[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

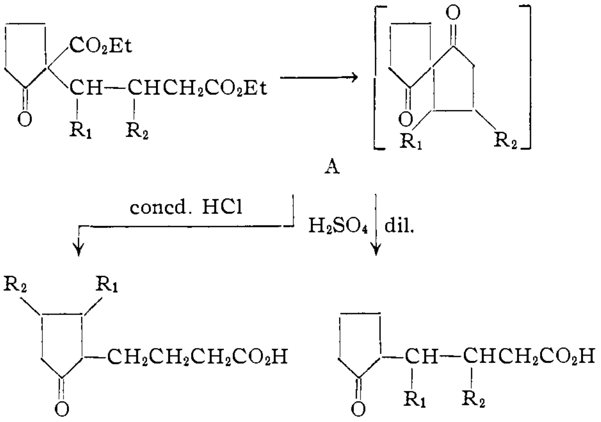
The Hydrolysis and Rearrangement of 2-Carbomethoxy-2-(*o*-cyanobenzyl)-1-tetralone

BY WERNER HERZ

RECEIVED MARCH 6, 1957

The hydrolysis of the title compound was studied in an attempt to gain further information on the scope and mechanism of the acid-catalyzed rearrangement of certain ε-ketoacids. The initial product, 2-*o*-(cyanobenzyl)-1-tetralone (II), when subjected to further acid hydrolysis furnished the spirodiketone III which was stable to acid and was cleaved by base to 2-(*o*-carboxybenzyl)-1-tetralone (IV). Basic hydrolysis of II caused rearrangement and resulted in the formation of 2-β-(*o*-carboxyphenyl)-1-indanone (V). The results are interpreted as providing evidence for the mechanism proposed previously.

To explain the acid-catalyzed rearrangement of the ketoacid, 2-(2′-oxocyclohexyl)-methyl-6-chloronicotinic acid, Ramirez and Paul[1] postulated the intervention of an intermediate spirodiketone. We have used this idea by suggesting that the spirodiketone A is a possible intermediate in the rearrangement which occurs when β-ketoesters of the type shown are hydrolyzed with strong mineral acid.[2,3]

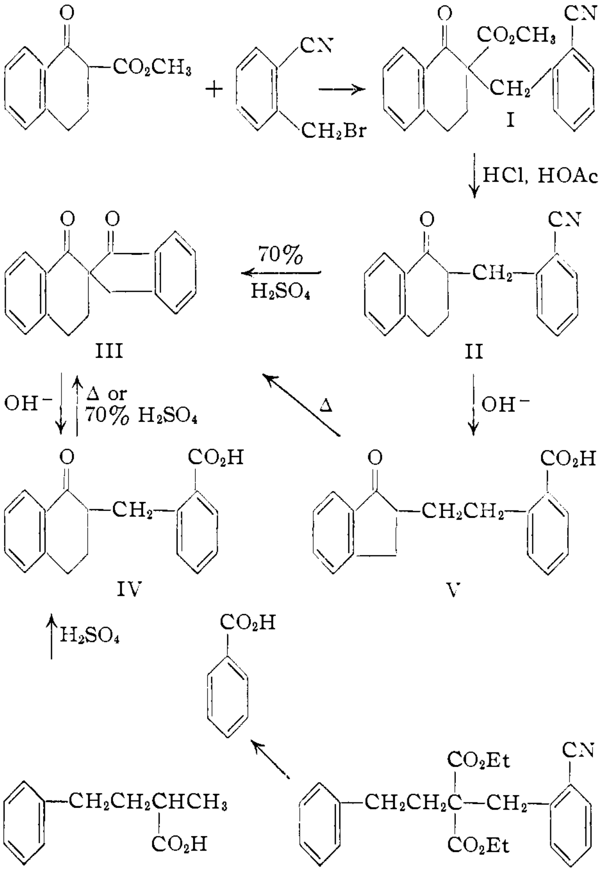


Further evidence for this view has been presented recently.[4]

It was thought that the system outlined in the accompanying chart might provide a test of this hypothesis.

