filtered, and concentrated to yield 0.60 g. of a pale green oil. The infrared spectrum showed strong hydroxyl absorption and a nonconjugated nitrile band at 4.45 μ. The liquid was distilled at atmospheric pressure, and the distillate purified by chromatography in ether over alumina. Its infrared spectrum was then identical with that of authentic cinnamonitrile.

The aqueous washings were treated with Brady's reagent, and afforded 1.02 g. of *acetone 2,4-dinitrophenylhydrazone*, m.p. and mixed m.p. 125–126°.

Acknowledgment. The author gratefully acknowledges the support of this research by the Standard Oil Co. of New Jersey during the summer of 1959, and thanks also The Quaker Oats Chemical Co. for a generous gift of ethyl tetrahydrofuroate, the Victor Chemical Co. for a gift of polyphosphoric acid, Dr. W. I. Taylor for a sample of bullatenone, and Mr. Irwin Kuntz for his aid in obtaining and interpreting the NMR spectra. A preliminary study of the reactions of 2,2-diphenyltetrahydropyran-3-one oxime was carried out by Harold L. Wentz as part of his senior thesis (Princeton University, 1959).

PRINCETON, N. J.

[CONTRIBUTION NO. 1640 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Studies on 1,5-Diphenyl-2,3-pyrrolidinedione and Related Compounds[1,2]

HARRY H. WASSERMAN AND RICHARD C. KOCH[3]

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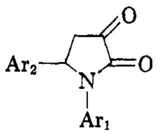
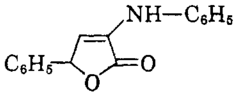
Details are given of structural studies on the Schiff and Gigli compound. This work, previously reported in preliminary form,[1] is in agreement with the most recent findings of Meyer and Vaughan.[8] A synthesis of 1,5-diphenyl-2,3-pyrrolidinedione and its reaction with ozone are described.

In seeking model α-keto-γ-lactams for other studies, we had occasion to reinvestigate the compounds, generally considered to be 1,5-diaryl-2,3-pyrrolidinediones I,[4] obtained in the condensation of pyruvic acid with aromatic aldehydes and aryl amines. The prototype of such products, A, $C_{16}H_{13}NO_2$, m.p. 161° was first prepared by Schiff and Gigli[5] from pyruvic acid and benzalaniline, and, until very recently, was formulated as Ia.



I

Ia. $Ar_1 = Ar_2 = C_6H_5$



II

Although structure Ia accommodates the behavior of A in many respects, there are certain properties of this material which appeared exceptional on the basis of the pyrrolidinedione formulation. In particular, the infrared spectrum, exhibiting bands at 5.68 and 6.01 μ, the ready displacement of aniline from A by amines,[6] and the thermal decarboxylation to cinnamylideneaniline[7] cannot be reconciled easily with structure Ia or with its enolic tautomer. On the other hand, as was outlined earlier[1] (and as has been shown independently by Meyer and Vaughan[8]), the alternative enamino lactone II[9] readily accommodates these and other known properties of A. Our studies on this problem[1] are now presented in detail.

Authentic 1,5-diphenyl-2,3-pyrrolidinedione. We sought to distinguish between the two possible structures for A by first synthesizing authentic 1,5-diphenyl-2,3-pyrrolidinedione by an unambiguous route. The starting material for this preparation was 4-carbethoxy-1,5-diphenyl-2,3-pyrrolidinedione (III), reported in the early literature[10] and recently synthesized independently by Southwick.[11] The properties[5,10–12] of this and related 4-carbalkoxy-2,3-pyrrolidinediones are in complete accord with the assigned structures.

It was expected that hydrolysis of the ester, followed by decarboxylation, would provide a simple route to Ia. However, repeated attempts to effect this hydrolytic cleavage using both acidic and basic reagents were unsuccessful. The drastic conditions required for reaction brought about

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(1) A preliminary account of this work has appeared previously: H. H. Wasserman and R. C. Koch, *Chem. & Ind. (London)*, 428 (1957).

(2) From the doctoral dissertation of R. C. Koch, Yale University, 1957.

