Rearrangement Reactions of Phenyl Chloroformate Derivatives of 2-Hydroxyaminoacetanilides to Hydantoins, Ureas and Hydantoic Acid Derivatives

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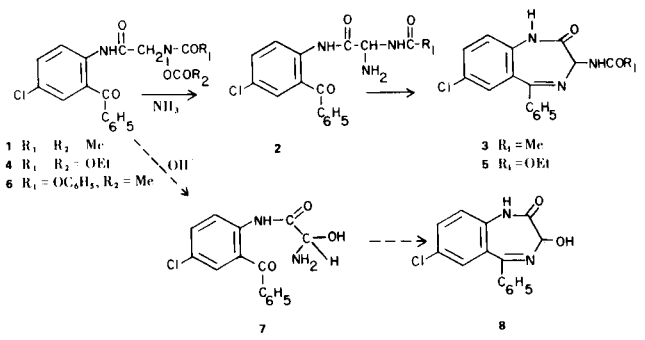
Alkaline treatment of 2′-benzoyl-2-(*N*-carbophenoxy-*N*-hydroxyamino)-4′-chloroacetanilide (**10**) and its corresponding acetate **6** afforded respectively 5-(2-benzoyl-4-chlorophenyl)-3-hydroxyhydantoic acid (**12**) and 6-chloro-4-phenylquinazolone (**13**). A study of the course of the reaction was carried out with the corresponding compounds that are devoid of the 2-benzoyl group. An elucidation of the rearrangement is based on the isolation and independent synthesis of the heterocyclic intermediates.

The syntheses of 2-(*N*-acetoxy-*N*-acetylamino)acetanilides (**1**) as well as their usefulness as intermediates in the preparation of various 2-acetamido-2-aminoacetanilides (**2**) has been reported (2). Certain 2′-benzoyl-2-acetamido-2-aminoacetanilides (**2**) have also been shown to be useful intermediates in the preparation of 3-acetamido-1,4-benzodiazepines (**3**) (3). We have also reported on the preparation of related urethanes **4** and have shown how these undergo an elimination-addition reaction followed by cyclization to afford the 1,4-benzodiazepine-3-carbamate (**5**) (4). It was anticipated that the phenyl urethane **6**, which would be more susceptible to hydrolysis, might hydrolyze subsequent to undergoing the elimination-addition reaction to afford the 2-amino-2-hydroxy acetanilide (**7**). *In situ* cyclization of the labile intermediate might then afford a direct route for the preparation of 3-hydroxy-1,4-benzodiazepines, such as oxazepam (**8**),

Figure 1



Indeed, the urethane **6** readily rearranged upon treatment with base; however, the course of the reaction was entirely different from the reactions observed previously. The products that were obtained and the reactions that occurred are described below.

The desired 2-(*N*-acetoxy-*N*-carbophenoxyamino)acetanilide (**6**) was prepared by acylation of 2′-benzoyl-4′-chloro-2-hydroxyaminoacetanilide (**9**) (2) with phenyl chloro formate followed by acetylation with acetic anhydride. Treatment of **6** with alcoholic alkali gave none of the anticipated 2-amino-2-hydroxyacetanilide **7** or its expected cyclization product **8**. Instead, 6-chloro-4-phenylquinazolone (**13**) was isolated and identified by comparison with authentic material (5). When the intermediate **10** was treated in a similar manner with alkali, a substance identified as 5-(2-benzoyl-4-chlorophenyl)-3-hydroxyhydantoic acid (**12**) was isolated.

In addition to having elemental analyses that are consonant with the acid **12**, the proposed structure is further supported by the nmr spectrum in deuteriochloroform which has a singlet at δ 4.5 (2H) for the methylene, a multiplet at δ 7.3-7.7 for seven aromatic protons, and a doublet at 8.18 (J = 10 Hz) for the aromatic proton ortho to the amide. The ir spectrum (potassium bromide) shows a broad band at 3.15 μ and sharp bands at 5.68, 6.05, and 6.15 μ which can be assigned to the hydroxyl, and to carboxylic acid, diaryl ketone, and amide carbonyls.