Acid hydrolysis of I or II should furnish IV (without rearrangement), V (with rearrangement) or a mixture of IV and V. Hydrolysis of the spirodiketone III, which has been known since 1924 when Leuchs and Reinhart obtained it by cyclization of benzyl-β-phenylethylmalonyl chloride in the presence of ferric chloride,[5] would also be expected to yield V, or a mixture of IV and V if hydrolysis of I or II were accompanied by rearrangement and if III were an intermediate.

Unfortunately compound I, synthesized in the manner shown, and its derivatives proved rather refractory toward acid hydrolysis. Choice of the homogeneous medium (hydrochloric acid–acetic acid) which had been successful in earlier instances[3,4] furnished II as sole product. Further hydrolysis of II, using 70% sulfuric acid, resulted in the formation of a substance which was identified as the spirodiketone III by elementary analysis, infrared spectrum (indanone carbonyl at 1710 cm.$^{-1}$, tetralone carbonyl at 1670 cm.$^{-1}$) and synthesis from 2-*o*-carboxybenzyl-1-tetralone (IV, *vide infra*).



Upon alkaline hydrolysis of III, Leuchs and Reinhart[5] obtained a compound from which III could be regenerated by distillation and to which formula IV, rather than V, was ascribed on rather insecure grounds. Repetition of this work has now shown that the assumption of the German workers was correct. The infrared spectra of the compound and of its methyl ester indicated that an α-tetralone rather than an indanone structure was present. This was confirmed by an unequivocal synthesis of IV from diethyl *o*-cyanobenzyl-β phenylethylmalonate in the manner shown on the chart. An attempt to prepare IV by a simpler route involving as the initial step the condensation of 1-tetralone with phthalaldehydic acid failed due

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[1] F. Ramirez and A. P. Paul, THIS JOURNAL, **77**, 1035 (1955).

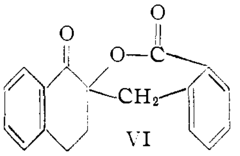
[2] W. Herz, *ibid.*, **78**, 1485, 2529 (1956).

[3] W. Herz, *J. Org. Chem.*, **22**, 585 (1957).

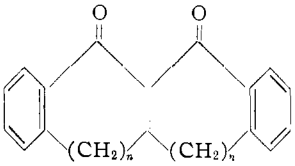
[4] D. K. Banerjee and T. R. Kasturi, THIS JOURNAL, **79**, 926 (1957).

[5] H. Leuchs and F. Reinhart, *Ber.*, **57**, 1208 (1924).

to facile lactonization of the primary condensation product which resulted in VI.