(3) Chas. Pfizer and Co. Inc., Groton, Conn. Celanese Corp. Fellow, 1955–56.

(4) For leading reference, *cf.* R. C. Elderfield, *Heterocyclic Compounds*, Vol. IV, John Wiley and Sons, Inc., New York, 1952, pp. 25–29; W. R. Vaughan, *J. Org. Chem.*, **20**, 1613 (1955).

(5) R. Schiff and L. Gigli, *Ber.*, **31**, 1306 (1898).

(6) L. G. Montón, Doctoral thesis, *Eidgenossische Technische Hochschule*, Zurich, 1951.

(7) W. R. Vaughan and L. R. Peters, *J. Org. Chem.*, **18**, 405 (1953).

(8) W. L. Meyer and W. R. Vaughan, *J. Org. Chem.*, **22**, 1560 (1957).

(9) K. Garzarolli-Thurnlackh, *Monatsh.*, **20**, 480 (1899).

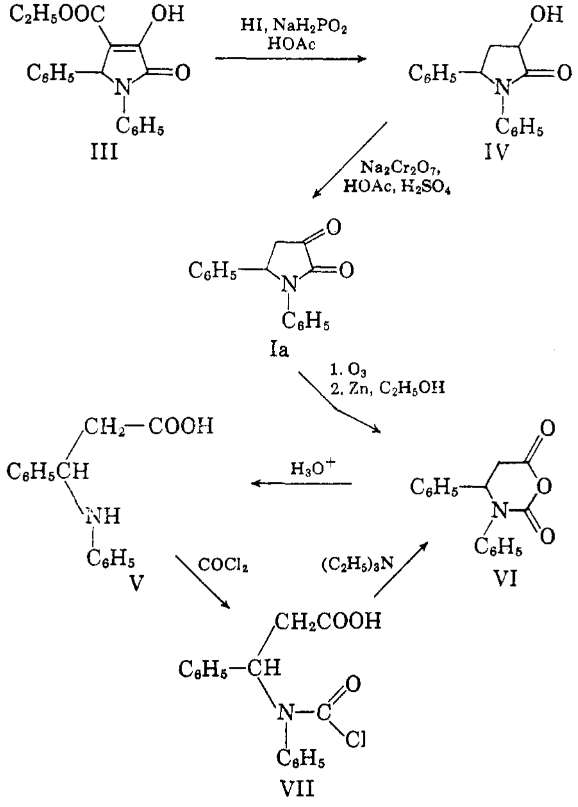
(10) (a) R. Schiff and L. Bertini, *Ber.*, **30**, 601 (1897); (b) L. J. Simon and A. Conduché, *Ann. chim. phys.*, [8], **12**, 5 (1907).

(11) P. L. Southwick and L. L. Seivard, *J. Am. Chem. Soc.*, **71**, 2532 (1949); P. L. Southwick and R. T. Crouch, *J. Am. Chem. Soc.*, **75**, 3413 (1953).

(12) P. L. Southwick, E. P. Previc, J. Casanova, Jr., and E. H. Carlson, *J. Org. Chem.*, **21**, 1087 (1956).

secondary reactions, and complex mixtures were formed.[13] The presence of the desired compound in some of the strongly acidic reaction mixtures was indicated by the characteristic band at 5.65 μ in the infrared, but this product could not be isolated.

The preparation of Ia was eventually achieved by a modified route. When III was refluxed with concentrated hydriodic acid (47%) in glacial acetic acid, hydrolysis, decarboxylation, and reduction took place to yield 3-hydroxy-1,5-diphenyl-2-pyrrolidone (IV). The reduction step was evidently brought about by the hypophosphorus acid present as a stabilizer in commercial hydriodic acid. Thus, while varying results were obtained with hydriodic acid, depending upon the batch of reagent used, addition of sodium hypophosphite to the reaction mixture consistently gave good yields of IV, m.p. 201–212°.[14]



Oxidation of IV to the pyrrolidinedione failed with copper acetate, bismuth oxide, *N*-bromoacetamide, and chromic anhydride–pyridine complex.[15] The reaction was finally carried out successfully by means of dichromate in acetic acid–sulfuric acid. The product, Ia,[16] m.p. 158–159°, was purified with some difficulty due to its instability. It was readily transformed under a variety of conditions into a sparingly soluble product, presumably by a dimerization reaction of the type described by Southwick.[12,17]

The pyrrolidinedione Ia shows the expected absorption in the infrared at 5.65 and 5.84 μ in good agreement with the absorption of related *N*-substituted pyrrolidinediones reported by Southwick.[12] Conclusive proof of structure was provided by its degradation with ozone as described below.

