Reactions of 3,4-Disubstituted 4-Oxazolin-2-ones. III.[1] The Reaction of 3,4-Diphenyl-4-oxazolin-2-one with Organic Nitrites

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Received February 19, 1968

The reaction of 3,4-diphenyl-4-oxazolin-2-one (**4**) with benzyl, *n*-butyl, or *n*-amyl nitrite under acidic conditions leads to 4-alkoxy-3,4-diphenyl-5-oximinooxazolidin-2-ones (**6a**, **6b**, and **6c**, respectively), *via* addition of the nitrite ester to the double bond and rearrangement of the unstable intermediate 5-nitroso-2-oxazolidinone **5**. Compound **6a** was chosen for further chemical investigation; it rearranged in the presence of bases to 5-benzyloxy-4,5-diphenyl-3-hydroxyhydantoin (**8**), which was converted into 4,5-diphenyl-5-hydroxyhydantoin (**10**). The latter compound was independently synthesized through a novel route.

Previous work[1] from this laboratory has dealt with some unusual reactions of 3,4-disubstituted 4-oxazolin-2-ones (such as **1**), whose unexpected reactivity has been correlated with the lack of a substituent at position 5. In the course of our study, we investigated the reaction of 3,4-diphenyl-4-oxazolin-2-one (**4**, Scheme I) with alkyl nitrites under acidic conditions. By analogy with the behavior of compound **4** toward bromine,[1a] and of other heterocycles, *e.g.*, pyrazolin-5-ones, toward bromine or alkyl nitrites,[3] a substitution with formation of the 5-nitroso derivative **2** was anticipated. However, the analytical data for the products of the reactions between **4** and benzyl, *n*-butyl, or *n*-amyl nitrite (50–75% yield) indicated that *addition* of the reagents to the oxazolone had taken place. Structures **3** or **5**, which could be expected from these additions, were not in agreement with the ir spectra, which showed absorption in the 3-μ region (hydroxyl), and two strong bands in the 5.5–5.8-μ region (C=O and possibly C=N). These data rather pointed to the oximino structures **6a**, **b**, and **c**, which are tautomeric with those of type **5**. No evidence was found for the presence of even small amounts of the latter forms, which certainly are intermediates of the reaction.

Compound **6a** (R = benzyl) was selected for further chemical investigation, in view of the greater reactivity and ease of characterization shown by benzyl derivatives. Acetylation and benzoylation of **6a** gave the acetate and benzoate **7a** and **b**, respectively, thus providing further evidence for the presence of the oximino group. Treatment of **6a** with bases (KOH in ethanol, pyridine, etc.) produced an alkali-soluble compound, which gave a positive ferric chloride test for hydroxamic acid, and showed in its ir spectrum the typical hydantoin carbonyl absorption[4] (λ_{CO} 5.58, 5.72 μ). These data, and the reported similar case of the facile isomerization of phthaloxime to N-hydroxyphthalimide,[5] led us to formulate this compound as 5-benzyloxy-1,5-diphenyl-3-hydroxyhydantoin (**8**, Scheme II). Further structural proofs were obtained as follows. Attempts to remove the 3-hydroxy group by reduction with zinc in acetic acid, according to a procedure which has proven useful in a similar case,[6] gave, besides the expected benzyloxyhydantoin **9**, benzyl acetate and a product clearly originating from debenzylation of **9**, which was identified as 1,5-diphenyl-5-hydroxyhydantoin (**10**). The latter compound could also be obtained on treatment of **9** with zinc chloride in acetic acid. 1,5-Diphenyl-5-hydroxyhydantoin has been prepared[7,8] by chromic acid oxidation of 1,5-diphenylhydantoin. However, for an independent preparation of compound **10** the procedure outlined in the sequence **14** → **17** was preferred. Treatment of 2-aminoacetophenone hydrochloride (**14**) with phenyl isocyanate (**15**) according to an usual procedure for the preparation of imidazolones,[9] gave 3,4-diphenyl-4-imidazolin-2-one (**16**). Treatment of **16** with bromine in acetic acid in the presence of sodium acetate gave 5-acetoxy-1,5-diphenylhydantoin[10] (**17**), whose deacetylation afforded a product which was identical with **10**. On the other hand, **17** could be obtained on treatment of **10** with acetic anhydride.