VI

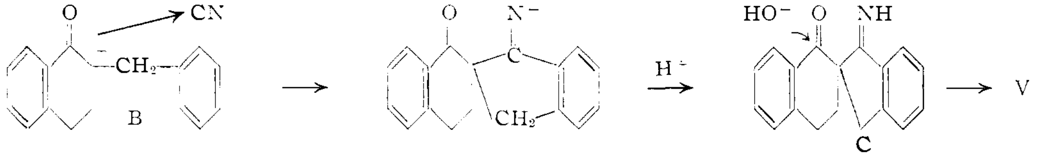


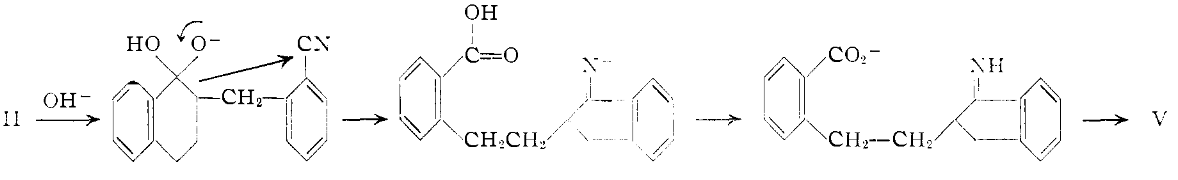
VII

The manner in which III is cleaved by alkali presents certain points of interest. Cleavage of β-diketones by base is thought to proceed primarily in that direction which yields the stronger acid.[6] In the case of III there would appear to be little difference in the acidity of the two products IV and V and one might expect a mixture. On the other hand, the generalizations formulated by Brown, Brewster and Shechter[7] suggest that attack by hydroxyl ion should occur preferentially on the tetralone carbonyl group instead of on the indanone carbonyl as actually observed. However, there is evidence[6] that steric hindrance may be a factor in the alkaline cleavage of β-diketones and the results of Leuchs and co-workers indicate that in spirodiketones of type III, a tetralone carbonyl is very much more hindered than an indanone. Thus VII $(n = 1)$ easily formed a diphenylhydrazone and a monoxime[8] whereas VII $(n = 2)$ yielded neither a phenylhydrazone nor an oxime.[5] Leuchs and Reinhart[5] reported also that the spiroketone III was unreactive toward phenylhydrazine and hydroxylamine. Hence preferential cleavage of the indanone ring of III is quite possibly due to steric factors.

While the stability of III toward further treatment with acid prevented the realization of our original plan, the formation of III from II under strongly acidic conditions demonstrates that an acid-catalyzed intramolecular Claisen-type condensation may indeed be induced in appropriate derivatives of ε-ketoacids and strongly supports the hypothesis that spirodiketones are intermediates in the acid-catalyzed rearrangement of such compounds. In fact, IV itself was converted to III on treatment with 70% sulfuric acid.[9]

The *alkaline* hydrolysis of II furnished, rather surprisingly, not the ketoacid IV but an isomeric ketoacid of higher m.p. whose derivatives clearly differed from the corresponding derivatives of IV. The infrared spectra of the new substance and of its methyl ester indicated the presence of an indanone moiety (C=O at 1712 cm.$^{-1}$, masked in the ester by the presence of the conjugated keto group). Since the new ketoacid also was converted to the spirodiketone III on distillation, its structure must be V. Now IV and its methyl ester are not converted to V on refluxing with base; hence the formation of V by hydrolysis and rearrangement of II must be ascribed to the more clearly pronounced electrophilic properties of the carbon atom of the cyanide function.[10] A possible mechanism involves an attack by the carbanion B, formed from II under the influence of base, on the cyanide group. Since alkali cleaves III to IV, it would then be necessary to postulate that the conversion of C to III by hydrolysis of the imino function proceeds at a much slower rate than the conversion of C to V, *i.e.*, the hydroxyl ion must attack preferentially the tetralone carbonyl group as shown. In view of the apparent steric requirements discussed earlier, this does not seem likely. Alternatively, attack by base on the tetralone carbonyl may precede the displacement shown below; hydrolysis of the imino derivative would then proceed normally with formation of V.





Acknowledgment.—This work was supported in part by grants from the National Science Foundation and the Research Council of the Florida State University. I also wish to express my thanks to Dr. H. M. Walborsky for stimulating discussions.

Experimental[11]

2-(*o*-Cyanobenzyl)-2-carbomethoxy-1-tetralone (I).—To a suspension of 1.75 g. of powdered sodium in 150 ml. of toluene was added, with heating and stirring, 15.4 g. of 2-carbomethoxy-1-tetralone.[12] After two hours a solution of 15 g.

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(6) For a discussion with references, see H. H. Wasserman in "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley & Sons, Inc., New York, N. Y., 1956, p. 371.

(7) H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954). For another instance which departs from this generalization see C. Mannich, *Ber.*, **74**, 557, 1007 (1941).

(8) H. Leuchs and D. Radulescu, *ibid.*, **45**, 189 (1912).

(9) This observation suggests that the formation of III from II may proceed *via* IV by initial hydrolysis of the nitrile group under the influence of acid.

(10) Attempts to prepare the amides of IV and V in order to study their behavior under the influence of base are described in the Experimental part.

(11) Melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford, England. Infrared spectra were run by Miss Martha Brackett and Mr. Joseph Kovacic on a Perkin-Elmer model 21 double beam instrument. Ultraviolet spectra were determined by Mrs. Shirley Ann Pinner and Miss M. T. Esquivel on a Beckman model DKI recording spectrophotometer.