Whereas Ia could be recovered unchanged after prolonged treatment with ozone in methylene chloride at −60°, reaction was observed under the following conditions. The methylene chloride solution was saturated with ozone at −60°, and, after zinc and aqueous alcohol were added, the reaction mixture was allowed to remain at room temperature. A product was thereby obtained which showed characteristic bands of an anhydride at 5.54 and 5.73 μ.[18] This product underwent ready hydrolysis in acid to β-anilino-β-phenylpropionic acid (V) and appeared to be *N*-carboxy-β-anilino-β-phenylpropionic acid anhydride (VI). An independent preparation of VI and infrared comparison established the structure of this ozonolysis product. The synthesis was accomplished by conversion of β-anilino-β-phenylpropionic acid (V) to the chlorocarbonyl derivative (VII) with phosgene, followed by cyclization in ether with triethylamine to the authentic anhydride.[19] Ozonization of Ia thus appears to have resulted in an oxidative ring enlargement analogous to the conversion of isatin to isatoic anhydride by chromic anhydride and to the

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[13] Substitution of the phenyl group in the 5-position of III appears to provide a steric effect which hinders hydrolysis of the adjacent ester group. In related cases where 5-substituents are absent, 4-carbalkoxy-2,3-pyrrolidinediones undergo ester hydrolysis under milder conditions.[12]

[14] In an independent preparation of the alcohol IV by the nitrous acid deamination of the corresponding 3-amino pyrrolidone, Meyer and Vaughan, *J. Org. Chem.*, **22**, 1554 (1957), obtained a product, m.p. 148–150°, which on oxidation yielded crude Ia. Dr. Meyer has informed us privately of his studies on the alcohols prepared by the two routes, from which he concludes that the difference in the melting points is due to diastereoisomerism. It is interesting to note that the melting behavior of the acetate of IV (see Experimental section) is suggestive of a mixture of isomers.

[15] The resistance of 3-hydroxypyrrolidines to oxidation has also been noted by J. E. McKeon, Ph.D. dissertation, Yale University, 1960, and by J. Meinwald and O. L. Chapman, *J. Am. Chem. Soc.*, **80**, 633 (1950).

[16] Meyer and Vaughan, *cf.* ref. 14, have independently prepared crude Ia from III and have shown that the previously uncharacterized pyrolysis product of III [W. R. Vaughan and D. I. McCane, *J. Org. Chem.*, **20**, 143 (1955)] is Ia, formed by thermal decarbethoxylation. Additional directions for the preparation of Ia are given by W. R. Vaughan and I. S. Covey, *J. Am. Chem. Soc.*, **80**, 2197 (1958) and W. R. Vaughan and R. C. Tripp, *J. Am. Chem. Soc.*, **82**, 4370 (1960).

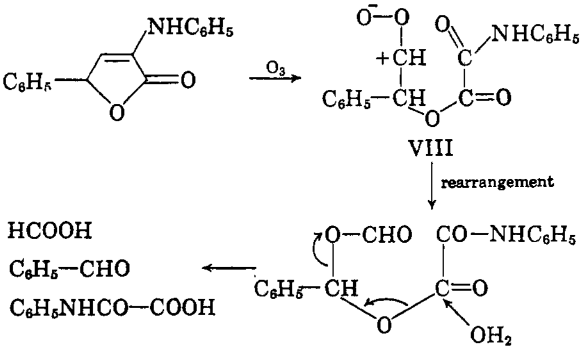
[17] Similar dimerizations have been observed in the case of a 3-ketopyrrolidine by A. A. Patchett and B. Witkop, *J. Am. Chem. Soc.*, **79**, 185 (1957), and the open chain α-keto amide, pyruvanilide, by J. V. Scudi, *J. Am. Chem. Soc.*, **59**, 1403 (1937).