The formation of 6-chloro-4-phenylquinazolone (**13**) and 5-(2-benzoyl-4-chlorophenyl)-3-hydroxyhydantoic acid (**12**) may be explained by the sequence of reactions outlined in Figure 2. It is postulated that the initial reaction that occurred when both **10** and **6** were treated with alkali was cyclization to form the hydantoins **11** and **14**. The hydantoin **11** was then hydrolyzed to 5-(2-benzoyl-4-chlorophenyl)-3-hydroxyhydantoic acid (**12**). The hydantoin **14** could either follow a similar course to give the

intermediate hydantoic acid **15a**, or it could undergo the elimination-addition reaction to give the 4-hydroxyhydantoin **15b**. Intermediate **15a** or **15b** could then undergo either elimination-addition or hydrolysis to give the unstable α-hydroxy acid **16**, which upon elimination of glyoxylic acid afforded the 4-chloro-2-benzoylphenyl urea (**17**). *In situ* cyclization of the urea by elimination of water gave the isolated 6-chloro-4-phenylquinazolone (**13**).

In order to study the course of these reactions more thoroughly, we investigated the chemistry of the corresponding compounds without the 2-benzoyl group. The absence of the benzoyl group facilitated isolation of the corresponding intermediates that were postulated in Figure 2. Also, independent syntheses of the various intermediates were more facile when the benzoyl group was not present. The *N*-hydroxyphenylurethane **19** was prepared in similar fashion to **10** by acylation of **18** (3) with phenylchloroformate. Acetylation with acetic anhydride produced 2-(*N*-acetoxy-*N*-carbophenoxyamino)-4′-chloroacetanilide (**20**).

As was expected on the basis of the postulated reaction scheme of Figure 2, treatment of **20** with sodium hydroxide (conditions *A*) afforded *p*-chlorophenylurea (**24**) (6), the intermediate that corresponds with **17**. By simply heating **20** in refluxing ethanol (conditions *B*), we were able to prepare the intermediate *N*-acetoxyhydantoin **21**. Since neither **22a** nor **22b** has been isolated from the alkaline reaction, the question of whether ring opening of **21** proceeds or follows elimination-addition still cannot be fully resolved.

Treatment of the *N*-hydroxyurethane **19** with sodium hydroxide produced the expected 5-*p*-chlorophenyl-3-hydroxyhydantoic acid (**26**) that corresponds with **12** in Figure 2. As would be expected on basis of reported hydantoin chemistry (7), base hydrolysis of **25**, which was prepared as described below, gave **26**, thereby confirming the postulated intermediacy of the *N*-hydroxyhydantoin **25**.

In addition to having elemental and spectral analyses that were consonant with the proposed structures, some intermediates were prepared by independent syntheses. The 3-hydroxy-5-*p*-chlorophenylhydantoic acid **26** was prepared by condensing *p*-chlorophenylisocyanate with *N*-hydroxyaminoacetic acid. Since the hydantoic acid **26** gave the deep red color with ferric chloride that is characteristic of hydroxamic acids and since mild acetylation of **26** gave **22a**, which exhibits the characteristic *N*-acetyl absorption in the infrared, it can be concluded that the

