The temperature was maintained at 60–70° throughout the addition and for 30 minutes thereafter. The mixture was cooled, filtered and evaporated to crystallization. The solid was collected and crystallized from aqueous alcohol; yield 2.7 g., m.p. 85–87°. Recrystallization raised the m.p. to 87–88°. The product did not respond to the ammoniacal silver nitrate test.

Anal. Calcd. for $C_{13}H_{17}NO_2$: N, 6.39. Found: N, 5.81.

Acknowledgments.—The authors express their sincere thanks to the Eli Lilly Company, Indianapolis, Indiana, for the financial support of this work and to Messrs. W. L. Brown, H. L. Hunter, W. J. Schenck and G. M. Maciak of the Lilly Research Laboratories for the analytical work. Thanks are due also to Dr. F. E. Cislak, Reilly Tar and Chemical Corporation, Indianapolis, for generous gifts of 3-methyl-1-pentyne-3-ol.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1]]

Reaction of Diacetyl and Cyclohexylamine

BY J. F. CARSON

RECEIVED APRIL 14, 1953

Diacetyl and anhydrous cyclohexylamine react at 0–25° to yield, as the principal product, the new crystalline 1,4-dicyclohexylimino-2,5-dimethyl-2-hydroxycyclohexene, I. This colorless crystalline compound when dissolved in methanol readily eliminates water under unusually mild conditions to yield the yellow crystalline diimine, N,N′-dicyclohexyl-2,5-dimethyl-1,4-benzoquinonediimine, VI. The diimine has interesting thermochromic properties. Solutions in methanol are yellow at 25° or above and red at 0° or below.

In connection with investigations on the non-enzymatic browning of vegetables, the reactions of some simple α-hydroxy-carbonyl and dicarbonyl compounds with primary aliphatic amines have been investigated.[2] In particular, the reactions of diacetyl have been examined, since diacetyl has been reported as a degradation product[3] resulting from the reaction of sugars and amino acids. Dicarbonyl compounds may also be of significance inasmuch as they effect the Strecker degradation of α-amino acids.[4] Reaction of diacetyl with methylamine, ethylamine or *n*-butylamine in aqueous solution at *p*H 7.0 (buffered with phosphate) at 25° slowly deposits intensely colored blue or purple precipitates which on longer standing gradually turn brown. Difficulties in the isolation of pure constituents from these reactions led to investigations under anhydrous conditions. These reactions, however interesting, have not yielded a satisfactory explanation of reactions in aqueous systems.

Reaction of diacetyl with a number of primary aliphatic amines yielded only brown resins or oils except in the case of cyclohexylamine. Reaction of diacetyl with excess anhydrous cyclohexylamine at 0–25° yielded the new compound I and traces of diacetyldicyclohexylimine II. The new dicyclohexyliminodimethylcyclohexenol derivative I is a colorless crystalline compound, very unstable in polar solvents at 25° but moderately stable in hydrocarbons. The compound is isolated and purified by recrystallizing from hexane at −20° or lower, the diacetyldicyclohexylimine II accumulating in the mother liquors. Although yields of the crude product are good, losses in recrystallization result in low yields (25–33%) of pure product.

Evidence for the structure of the new compound is obtained from elemental analysis, catalytic hydrogenation with the absorption of three moles of hydrogen, and particularly from the facile decomposition of the compound to a N,N′-dicyclohexylquinonediimine VI. In the ultraviolet, the compound has a maximum at 257 mμ (isoöctane). Infrared spectrum shows strong absorption at 6.12 and 6.20 μ and weak absorption at 6.28 μ in the region of C=C or C=N stretching. Strong absorption at 2.98 μ indicates that the oxygen atom is present as a hydroxyl group. One may speculate that the reaction proceeds first by an aldol condensation of two molecules of monocyclohexylimine III to yield IV followed by an internal aldolization accompanied by loss of the elements of water to yield I. Diacetyl in the presence of strong aqueous alkali is reported to condense in a similar manner to yield 2,5-dimethyl-1,4-benzoquinone.[5]

The new compound I undergoes an interesting solvolysis in methanol to the yellow crystalline N,N′-dicyclohexyl-2,5-dimethyl-1,4-benzoquinonediimine (VI) by loss of the *t*-hydroxyl group. The decomposition proceeds in good yield in methanol at 25° over a three-day period or in a few minutes in boiling methanol. The reaction also takes place in ethanol or isopropyl alcohol but more slowly. In the presence of chloroform, pyridine or acetic acid, compound I decomposes to give brown resinous material.