Debenzylation of **8** with zinc chloride in acetic acid gave the desired 3,5-dihydroxyhydantoin **11** (λ_{OH} 3.0; λ_{CO} 5.62, 5.85 μ) in good yield. However, attempts to reduce **11** to **10** with zinc in acetic acid constantly gave a different compound, also obtained in minute yield as a by-product in the reduction of **8** with the same reagent. The compound could also be obtained in good yield on treatment of **10** with zinc in acetic acid and *was reconverted into* **10** *by chromic acid oxidation*. These data, together with analytical and spectral evidence, led us to formulate the compound as N-mandelyl-N′-phenylurea (**12**). Indeed, elemental analysis indicated the formula $C_{15}H_{14}N_2O_3$, the ir spectrum showed bands at 2.97, 3.05 μ (OH and/or NH) and a strong carbonyl band at 5.85 μ, and the nmr spectrum showed, besides the aromatic protons, three broad signals at δ 10.3, 9.2, and 4.25 (1 H each), attributable to different types of active hydrogen, and a singlet at 5.16 (1 H, benzyl proton).

It may be assumed that small amounts of the open-chain tautomers **18** exist at equilibrium in solutions of **10**

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[1] For parts I and II of the series, *cf.* (a) M. F. Saettone, *J. Org. Chem.*, **31**, 1959 (1966); (b) M. F. Saettone and A. Marsili, *Tetrahedron Lett.*, 6009 (1966).

[2] Taken in part from the doctoral thesis of E. Bucci.

[3] See, *e.g.*, "The Chemistry of Heterocyclic Compounds," Vol. 20, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1964, pp 81, 85.

[4] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p 221.

[5] L. A. Carpino, *J. Amer. Chem. Soc.*, **79**, 98 (1957).

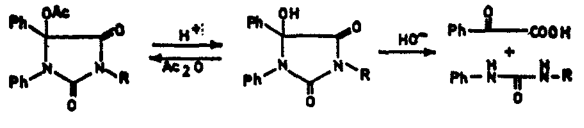
[6] J. A. Moore and J. Binkert, *ibid.*, **81**, 6038 (1959).

[7] H. Aspelund, *Acta Acad. Aboensis, Math. Phys.*, **23**, 11 (1962).

[8] G. A. Holmberg, *Acta Chem. Scand.*, **4**, 821 (1950).

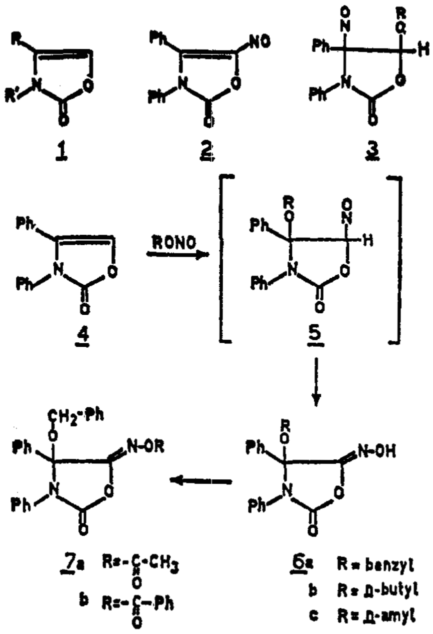
[9] See, *e.g.*, P. Fritsch, *Ber.*, **26**, 427 (1893).

[10] This synthesis is the outcome of independent work on the bromination of 5-unsubstituted 4-imidazolin-2-ones, which will be published at a later date. The structure of compounds of type **17** was proven through the following sequence.