[18] Several *N*-carboxy anhydrides of α-amino acids have been reported to absorb at 5.38–5.40 μ and 5.59–5.66 μ by K. D. Kopple and J. J. Katz, *J. Am. Chem. Soc.*, **78**, 6199 (1956), and M. Idelson and E. R. Blout, *J. Am. Chem. Soc.*, **79**, 3948 (1957). The six-membered anhydride VI would be expected to show two bands at slightly higher wave lengths.

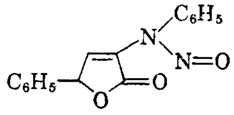
oxidative cleavage of α-dicarbonyl compounds by peroxidic reagents.[20,21]

Studies on A, the Schiff and Gigli compound. The synthetic and degradative work described above clearly establishes the nonidentity of A with authentic 1,5-diphenyl-2,3-pyrrolidinedione. As stated earlier,[1,8] the only reasonable alternative for A is the enamino lactone II. Structure II readily accommodates all the known chemistry of A, including the conversion to methyl benzalpyruvate and aniline hydrochloride by methanolic hydrogen chloride, and the decarboxylation to cinnamylidineaniline.

A further aspect of the chemistry of A which deserves consideration in the light of structure II is the behavior on ozonolysis reported by Montón.[6] The isolation of benzaldehyde and oxanilic acid from this reaction can be explained in terms of zwitterion formation (VIII) followed by rearrangement as shown.[22]



The infrared spectrum of A, showing a strong carbonyl peak at 5.68 μ, is in good agreement with the spectra of other α,β-unsaturated lactones.[23] Although one cannot distinguish conclusively between —NH and —OH by the 2.98 μ band in the spectrum, the resistance to acylation and absence of a color reaction with ferric chloride argue against the presence of enolic hydroxyl. In addition, we have obtained unequivocal evidence for the presence of an —NH grouping in A by the preparation of an *N*-nitroso derivative (IX).[24] This compound, prepared by reaction with sodium nitrite in glacial acetic acid, shows no peaks in the 3 μ region of the infrared but does absorb strongly at 6.71 μ, in good agreement with the absorption reported for monomeric *N*-nitroso derivatives.[25] Denitrosation of the nitroso derivative by aqueous hydrogen chloride regenerates A.



IX

EXPERIMENTAL[26]

The Schiff and Gigli compound (A) was prepared according to the method of Vaughan and Peters.[27] The infrared spectrum in chloroform shows bands at 2.98 (N—H), 5.68 (lactone (C=O), 6.01 (C=C), and 6.53 μ (N—H).

N-Nitroso derivative IX *of the Schiff and Gigli compound.* To a suspension of 1.0 g. (4 mmoles) of finely divided compound A in 30 ml. of glacial acetic acid, there was added in small portions, at 15–18°, 0.28 g. (4 mmoles) of sodium nitrite (45 min). As the reaction proceeded, the solid dissolved. The resulting orange-yellow solution was left at 15–18° for another 45 min. and then poured onto cracked ice with vigorous stirring. (From this point on, all operations were carried out in the cold room at 5°.) The resulting yellow precipitate was collected by filtration, washed repeatedly with distilled water, and dried under vacuum over calcium chloride; yield, 1.0 g. (89%), m.p. 74–76° dec. The product was recrystallized rapidly twice by dissolving it in methylene chloride, diluting with several volumes of pentane, and storing the mixture in the deep-freeze for 30 min. Microscopic yellow rods, m.p. 79.0–79.5° dec., were thus obtained; $\lambda_{max}^{CHCl_3}$ 5.62 (lactone C=O), 6.06 (C=C), 6.71 μ (N—NO); there was no absorption in the region of 2.98 or 6.53 μ.

Anal. Calcd. for $C_{16}H_{12}N_2O_3$: C, 68.56; H, 4.32; N, 10.00. Found: C, 68.41; H, 4.14; N, 9.82.

Solutions of the compound decomposed overnight even at −1°, and a sample stored under vacuum at 5° darkened within a week.