Figure 2

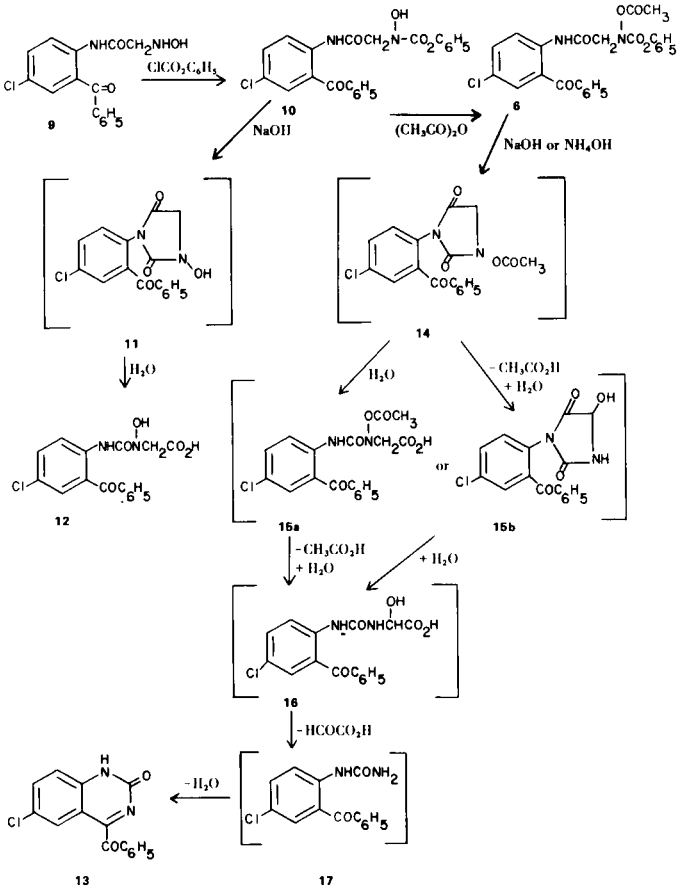
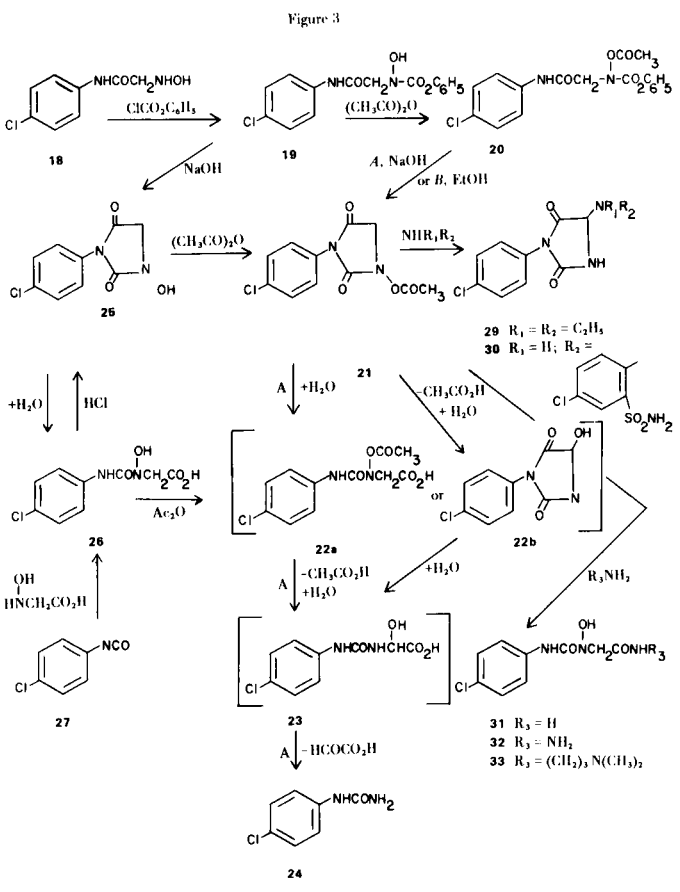


Figure 3



nitrogen atom of *N*-hydroxyaminoacetic acid added to the isocyanate. The 3-hydroxy-*p*-chlorophenylhydantoic acid (**26**), prepared from *N*-hydroxyaminoacetic acid, was cyclized in hydrochloric acid to the corresponding *N*-hydroxyhydantoin **25**, which corresponds with intermediate **11** in the postulated reaction scheme. Acetylation of **25** gave, as expected, the compound **21** also prepared from **20**.

The reactions of 1-acetoxy-3-*p*-chlorophenylhydantoin (**21**) with amines to give the 5-amino compounds indicate that the elimination-addition reaction could occur prior to ring opening. When the *N*-acetoxyhydantoin **21** was treated with diethylamine, acetic acid was eliminated and diethylamine added to the C=N to give **29**. Likewise, reaction of **21** with a mixture of 2-amino-4-chlorobenzenesulfonamide gave 3-(*p*-chlorophenyl)-5-(5-chloro-2-sulfamylanilino)hydantoin **30**. The compounds **29** and **30** had elemental and spectral (ir and nmr) analyses that were consistent with the postulated structures.

A distinctly different reaction occurred when *N*-acetoxyhydantoin **21** was treated with certain amines. Both the acetoxy group and the hydantoin underwent aminolysis. For example, ammonia, hydrazine, and dimethylaminopropylamine condensed with **21** to give the amides **31**, **32**, and **33**. These structures were also supported by elemental and spectral analyses.

EXPERIMENTAL (8)

2-[Carboxy(hydroxy)amino)-2′-benzoyl-4′-chloroacetanilide, Phenyl Ester (**10**).

