[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

A Study of the Structure of Some Derivatives of 5-(*o*-Nitrobenzylidene)-Hydantoin[1]

BY HENRY R. HENZE AND GEORGE R. ALLEN, JR.

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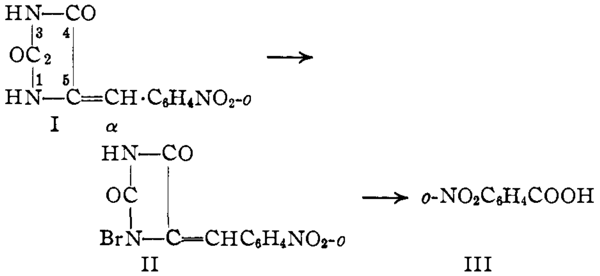
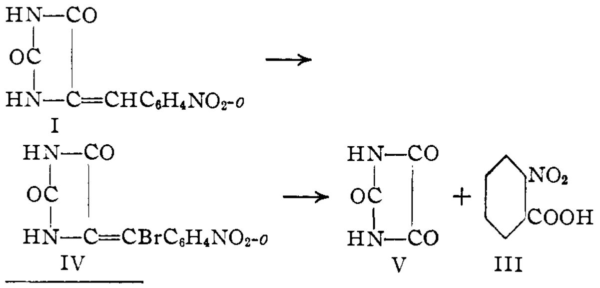
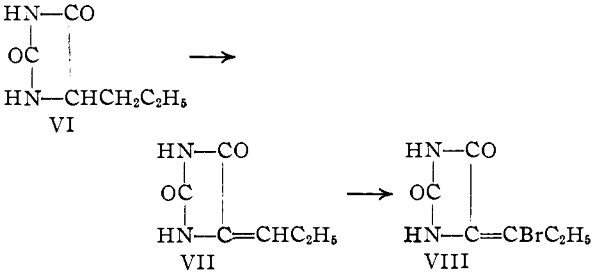
The published structures of certain reaction products of 5-(*o*-nitrobenzylidene)-hydantoin have been shown to be in error and are herein correctly formulated.

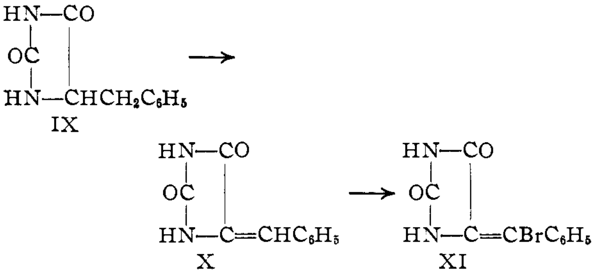
Recently, while we were studying the bromination of 5-propylidenehydantoin, we became aware of the publication by Kozak and Musial[2] who, in describing the chemical behavior of 5-(*o*-nitrobenzylidene)-hydantoin (I), stated that its bromination, chlorination and nitration led to substitution on the nitrogens of the hydantoin nucleus. For example, they reported that interaction of I with bromine led to the formation of a monobromo derivative to which they assigned the structure of 1-bromo-5-(*o*-nitrobenzylidene)-hydantoin (II). The sole evidence recorded in support of this formation was that upon oxidation of II, with alkaline potassium permanganate solution, *o*-nitrobenzoic acid (III) was obtained.


I α II III

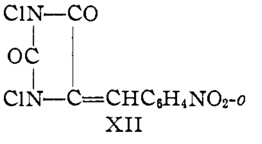
From our previous experiences, it seemed far more probable that bromination of I should produce 5-(α-bromo-*o*-nitrobenzylidine)-hydantoin (IV). We, therefore, have resynthesized this brominated hydantoin, II or IV, and demonstrated that its bromine is unreactive toward iodides.[3] Accordingly, the monobromo compound was subjected to ozonolysis, from which both *o*-nitrobenzoic acid (III) and parabanic acid (V) were isolated.[4] Since the result of the simultaneous action of one equivalent of bromine and ozone on 5-propylhydantoin[5] (VI) had led to the formation of 5-propylidenehydantoin (VII) and 5-(α-bromopropylidene)-hydantoin (VIII), it seemed logical to expose 5-benzylhydantoin (IX) similarly to the simultaneous action of bromine and ozone. From such an experiment, the known 5-benzylidenehydantoin[6] (X) and its monobromo derivative XI were isolated. These facts appear to make it conclusive that the monobromo derivative of Kozak and Musial should be formulated as IV.