(12) W. E. Bachmann and D. G. Thomas, THIS JOURNAL, **63**, 598 (1941).

of 2-bromo-*o*-tolunitrile[13] in 80 ml. of toluene was added and the reaction mixture was stirred and refluxed for an additional 20 hours, allowed to cool and diluted with water. The toluene layer was separated, washed with cold 10% sodium hydroxide solution and water, the water layers were extracted with ether and the combined organic layers were dried and concentrated *in vacuo*. The viscous residue was stirred with petroleum ether (b.p. 30–60°) and the petroleum ether was decanted. The undissolved oil crystallized on stirring with hexane; wt. of crude brown solid 17.4 g. The petroleum ether deposited an additional 2.1 g. of creamy crystals, total yield 19.5 g. (83%). Several recrystallizations from ethanol furnished colorless crystals, m.p. 114.5–115.5°. Attempts to prepare a semicarbazone and a dinitrophenylhydrazone resulted in recovery of starting material. The infrared spectrum (CCl_4 solution) had bands at 2225 (–CN), 1739 (ester) and 1692 cm.$^{-1}$ (ketone).

Anal. Calcd. for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39. Found: C, 75.20; H, 5.32; N, 4.35.

2-(*o*-Cyanobenzyl)-1-tetralone (II).—A solution of 2 g. of the preceding β-ketoester in 25 ml. of acetic acid and 15 ml. of concd. hydrochloric acid was refluxed overnight. The mixture was cooled and diluted with water. An oil separated which solidified on standing. The crude product, wt. 1.7 g., was recrystallized repeatedly from ethanol. The colorless needles melted at 102–103.5°. They were insoluble in sodium bicarbonate solution and liberated ammonia on treatment with hot base. The infrared spectrum (CCl_4 solution) had bands at 2225 (–CN) and 1689 cm.$^{-1}$ (ketone).

Anal. Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.73; N, 5.36. Found: C, 82.55; H, 5.65; N, 4.87.

The dinitrophenylhydrazone, orange needles from ethyl acetate, melted at 231–232.5°.

Anal. Calcd. for $C_{24}H_{19}N_5O_4$: C, 65.30; H, 4.34; N, 15.87. Found: C, 65.10; H, 4.33; N, 15.80.

2-β-(*o*-Carboxyphenyl)-ethyl-1-indanone (V).—A mixture of 4 g. of II, 6 g. of sodium hydroxide and 30 ml. of water was refluxed for 18 hours until the evolution of ammonia had ceased. The solution was cooled, diluted with water, extracted with ether and acidified. An oil separated which crystallized on standing. It was filtered, taken up in hot benzene, treated with charcoal, concentrated and allowed to cool. The precipitate weighed 1.35 g., m.p. 135–139° (dilution of the mother liquors with petroleum ether yielded an additional 0.72 g. of lower m.p. range). Two additional recrystallizations from benzene gave colorless crystals, m.p. 144–145°. The infrared spectrum ($CHCl_3$) showed bonded hydroxyl due to the acid function and a broad asymmetrical carbonyl band which on further dilution exhibited subpeaks at 1712 and 1690 cm.$^{-1}$ (indanone carbonyl and conjugated carboxylic acid). A second run, using 15 g. of II, furnished a first crop weighing 8.5 g., m.p. 129–136°, which subsequent recrystallization raised to 136–139°, and 1.7 g. from the mother liquors, m.p. 95–111°. The range in m.p.'s suggests that the hydrolysis of II gives rise to some IV also; however, fractional crystallization did not give rise to a pure fraction corresponding to IV nor was it possible to identify IV as a contaminant by inspection of the infrared spectrum.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.73. Found: C, 76.90; H, 5.76.

Only starting material was recovered when attempts were made to prepare a semicarbazone. The dinitrophenylhydrazone, orange-red felted needles from ethyl acetate, melted at 218.5–219.5°.

Anal. Calcd. for $C_{24}H_{20}N_4O_6$: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.75; H, 4.31; N, 11.80.