A mixture of 4.0 g. of 2′-benzoyl-4′-chloro-2-hydroxyaminoacetanilide (**9**) (2), 10 ml. of phenylchloroformate and 100 ml. of chloroform was refluxed for 30 minutes. The solvent was removed *in vacuo* and the residue crystallized by addition of 60 ml. of ethanol. Recrystallization from acetonitrile gave 2.5 g. (45%) of **10**, m.p. 171-173°; ir μ 3.20 (broad NH and OH), 5.80 (carbamate CO), 5.86 (amide CO), 6.12 (diaryl ketone), 6.63 (amide II); nmr (deuteriochloroform): δ 4.5 (s, 2), 7.1-7.7 (m, 12), 7.88 (s, 1), 8.42 (d, 1, J = 10 Hz), 10.91 (s, 1).

Anal. Calcd. for $C_{22}H_{17}ClN_2O_5$: C, 62.19; H, 4.03; Cl, 8.35; N, 6.60. Found: C, 62.12; H, 3.94; Cl, 8.3; N, 6.42.

2-[Carboxy(hydroxy)amino]-4′-chloroacetanilide, Phenyl Ester (**19**).

Preparation from 5.0 g. of 4′-chloro-2-hydroxyaminoacetanilide (**18**) (3) and 7.0 ml. of phenylchloroformate according to the above procedure and recrystallization from 2-propanol gave **19**, m.p. 209-211°; ir μ 3.1, 5.75 (ester), 5.90 (amide).

Anal. Calcd. for $C_{15}H_{13}ClN_2O_4$: C, 56.17; H, 4.08; Cl, 11.05; N, 8.74. Found: C, 56.25; H, 4.07; Cl, 11.2; N, 8.60.

2-[Carboxy(hydroxy)amino]-2′-benzoyl-4′-chloroacetanilide acetate, Phenyl Ester (**6**).

A solution of 2.0 g. of 2-[carboxy(hydroxy)amino]-2′-benzoyl-4′-chloroacetanilide, phenyl ester (**10**) and 25 ml. of acetic anhydride was warmed on the steam bath for 20 minutes. The solvent was removed *in vacuo* and the residue recrystallized from 2-propanol giving 1.0 g. (50%) of **6**, m.p. 127-129°; nmr (deuteriochloroform): δ 2.17 (s, 3), 4.46 (s, 2), 7.05-7.70 (m, 12), 8.41 (d, 1, J = 9.5 Hz), 11.0 (s, 1).

Anal. Calcd. for $C_{24}H_{19}ClN_2O_6$: C, 61.74; H, 4.10; Cl, 7.60; N, 6.00. Found: C, 61.64; H, 4.07; Cl, 7.7; N, 6.00.

2-[Carboxy(hydroxy)amino-4′-chloroacetanilide, Phenyl Ester, Acetate (**20**).

2-[Carboxy(hydroxy)amino]-4′-chloroacetanilide, phenyl ester, 6.6 g. (**19**) and 35 ml. of acetic anhydride were combined as described above. The acetate **20**, 5.4 g., m.p. 148-151°, which precipitated out of the reaction mixture, was collected and washed with hexane; ir μ 5.59 (N-OAc), 5.72 (ester), 5.90 (amide); nmr (DMSO-d_6): δ 2.29 (s, 3), 4.52 (s, 2), 6.75-7.86 (m, 9).

Anal. Calcd. for $C_{17}H_{15}ClN_2O_5$: C, 56.28; H, 4.17; Cl, 9.77; N, 7.72. Found: C, 56.15; H, 4.02; Cl, 9.5; N, 7.89,

5-[2-Benzoyl-4-chlorophenyl]-3-hydroxyhydantoic Acid (**12**).

To a suspension of 4.45 g. of 2-[carboxy(hydroxy)amino]-2′-benzoyl-4′-chloroacetanilide, phenyl ester (**10**) in 60 ml. of ethanol was added 20 ml. of 4 *N* sodium hydroxide and the reaction mixture was gently warmed on the steam bath until an orange colored sodium salt formed. The reaction mixture was acidified with 60 ml. of 4 *N* hydrochloric acid, heated for 5 minutes, diluted with water and cooled. The precipitate was filtered and washed with chloroform giving 1.4 g. (39%) of product, m.p. 153-155°.

Anal. Calcd. for $C_{16}H_{13}ClN_2O_5$: C, 55.19; H, 3.76; Cl, 10.11; N, 8.00. Found: C, 55.32; H, 3.94; Cl, 10.2; N, 7.81.