I IV V III


VI VII VIII


IX X XI

Kozak and Musial had allowed I to react with an excess of chlorine and believed that, as a result, 1,3-dichloro-5-(*o*-nitrobenzylidene)-hydantoin (XII) ($C_{10}H_5Cl_2N_3O_4$) was obtained. We have repeated the synthesis of XII and subjected it to ozonolysis; once more, the products of cleavage were III and IV. In order to show that the two chloro atoms of XII differed from each other in chemical behavior, an acetone solution of XII was refluxed with zinc; a monochloro product XIII, $C_{10}H_6ClN_3O_4$, melting with decomposition at 245–247°, was produced. This same product XIII could be obtained when potassium iodide was allowed to


XII

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[1] Constructed from Part I of the Ph.D. dissertation of George R. Allen, Jr., The University of Texas, June, 1953.

[2] J. Kozak and L. Musial, *Bull. intern. acad. polonaise*, **1940A**, 432 (1930).

[3] It would seem highly probable that the bromine atom in a –CONBr– structure should liberate iodine from acidified potassium iodide solution.

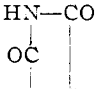
[4] The activation of the halogen in IV $C{=}C(Cl)C_6H_4NO_2$ would seem to be somewhat analogous to that in an acyl halide $O{=}C(Cl)R$, hence an aroyl halide, benzoyl chloride, was exposed to the same ozonolysis conditions as the bromohydantoin derivative and yielded benzoic acid.

[5] E. J. McMullen, H. R. Henze and B. W. Wyatt, submitted for publication.

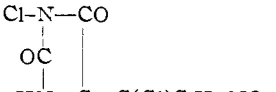
[6] H. L. Wheeler and C. Hoffman, *Am. Chem. J.*, **45**, 368 (1911).

react with an acetic acid solution of XII.[7] The product XIII was inactive toward aqueous potassium permanganate solution, bromine in carbon tetrachloride and concentrated ammonium hydroxide solution, but was readily soluble in very dilute sodium hydroxide solution from which it was regenerated by carbon dioxide.

The monochloro derivative XIII could be prepared directly from I by a brief chlorination (1 equivalent) in glacial acetic acid. By subsequent chlorination, XIII was converted into the dichloro XII. Since ozonolysis of XIII, like that of XII, yielded III and V, compounds XIII and XII may be formulated as being, respectively, 5-(α-chloro-*o*-nitrobenzylidene)-hydantoin and 3-chloro-5-(α-chloro-*o*-nitrobenzylidene)-hydantoin.

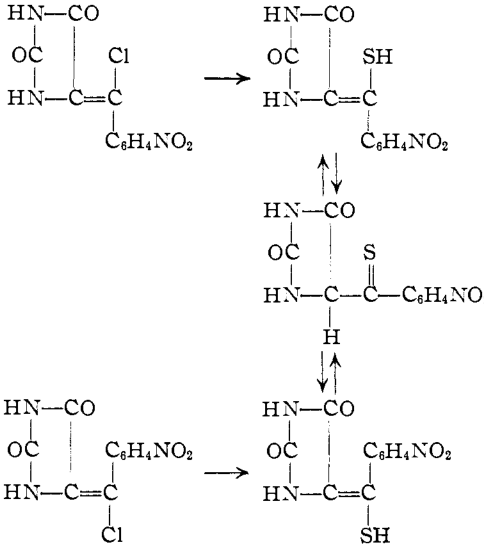


XIII



XII

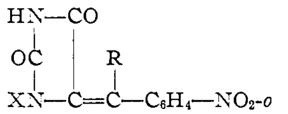
The behavior of XIII and XIV toward potassium bisulfide was of interest in that both compounds formed the same mercapto derivative; this fact is to be explained on the basis of a mercapto-thiocarbonyl tautomerism.