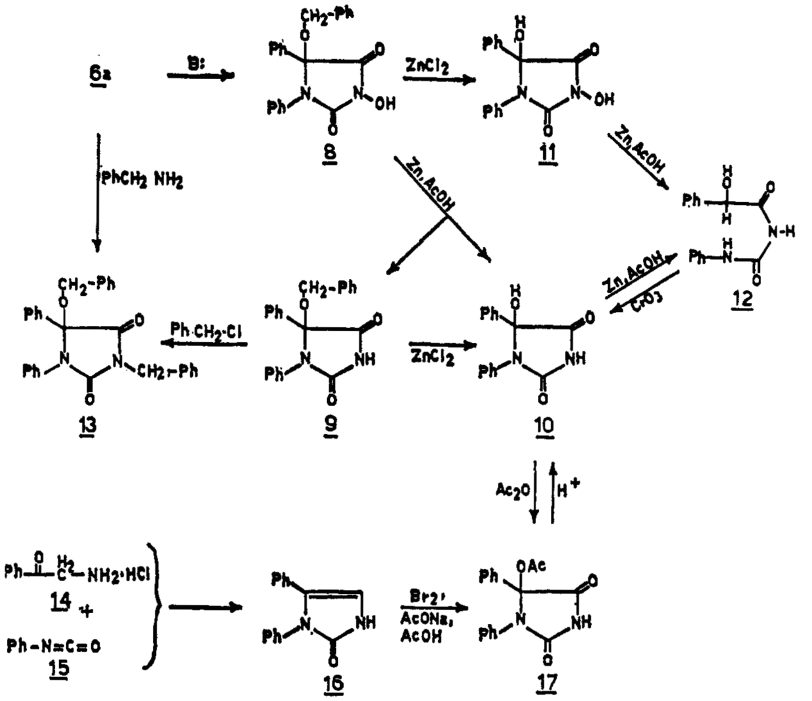


For an analogous reaction, *cf.* H. Greenberg, T. Van Es, and O. G. Backeberg, *J. Org. Chem.*, **31**, 3951 (1966).

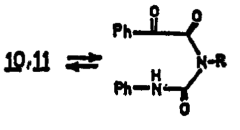
SCHEME I



SCHEME II



and **11**, so that reduction of the phenylglyoxylyl derivative **18** may occur to give the mandelyl derivative **12**. On the other hand, oxydation of **12** would reconvert the product into **18** (R = H), and hence into **10**. These data are in agreement with the known facile interconversion of mandelic and phenylglyoxylic acid.[11]



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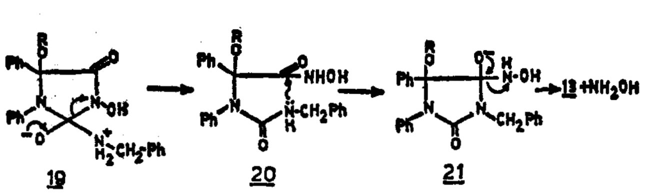
A further transformation of **6a** follows. Treatment of the compound with benzylamine in the absence of solvent gave 3-benzyl-5-benzyloxy-1,5-diphenylhydantoin (**13**). The structure of **13** was proved through its preparation from the sodium salt of **9** and benzyl chloride. Since a treatment of **6a** with benzylamine in benzene solution had given the benzylamine salt of **8**, the formation of **13** should involve rearrangement of **6a** to **8** and further interaction of benzylamine with the latter. The reaction probably involves attack by the amine on one of the carbonyl groups of **8** to yield **13** through the intermediates **19**, **20**, and **21** (or the analogous ones deriving from attack on the 4-oxo group).