6-Chloro-4-phenyl-2(1*H*)quinazolinone (**13**) (5).

Method A.

To a suspension of 1.0 g. of 2-[carboxy(hydroxy)amino]-2′-benzoyl-4′-chloroacetanilide, acetate phenyl ester (**6**) in 20 ml. of ethanol was added 5 ml. of 4 *N* sodium hydroxide solution with stirring. After 1 hour, during which time a yellow solution developed, 40 ml. of water was added, and the resultant precipitate was filtered. Acidification of the filtrate with hydrochloric acid caused the above titled compound **13** to separate as a solid, m.p. 305° dec.

Method B.

To a suspension of 1.0 g. of compound **6** in 15 ml. of 1,2-dimethoxyethane was added with stirring 5 ml. concentrated ammonium hydroxide. After standing for 72 hours, the solution was diluted with a large volume of water to give 0.6 g. of compound **13**, m.p. 305°.

3-(*p*-Chlorophenyl)-1-hydroxyhydantoin, Acetate (**21**).

A solution of 4.5 g. of 2-[carboxy(hydroxy)amino]-4′-chloroacetanilide, phenyl ester, acetate **20** was refluxed in 20 ml. of ethanol for 15 minutes. The solution was chilled to cause the precipitation of 2.3 g. of product, m.p. 116-118°; ir μ 5.8 (*N*-$OCOCH_3$), 5.7-5.8 (broad, CONCO); nmr (DMSO-d_6): δ 2.28 (s, 3), 4.53 (s, 2), 7.42-7.85 (m, 4).

Anal. Calcd. for $C_{11}H_9ClN_2O_4$: C, 49.18; H, 3.38; N, 10.43. Found: C, 49.33; H, 3.46; N, 10.17.

5-(*p*-Chlorophenyl)-3-hydroxyhydantoic Acid, Acetate (**22a**).

To 200 ml. of acetic anhydride warmed on a steam bath was added 20.0 g. of 5-(*p*-chlorophenyl)-3-hydroxyhydantoic acid (**26**) in several portions. The mixture was hand agitated to dissolve the solid, and the resulting solution was heated an additional 5 minutes. After the excess acetic anhydride was evaporated *in vacuo*, ether was added to the residue, and the mixture was chilled at 4°. Filtra-

tion of the mixture afforded 8.66 g. of crude product which was purified by recrystallization from ethanol to give 6.29 g. of **22a**, m.p. 150-152° dec.; ir μ 2.99 (amide NH), 3.36 (broad, acid OH), 5.54 (*N*-acetoxy CO), 5.81 (carboxyl), 6.01 (amide CO), 6.24 (aromatic), 6.48 (amide II), 6.71 (aromatic); nmr (DMSO-d_6): δ 2.22 (s, 3), 4.35 (s, 2), 7.55 (q, 4, J = 9 Hz, δ_{AB} = .26 ppm), 9.32 (s, 1).

Anal. Calcd. for $C_{11}H_{11}ClN_2O_3$: C, 46.06; H, 3.86; N, 9.77; Cl, 12.37. Found: C, 46.35; H, 3.63; N, 9.84; Cl, 12.2.

Preparation of *p*-Chlorophenylurea (**24**).

A. From Compound **21**.

A sample of 0.5 g. of **21** was added to an excess dilute sodium hydroxide solution with stirring. An exothermic reaction took place during which time the compound dissolved, followed by the appearance of a precipitate. The reaction mixture was heated to boiling, cooled, and filtered to afford product **24**, m.p. 204-206°.

B.

To a solution of *p*-chloroaniline in excess dilute hydrochloric acid was added a solution of potassium isocyanate. The resultant product, a white solid with m.p. 204-206°, was the same as that prepared by method A from compound **21**.

3-(*p*-Chlorophenyl)-1-hydroxyhydantoin (**25**).

A slurry of 5.00 g. (20.4 mmoles) of 5-(*p*-chlorophenyl)-3-hydroxyhydantoic acid in 100 ml. of 6 *N* hydrochloric acid was heated with stirring in an oil bath at 150°. After 25 minutes, product in the form of needles separated in the presence of a small amount of undissolved starting material. Heating was continued for an additional 5 minutes and the mixture was allowed to cool gradually to room temperature. Filtration of the colorless needles afforded 2.5 g. of product, m.p. 168-170°. Recrystallization from acetonitrile afforded 1.46 g. of **25**, m.p. 167-169°; ir μ 3.30 (OH), 5.65 and 5.85 (CONCO); nmr (DMSO-d_6): δ 4.31 (s, 2), 7.25-7.85 (m, 4).