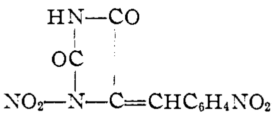
Kozak and Musial had found that heating I with concentrated nitric acid resulted in formation of a dinitro product which they formulated as 1-nitro-5-(*o*-nitrobenzylidine)-hydantoin.[8] When this treatment with concentrated nitric acid was repeated by us, only a small yield of XV could be obtained for the chief chemical attack was one of oxidative-cleavage of I at the 5-α-double bond. However, again ozonolysis was resorted to and XV yielded parabanic acid (V). Therefore, XV was subjected to hydrolysis in acid medium, from which the known (*o*-nitrophenyl)-nitromethane[9] was recovered. This seems to require that XV be reformulated as 5-(α,*o*-dinitrobenzylidene)-hydantoin (XVI).

TABLE I

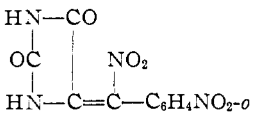
ULTRAVIOLET ABSORPTION SPECTRA OF HYDANTOINS



R-	X-	Maxima, mμ	$\epsilon \times 10^3$	Minima, mμ	$\epsilon \times 10^3$
H	H	296	13.9	246	7.88
Cl (lower m.p.)	H	275	14.6	250	11.80
Cl (higher m.p.)	H	275	14.4	250	11.75
Br	H	278	14.9	250	10.60
NO_2	H	275	14.00	250	10.00
SH	H	265	5.53	250	4.58
Cl	Cl	275	13.75	250	9.28



XV



XVI

Experimental

Condensation of Hydantoin with *o*-Nitrobenzaldehyde.—Through use of the procedure of Kozak and Musial, in which hydantoin and *o*-nitrobenzaldehyde are heated with fused zinc chloride, 5-(*o*-nitrobenzylidene)-hydantoin (I) was obtained in variable yields (45–80%). The reaction product was not of purity sufficient for subsequent use. After a minimum of three recrystallizations from glacial acetic acid the white compound melted at 280–282° dec.[10] The purified product was never obtained in greater than 50% yield.

In attempts to obtain I in better yield, a mixture of hydantoin, *o*-nitrobenzaldehyde, fused sodium acetate and glacial acetic acid containing acetic anhydride was heated; the unreacted aldehyde was recovered (96%). Likewise the condensation could not be effected through attempted use of piperidine as a catalyst, or through heating the reactants with fused zinc chloride in glacial acetic acid.

Condensations using 2-Thiohydantoin. A.—Following the procedure of Namjoshi and Dutt,[11] *o*-nitrobenzaldehyde and 2-thiohydantoin were allowed to reflux with acetic anhydride for three hours. The hot, red solution was poured into cold water; an oily liquid formed, but, by warming the mixture on a steam-bath, it was converted into a crystalline solid. The latter (0.25 g.) melting at 240–241°, proved to be acetyl-5-(*o*-nitrobenzylidene)-2-thiohydantoin. Additional product (representing 26% conversion) was obtained by concentration of the mother liquor.

The acetylated derivative was heated in 20% sodium hydroxide solution for one hour; acidification yielded 5-(*o*-nitrobenzylidene)-2-thiohydantoin (75% conversion); m.p. 242–246° dec.

B.—The method of Wheeler and Brautlecht[12] was used to

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[7] In one repetition of this experiment, with only very little difference in the method of isolating the reaction product, another monochloro derivative XIV was isolated. Although XIV melted with decomposition at 144.0–145.5°, it was isomeric with XIII. Mixtures of XIII and XIV began melting slightly about 122–126° but fusion was not complete until about 142°. Subsequently, the chemical behavior of XIII and XIV indicates that these two products are the anticipated geometrical isomers.

[8] Kozak and Musial seem to have based this assignment of structure of XV upon the fact that Biltz and Slotta (*J. prakt. Chem.*, **113**, 247 (1926)) had found that a 1-nitro derivative resulted from the nitration of 3,5,5-trimethylhydantoin. Since the latter does not possess an unsaturated substituent at the 5-position of the hydantoin nucleus the chemical behavior of the trialkylated hydantoin should be expected to differ from that of XV. Likewise, certain work of Grimaux [*Bull. soc. chim.*, [2] **23**, 49 (1876); *Ann. chim. phys.*, [5] 11, 358 (1877)] indicated that the attachment of the nitro groups in substituted C-5 unsaturated hydantoin derivatives is to the α-position. This work was later verified by Davidson and Johnson (THIS JOURNAL, **47**, 561 (1925); Davidson, *ibid.*, **47**, 1722 (1925)).

