presence of substantial amounts of polymeric material. In view of these properties the polysubstituted triptych-boroxazolidines do not appear to be particularly desirable units for attachment to amino acid moieties for the preparation of water-stable compounds.

Experimental[5]

Triethanolamine Derivatives of General Structure III.—The triethanolamine derivatives listed in Table I were prepared by the addition of the appropriate epoxide to a chloroform solution of the appropriate diethanolamine. After the initial exothermic reaction had subsided, the solution was refluxed for several hours and the product then worked up in the usual way and purified by distillation through a short Vigreux column.

Triptych-boroxazolidines of General Structure IV.—The triptych-boroxazolidines listed in Table II were prepared by treating the triethanolamine (III) with an equivalent amount of tri-*n*-butyl borate, distilling the *n*-butyl alcohol, and purifying the residue by recrystallization wherever possible.

Analytical Methods.—Basic nitrogen was determined by titration with 0.1 *N* perchloric acid in glacial acetic acid using Methyl Violet as indicator.[6] For the triptych-boroxazolidines a 0.2–0.3-g. sample was dissolved in 50 ml. of 0.1 *N* perchloric acid in acetic acid, and the solution was heated on the steam bath for 15 min. After cooling to room temperature, the excess perchloric acid was back titrated with 0.1 *N* sodium acetate in glacial acetic acid. Boron content was determined by the method of Thomas.[7]

Acknowledgment.—We are indebted to Mrs. Franziska Schleppnik for carrying out all of the nitrogen and boron analyses as well as many of the chemical preparations reported herein.

[5] All melting points were determined on a Kofler hot stage calibrated against compounds of known melting point. All boiling points are uncorrected.

[6] E. F. Hillebrand and C. A. Pentz in "Organic Analysis," Vol. III, Interscience, Inc., New York, 1956, p. 145.

[7] L. H. Thomas, *J. Chem. Soc.*, 820 (1946).

Reaction of Dichlorocarbene with Imines

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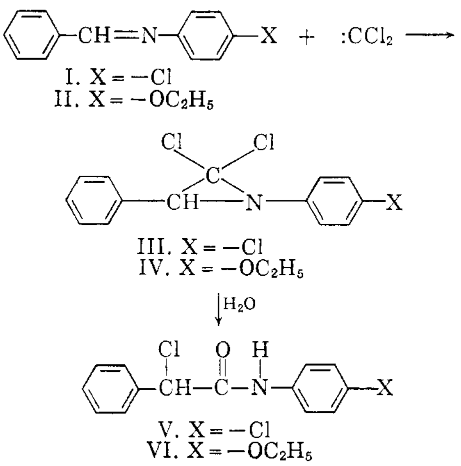
Received March 15, 1962

Addition of dichlorocarbene to the carbon-nitrogen double bond of benzalaniline has been described.[3] This reaction has been extended to other imines and an iminium salt.

The reaction of benzylidene *p*-chloroaniline (I) with dichlorocarbene generated *in situ* from potassium *t*-butoxide and chloroform resulted in a 68% yield of 1-*p*-chlorophenyl-3-phenyl-2,2-dichloroethylenimine (III). Similarly dichlorocarbene was added to benzylidene-*p*-phenetidine (II) to produce 1-*p*-ethoxyphenyl-3-phenyl-2,2-dichloroethylenimine (IV) in 91% yield. The hydrolysis of these products formed the corresponding α-chloro-α-phenylacetanilides (V and VI) in quantitative yields.