Anal. Calcd. for $C_9H_7ClN_2O_3$: C, 47.70; H, 3.11; N, 12.36; Cl, 15.64. Found: C, 47.33; H, 3.27; N, 12.21; Cl, 15.8.

5-(*p*-Chlorophenyl)-3-hydroxyhydantoic Acid (**26**).

Procedure A. From Rearrangement of **19**.

A slurry of **10** g. (31.2 mmoles) of 2-[carboxy(hydroxy)amino]-4'-chloroacetanilide, phenyl ester in 100 ml. of ethanol was treated with 40 ml. of 4 *N* sodium hydroxide. The mixture was warmed on a steam bath until a clear, yellow solution was obtained and then chilled and diluted with 50 ml. of water. Acidification with 80 ml. of 6 *N* hydrochloric acid followed by further dilution and cooling afforded 5.6 g. of precipitate (m.p. 158-160°). Recrystallization from 125 ml. of 1:3 ethanol-water gave 4.3 g. (57% yield) of **26**, m.p. 160-162°; nmr (DMSO-d_6): δ 4.30 (s, 2), 7.45 (d, 2 J = 9 Hz), 7.92 (d, 2 J = 9 Hz).

Procedure B.

A slurry of *N*-hydroxyaminoacetic acid (13.67 g., 0.141 mole) in 40 ml. of dry 1,2-dimethoxyethane was stirred and treated gradually with a solution of 23.1 g. (0.171 mole) of *p*-chlorophenylisocyanate **27** in 20 ml. of dry 1,2-dimethoxyethane. After the exothermic reaction ceased, the mixture was stirred at 28° for 1.5 hours. Filtration of crystalline material gave 24.37 g. (71%) of 5-(*p*-chlorophenyl)-3-hydroxyhydantoic acid **26**, m.p. 156-157°. The material was identical with that prepared by Procedure A.

3-(*p*-Chlorophenyl)-5-diethylaminohydantoin (**29**).

To a slurry of 1.0 g. (3.7 mmoles) of 3-(*p*-chlorophenyl)-1-hydroxyhydantoin acetate (**21**) in 10 ml. of ethanol was added 2 ml. of diethylamine. After the heat of reaction subsided the solution was diluted with an equal volume of water and chilled. The crystalline solid was filtered and washed successively with water and acetonitrile to give 1.0 g. of **29**, m.p. 156-158°; ir μ 3.11 (NH), 5.66 and 5.80 (CONCO); nmr (deuteriochloroform): δ 1.1 (t, 6, J = 7 Hz), 2.75 (q, 4, J = 7 Hz), 5.02 (s, 1), 7.15 (s, 1), and 7.2-7.7 (m, 4).

Anal. Calcd. for $C_{13}H_{16}ClN_3O_2$: C, 55.43; H, 5.72; Cl, 12.59; N, 14.92. Found: C, 55.49; H, 5.76; Cl, 12.60; N, 14.67.

3-(*p*-Chlorophenyl)-5-(5-chloro-2-sulfamylanilino)hydantoin (**30**).

To a mixture of 2.0 g. of 3-(*p*-chlorophenyl)-1-hydroxyhydantoin, acetate (**21**), 2.0 g. of 2-amino-4-chlorobenzenesulfonamide and ethanol was added with stirring a solution of 1 ml. of triethylamine in ethanol. The slightly exothermic reaction was allowed to stand for 10 minutes and concentrated to dryness *in vacuo*. The residue was dissolved in ether, washed with water, concentrated to dryness, and recrystallized from benzene yielding 1.3 g. of impure product. Recrystallization from acetonitrile gave **30**, m.p. 240-243°; ir μ 3.11 broad (NH's), 5.61 and 5.83 (CONCO), 7.55 and 8.75 (SO_2).

Anal. Calcd. for $C_{15}H_{12}Cl_2N_4O_4S$: C, 43.38; H, 2.91; N, 13.49; Cl, 17.08; S, 7.72. Found: C, 43.68; H, 2.99; N, 13.59; Cl, 16.9; S, 7.2.

5-(*p*-Chlorophenyl)-3-hydroxyhydantoic Acid, Hydrazide (**32**).