[9] A. F. Holleman, *Rec. trav. chim.*, **15**, 365 (1896).

[10] J. Kozak and L. Musial, ref. 2, reported m.p. 278–280° dec.

[11] V. G. Namjoshi and S. Dutt, *J. Ind. Chem. Soc.*, **8**, 244 (1931).

[12] H. L. Wheeler and C. A. Brautlecht, *Am. Chem. J.*, **45**, 446 (1911).

prepare 5-(*o*-nitrobenzylidene)-2-thiohydantoin in 49% yield, yellow crystalline solid, m.p. 244–247° dec.

Desulfurization of 5-(*o*-Nitrobenzylidene)-2-thiohydantoin.—Following a desulfurization procedure developed by Johnson, *et al.*,[13] a suspension of this thiohydantoin was heated with chloroacetic acid solution at reflux for four hours to produce 5-(*o*-nitrobenzylidene)-hydantoin[14] (I), 91% yield, m.p. 272-277° dec.; after recrystallization from glacial acetic acid, m.p. 280–282° dec.

Bromination of 5-(*o*-Nitrobenzylidene)-hydantoin (I).—A mixture of 3.56 g. (0.015 mole) of I and 100 ml. of glacial acetic acid was heated until solution occurred, then 0.84 ml. (0.015 mole) of bromine in 30 ml. of glacial acetic acid was added dropwise (90 minutes) to the stirred solution. After 3 hours, the brownish-yellow mixture was chilled; solid material separated, was filtered off and washed with 100 ml. of petroleum ether (b.p. 60–68°). Recrystallization from glacial acetic acid gave 3.70 g. (78% yield) of the monobromo derivative of 5-(*o*-nitrobenzylidene)-hydantoin as yellow crystals, m.p. 245.0–247.5° dec. After further recrystallization from ethyl alcohol, the product[15] IV melted with decomposition at 247–248°.

A portion of IV was dissolved in 50% chloroform–glacial acetic acid solution and treated with a crystal of potassium iodide; no perceptible coloration of the solution was noted until after a very small amount of N-bromosuccinimide had been added.

Ozonolysis of IV.—A stream of ozone in oxygen was passed into a suspension of 2.0 g. (0.006 mole) of IV in 200 ml. of glacial acetic acid; after about 250 minutes all solid material had dissolved and the solution had changed in color from yellow to orange, zinc dust and 50 ml. of ice-water were added, the mixture was filtered and the filtrate was concentrated *in vacuo* to about 25 ml. Solid separated, and was removed and washed with acetone; m.p. 246–248°, weight 1.55 g. (77% recovery).

The filtrate was further concentrated, chilled and filtered to obtain 0.07 g. (43% yield of material ozonized) of parabanic acid, m.p. 241–243° dec. The filtrate was again concentrated; upon addition of water, light yellow needles of *o*-nitrobenzoic acid (m.p. 144-145°) separated.

Bromination of 5-Benzylhydantoin in the Presence of Ozone.—A solution of 3.27 g. (0.017 mole) of 5-benzylhydantoin in 60 ml. of glacial acetic acid was treated with 2.1 ml. (6.7 g. or 0.042 mole) of bromine before a stream of ozone–oxygen was bubbled in (5 l. per hr.) during 15 hours; the color of the reaction mixture progressively lightened to a final light yellow. The solution was diluted with 60 ml. of water and subjected to steam distillation until about 500 ml. of distillate had been collected. The residual material was chilled causing separation of authentic 5-(α-bromobenzylidene)-hydantoin[16] (XI); 0.54 g., m.p. 233–237° dec.

The filtrate was resubjected to steam distillation, the residual solution was concentrated by evaporation; addition of water and chilling caused precipitation of 1.15 g. (36% yield) of authentic 5-benzylidenehydantoin[17] (X).

Nitration of 5-(*o*-Nitrobenzylidene)-hydantoin (I).—A solution of 1.62 g. (0.006 mole) of I in 16.5 ml. of concentrated nitric acid was heated until oxides of nitrogen ceased to be evolved. The hot solution was poured into ice-water; solid material appeared, was removed by filtration and was recrystallized from alcohol as a light yellow solid XVI, 0.15 g., 8% yield, m.p. 225–227° dec.[18]

The filtrate from XVI was evaporated to about 20 ml. and chilled; a yellow solid appeared, was filtered off and recrystallized from water; 0.60 g. (62% conversion), m.p. 145–146°; did not depress the m.p. of authentic *o*-nitrobenzoic acid. Further concentration and subsequent chilling of the acidic filtrate yields parabanic acid, melting with decomposition at 240°.