The interest of the presently reported reaction of **4** with organic nitrites lies mainly in the fact that the products result, at least formally, from an *addition* of the reagent to the substrate, rather than from the usual substitution. To our knowledge, similar cases of addition of organic nitrites to double bonds have not yet been reported. Three factors appear to play an important role in this reaction: (1) the particular enamide enol ester structure of compound **4** (no similar addition takes place when compounds possessing normal olefinic double bonds are used as substrates); (2) lack of substituents at the 5 position of the oxazolinone (5-substituted oxazolinones, *e.g.*, 3,4-diphenyl-5-methyl-4-oxazolin-2-one, where transformation of a nitroso derivative of type **5** into the tautomeric oximino derivative **6** is impossible, *do not* undergo nitrite addition); (3) presence of hydrogen chloride (compound **4** is recovered unchanged when the reaction is carried out in the absence of acid). However, the data gathered so far do not allow formulation of a definite mechanism for the reaction under discussion. The role of hydrogen chloride could be tentatively explained in terms of an activation, through protonation, of the organic nitrite. Clearly, a two-stage ionic mechanism should be rejected because it cannot be seen why a carbonium ion, formed by interaction of NO^+ with the substrate, should react only with the alcohol and not with the chloride ion. Furthermore, if free alcohol were formed, it should, at least in the case of the reaction with benzyl nitrite, be very rapidly transformed into alkyl chloride. An alternative mechanism, involving addition of nitrosyl chloride (formed by interaction of the organic nitrite with hydrogen chloride[12]) to **4**, and reaction of the intermediate chloro oxime with the alcohol seems even less likely. Indeed, such a chloro oxime, once formed, should be rather stable in the presence of a high concentration of chloride ions. Anyway, no chlorinated products were isolated from the reactions. We resist the temptation of proposing any definite representation of the transition state of the reaction; however, we think that a four-center mechanism, basically similar to that proposed by

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(11) See, *e.g.*, L. Claisen, *Ber.*, **10**, 844 (1877); R. Meyer and A. Baur, *ibid.*, **13**, 1495 (1880).

(12) L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 324 (1951).

Meinwald, *et al.*,[13] for the addition of nitrosyl chloride to norbornene, might be operative in the present case.

Further work on this and related reactions is underway in order to clarify their mechanism.

Experimental Section[14]

Reactions of 3,4-Diphenyl-4-oxazolin-2-one with Nitrites. A. Reaction with Benzyl Nitrite.—A solution of **4**[1a] (15.0 g) in anhydrous tetrahydrofurane (15 ml) was saturated with dry hydrogen chloride, while cooling at 0–5°. To the stirred and cooled solution, freshly prepared benzyl nitrite[15] (9.0 g) was added dropwise. Each addition caused the solution to assume a dark-red color, which disappeared on stirring. Evaporation of the solvent under reduced pressure gave an oily residue, which solidified on trituration with petroleum ether. Recrystallization of the crude product (14.2 g) from benzene–petroleum ether gave pure 4-benzyloxy-3,4-diphenyl-5-oximinooxazolidin-2-one (**6a**): mp 205–208° dec; ir, $\lambda_{\max}$ 3.0, 5.50, 5.80, 6.90, 7.35, 8.90, 9.80, 10.0, 11.28, 12.35, and 14.0 μ.

Anal. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.77; H, 4.96; N, 7.44.

B. Reaction with *n*-Butyl Nitrite.—The reaction was carried out as indicated under A, using freshly prepared *n*-butyl nitrite.[16] The crude 4-*n*-butyloxy-3,4-diphenyl-5-oximinooxazolidin-2-one (**6b**, 76% yield) melted at 178–181° dec after recrystallization from benzene–petroleum ether: ir, λ_{OH} 3.0, λ_{CO} 5.51, 5.83 μ.

Anal. Calcd for $C_{19}H_{20}N_2O_4$: C, 67.04; H, 5.92; N, 8.23. Found: C, 66.81; H, 5.95; N, 8.38.

C. Reaction with *n*-Amyl Nitrite.—This reaction was also carried out as described under A, using freshly prepared *n*-amyl nitrite,[16] to give 4-*n*-amyloxy-3,4-diphenyl-5-oximinooxazolidin-2-one (**6c**, 49% yield): mp 151–153° from benzene–petroleum ether; ir, λ_{OH} 2.98, λ_{CO} 5.50, 5.82 μ.

Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.64; H, 6.32; N, 7.96.

Acetylation and Benzoylation of 6a.—Treatment of **6a** with acetic anhydride in pyridine at 100° for 6 hr gave, after the usual work-up, the acetyl derivative **7a** in 89% yield: mp 139–141° after crystallization from benzene–petroleum ether; ir, λ_{CO} 5.50, 5.59 (sh), 5.90 μ.

Anal. Calcd for $C_{24}H_{20}N_2O_5$: C, 69.22; H, 4.84; N, 6.73. Found: C, 68.97; H, 4.92; N, 6.91.

The benzoylation of **6a** was carried out as follows. To a solution of **6a** (0.5 g) in anhydrous pyridine (5.0 ml) was added 0.3 g benzoyl chloride. The mixture was heated at 100° for 4.5 hr, then was poured into water (50 ml). The solid which separated was collected, washed with 10% HCl, and extracted with ether. The ethereal solution was washed with 10% Na_2CO_3 and water, dried ($MgSO_4$), and evaporated to yield the benzoyl derivative **7b** (0.52 g): mp 131–133° from benzene–petroleum ether; ir, λ_{CO} 5.50, 5.69, 5.95 μ.

Anal. Calcd for $C_{29}H_{22}N_2O_5$: C, 72.79; H, 4.63; N, 5.86. Found: C, 72.80; H, 4.83; N, 5.83.

5-Benzyloxy-1,5-diphenyl-3-hydroxyhydantoin (8).—A solution of **6a** (0.5 g) in ethanolic 2% KOH (37.5 g) was refluxed 30 min, then diluted with water, and acidified with dilute HCl. The precipitate was collected, dried (0.49 g), and crystallized from benzene–petroleum ether to afford pure **8**: mp 166–168°; ir, $\lambda_{\max}$ 3.10, 5.58, 5.75, 6.89, 7.40, 8.55, 9.50, 13.35, 14.15 μ.

Anal. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.71; H, 5.01; N, 7.25.

An ethanolic solution of **8** turned red on addition of a few drops of $FeCl_3$ solution (hydroxamic acid).[17]

Treatment of **6a** at reflux temperature with tertiary aromatic or aliphatic amines (pyridine, triethylamine, etc) produced **8** in lesser (50–70%) yield.

Reaction of 8 with Zinc in Acetic Acid.—To a solution of **8** (1.5 g) in glacial acetic acid (25 ml) was added 1.5 g of finely powdered zinc. The mixture was refluxed 3 hr, then the excess zinc was filtered off, and the filtrate was evaporated at reduced pressure. The oily residue (A) was washed several times with water, and solidified on trituration. Crystallization of this material from ethanol afforded 0.46 g of **5-benzyloxy-1,5-diphenylhydantoin** (**9**): mp 176–178° after crystallization from benzene–petroleum ether; ir, λ_{NH} 3.15, 3.28, λ_{CO} 5.61, 5.85 μ.

Anal. Calcd for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82. Found: C, 73.98; H, 5.16; N, 7.56.

Extraction with ether of the aqueous washings of the residue (A), followed by evaporation of the dried ($MgSO_4$) ethereal extract, afforded 90 mg of a compound, mp 146–148°, identified as **N-mandelyl-N′-phenylurea** (**12**, see below).

The mother liquors from **9** were diluted with water and extracted with ether. Evaporation of the dried ($MgSO_4$) ethereal extract gave an oily residue (B), which solidified on washing and trituration with petroleum ether to afford **1,5-diphenyl-5-hydroxyhydantoin** (**10**, 0.34 g): mp 185–187° (lit.[7,8] mp 182–183°) after crystallization from benzene; ir, λ_{OH} 3.0, λ_{CO} 5.62, 5.85 μ.

