original suspension. The mixture was left at 31° for 36 hours, and then it was refluxed for one hour. It was then treated as before, yielding 0.65 g. of crude IVb, m.p. 150–152° dec. Recrystallization of the combined batches of crude material from methanol yielded pure IVb, m.p. 154.5–155.5°.

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(17) F. Straus, *Ann.*, **383**, 308 (1912); J. U. Nef, *ibid.*, **280**, 295 (1894).

(18) A. Ulrich, *Ber.*, **37**, 1688 (1905).

Acknowledgment.—Microanalyses for carbon, hydrogen and nitrogen were performed by Miss H. Beck, Mrs. C. White and Miss J. Sorenson. This investigation was made possible by a grant-in-aid of research by American Viscose Corporation.

EVANSTON, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

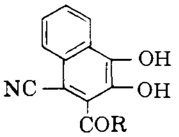
Studies on 4-Substituted-β-naphthoquinones

BY WILLIAM IBRAHIM AWAD AND MOHAMED SHAWKEY HAFEZ

RECEIVED FEBRUARY 10, 1958

The infrared curves of 1,2-dihydroxy-3-aceto-4-cyanonaphthalene and 2,3-dihydroxyacetophenone are discussed. A comparison between the ultraviolet curves of 1,2-diacetoxy-4-cyanonaphthalene and 1,2-diacetoxy-3-aceto-4-cyanonaphthalene is discussed. The photochemical reaction of some aldehydes with β-naphthoquinone, 4-cyanomethyl-1,2-naphthoquinone, 4-chloro-1,2-naphthoquinone and 4-aryloxy-1,2-naphthoquinones is investigated. The 4-aryloxy-1,2-naphthoquinones are prepared by the interaction of 4-chloro-1,2-naphthoquinone and phenols in the presence of pyridine.

Schönberg, Awad and Mousa[1] found that when 4-cyano-1,2-naphthoquinone was exposed to sunlight in the presence of an aliphatic aldehyde, *e.g.*, acetaldehyde or propionaldehyde, an orange compound of constitution I was obtained.



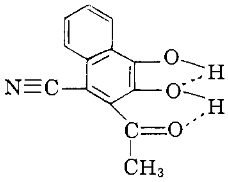
Ia, R = $-CH_3$
Ib, R = $-C_2H_5$

The chemical evidence supporting structure I has been described before.[1] Spectroscopic data of I and some related compounds are discussed here. The infrared[2] curve of Ia shows that the carbonyl group stretching frequency is at 1640 cm.$^{-1}$, which corresponds to a chelated carbonyl group. Similar values have been observed with *o*-hydroxyacetophenone (1639–1613 cm.$^{-1}$)[3a] and 3-hydroxy-2-acetonaphthalene (1657 cm.$^{-1}$).[3b] Compound Ia shows also strong absorption due to the —C≡N radical at (2190 cm.$^{-1}$)[4a]; no free –O–H stretching frequency (3650–3690 cm.$^{-1}$)[4b] could be observed. In similar cases the absence of free -OH absorption in the fundamental region has been reported (ref. 3b, p. 91).

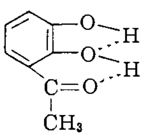
The absorption at 3460 cm.$^{-1}$ (which persists in concentrated and dilute chloroform solution) is to be attributed to hydrogen bonding by the hydroxyl group in the α-naphthyl position to the other hydroxyl group in the β-naphthyl position. The chelated hydroxyl group (*i.e.*, that in the β-naphthyl position) would be expected to give a broad band extending over the region (3400–2600 cm.$^{-1}$).[5] The wide base of the peak with maximum at 3460 cm.$^{-1}$ on its low frequency side, clearly indicates the presence of such a broad peak of relatively low intensity.

These data show that a sort of double chelation exists in the molecule and the structure of Ia is thus better represented as II.

A similar hydrogen bond was assigned to pyrogallol by Pauling[6] to account for its infrared spectrogram (overtone region).



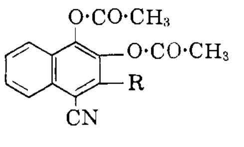
II



III

Further evidence for structure II is deduced by comparing its infrared curve (potassium bromide technique) and that of 2,3-dihydroxyacetophenone (III); III shows absorption bands at 1640 cm.$^{-1}$ (chelated carbonyl group) and at 3300 cm.$^{-1}$ (which is to be attributed to hydrogen bonding by the hydroxyl group). Again no free –OH stretching frequency could be observed.

More evidence for structure II is deduced from the comparison of the ultraviolet[7] curve of its diacetate IV and the ultraviolet[7] curve of 1,2-diacetoxy-4-cyanonaphthalene (V) prepared according to reference 1. These ultraviolet curves show that both IV and V are of analogous structure.



IV, R = $COCH_3$
V, R = H

	λ_{max}	E_{max}	λ_{max}	E_{max}	λ_{max}	E_{max}
IV	243	42200	305	6400	329	3600
V	231	50600	299	7600	328	3300

The colors of II (orange-red)[1] and III (deep-yellow)[8] have been attributed to the contribution of *o*-quinonoid structure VI, since the diacetates of II and III are colorless. If this assumption is valid *o*-

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[1] A. Schönberg, W. I. Awad and G. A. Mousa, THIS JOURNAL, **77**, 3850 (1955).

[2] Baird Double beam instrument with sodium chloride prism using the potassium bromide wafer technique on solids. The cell was 0.5 mm. and the concentration was 0.5% in potassium bromide wafer.

[3] (a) W. Gordy, *J. Chem. Phys.*, **8**, 516 (1940); (b) compare L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," first edition, reprinted 1956, Methuen and Co. Ltd., London, p. 124.

[4] (a) *Ibid.*, p. 223; (b) *ibid.*, p. 84.

[5] *Cf.* M. St. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957), with special reference to p. 29. This idea and reference were suggested by one of the referees.

[6] Linus Pauling, "The Nature of the Chemical Bond," 2nd. ed., Geoffrey Cumberlege, Oxford University Press, London, 1950, p. 325.

[7] Unicam Spectrophotometer, cell 1 cm., using ethyl alcohol as a solvent.

[8] H. v. Krannichfeldt, *Ber.*, **46**, 4017, 4018 (1913).