The methyl ester was prepared by passing gaseous hydrogen chloride through an ice-cold solution of 1 g. of the acid in 20 ml. of anhydrous methanol for three hours. After three days the solvent was removed at reduced pressure; the residue crystallized on standing and rubbing with low-boiling petroleum ether. Recrystallization from methanol furnished 0.7 g. of colorless needles, m.p. 71–71.5°. The infrared spectrum ($CHCl_3$) exhibited one band at 1712 cm.$^{-1}$ (composite of conjugated ester and indanone carbonyl).

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.27; H, 6.29.

The acid was unchanged when refluxed for two hours with 1:2 mixture of hydrochloric acid–acetic acid, but gave the spirodiketone III on distillation *in vacuo* or on refluxing with sulfuric acid. Attempts to prepare the amide by ammonolysis of the ester yielded starting material; ammonolysis of the acid chloride gave an amorphous solid which melted over a wide range.

The ethylene dithioketal was prepared by mixing 0.5 g. of the ketoacid with 1 ml. of ethanedithiol and 1 ml. of boron trifluoride etherate. The product was filtered, washed with a little methanol (yield of crude product 0.49 g.) and recrystallized several times from methanol. The colorless crystals melted at 141.5–142°.

Anal. Calcd. for $C_{20}H_{20}O_2S_2$; C, 67.38; H, 5.66. Found: C, 67.43; H, 5.80.

Desulfurization of the thioketal or Wolff–Kishner reduction of the ketoacid resulted in glassy acidic material which could not be recrystallized satisfactorily. Attempts to prepare derivatives (amides, esters) resulted in oils or fractions which did not exhibit sharp m.p.'s.

2,3,6,7-Dibenzo-1,5-spiro[5,6]decanedione (**III**).—A mixture of 1 g. of the ketonitrile II, 10 ml. of water and 10 ml. of concd. sulfuric acid was refluxed for 18 hours, cooled, diluted with water and chilled. The oil which separated solidified gradually, wt. 0.7 g. Recrystallization from ethanol furnished beautiful colorless rhombs, m.p. 109–110°, lit.[5] 111–112°. The infrared spectrum exhibited two strong carbonyl bands at 1710 (indanone) and 1670 cm.$^{-1}$ (tetralone).

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42: H, 5.38. Found: C, 82.69; H, 5.35.

The ultraviolet spectrum (95% ethanol) had maxima at 252 mμ (ε 32000) and 295 mμ (ε 5690). The K-band appears to be somewhat more intense than expected of the arithmetical sum of tetralone and indanone chromophores[14]; this may indicate a small degree of interaction of the type observed in alicyclic systems.[15]

When the ketoacid V was heated in a short-path still, an amber-colored liquid which set to a glass distilled at 220–230° (1.5 mm.). It became crystalline on stirring with petroleum ether (b.p. 30–60°); recrystallization from benzene–ligroin furnished the spirodiketone, m.p. 109–110°. Similarly, distillation of the isomeric ketoacid IV yielded the spirodiketone, m.p. 108.5–109.5°, mixed m.p. with IV 91–102°.

A mixture of 0.4 g. of the spirodiketone, 2 g. of sodium hydroxide and 15 ml. of water was refluxed overnight. The basic solution was filtered, acidified and extracted with ether; the ether extracts were dried and the ether removed. The residue solidified on rubbing with petroleum ether; wt. 0.28 g. Recrystallization from benzene–ligroin furnished needles, m.p. 112–114°, mixed m.p. with starting material 91–102°, mixed m.p. with IV 112–115°, whose infrared spectrum was identical with that of IV.

Diethyl β-Phenylethyl-*o*-cyanobenzylmalonate.—To a suspension of 4.6 g. of powdered sodium in 200 ml. of toluene was added, with heating and stirring, 52.8 g. (0.2 mole) of diethyl β-phenylethyl-*o*-tolunitrile. Sodium bromide began to precipitate almost immediately. Refluxing and stirring was continued for 18 hours. The mixture was cooled, diluted with water, the toluene layer washed with water and the aqueous washings extracted with ether. The combined organic layers were dried, concentrated and fractionated in a short-path still. The product, which was still somewhat colored, boiled at 222–232° (1.5 mm.), wt. 51 g. (67%). A small sample was redistilled for analysis, b.p. 210–212° (0.8 mm.), n^{22}D 1.5353.