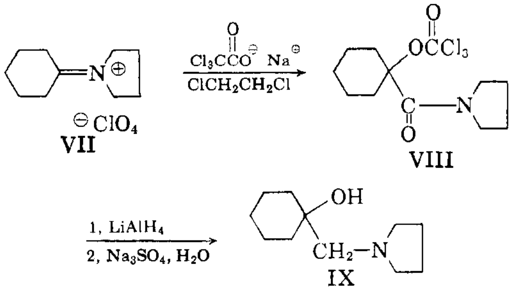


I. $X = -Cl$
II. $X = -OC_2H_5$

III. $X = -Cl$
IV. $X = -OC_2H_5$

V. $X = -Cl$
VI. $X = -OC_2H_5$

Treating an iminium salt, 1-cyclohexenyl-N-pyrrolidinium perchlorate (VII), with dichlorocarbene, generated by refluxing sodium trichloroacetate in ethylene dichloride,[4] resulted in the formation of *N*-(1-trichloroacetoxy-1-carboxycyclohexyl)pyrrolidine (VIII) in 29% yield. From the evolution of hydrogen chloride gas by the reaction mixture and from the composition of the final product, there evidently was residual water present in the sodium trichloroacetate, as the ethylene dichloride and the reaction apparatus were dry. The product was identified by its analysis, molecular weight, and infrared absorption spectrum. The infrared spectrum exhibited maxima at 1755 and 1625 cm.$^{-1}$; the former was due to C=O stretching of the trichloroacetoxy group, and the latter to C=O stretching of a tertiary amide group. Further proof of structure of VIII was given by reduction with lithium aluminum hydride, which resulted in the formation of 1-(N-pyrrolidylmethyl)-1-hydroxycyclohexane (IX). It was rather unexpected to find the trichloroacetoxy group in place of the chlorine atom at the 1-position in VIII. The trichloroacetoxy compound was prob-



VII

VIII

IX

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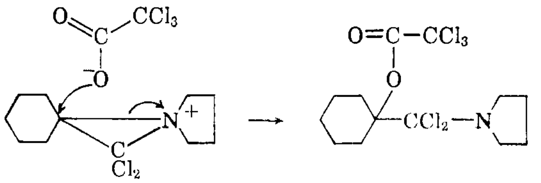
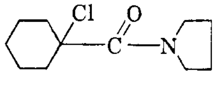
[2] To whom inquiries should be addressed.

[3] E. K. Fields and J. M. Sandri, *Chem. Ind.* (London), 1216 (1959).

[4] W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).



ably formed by attack of trichloroacetate ion on the intermediate imine rather than by displacement of the 1-chlorine atom from the alternative intermediate



The corresponding N-(1-bromo-1-carboxycyclohexyl)pyrrolidine under the same conditions failed to react with sodium trichloroacetate.

Experimental

1-*p*-Chlorophenyl-3-phenyl-2,2-dichloroethylenimine (III).—To a stirred slurry of 21.6 g. (0.1 mole) of benzylidene-*p*-chloroaniline,[5] m.p. 60–61° (reported m.p. 62°), 44.9 g. (0.4 mole) of potassium *t*-butoxide and 250 ml. of hexane were slowly added 47.8 g. (0.4 mole) of chloroform. The reaction mixture was stirred at room temperature for 16 hr. The mixture was filtered with the aid of suction, the residue was washed three times with hexane, and the solvent was removed *in vacuo* from the combined filtrates, leaving a crystalline product. After two recrystallizations from pentane, 20.4 g. (68%) of 1-*p*-chlorophenyl-3-phenyl-2,2-dichloroethylenimine was obtained as light tan crystals, m.p. 71–72°. The band at 1620 cm.$^{-1}$ that was present in the infrared spectrum of the starting material was absent in the product.

Anal. Calcd. for $C_{14}H_{10}Cl_3N$: C, 56.3; H, 3.4; Cl, 35.6; N, 4.7. Found: C, 56.1; H, 3.6; Cl, 35.3; N, 4.7.

α-Chloro-α-phenyl-*p*-chloroacetanilide (V).—In contact with an excess of water at 25° for 24 hr., 1-*p*-chlorophenyl-3-phenyl-2,2-dichloroethylenimine hydrolyzed to α-chloro-α-phenyl-*p*-chloroacetanilide in quantitative yield. The product crystallized from 95% ethanol as colorless needles, m.p. 160–161°.

Anal. Calcd. for $C_{14}H_{11}Cl_2NO$: C, 60.0; H, 4.0; Cl, 25.3; N, 5.0. Found: C, 59.8; H, 4.2; Cl, 24.8; N, 4.7.