Denitrosation of the N-nitroso derivative IX. A solution of 0.22 g. (0.8 mmole) of the *N*-nitroso derivative (IX) in 20 ml. of methylene chloride was shaken for 10 min. with 5 ml. of concd. hydrochloric acid. The dark organic layer was washed with water, dried over sodium sulfate, and concentrated to dryness under vacuum, leaving 0.20 g. (0.8 mmole) (100%) of crude solid. After thorough washing with absolute ethanol and two recrystallizations from the same solvent,

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(19) The method of preparation followed the procedure of L. Birkofer and H. Kachel, *Naturwiss.*, **41**, 576 (1954) for the preparation of *N*-carboxy-β-amino acid anhydrides. See also L. Birkofer and R. Modic, *Ann.*, **604**, 56 (1957). We are indebted to J. J. Keggi and D. F. Tavares for assistance in the preparation of VI.

(20) H. Kolbe, *J. prakt. Chemie*, **30**, 467 (1884).

(21) J. E. Leffler, *J. Org. Chem.*, **16**, 1785 (1951).

(22) R. Criegee, *Rec. Chem. Progress*, **18**, 111 (1957); P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

(23) R. N. Jones and C. Sandorfy, *Technique of Organic Chemistry*, Vol. IX, A. Weissberger, ed., Interscience Publishers, Inc., New York, 1956, p. 455; P. Yates and G. H. Stout, *J. Am. Chem. Soc.*, **76**, 5110 (1954); R. N. Jones *et. al., Can. J. Chem.*, **37**, 2007 (1959).

(24) Meyer and Vaughan[14] obtained a compound, m.p. 216–216.5° dec., to which they assigned structure IX. We have found that this product, formed from A and sodium nitrite in *hot* acetic acid, shows absorption at 5.56, 6.33, and 6.63 μ, and can be recovered unchanged under the conditions which bring about denitrosation of the low-melting isomer. The two nitroso derivatives are not interconverted on heating in solvents. While we feel that the properties of the high-melting product are not in accord with IX, there is still insufficient evidence to permit a rigorous alternative structural assignment. We thank Dr. Richard Waterfield for information on the spectrum and chemical behavior of the 216° melting isomer.

(25) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 4172 (1955).

(26) Melting points are uncorrected. Microanalyses are by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Infrared spectra were determined with a Perkin-Elmer double beam infrared spectrophotometer, Model 21, and calibrated against the water vapor absorption band at 5.882 μ.

(27) W. R. Vaughan and L. R. Peters, *J. Org. Chem.*, **18**, 382 (1953).

the product melted at 159–160° dec. alone, and on admixture with A (reported[27] m.p. 160–160.5°). The infrared spectrum of the solid was identical with that of A.

4-Carbethoxy-1,5-diphenyl-2,3-pyrrolidinedione (III). The procedure of Southwick and Seivard[11] was followed, except that the reaction mixture was not heated, but left at room temperature for 4 days instead. During this time, 97.2 g. (77%) of yellow powder, m.p. 169–172°, was collected in three crops and washed thoroughly with ice cold ether. Recrystallization from a large volume of 95% alcohol afforded 90 g. (72%) of colorless crystals, m.p. 171.5°–174° (reported m.p.[10,11] 171°, 173°); $\lambda_{max}^{CHCl_3}$ 2.93 (OH), 5.84 (conjugated ester C=O), 5.93 (lactam C=O), and 6.06 μ (C=C).

Attempted acid hydrolysis of III. (a) Solutions of III in concentrated sulfuric acid, in 70% sulfuric acid, and in a mixture of 47% hydriodic acid and acetic acid were left at room temperature for 3 days, then poured onto ice. Ether extraction gave only starting material in every case.

(b) III was heated with various mineral acids (hydrochloric, hydrobromic, sulfuric) of various concentrations (10–70%) for periods of time ranging from 6 min. to 23 hr., with or without the addition of alcohol or acetic acid to effect solution. Samples of the reaction mixtures were withdrawn periodically, diluted with water, and extracted with ether or chloroform. At varying stages of the reaction, the extracted material usually showed a weak to medium sharp band at 5.65 μ in the infrared. Continued heating failed, however, to increase the intensity of this band and led only to dark, complex mixtures from which the desired product could not be isolated.

