Anal. Calcd. for $C_{20}H_{32}N_2O$: C, 75.90; H, 10.19; N, 8.85; mol. wt., 316. Found: C, 76.1; H, 10.1; N, 8.71; mol. wt. (Signer isothermal distillation in ether *vs.* azobenzene as standard), 315.

From the mother liquors, small quantities of diacetyldicyclohexylimine II m.p. 81–82° could be obtained, identical with the product resulting from the reaction of acetoin and cyclohexylamine.[2] When this reaction was attempted with ethylamine, *n*-butylamine, *s*-butylamine or benzylamine, only dark oils or resins were obtained.

Catalytic Hydrogenation of I.—A solution of 603 mg. (1.91 millimoles) of I in 40 ml. of ethyl acetate containing 20 mg. of platinum oxide was shaken with hydrogen at 27° and 760 mm. Absorption of hydrogen was complete in 90 minutes, *V* (S.T.P.), 119.4 cc. equivalent to 2.8 moles of hydrogen per mole of compound. The product was a colorless noncrystallizing oil.

N,N′-Dicyclohexyl-2,5-dimethyl-1,4-benzoquinonediimine (VI).—One gram of the colorless dicyclohexyliminocyclohexenol I was dissolved in 100 ml. of methanol and allowed to stand three days at 25°. The solution became yellow in a few hours and gradually deposited amber crystals. The mixture was cooled to −20°, the solution changing from yellow to red. Filtration yielded 700 mg. of the yellow crystalline product. An additional 120 mg. was obtained from the mother liquor. For analysis, the compound was recrystallized from 150 parts of methanol. The compound can be obtained more quickly by refluxing solutions of I in methanol for 10–15 minutes. The compound melts at 145.6–147° without decomposition. Three yellow to amber polymorphic forms have been detected in products recrystallized from methanol, plates, needles and hexagonal prisms of which the latter is the stable phase; ultraviolet absorption in isoöctane: λ_{max} 288 mμ, ε 40,100; inflection λ 295–300 mμ, ε 35,500.

Anal. Calcd. for $C_{20}H_{30}N_2$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.3; H, 10.1; N, 9.27.

Catalytic Hydrogenation of VI.—A solution of 685 mg. (2.29 millimoles) of the quinonediimine VI in 40 ml. of ethyl acetate containing 18 mg. of platinum oxide when shaken with hydrogen at room temperature and atmospheric pressure absorbed 47.2 cc. (S.T.P.) equivalent to 0.92 mole/mole of compound. The reduction product, N,N′-dicyclohexyl-2,5-dimethyl-*p*-phenylenediamine, was obtained crystalline on evaporation of the reduction solution, and for analyses was recrystallized twice from hexane at −20°, colorless needles, m.p. 119.5–120.5°; ultraviolet absorption in isoöctane: λ_{max} 255 mμ, ε 15,400; λ_{max} 323 mμ, ε 3,070.

Anal. Calcd. for $C_{20}H_{32}N_2$: C, 79.94; H, 10.73; N, 9.32. Found. C, 80.1; H, 10.6; N, 9.28.

Acid Hydrolysis of N,N′-Dicyclohexyl-2,5-dimethyl-1,4-benzoquinonediimine.—Quinonediimine VI (580 mg., 0.00195 mole) was suspended in 50 ml. of absolute ethanol. Upon the addition of 15 ml. of 6 *N* hydrochloric acid, the yellow compound immediately dissolved to give a deep red solution which faded in a few minutes to yellow. The yellow solution, after standing overnight, was extracted four times with 30-ml. portions of pentane. Evaporation of the hydrocarbon solution yielded yellow crystalline material which was recrystallized from 10 ml. of methanol giving 182 mg. (69%) of 2,5-dimethyl-1,4-benzoquinone, m.p. 123–124°; ultraviolet absorption spectrum in isoöctane: λ_{max} 248 mμ, ε 20,900; inflection λ 253–256 mμ, ε 18,400; λ_{max} 304, ε 268.

Anal. Calcd. for $C_8H_8O_2$: C, 70.58; H, 5.93. Found: C, 70.2; H, 5.98.

The acid solution after extraction with hydrocarbon was converted to the *p*-toluenesulfonamide in the usual manner.[9]

The derivative melted at 85.5–86.4°, undepressed when mixed with an authentic sample.