The structure of N,N′-dicyclohexyl-2,5-dimethyl-1,4-benzoquinonediimine (VI) was established by elemental analysis and by acid hydrolysis to cyclohexylamine and *p*-xylo-*p*-quinone. On hydrogenation in the presence of platinum oxide, VI absorbs one mole of hydrogen giving the crystalline aromatic diamine, N,N′-dicyclohexyl-2,5-dimethyl-*p*-phenylenediamine—supporting evidence of a qui-

---

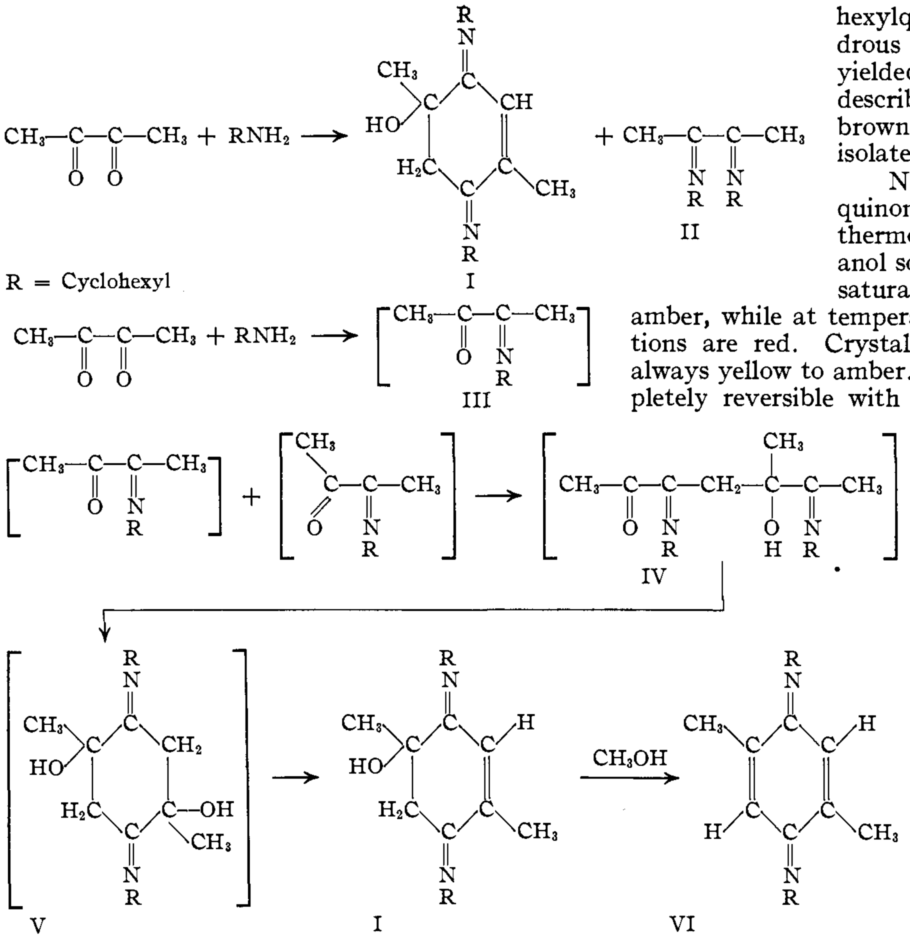
[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Presented at 123rd National Meeting of American Chemical Society, Los Angeles, March, 1953. Article not copyrighted.

[2] J. F. Carson, THIS JOURNAL, **75**, 4337 (1953).

[3] Report of Non-Enzymatic Browning Conference, Quartermaster Food and Container Institute for the Armed Forces, Feb. 1, 1952, published by Research and Development Associates, Food and Container Institute, Inc., Aug., 1952, pp. 31–34.

[4] A. Schönberg, R. Moubasher and A. M. Mostafa, *J. Chem. Soc.*, 176 (1948).

[5] H. von Pechmann and E. Wedekind, *Ber.*, **28**, 1846 (1895).



nonediimine structure. In the infrared, VI has two bands in the range of 6.2–6.4 μ which may be attributed to C=C or C=N unsaturation. In the ultraviolet, the quinonediimine has strong absorption with a maximum at 288 mμ and an inflection at 295–300 mμ. The hydrolysis product, *p*-xylo-*p*-quinone, has a similarly shaped maximum and inflection, but the maximum is at 248 mμ and the inflection at 253–258 mμ. The hypsochromic shift on going from the quinonediimine to the quinone was unexpected, since the C=N group is ordinarily a weaker chromophore than the C=O group.