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.15; H, 4.51; N, 10.44. Found: C, 66.96; H, 4.54; N, 10.35.

Evaporation of the petroleum ether washings of the residue (B) gave a small amount of an oil which was identified as **benzyl acetate** by comparison with an authentic sample.

Reaction of 9 with Zinc Chloride.—A solution of **9** (0.2 g) in glacial acetic acid (12 ml) containing 0.2 g of recently fused zinc chloride was refluxed 2.5 hr and then was poured into water (200 ml). The mixture was extracted with ether; the ethereal extract was washed with 10% Na_2CO_3 and water, dried ($MgSO_4$), and evaporated to yield an oil which solidified on treatment with petroleum ether. The solid (0.12 g) was identified as **10**. Evaporation of the petroleum ether washings from **10** gave benzyl acetate.

Structure Proof of 10. A. 3,4-Diphenyl-4-imidazolin-2-one (16).—A mixture of 2-aminoacetophenone hydrochloride[18] (6.0 g), phenyl isocyanate (4.4 g), and anhydrous pyridine (15 ml) was heated 3 hr at 120°. A solid began to separate from the hot mixture after 1–2 hr. This was collected and crystallized from chloroform, then from ethanol, to afford 5.0 g of pure **3,4-diphenyl-4-imidazolin-2-one** (**16**): mp 241–244°; ir, λ_{NH} 3.15, 3.30 (sh), λ_{CO} 5.95 μ.

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.26; H, 5.31; N, 11.98.

B. 5-Acetoxy-1,5-diphenylhydantoin (17).—To a solution of **16** (1.5 g) and freshly fused sodium acetate (1.5 g) in glacial acetic acid (30 ml) was slowly added, at room temperature, a 0.4 *M* solution of bromine in glacial acetic acid (32.5 ml). The mixture was then poured into cold water (500 ml), and the product which separated was collected, dried (0.9 g), and crystallized from ethanol–benzene to afford pure **17**: mp 196–198°; ir, λ_{NH} 3.18, 3.29, λ_{CO} 5.59, 5.70 (sh), 5.80 μ.

Anal. Calcd for $C_{17}H_{14}N_2O_4$: C, 65.80; H, 4.55; N, 9.03. Found: C, 66.01; H, 4.65; N, 8.96.

C. Conversion of 17 into 10, and Vice Versa.—Compound **17** (0.1 g) was added, with stirring, to cold concentrated H_2SO_4 (5 ml). The solution, which had an intense red color, was then poured onto cracked ice. The white solid which separated was collected, washed with water, dried (83 mg), and identified as **10**.

A solution of **10** (1.0 g) in a mixture of acetic anhydride (10 ml) and pyridine (1.0 ml) was heated 3 hr at 100°. Evaporation of the solvents under reduced pressure gave a solid residue which was crystallized from benzene–ethanol to yield 0.9 g of pure **17**.

Reaction of 8 with Zinc Chloride. 3,5-Dihydroxy-1,5-diphenylhydantoin (11).—A solution of **8** (0.50 g) and freshly fused zinc chloride (0.24 g) in glacial acetic acid (5.0 ml) was refluxed 2.5 hr, then was poured into water (50 ml). The aqueous solution was extracted with ether; the dried ($MgSO_4$) ethereal extract was evaporated to give a residue which solidified on trituration with petroleum ether. Crystallization of this material from benzene gave pure **11** (0.3 g): mp 101–103°; ir, λ_{OH} 3.0; λ_{CO} 5.61, 5.81 μ.

Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.26; N, 9.86. Found: C, 63.22; H, 4.31; N, 9.72.

N-Mandelyl-N′-phenylurea (12). A. From 11.—Powdered zinc (0.5 g) was added to a solution of **11** (0.28 g) in glacial acetic acid (5.0 ml); the mixture was refluxed 15 min and then poured

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(13) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Amer. Chem. Soc.*, **85**, 2513 (1963); **86**, 4074 (1964).