(9) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 48.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, FOUAD I UNIVERSITY]

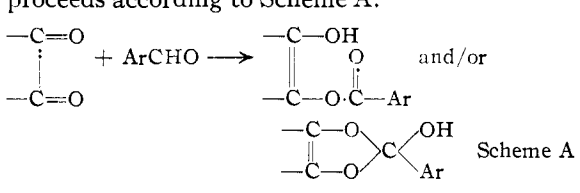
Experiments with 1,2-Benzophenazine-3,4-quinone. Thermochromic Effects Based on Lactam–Lactim Tautomerism

BY ALEXANDER SCHÖNBERG, AHMED MUSTAFA AND SALAH MOHAMED ABDEL DAYEM ZAYED

RECEIVED MARCH 19, 1953

1,2-Benzophenazine-3,4-quinone gives violet photo-addition products in sunlight with benzaldehyde and *p*-methoxybenzaldehyde. Their solutions in ethyl benzoate show reversible thermochromic changes (violet-brown $\underset{\text{hot}}{\overset{\text{cold}}{\rightleftarrows}}$ orange) attributed to reversible tautomeric changes (lactam–lactim tautomerism). 1,2-Benzophenazine-3,4-quinone by the action of phenylmagnesium bromide, followed by hydrolysis is reduced to the violet hydroquinone, and reacts with ethereal diazomethane solution to give the corresponding methylene ether.

It has been shown that the photo-addition of aldehydes to *o*-quinones is a general reaction which may be carried out with *o*-benzoquinone, β-naphthoquinone, phenanthraquinone, acenaphthenequinone and/or their derivatives.[1] The reaction proceeds according to Scheme A.



Scheme A

We have now allowed the yellow 1,2-benzophenazine-3,4-quinone (I) to react with benzaldehyde and *p*-methoxybenzaldehyde and find that addition takes place in molecular proportions. The products were, however, not yellow as expected (*cf.* the pale yellow or yellow color of 3,4-diacetoxy-1,2-benzophenazine (IIc) and 3,4-dimethoxy-1,2-benzophenazine (IIb),[2] respectively), but formed deep violet crystals. It is believed that these substances have constitution IIIb and are therefore not true derivatives of the 3,4-dihydroxy-1,2-benzophenazine (IIa). Badger and co-workers[2] have shown that the substance, formerly believed to be IIa obtained from the quinone I by the action of phenylhydrazine, is in reality IIIa which explains its blue-violet color. The photo-products IIIb are soluble in aqueous alkali, to give orange or orange-brown solutions. The violet IIIb (Ar = C_6H_5) dissolves

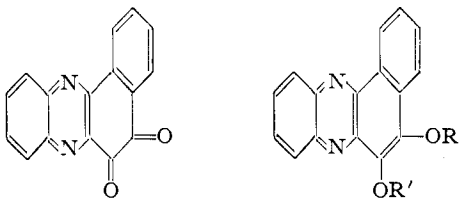
(1) A. Schönberg, N. Latif, R. Moubasher and A. Sina, *J. Chem. Soc.*, 1364 (1951).

(2) G. Badger, R. S. Pearce and R. Pettit, *ibid.*, 3204 (1951).

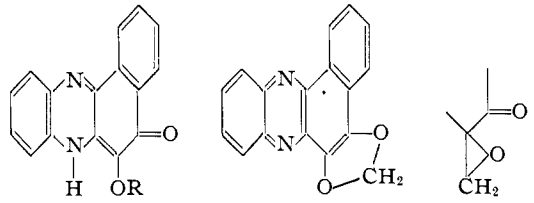
in decalin in which it is difficultly soluble at room temperature, giving a yellow solution, the color change probably being due to the change into IId (Ar = C_6H_5).

Reactions of I with the Grignard Reagent, and with Diazomethane, Respectively.—It has been shown[3] that some *o*-quinone derivatives are reduced by Grignard reagents, whereas normally, *e.g.*, in the case of phenanthraquinone and phenylmagnesium bromide, addition takes place. It has now been found that I, by the action of phenylmagnesium bromide followed by hydrolysis, is readily reduced to IIIa. The violet reduction product was identified as the diacetate IIc; the same diacetate has been obtained[2] by the action of acetic anhydride on IIIa, prepared by the action of phenylhydrazine on I.