Anal. Calcd. for $C_{23}H_{25}NO_4$: C, 72.80; H, 6.64; N, 3.69. Found: C, 72.99; H, 6.40; N, 3.55.

β-Phenylethyl-*o*-carboxybenzylmalonic Acid.—A mixture of 50 g. of the malonic ester, 50 ml. of water, 100 g. of potassium hydroxide and 450 ml. of *n*-amyl alcohol was refluxed in a copper flask for three days until the evolution of ammonia had stopped. Water was added and most of the amyl alcohol was removed by distillation. The aqueous resi-

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[13] Fa-Ki Tcheou, Yu-Tsun Shih and Kwan-Liang Lee, *J. Chinese Chem. Soc.*, **17**, 150 (1950).

[14] W. M. Schubert and W. A. Sweeney, THIS JOURNAL, **77**, 2297 (1955).

[15] D. J. Cram and H. Steinberg, *ibid.*, **76**, 2753 (1954).

due was extracted with ether and acidified. An oil separated which crystallized on standing; wt. 45.4 g. (100%) of crude material. Several recrystallizations from dilute aqueous methanol furnished colorless needles soluble in hot water; m.p. 173° with gas evolution. Analysis indicated that it was a hydrate.

Anal. Calcd. for $C_{19}H_{18}O_6 \cdot H_2O$: C, 63.33; H, 5.59. Found: C, 63.77; H, 5.36.

2-*o*-Carboxybenzyl-4-phenylbutyric Acid.—The crude malonic acid, wt. 44.5 g., was heated at 190° until the evolution of carbon dioxide had stopped. The material crystallized on standing. It was taken up in 200 ml. of hot ethanol, treated with charcoal, filtered, concentrated to about 150 ml., diluted with water, reheated and allowed to cool. There was obtained 32.5 g. (84%) of cream-colored crystals, including material recovered from the mother liquors. Further recrystallizations from aqueous ethanol furnished colorless needles, m.p. 149–149.5°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.25; H, 6.02.

2-(*o*-Carboxybenzyl)-1-tetralone (IV).—A solution of 15 g. of the preceding acid in 120 ml. of concd. sulfuric acid was kept at room temperature for two hours (if during the mixing and subsequently the temperature was allowed to rise, the desired product was contaminated by considerable amounts of the spirodiketone) and then poured over cracked ice. The precipitate was filtered (wt. 13 g., 92%) and recrystallized several times from benzene–petroleum ether. The shiny white needles melted at 115–116°, lit. 113–115°.[5] The infrared spectrum exhibited typical acid–OH absorption and an asymmetrical carbonyl band centered at 1685 cm.$^{-1}$ (conjugated ketone) with indications of bands near 1705 (dimeric carboxyl) and 1735 cm.$^{-1}$ (monomeric carboxyl). The substance was somewhat sternutatory, as observed previously.[5]

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.73. Found: C, 77.21; H, 5.89.

Several attempts to prepare a semicarbazone resulted in recovery of starting material. The dinitrophenylhydrazone, orange-red crystals from ethyl acetate, melted at 240° (dec).

Anal. Calcd. for $C_{24}H_{20}N_4O_6$: C, 62.60; H, 4.38; N, 12.1. Found: C, 62.91; H, 4.57; N, 11.9.

The methyl ester was prepared by saturating a solution of 1 g. of IV in 25 ml. of methanol with dry hydrogen chloride in the cold and allowing to stand for several days. The solvent was removed at reduced pressure and the residue was recrystallized several times from methanol. The product, m.p. 86.5–88°, exhibited two strong bands in the carbonyl region of the infrared spectrum, 1719 (conjugated ester) and 1680 cm.$^{-1}$ (tetralone).

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.48; H, 6.47.