(14) Melting points were determined on a Kofler apparatus, and are not corrected; ir spectra were recorded on Nujol mulls and the nmr spectrum on a deuteriochloroform solution with tetramethylsilane as internal standard. Identity of compounds was verified by mixture melting point and comparison of ir spectra. Petroleum ether refers to the fraction of boiling range 60–80°.

(15) A. Bayer and V. Villiger, *Ber.*, **34**, 755 (1901).

(16) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co. Ltd., London, 1956, p 306.

(17) See ref 16, p 1062.

(18) C. Mannich and F. L. Hahn, *Ber.*, **44**, 1542 (1911).

into water. The solid which separated was collected and crystallized from benzene–petroleum ether to give pure **12** (0.2 g): mp 146–148°; ir, λ_{max} 2.97, 3.05, 5.85, 5.90 (sh), 6.41, 6.75, 8.10, 8.51, 9.39, 13.16 μ; for nmr, see text.

Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.65; H, 5.22; N, 10.37. Found: C, 66.63; H, 5.27; N, 10.54.

B. From **10**.—Treatment of **10** with zinc in acetic acid as described for **11** gave N-mandelyl-N′-phenylurea (**12**) in 75% yield.

Oxidation of 12 to 10.—To a cooled solution of **12** (0.27 g) in acetone (10 ml) was slowly added an 8 *N* solution of CrO_3[19] (2.0 ml). The mixture was heated 5 min at 50°, then was poured into cold water. The solid which separated (0.15 g) was identified as **10**.

3-Benzyl-5-benzyloxy-1,5-diphenylhydantoin (13). A. From 6a.—A solution of **6a** (0.5 g) in benzylamine (10 ml) was heated 6 hr at 175°, then was poured into water (50 ml). The yellow oil which separated was extracted several times with hot petroleum ether. The combined extracts were washed with dilute HCl and water, dried ($MgSO_4$), and evaporated to yield 0.3 g of **13**: mp 121–123° after crystallization from benzene–petroleum ether; ir, λ_{CO} 5.62, 5.81 μ.

Anal. Calcd for $C_{29}H_{24}N_2O_3$: C, 77.66; H, 5.39; N, 6.25. Found: C, 77.51; H, 5.52; N, 6.41.

B. From **9**.—To a solution of **9** (0.1 g) and benzyl chloride (0.1 g) in 95% ethanol (7.0 ml) was added a 0.11 *N* solution of KOH in ethanol (2.7 ml). The mixture was refluxed 2 hr; then it was diluted with water and extracted with ether. The dried ($MgSO_4$) ethereal extract was evaporated to give a residue which solidified on trituration with ethanol. This product (80 mg) was crystallized from benzene–petroleum ether to give pure **13**.

Registry No.—**6a,** 16710-18-2; **6b,** 16710-19-3; **6c,** 16710-20-6; **7a,** 16710-21-7; **7b,** 16710-22-8; **8,** 16710-23-9; **9,** 16710-24-0; **10,** 15903-38-5; **11,** 16710-26-2; **12,** 16710-27-3; **13,** 16709-72-1; **16,** 16709-73-2; **17,** 16709-74-3.

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[19] C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

Synthesis and Reactions of "Anhydrochloralurethans"

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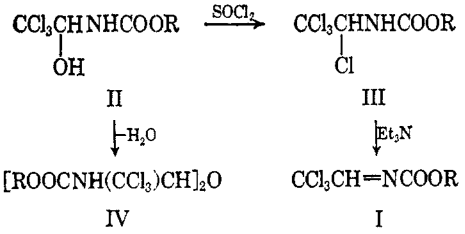
Received February 13, 1968

The previously unreported anhydrochloralurethans (I) are obtained by dehydrochlorination of alkyl 1,2,2,2-tetrachloroethylcarbamates (III). Reaction of I with water, alcohols, and amines affords chloral O,N- and N,N-acetals. The latter compounds are also produced in the reaction of chloralurethans (II) with alkyl and aryl isocyanates. Treatment of II and III with carbonyl chloride in the presence of N,N-dimethylformamide as the catalyst gives rise to the formation of 1,2,2,2-tetrachloroethyl isocyanate (XI), which undergoes the Michalis–Arbuzov reaction with triethyl phosphite to afford diethyl 1-isocyanato-2,2,2-trichloroethylphosphonate (XII).