Reductive cleavage of 4-carbethoxy-1,5-diphenyl-2,3-pyrrolidinedione (III). *Formation of 3-hydroxy-1,5-diphenyl-2-pyrrolidone* (IV). A mixture of 10 g. (0.031 mole) of 4-carbethoxy - 1,5 - diphenyl - 2,3 - pyrrolidinedione(III), 10 g. (0.094 mole) of sodium hypophosphite, 50 ml. of 47% hydriodic acid (sp. gr. 1.5), and 50 ml. of glacial acetic acid was refluxed for 3 hr. The solution was then diluted to 500 ml. with ice water and extracted repeatedly with chloroform. The combined extracts were washed with water, aqueous bicarbonate solution, and again twice with water, dried over sodium sulfate, filtered, and concentrated to dryness under vacuum. The residue was washed with benzene until white, [4.33 g. (55%) of fine crystals, m.p. 200–203.5°] and then recrystallized from benzene affording 3.94 g. (50%) of microscopic needles, m.p. 204–206°. Two further recrystallizations gave an analytical sample, m.p. 206–207°; $\lambda_{max}^{CHCl_3}$ 2.87 (OH), 5.88 μ (lactam C=O); λ_{max}^{KBr} 3.04, 5.95 μ.

Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.84; H, 5.97; N, 5.31.

The acetyl derivative was prepared by dissolving 0.33 g. (1.3 mmoles) of the crude hydroxylactam (IV) in 1.7 ml. (1.9 g., 24 mmoles) of acetyl chloride, allowing the reaction mixture to stand at room temperature for 1 hr., and then concentrating it under reduced pressure. The residue was dissolved in methylene chloride, and the solution was washed with dilute bicarbonate, then twice with water, dried over magnesium sulfate, clarified by filtration through a filter pad, and concentrated to dryness in a stream of nitrogen. The oily residue, which crystallized on cooling, weighed 0.38 g. (99%). Recrystallization from benzene afforded 0.19 g. (50%) of silky white needles. On a hot stage, part of the crystals melted at 103.5°, the remainder melting at 110.5°. An analytical sample was obtained from 4:1 cyclohexane-benzene; m.p. 115.0–115.5° and 117.5–118.5°; λ_{max}^{Nujol} 5.73 (ester C=O) and 5.83 μ (lactam C=O); no absorption around 3 μ.

Anal. Calcd. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.27; H, 5.93; N, 4.79.

Attempted oxidation of 3-hydroxy-1,5-diphenyl-2-pyrrolidone (IV). Oxidation failed to occur with a variety of reagents: (a) cupric acetate (1 equiv.) in 50% aqueous acetic acid which were tried at 85° for 10 hr. There was no precipitate of red copper oxide; (b) bismuth oxide (excess) in glacial acetic acid at reflux for 1.5 hr. and at room temperature for 10 hr. There was no precipitate of black bismuth; (c) chromic anhydride–pyridine complex (3.8 equiv.) in pyridine at room temperature overnight; (d) *N*-bromosuccinimide (1.25 equiv.) in acetone, with water and acetic acid added, at room temperature overnight; (e) *N*-bromoacetamide (4 equiv.) in butanol, with aqueous pyridine added, at room temperature for 48 hr. Unchanged starting material was recovered in (c), (d), and (e).

Oxidation of 3-hydroxy-1,5-diphenyl-2-pyrrolidone (IV). *Formation of 1,5-diphenyl-2,3-pyrrolidinedione* (Ia). To a solution of 2.02 g. (8 mmoles) of 3-hydroxy-1,5-diphenyl-2-pyrrolidone (IV) in 60 ml. of glacial acetic acid was added dropwise, at 15–18°, an ice cold solution of 1.19 g. (4 mmoles) of sodium dichromate dihydrate in 4 ml. of 20% sulfuric acid (30 min.). Green chromic sulfate precipitated gradually during the addition. The reaction mixture was left at room temperature for 10 min., diluted to 600 ml. with ice water, and extracted repeatedly with chloroform. The combined extracts were washed with water, aqueous barium chloride, and again twice with water, dried over sodium sulfate, and concentrated to dryness under reduced pressure at room temperature. The residue was washed thoroughly with ether, leaving 1.38 g. (69%) of yellow powder, m.p. 155–156° dec. Crystallization from methylene chloride by addition of pentane afforded tiny prisms, m.p. 158.5–159° dec. Two recrystallizations from benzene and two more from methylene chloride–pentane afforded an analytical sample, m.p. 158–159° dec. (reported[16] m.p. 158–159°, 162–163°, 159–162°, 164–165°); no color reaction with alcoholic ferric chloride.