To a suspension of 4 g. (14.9 mmoles) of 3-(*p*-chlorophenyl)-1-hydroxyhydantoin acetate (**21**) in 75 ml. of ethanol was added dropwise a solution of 8 ml. of hydrazine hydrate in 20 ml. of ethanol. After the mixture was stirred at room temperature for one hour it was diluted with 300 ml. of water and chilled in an ice bath. Filtration of the precipitate afforded 2.8 g. (75%) of **32**, m.p. 153-155°; ir (potassium bromide): μ 3.06 (NH), 3.65 broad (OH), 6.01 (amide CO), 6.60 (amide II); nmr (DMSO-d_6): δ 4.09 (s, 2, exchanges in deuterium oxide), 4.26 (broad s, 2), 7.48 (q, 4, J = 9, δ_{AB} = .41 ppm), 9.08 (m, 2), and 9.88 (s, 1).

Anal. Calcd. for $C_9H_{11}ClN_4O_3$: C, 41.78; H, 4.29. Found: C, 41.86; H, 4.26.

5-(*p*-Chlorophenyl)-*N*-[3-(dimethylaminopropyl]-3-hydroxyhydantamide (**33**).

To a solution of 5 ml. of 3-dimethylaminopropylamine and 40 ml. of ethanol was added 2.0 g. of 3-(*p*-chlorophenyl)-1-hydroxyhydantoin, acetate (**21**). The slightly exothermic reaction was allowed to stand for 10 minutes and the solvent was removed *in vacuo*. The solid was recrystallized from benzene and then acetonitrile yielding 1.0 g. of product, m.p. 133-135°; ir μ 3.06 (amide NH), 4.12 broad (N-OH), 5.96 and 6.06 (amide CO), 6.58 broad (amide II).

Anal. Calcd. for $C_{14}H_{21}ClN_4O_3$: C, 51.15; H, 6.44; N, 17.04. Cl, 10.78. Found: C, 51.39; H, 6.25; N, 16.86; Cl, 10.80.

5-(*p*-Chlorophenyl)-3-hydroxyhydantoic Acid Amide (**31**).

A mixture of 1.0 g. of 3-(*p*-chlorophenyl)-1-hydroxyhydantoin, acetate (**21**), alcohol and ammonium hydroxide was warmed for several minutes, diluted with water and concentrated to a small volume. The resultant precipitate was collected and recrystallized from acetonitrile giving **31**, m.p. 161-163°; ir μ 3.00 and 3.13 (NH), 3.55 (OH and CH_2), 6.01 and 6.14 (amide CO), 6.52 (amide II).

Anal. Calcd. for $C_9H_{10}ClN_3O_3$: C, 44.37; H, 4.15; N, 17.25; Cl, 14.35. Found: C, 44.68; H, 4.04; N, 17.04; Cl, 14.82.

NOTES AND REFERENCES

(1) Presented in part at the Deuxieme Congress International De Chemie Heterocyclique July 7-11, 1969, Montpellier France,

(2) S. C. Bell, R. J. McCaully, and S. J. Childress, *Tetrahedron Letters*, 2889 (1965).

(3) S. C. Bell, R. J. McCaully, and S. J. Childress, *J. Org. Chem.*, 33, 216 (1968).

(4) S. C. Bell, *ibid.*, 33, 828 (1968).

(5) T. S. Sulkowski and S. J. Childress, *ibid.*, 27, 4424 (1962).

(6) Doht, *Monatsh. Chem.*, 27, 216 [B. Prager, P. Jacobson, P. Schmidt and D. Stern, "Beilsteins Handbuch der Organischem Chemie 4th Ed., Vol. 12, Julius Springer, Berlin, 1929, p. 615.]

(7) E. Ware, *Chem. Rev.*, 46, 403 (1950).

(8) Melting points were determined in a capillary tube using a Thomas-Hoover melting point apparatus and are uncorrected. Ir spectra were obtained in potassium bromide discs using a Perkin-Elmer spectrophotometer Model 21. Nmr spectra were determined with a Varian Model A-60 spectrometer using TMS as the internal reference. Combustion elemental analyses were carried out by the Analytical Section of these laboratories on a Perkin-Elmer Model 240 elemental analyzer. The analyses and spectra were obtained under the supervision of Mr. Bruce Hofmann whose assistance was greatly appreciated.