The yellow 3,4-methylenedihydroxy-1,2-benzophenazine (IV) has been obtained by the action of ethereal diazomethane solution on I. On treatment with hydrochloric acid in the presence of acetic acid, IV yields IIIa. This excludes the formation of a methylene oxide derivative (*cf.* IVa abbreviated formula). Methylene ethers from 1,2-diketones and *o*-quinones by the action of diazoalkanes have been obtained frequently,[4] whereas the formation of an ethylene oxide is rare. It has, however, been observed in the case of phenanthraquinone and diazomethane, especially in the presence of methyl alcohol.[5]



I (yellow) IIa, R = R′ = H
IIb, R = R′ = CH_3(yellow)
IIc, R = R′ = $-COCH_3$ (pale yellow)
IId, R = H, R′ = –COAr
(lactim form and its derivatives)



IIIa, R = H (violet-blue) IV (yellow) IVa
IIIb, R = –COAr (violet)
(lactam form and its derivatives)

Thermochromism Based on Lactam–Lactim Tautomerism.—It was found that the solution of the violet photochemical addition products IIIb, (Ar = C_6H_5, Ar = *p*-$CH_3OC_6H_4$) of I with benzaldehyde and *p*-methoxybenzaldehyde in ethyl benzoate, believed to have constitutions IIIb, show thermochromic properties. Cold dilute solutions are violet-brown and much more intense in color than hot solutions which are orange. The phenomenon cannot be explained by assuming that the photo-addition products IIIb dissociate on warming into their generators (aldehyde + I) which recombine in the cold, because no combination of these generators takes place in the absence of light. It is proposed that the change is due to a lactam–lactim tautomerism (IIIb ⇆ IId), the cold (hot) solutions contain the lactam form in relative higher (lower) concentrations.[5a] This change of color with temperature using the same solvent should be compared with the change of color effected in the case of IIIa by the same temperature, but using different solvents. The tautomeric system (IIa ⇆ IIIa) dissolved in dioxan is dark reddish-brown (relatively great concentration of the lactim form). In aqueous dioxan the color is deep blue corresponding to the increased proportion of the lactam form[2] IIIa.

Experimental

General Remarks.—The benzene (thiophene-free) used was dried over metallic sodium. Ethyl benzoate (Schering–Kahlbaum) was purified by shaking with sodium carbonate for 24 hours, followed by filtration and distillation.

Photo-addition of Aromatic Aldehydes to 1,2-Benzophenazine-3,4-quinone. (a) Anisaldehyde.—A Schlenk tube (Pyrex glass)[6] containing, partially dissolved and partially suspended, 0.7 g. of I, 1 g. of *p*-methoxybenzaldehyde and 15 ml. of benzene was sealed in a stream of dry carbon dioxide and exposed to sunlight for 10 days (August). The red benzene solution was filtered from the solid contents, which were washed with acetone and crystallized several times from acetic acid as red-violet crystals, m.p. 249° (violet melt). The substance (IIIb, Ar = *p*-$CH_3OC_6H_4$-) is difficultly soluble in cold benzene and in xylene; it dissolves in concentrated sulfuric acid with a green color, and is difficultly soluble in dilute potassium hydroxide with an orange color. Its alkaline solution on acidification gives a violet color with formation of a violet deposit. *Anal.* Calcd. for $C_{24}H_{16}N_2O_4$: C, 72.7; H, 4.0; N, 7.1. Found: C, 72.5; H, 3.9; N, 6.9. Yield *ca.* 70%.

Dark Experiment.—The above experiment was repeated in the dark; I was recovered unchanged or almost unchanged.

(b) Benzaldehyde.—A mixture of 0.7 g. of I, 1.5 g. of freshly distilled benzaldehyde and 10 ml. of benzene was exposed to sunlight for 10 days (August) as described above. The solid contents of the reaction tube were collected, and crystallized from acetic acid as violet crystals, m.p. *ca.* 230°. *Anal.* Calcd. for $C_{23}H_{14}N_2O_3$: C, 75.4; H, 3.8; N, 7.6. Found: C, 74.6; H, 3.8; N, 7.7. The substance (IIIb, Ar = C_6H_5) is difficultly soluble in cold benzene, and in cold decalin with a yellow color and dissolves in concentrated sulfuric acid with an orange-brown color. It dissolves in aqueous sodium hydroxide with an orange-brown color, and on acidification with hydrochloric acid, a violet deposit is formed which redissolves in aqueous sodium hydroxide; yield, *ca.* 65%.