Anal. Calcd. for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57; mol. wt., 251. Found: C, 76.28; H, 4.94; N, 5.45; mol. wt., 242 (ebullioscopic in chloroform).

Infrared spectra of the product in chloroform and in potassium bromide disc showed sharp bands at 5.65 and 5.84 μ; hydroxyl absorption could not be detected. The spectra were distinctly different from those of the Schiff and Gigli compound (A), m.p. 161° dec. A mixture of the two compounds decomposed at 139°. Ia was inert to nitrous acid under the conditions used to nitrosate A.

Solutions of Ia in polar solvents (alcohol, acetic acid) turned red within a few minutes when heated. The compound readily underwent a transformation to a sparingly soluble white solid which appears to correspond to the dimerization of 2,3-pyrrolidinediones reported by Southwick.[12] This solid was formed when Ia, in methylene chloride–ether, was filtered through charcoal, when Ia was chromatographed on silene EF-Supercel in benzene, and when, Ia was sublimed *in vacuo* (110° at 0.5 mm.) to yield white crystals, m.p. 172–173°, sparingly soluble in chloroform; $\lambda_{max}^{CHCl_3}$ 5.64 m, 5.84 s, 5.90 s, and 7.33 μ s.

β-Anilino-β-phenylpropionic acid N-carboxyanhydride (VI).[14] β-Anilino-β-phenylpropionic acid,[19] 4.0 g. (0.0166 mole), was dissolved in 200 ml. of dioxane (purified by passing it through a column of alumina and drying over Drierite). Gaseous phosgene was slowly led into the solution, maintained at 32–36°, until the absorption of phosgene ceased (4 hr.). The solution was then flushed thoroughly with nitrogen and concentrated to dryness under vacuum. The residual white solid was dissolved in 175 ml. of ether, 2.2 ml. (1.6 g., 0.016 mole) of triethylamine was added, and after 30 min. the resulting precipitate of triethylamine hydrochloride was removed by filtration. The solvent was evaporated under vacuum, and after washing with ether, there remained 1.9 g. (43%) of crystalline, white solid, m.p. 131–132° dec. An analytical sample was obtained by three recrystallizations from benzene-cyclohexane; m.p. 134–134.6° dec.; $\lambda_{max}^{CHCl_3}$ 5.54 μ and 5.73 μ.

Anal. Calcd. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 72.19; H, 4.96; N, 5.28.

Ozonolysis of 1,5-diphenyl-2,3-pyrrolidinedione (Ia). (a)

Ozonized oxygen was led into a solution of 0.4 g. (1.6 mmoles) of Ia in 300 ml. of methylene chloride, cooled in a Dry Ice-acetone bath for 24 hr. The solution was then flushed thoroughly with oxygen and concentrated to dryness under vacuum at room temperature. The infrared spectrum of the solid residue was identical with that of the starting material.

(b) A solution of 0.050 g. (0.2 mmole) of Ia in 30 ml. of methylene chloride was cooled in a Dry Ice-acetone bath and saturated with ozone (bright blue color). Zinc dust (0.85 g., 13 mmoles) and 1 ml. of 50% ethanol were then added, and the mixture was allowed to come to room temperature. After standing at room temperature for 1 hr., the mixture was dried over sodium sulfate, filtered, and concentrated to dryness under vacuum at room temperature. The residue was redissolved in methylene chloride, and the above procedure was repeated twice. Treatment of the resulting mixture with ether gave an insoluble fraction (mostly poly-β-anilino-β-phenylpropionate, as shown by the infrared). Evaporation of solvent left a residue which, by comparison of infrared spectra, was shown to be β-anilino-β-phenylpropionic acid *N*-carboxyanhydride (VI).