Hydrolysis of the methyl ester with acid or base resulted in regeneration of IV. When IV was refluxed with a mixture of acetic acid and hydrochloric acid only starting material was recovered. Refluxing with 70% sulfuric acid converted IV to the spirodiketone III.

Attempts were made to prepare the amide of ketoacid IV by partial hydrolysis of the ketonitrile II with hydrogen peroxide (recovery of impure starting material) and sulfuric acid (formation of the spirodiketone), ammonolysis of the methyl ester of IV (recovery of starting material) and ammonolysis of the acid chloride of IV (formation of an amorphous neutral solid which could not be converted to material melting sharply but whose infrared spectrum indicated the presence of at least some amide).

2-(*o*-Carboxybenzyl)-1,2,3,4-tetrahydronaphthalene.—Reduction of 1 g. of ketoacid IV by the Huang-Minlon modification of the Wolff–Kishner reaction resulted, after several recrystallizations, in 0.5 g. of colorless crystals, m.p. 160.5–162°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.37; H, 6.90.

Condensation of 1-Tetralone and Phthalaldehydic Acid.—To a solution of 1 g. of 1-tetralone and 1 g. of phthalaldehydic acid in 10 ml. of ethanol was added 0.2 ml. of 40% potassium hydroxide solution. After standing overnight, the purple solution was diluted with water and acidified. A yellow oil separated and solidified on standing, wt. 1.3 g. Two recrystallizations from benzene–ligroin (b.p. 65–110°) resulted in needles which melted unsharply in the range 121–126°. A third recrystallization produced a sudden rise to 136.5–138°; further purification did not alter the m.p. The infrared spectrum had bands at 1760 (lactone) and 1680 (2-tetralone); this together with the analysis indicated structure VI. Although the substance was neutral it dissolved in dilute alkali. Neutralization of the alkaline solution reprecipitated the lactone.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.39; H, 5.08.

The red dinitrophenylhydrazone was recrystallized from ethyl acetate, m.p. 262–263°.

Anal. Calcd. for $C_{24}H_{18}N_4O_6$: C, 62.88; H, 3.96. Found: C, 62.99; H, 4.07.

TALLAHASSEE, FLORIDA

[CONTRIBUTION NO. 229 FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO., INC.]

Products of the Photochemical Decomposition of N,N'-Disubstituted *p*-Quinonediimine-N,N'-dioxides

BY C. J. PEDERSEN[1]

RECEIVED MARCH 19, 1957

A new class of photochemical reaction has been discovered. N,N'-Disubstituted *p*-quinonediimine-N,N'-dioxides (I) when exposed to light of 300–450 mμ wave lengths, decompose very rapidly and quantitatively into N-substituted *p*-quinoneimine-N-oxides (IV) and azo compounds, and the resulting N-oxides decompose into *p*-quinone and azo compounds. The two reactions can be separated because the wave length required for the second is approximately 20 mμ shorter than for the first. The composition of the azo compounds depends upon the substituents on the nitrogen atoms: nitrogen atoms attached to similar groups react at about the same rate, but the nitrogen atom carrying an aromatic group reacts more readily than the nitrogen atom attached to an aliphatic group. Mixtures of azo compounds, including unsymmetrical ones, are obtained from unsymmetrically substituted N,N'-dioxides II or from mixtures of symmetrically substituted N,N'-dioxides I and III.

During the preparation of N,N'-disubstituted *p*-quinonediimine-N,N'-dioxides (I),[2] it was observed that solutions of these compounds are very sensitive to light. For example, a 1-cm. layer of a 10^{-5} molar solution of N,N'-diphenyl-*p*-quinonediimine-N,N'-dioxide in benzene, which is light yellow in color, is decolorized within one second by direct sunlight. A stronger solution which had been exposed to sunlight for several days was found to contain azobenzene. It thus appeared that the compound had decomposed intramolecularly into azobenzene and *p*-quinone, and the

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(1) Elastomer Chem. Dept., E. I. du Pont de Nemours and Co., Inc.

(2) C. J. Pedersen, THIS JOURNAL, **79**, 2295 (1957).