Investigation of the Stability of Ethyl Benzoate Solutions of IIIb (Ar = C_6H_5) toward Heat.—Twenty ml. of a solution (prepared by dissolving 20 mg. of IIIb, Ar = C_6H_5 in 25 ml. of ethyl benzoate) was divided into two equal parts and each of them placed in one of two Schlenk tubes (A and B) having the same shape and size. A and B were then sealed in a stream of dry pure nitrogen. A was kept in ice, B was heated (bath temp., 170°) for three minutes and then immersed in an ice-bath. After some time, the color of the solutions in A and B was undistinguishable.[7] The process of

(3) A. Schönberg and N. Latif, *J. Chem. Soc.*, 446 (1952).

(4) *Cf.* the action of diazoalkanes on benzil (H. Biltz and H. Paetzold, *Ann.*, **433**, 71, 81 (1923)), on β-naphthoquinone derivatives (L. F. Fieser and J. L. Hartwell, THIS JOURNAL, **57**, 1479 (1935)), on phenanthraquinone and chrysenequinone (A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 746 (1946)), and on *o*-benzoquinone derivatives (A. Schönberg, W. I. Awad and N. Latif, *ibid.*, 1368 (1951); A. Schönberg and N. Latif, ref. 3).

(5) F. Arndt, J. Amende and W. Ender, *Monatsh.*, **59**, 210 (1932).

(5a) The variation of the position of the equilibrium between two tautomeric forms with temperature, *e.g.*, in the case of ethylacetoacetate, already has been established by determination of the refractive indexes (K. G. Falk, THIS JOURNAL **31**, 106 (1909)) and by determination of the densities (J. Traube, *Ber.*, **29**, 1719 (1898)).

(6) *Cf.* A. Schönberg and A. Mustafa, *Chem. Revs.*, **40**, 199 (1947).

(7) The solutions were viewed perpendicular to the main axis of the Schlenk tubes.

heating the contents of B and cooling was repeated three times, the same result was obtained in each case, showing that during the heating of B, no decomposition or changes took place which effected the color of the recooled solution to the naked eye.

Thermochromic Changes of Ethyl Benzoate Solutions of IIIb (Ar = C_6H_5).—Twenty ml. of the above solution was divided into two equal parts and placed in two Schlenk tubes (A and B) as described above. A was placed in an ice-bath and the level of the solution was marked. A and B were then heated (bath temp., 170°) for three minutes and the level of the solution in A was marked (C). On cooling (ice-bath), ethyl benzoate was added to A to bring the level of the solution to mark C and then A and B were sealed in a stream of dry pure nitrogen. B was heated to 170° for three minutes, when the solution acquired an orange color, compared with the violet-brown color of the cold solution in (A) (ice-bath). This experiment was repeated three times with the same result. When B was cooled in ice, the color of the solutions in A and B were of the same shade, but the intensity of the color was a little less in A, owing to the fact that the solution in B at 0° is more concentrated than that in A, whereas the concentrations of both solutions are the same at 170°.

Experiments similar to those carried out with IIIb (Ar = C_6H_5) were carried out with IIIb (Ar = p-$CH_3OC_6H_4$-) giving similar results.

Action of Phenylmagnesium Bromide on I.—To a Grignard solution (prepared from 0.8 g. of magnesium, 6 g. of bromobenzene and 40 ml. of dry ether) was added 1 g. of I and 30 ml. of dry benzene. The resulting deeply violet colored reaction mixture was refluxed (water-bath) for two hours and kept aside overnight at room temperature. It was decomposed with cold saturated aqueous ammonium chloride solution and the resulting blue-violet precipitate was filtered off, washed with water and finally with cold alcohol. This was identified as IIa through the formation of the corresponding diacetate (IIc) (m.p. and mixed m.p.[2]); yield is *ca.* 60%.