In another preparation, 1 g. of I was dissolved in a mixture of 10 ml. each of concentrated nitric and sulfuric acids. The solution was heated on a steam-bath until evolution of oxides of nitrogen ceased (about one hour) and then was poured onto 200 g. of cracked ice. A yellow solid material resulted, was filtered and recrystallized from diluted alcohol; 0.2 g. (17% yield) of XVI, m.p. 225–226° dec.

Ozonolysis of XVI.—A 5% ozone in oxygen mixture was bubbled for 6 hours through a solution of 0.30 g. of XVI in 50 ml. of glacial acetic acid. After treatment with zinc dust and ice-water, the reaction mixture was filtered and the volume of the filtrate was reduced (*in vacuo*) to about 5 ml. Dilution with an equal volume of water caused precipitation of white, solid material. The latter (73 mg., 64% yield), after recrystallization from water melted with decomposition at 243–244°, and was identified as parabanic acid. No other fission product was isolated.

Hydrolysis of XVI.—A solution of 0.50 g. of XVI in 25 ml. of 50% alcohol-water and 5 ml. of concentrated hydrochloric acid was slowly evaporated on a steam-bath to a volume of 10 ml.; chilling caused separation of orange solid,[19] after recrystallization from alcohol, 75 mg., m.p. 74–76°. Extraction of the reaction mixture with ether yielded an additional 15 mg. melting at 73–75°; total yield 27% of the calculated quantity.

Preparation of a Dichloro Derivative of 5-(*o*-Nitrobenzylidene)-hydantoin.—Chlorine was bubbled for 30 minutes through a solution of 1.0 g. of 5-(*o*-nitrobenzylidene)-hydantoin in 50 ml. of glacial acetic acid; copious evolution of white fumes was noted during the initial minutes but ceased before the end of the period. The solution was concentrated to about 10 ml. under an air jet and was chilled without causing deposition of solid material. The addition was diluted with 50 ml. of water; chilling the turbid solution resulted in formation of 0.31 g. of colorless solid; m.p. 180–183° dec. Additional crops of the product (total weight 0.83 g., yield 64%) were obtained and all material[20] XII upon recrystallization from dilute alcohol melted with decomposition at 180–182°.

Ozonolysis of the Dichloro-5-(*o*-nitrobenzylidene)-hydantoin (XII).—A stream of ozone–oxygen was led during 6 hours into a suspension of 2.50 g. of XII in 50 ml. of glacial acetic acid; after 4 hours the mixture had become homogeneous. After treatment with zinc dust and ice-water, the mixture was filtered, and the filtrate subjected to steam distillation, about 2500 ml. of distillate being collected. The residual solution was evaporated to about 30 ml. and chilled to yield yellow material which was shown to be *o*-nitrobenzoic acid (0.30 g., 23% yield), m.p. 144–146°. From the mother liquor, parabanic acid (m.p. 241–243° dec.) was recovered in 21% yield.

Preparation of a Monochloro Derivative of 5-(*o*-Nitrobenzylidene)-hydantoin. A.—Chlorine was bubbled for 10 minutes through a warm solution of 2.10 g. of I in glacial acetic acid; initially evolution of copious white fumes was noted. The solution was evaporated to dryness under an air-jet, and the residue was recrystallized from dilute alcohol to obtain 1.65 g. (69% yield) of a monochloro-5-(*o*-nitrobenzylidene)-hydantoin (XIII), m.p. 245–246° dec.

Anal. Calcd. for $C_{10}H_6ClN_3O_4$: C, 44.77; H, 2.26; Cl, 13.25; N, 15.70. Found: C, 44.69; H, 2.29; Cl, 12.90; N, 15.81.

This chloro compound XIII could be crystallized from dioxane–water solution; was soluble in 10% sodium hydroxide solution from which it was recovered unchanged by bubbling carbon dioxide through the alkaline solution; it failed to liberate iodine from an acetone–water solution of potassium iodide.