(c) In another run, 0.5 g. (2 mmoles) of Ia was oxidized as described under (b). The final reaction mixture was heated on the steam bath with 50 ml. of 1*N* hydrochloric acid for 0.5 hr. The aqueous solution was then decanted from insoluble material and rendered alkaline with aqueous sodium bicarbonate. The basic solution was washed three times with ether, treated with Norite on the steam bath, filtered, cooled, acidified to *p*H 4 with 1*N* hydrochloric acid, and then extracted three times with ether. The combined extracts were dried over sodium sulfate, filtered through a charcoal column, and concentrated to dryness under vacuum. The final residue was submitted to sublimation at 110–114° (0.5 mm.). The infrared spectrum of the sublimate was superimposable on that of authentic β-anilino-β-phenylpropionic acid[11] (m.p. 133.5–134°). The admixture of the two samples melted at 133–134° (reported[11] m.p. 135–137°).

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NEW HAVEN, CONN.

[CONTRIBUTION NO. 689 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS & CO.]

Cycloalkylation Reactions of Divinylacetylene

C. T. HANDY AND R. E. BENSON

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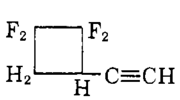
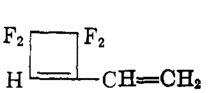
Bis(tetrahalocyclobutyl)acetylenes (Va and Vb) are formed in good yield by condensation of divinylacetylene with tetrafluoro- and chlorotrifluoroethylene. In contrast to the reaction of tetrafluoroethylene with monovinylacetylene, no product corresponding to the addition of tetrafluoroethylene to the acetylenic bond was found. The acetylenes Va and Vb are converted to bis(2-substituted 3,3-difluorocyclobutenyl)acetylenes by reaction with nucleophilic reagents.

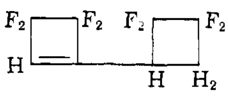
Previous studies in this laboratory have established that acetylenes undergo cycloaddition reactions with tetrafluoroethylene to give cyclobutene structures. Thus, 3,3,4,4-tetrafluorocyclobutene is formed from acetylene and tetrafluoroethylene at 250°,[1] and monovinylacetylene with tetrafluoroethylene gives the products I–III derived from cycloalkylation reactions at both the acetylenic and olefinic bonds.[2] Furthermore, substituted tetrafluorocyclobutanes are also formed by condensation of activated olefins with tetrafluoroethylene.[2]



I



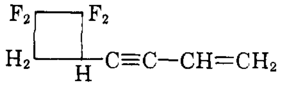
II



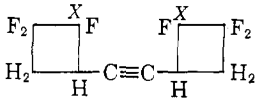
III

This paper reports the results of a study of the condensation of divinylacetylene with tetrafluoroethylene and chlorotrifluoroethylene together with an investigation of the resulting bis(tetrahalocyclobutyl)acetylenes.

Divinylacetylene reacts readily with tetrafluoroethylene at 125–140° and autogenous pressure to give 1,1,2,2-tetrafluoro-3-vinylethynylcyclobutane (IV) and bis(2,2,3,3-tetrafluorocyclobutyl)acetylene (Va). Either compound can be prepared as the major product by controlling the concentration of tetrafluoroethylene. In contrast to the reactions with either acetylene or monovinylacetylene, no product corresponding to the addition of tetrafluoroethylene to the acetylenic bond of divinylacetylene was isolated from these reactions. The structure assignments are based on elemental analyses and interpretation of the infrared, Raman, and NMR spectral data.



IV



Va. $X = F$
b. $X = Cl$

Similarly, reaction of divinylacetylene with chlorotrifluoroethylene at 150° and autogenous pressure produced bis(2-chloro-2,3,3-trifluorocyclobutyl)-acetylene (Vb), apparently as a mixture of stereoisomers. The structure assignment of Vb was made

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(1) J. L. Anderson, R. E. Putnam, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 382 (1961).

(2) D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1949).