The quinonediimines such as duroquinonediimine prepared by Kehrmann and Cordone[6] and N,N'-dimethylquinonediimine prepared by Willstätter and Pfannenstiel[7] are colorless compounds in contrast to the new quinonediimine reported here. Moreover, the N,N'-dimethyl-*p*-quinonediimine of Willstätter was reported to decompose readily in alcohol or water to yield brown material in contrast to our compound which is quite stable in this respect. Adams[8] has investigated the addition reactions of N-acyl substituted *p*-quinonediimides as the dibenzimides and dibenzenesulfonimides to yield aromatic derivatives. In particular, organic acids were found to add to the *p*-quinonedibenzimides to yield ring substituted acyldibenzoyl-*p*-phenylenediamines. Solution of the new dicyclohexylquinonediimine in anhydrous acetic or formic acids yielded intense red solutions as described by Adams,[8] but only brown resinous material could be isolated.

N,N'-Dicyclohexyl-*p*-xylo-*p*-quinonediimine has interesting thermochromic behavior in methanol solutions. At 25° or above, saturated solutions are yellow to amber, while at temperatures below 0°, the solutions are red. Crystalline products isolated are always yellow to amber. The color change is completely reversible with temperature, but is often very slow, varying from a few minutes to several days. In ethanol solutions, the color change is less pronounced, and in isopropyl alcohol the change is barely perceptible at −70°. The color change has not been observed in hydrocarbons, ether, chloroform or ethyl acetate. Possibly related to this phenomenon is the behavior of the compound to silicic acid. Attempted chromatography of the compound on two different commercial samples of silicic acid resulted in adsorption from hexane as a sharp non-mobile red band. Development with mixtures of ether, ethanol or ethyl acetate in hexane produced several yellow to brown bands from which only dark resins could be isolated. The precursor I dissolved in hexane behaved similarly in the presence of silicic acid.

Acknowledgment.—The author gratefully acknowledges the assistance of L. M. White and G. E. Secor for analyses, F. T. Jones for microscopic examinations and G. F. Bailey for spectrographic determinations.

Experimental

Reaction of Diacetyl and Cyclohexylamine.—Anhydrous cyclohexylamine (50 g., 0.5 mole) and diacetyl (15 g., 0.17 mole) were cooled to −10° and mixed in a 250-ml. flask with external cooling. The air in the flask was displaced by nitrogen, and the solution kept at 5° for 24 hours. The pale amber solution was then concentrated *in vacuo* $< 20°$ to a semi-crystalline mush, 50 ml. of hexane was stirred in, and the mixture left at −20° overnight. Filtration at −20° yielded 11 g. of tan crystalline material. An additional 18 g. of dark crystalline material was obtained by keeping the mother liquor in an acetone–Dry-Ice-bath for several days.

Several recrystallizations of the crude product from hexane at −20° yields the pure colorless dicyclohexyliminocyclohexenol I, 9 g. (33%). The large losses in recrystallization are a result of the high solubility of the compound in hydrocarbons and of the difficulty of separating traces of colored resinous material. Additional dark colored product may be obtained from the mother liquor sufficiently pure for the conversion to the quinonediimine VI. The new compound was obtained as coarse, colorless prisms, m.p. 101–102°; ultraviolet absorption: λ_{max} 257 mμ, ε 24,400 (isoöctane); λ_{max} 263 mμ, ε 22,400 (methanol).

---

(6) F. Kehrmann and B. Cordone, *Ber.*, **56**, 2398 (1923).

(7) R. Willstätter and A. Pfannenstiel, *ibid.*, **38**, 2244 (1905).

(8) R. Adams, *et al.*, THIS JOURNAL, **74**, 2593, 2597, 3657 (1952).

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 non-crystallizing 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.

ALBANY 6, CALIF.

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

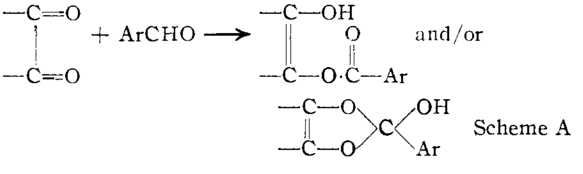
Experiments with 1,2-Benzophenazine-3,4-quinone. Thermochromic Effects Based on Lactam–Lactim Tautomerism

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).