B.—In another experiment, 3.5 g. of I was suspended in 45 ml. of glacial acetic acid containing one molar equivalent of chlorine; the well-stoppered container stood in the sunlight for 5 hours, the appearance of some of the suspended solid changed to coarser, larger crystals. Upon opening the container, copious evolution of hydrogen chloride was demonstrated. Removal of the suspended solid yielded 2.10 g. (60% recovery of unreacted I, m.p. 274–276° dec.

From the filtrate, light yellow, crystalline material was obtained, which, after recrystallization from dilute alcohol, melted with decomposition at 233–236° dec. The product was further purified and shown to be XIII; 1.05 g., 66% yield based on unrecovered I.

Chlorination of XIII.—Chlorine was passed for 15 minutes into a solution of 0.82 g. of the yellow monochloro derivative

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[13] T. B. Johnson, G. M. Pfau and W. W. Hodge, THIS JOURNAL, **34**, 1041 (1912).

[14] J. Kozak and L. Musial, ref. 2, reported m.p. 278–280° dec.

[15] J. Kozak and L. Musial, ref. 2, reported m.p. 247–248° dec.

[16] H. L. Wheeler, C. Hoffman and T. B. Johnson (*J. Biol. Chem.*, **10**, 147 (1911)) reported m.p. 240°.

[17] H. L. Wheeler and C. Hoffman, *Am. Chem. J.*, **45**, 368 (1911).

[18] J. Kozak and L. Musial, ref. 2, reported m.p. 224–226° dec.

[19] A. F. Holleman, ref. 9, reported that (*o*-nitrophenyl)-nitromethane melts at 72°.

[20] J. Kozak and L. Musial, ref. 2, reported the same m.p.

of 5-(*o*-nitrobenzylidene)-hydantoin (XII) in 50 ml. Heating the mixture on a steam-bath caused evolution of hydrogen chloride. From this solution there was obtained 0.65 g. (73% yield) of the colorless dichloro derivative of 5-(*o*-nitrobenzylidene)-hydantoin (XII), m.p. 178–180° dec.

Ozonolysis of XIII.—An ozone-oxygen mixture was passed through a solution of the monochloro derivative (0.35 g.) in 50 ml. of ethyl acetate; ozone was detectable in the effluent gas within 5 minutes; the solution had lost its original light yellow color after about 2 hours of gasification. Zinc dust and ice-water were added, the mixture was filtered; the filtrate yielded 130 mg. of *o*-nitrobenzoic acid (m.p. 145–146°) and 10 mg. of parabanic acid, m.p. 241–243° dec.

Difference in Activity of Halogen Atoms in the Dichloro-5-(*o*-nitrobenzylidene)-hydantoin (XII). A.—To 0.31 g. (0.001 mole) of II in 25 ml. of acetone was added 0.065 g. (0.001 gram-atom) of powdered zinc and the mixture was refluxed for 24 hours. The hot solution was filtered and the filtrate was shown to contain chloride ions; the solvent was evaporated from the filtrate. The residue was recrystallized from diluted alcohol to give 0.20 g. (67% yield) of 5-(α-chloro-*o*-nitrobenzylidene)-hydantoin (XIII).

B.—One-half gram of XII in 50% acetic acid solution was treated with one gram of potassium iodide; almost immediately, iodine was liberated. The solution was steam distilled and the residue concentrated to about 10 ml. before being ether extracted. After two recrystallizations from benzene, there was obtained 0.2 g. of crystals XIV, m.p. 144.0–145.5°.

Anal. Calcd. for $C_{10}H_6ClN_3O_4$: Cl, 13.25; N, 15.70. Found: Cl, 12.88; N, 15.83.

This material dissolved unaltered in 0.2 *N* sodium hydroxide solution and was inactive toward concentrated ammonium hydroxide solution. It did not exhibit any degree of unsaturation. A mixture of XIV with the higher-melting monochloro-5-(*o*-nitrobenzylidene)-hydantoin of m.p. 245–246° dec. melted over the range 126–135°; after cooling to a solid, upon reheating the mixture melted at 122–142°.

C.—In a repetition of experiment B, the higher melting geometrical isomer XIII was obtained and no evidence of presence of the lower-melting isomer XIV could be found.