Action of Ethereal Diazomethane Solution on I.—To a suspension of 1 g. of (I) in 50 ml. of dry ether was added an ethereal solution of diazomethane (prepared from 4 g. of nitrosomethylurea) and the reaction mixture was kept at 0° overnight and then treated with a fresh amount of ethereal diazomethane. During the reaction, the yellow solid I was gradually transformed into a pale yellow substance which was collected and crystallized from glacial acetic acid as pale yellow crystals, m.p. 228°. *Anal.* Calcd. for $C_{17}H_{10}N_2O_2$ requires C, 74.5; H, 3.6; N, 10.2. Found: C, 74.2; H, 3.7; N, 10.5. IV is difficultly soluble in benzene and ethyl alcohol and dissolves in concentrated sulfuric acid with a bluish-green color.

A solution of 0.2 g. of IV in 30 ml. of glacial acetic acid was treated with 0.5 ml. of concentrated hydrochloric acid and the reaction mixture was heated on a boiling water-bath for 15 minutes. It was then poured into ice-cold water and the blue-violet solid that separated was filtered off, washed with cold alcohol and identified as IIc as mentioned above.

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[CONTRIBUTION FROM THE GEORGETOWN UNIVERSITY MEDICAL CENTER]

N-Alkyl Saccharins and their Reduction Products

BY LEONARD M. RICE, CHARLES H. GROGAN AND E. EMMET REID[1]

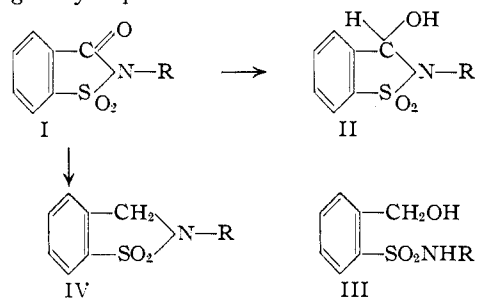
RECEIVED MARCH 12, 1953

The series of N-alkyl saccharins has been extended through dodecyl and representative members of the series have been reduced with lithium aluminum hydride. The reduction products were isolated and characterized chemically and by their infrared spectra. The products turned out unexpectedly to be N-alkyl derivatives of *o*-methylolbenzenesulfonamide. Dimethylformamide was found to be an excellent solvent for the synthesis of N-alkyl saccharins from the sodium saccharin salt and appropriate alkyl halides.

As part of a continuing study of the reduction of amides, we have extended the investigation of types of amides to include the N-alkyl saccharin, I, and have studied their reduction by means of lithium aluminum hydride. The N-alkyl saccharins, methyl through amyl, had been prepared previously by the reaction of sodium saccharin with an alkyl halide employing as a solvent a mixture of water and butyl carbitol.[2]

The series of N-alkyl saccharins has been extended from hexyl through dodecyl utilizing dimethylformamide as a solvent for the sodium saccharin salt. Just below its boiling point dimethylformamide dissolves about two-thirds of its weight of sodium saccharide, and it is a fair solvent for alkyl bromides. These saccharin derivatives were low melting solids which could be readily purified by vacuum distillation. The compounds prepared in this study and appropriate constants are shown in Table I.

It was of interest to study the behavior of these compounds on reduction with lithium aluminum hydride. Preliminary experiments indicated that the sulfone group was not reduced under the conditions employed and that all reduction observed took place at the carbonyl group. Reduction of the N-dodecyl derivative went smoothly and gave a product which, after recrystallization from benzene–petroleum ether, melted at 84°. Analysis, however, showed that no oxygen had been lost during the reduction. Since reduction of the sulfone group does not occur, partial or complete reduction of the carbonyl function gives three possibilities for the course of the reaction. These, as shown by formulas II, III and IV, are: partial reduction to yield a cyclic secondary alcohol, partial reduction with ring cleavage to yield a primary alcohol, and complete reduction to yield a ring methylene group as originally expected.



In all cases of representative members of this series studied, the sulfone group was unaffected and

(1) Professor Emeritus, Johns Hopkins University, Baltimore, Md.

(2) L. L. Merritt, Jr., Stanley Levey and H. B. Cutter, THIS JOURNAL, **61**, 15 (1939).