The synthesis of "anhydrochloralurethans" (I) was reported in 1891 by Moscheles.[1] However, Feist[2] had shown later that the compounds, isolated by Moscheles, had structure IV rather than I. In view of the anticipated reactivity of the imines I with regard to addition to the activated double bond, we attempted their synthesis from chloralurethans (II).[3] Since dehydration led to the formation of IV,[1,2] most likely *via* addition of unreacted II to the generated I, we selected a dehydrochlorination procedure.

Heating of chloralurethans (II) with thionyl chloride affords alkyl 1,2,2,2-tetrachloroethylcarbamates (III) in high yield (Scheme I). The dehydrochlorination of III in benzene, using triethylamine as the hydrogen chloride acceptor, proceeds at room temperature, and the previously unreported "anhydrochloralurethans" I are thus obtained in 40–50% yield of distilled product.

SCHEME I



$$\underset{\text{II}}{\underset{\text{OH}}{CCl_3CHNHCOOR}} \xrightarrow{SOCl_2} \underset{\text{III}}{\underset{\text{Cl}}{CCl_3CHNHCOOR}}$$

$$\text{II} \xrightarrow{-H_2O} \underset{\text{IV}}{[ROOCNH(CCl_3)CH]_2O} \qquad \text{III} \xrightarrow{Et_3N} \underset{\text{I}}{CCl_3CH{=}NCOOR}$$

The imines I are colorless liquids which darken on standing. Their structure was verified by elementary analysis, infrared ($\nu_{C=O}$ 1745 cm^{-1}, $\nu_{C=N}$ 1669 cm^{-1}) and nmr spectroscopy. For example, I ($R = C_2H_5$) shows the following signals (50% CCl_4, relative to TMS): singlet at 8.2 ppm, quartet at 4.3 ppm, and triplet at 1.38 ppm, with a relative intensity ratio of 1:2:3.

Likewise, ethyl 1-chloro-2,2,2-tribromoethylcarbamates obtained from ethyl 1-hydroxy-2,2,2-tribromoethylcarbamate[3] and thionyl chloride can be dehydrochlorinated to C-tribromomethyl-N-carboethoxyazomethine (V), as evidenced by infrared and nmr spectroscopy. However, the imine V is heat sensitive, and purification by vacuum distillation is not possible.[4,5]

The reactivity of the C=N double bond in I is evidenced by rapid and exothermic addition of water, alcohols, and amines to yield the corresponding hemiacetals II, O,N-acetals VI, and N,N-acetals VII (Scheme II). However, addition of hydrogen phosphite to afford the 1:1 adduct VIII is quite sluggish and requires the use of a base catalyst. For N-aroyl imines a similar activation of the C=N double bond toward addition of nucleophiles has been observed recently.[6]

The chloro group adjacent to nitrogen in alkyl 1,2,2,2-

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[1] R. Moscheles, *Ber.*, **24**, 1803 (1891).

[2] F. Feist, *ibid.*, **45**, 945 (1912).

[3] C. Bischoff, *ibid.*, **7**, 628 (1874).

[4] After completion of our investigation the *in situ* generation of I ($R = CH_2C_6H_5$) has been described, but purification by vacuum distillation was not possible because of heat sensitivity.[5]

[5] F. Weygand, W. Steglich, I. Lengyel, F. Fraunberger, A. Maierhofer, and W. Oettmeier, *Chem. Ber.*, **99**, 1944 (1966).

[6] S. W. Breuer, T. Bernath, and D. Ben-Ishai, *Tetrahedron Lett.*, 4569 (1966).