Preparation of 5-(α-Mercapto-2-nitrobenzylidene)-hydantoin. A. From the Higher Melting Monochloro-5-(*o*-nitrobenzylidene)-hydantoin (XIII).—To a solution of 1.05 g. (0.016 mole) of potassium hydroxide which had been saturated with hydrogen sulfide at 0°, was added 0.22 g. (0.00082 mole) of XIII and the solution was refluxed for one hour. The red solution was cooled, acidified with glacial acetic acid and refrigerated to precipitate solid material. The latter was removed and recrystallized from diluted alcohol; yield 0.16 g. (74%), m.p. 125–126°.

Anal. Calcd. for $C_{10}H_7N_3O_4S$: N, 15.85. Found: N, 15.82.

B. From the Lower Melting Monochloro-5-(*o*-nitrobenzylidene)-hydantoin (XIV).—Using the above procedure, 0.22 g. of XIV yielded 0.18 g. (83%) of the same sulfur derivative, m.p. 123–125°.

C. From the Bromo Derivative of 5-(*o*-Nitrobenzylidene)-hydantoin (XI).—In an analogous manner, 0.50 g. of XI, 2.10 g. of potassium hydroxide in 16 ml. of water saturated with hydrogen sulfide upon heating produced 0.36 g. (85% yield) of the crude sulfur product, m.p. 121–124°.

Ultraviolet Absorption Spectra of Solutions of Derivatives of 5-(*o*-Nitrobenzylidene)-hydantoin.—A Beckman Model DU Spectrophotometer was used to obtain the absorption spectra of ethyl alcoholic solutions of α-nitro, α-bromo, α-chloro, 3,α-dichloro and α-mercapto derivatives. All of these compounds exhibited maximum absorption at 275 mμ, and a minimum at 250 mμ. However, whereas the spectra of these compounds were highly similar in appearance the absorption spectrum of the mercapto derivative was quite easily recognized because of its lesser tendency to absorb.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

Kinetics of the Condensation of Dipyrrylmethenes with an α-Free Pyrrole[1]

BY ALSOPH H. CORWIN AND KENNETH W. DOAK[2]

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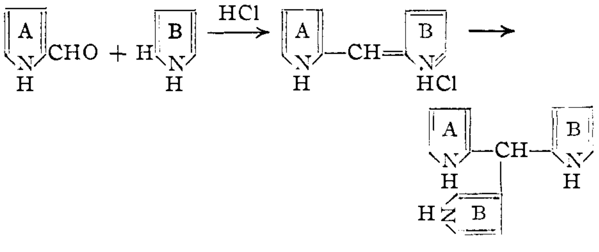
In a condensation with an α-free pyrrole, a dipyrrylmethene appears to be an electrophilic reagent. Substituents which make the bridge carbon more positive increase the rate of condensation. The rate depends on the concentrations of both the α-free pyrrole and the dipyrrylmethene. In a catalyzed reaction in benzene, monomeric acetic acid is the principal catalytic species at very low concentrations, while the dimer apparently becomes important at higher concentrations. Hydroxydipyrrylmethenes are very unreactive toward an α-free pyrrole, because of an unfavorable equilibrium. This alters the course of the aldehyde synthesis of dipyrrylmethenes from an N-methylpyrryl aldehyde and α-free pyrrole, so that two mono-N-methyldipyrrylmethenes have been isolated for the first time.

The mechanism of the aldehyde synthesis of dipyrrylmethenes has been studied by Corwin and Andrews,[3] and by Paden, Corwin and Bailey.[4] The condensation of a pyrryl aldehyde and an α-free pyrrole does not always give the expected dipyrrylmethene. The dipyrrylmethene formed may react further with the α-free pyrrole to form a tripyrrylmethane, which can undergo cleavage to form a different dipyrrylmethene and α-free pyrrole. Further condensations and cleavage may occur, so that three dipyrrylmethenes are possible, two symmetrical and one unsymmetrical. Corwin and Andrews,[3a] by changing substituents on the pyrrole nuclei, were able to isolate all three types of dipyrrylmethenes. This mechanism accounts for the failure of several attempts to synthesize a mono-N-methylmethene by the aldehyde synthesis.[3b]



This synthesis thus involves several competing reactions. The product isolated will be determined by the relative velocities of the competing reactions. Therefore, to determine the effects of sub-

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[1] Studies in the Pyrrole Series XXV. Paper XXIV, G. G. Kleinspehn and A. H. Corwin, THIS JOURNAL, **76**, 5641 (1954).

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