1-*p*-Ethoxyphenyl-3-phenyl-2,2-dichloroethylenimine (IV).—To a stirred mixture of 22.5 g. (0.1 mole) of benzylidene-*p*-phenetidine[6] (light yellow plates from 95% ethanol, m.p. 72–74°, reported m.p. 76°), 44.9 g. (0.4 mole) of potassium *t*-butoxide, and 350 ml. of hexane was added 47.8 g. (0.4 mole) of chloroform. The reaction mixture was stirred at room temperature for 18 hr., refluxed, and filtered. The residue was washed with hot hexane and the solvent was removed from the combined filtrates *in vacuo*, leaving 28.2 g. (91%) of crystalline residue. The product, 1-*p*-ethoxyphenyl-3-phenyl-2,2-dichloroethylenimine, crystallized from hexane in the form of colorless plates, m.p. 76.5–77.5°. The band at 1620 cm.$^{-1}$ that was present in the infrared spectrum of the starting material was absent in the product.

Anal. Calcd. for $C_{16}H_{15}Cl_2NO$: C, 62.4; H, 4.9; Cl, 23.0; N, 4.6. Found: C, 62.7; H, 5.1; Cl, 22.6; N, 4.5.

α-Chloro-α-phenyl-*p*-ethoxyacetanilide (VI).—A mixture of 1-*p*-ethoxyphenyl-3-phenyl-2,2-dichloroethylenimine and excess water was boiled for 5 min. After a strong evolution of hydrogen chloride gas a solid product, α-chloro-α-phenyl-*p*-ethoxyacetanilide, was produced in a quantitative yield. The product crystallized from methanol as colorless plates, m.p. 145–146.5°.

Anal. Calcd. for $C_{16}H_{16}NClO_2$: C, 66.3; H, 5.5; Cl, 12.3; N, 4.8. Found: C, 66.4; H, 5.9; Cl, 12.6; N, 4.8.

N-(1-Trichloroacetoxy-1-carboxycyclohexyl)pyrrolidine (VIII).—A stirred solution of 32.6 g. (0.13 mole) of 1-cyclohexenyl-*N*-pyrrolidinium perchlorate,[7,8] 48 g. (0.26 mole) of sodium trichloroacetate (Lachat Biochemical Company), and 300 ml. of dry ethylene dichloride was refluxed for 18 hr. The hot solution was filtered and the solvent was removed *in vacuo*. The residual solid was recrystallized from methanol, and a total of 13.0 g. (29%) of N-(1-trichloroacetoxy-1-carboxycyclohexyl)pyrrolidine, m.p. 165–166°, was obtained as colorless needles. The infrared spectrum (Nujol mull) exhibited maxima at 1755 and 1625 cm.$^{-1}$ and showed a molecular weight of 349: this was determined by calibration with the molar extinction coefficient of ethyl trichloroacetate.

Anal. Calcd. for $C_{13}H_{18}Cl_3NO_3$: C, 45.6; H, 5.3; Cl, 31.0; N, 4.1; mol. wt. 342. Found: C, 45.4; H, 5.2; Cl, 30.9; N, 4.1; mol. wt. 338 (ebullioscopic).

1-(N-Pyrrolidylmethyl)-1-hydroxycyclohexane (IX).—To a slurry of excess lithium aluminum hydride in 100 ml. of ether was added 1.5 g. (0.0045 mole) of N-(1-trichloroacetoxy-1-carboxycyclohexyl)pyrrolidine. The stirred reaction mixture was refluxed for 64 hr. A saturated aqueous solution of sodium sulfate was slowly added, the solution was filtered, and the solvent was removed from the solution. The residual oil was distilled through a good column, giving a colorless liquid, 1-(*n*-pyrrolidylmethyl)-1-hydroxycyclohexane, b.p. 44° (3 mm.), $n^{20}\text{D}$ 1.4881, $\nu^{\text{film}}_{\text{ma}}$ 3450 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{21}NO$: C, 72.1; H, 11.6; N, 7.6. Found: C, 72.3; H, 11.5; N, 7.5.

N-(1-Bromo-1-carboxycyclohexyl)pyrrolidine.—To a stirred mixture of 13.5 g. (0.09 mole) of cyclohexanecarbonyl chloride [b.p. 87° (27 mm.) $n^{24}\text{D}$ 1.4680; from thionyl chloride and cyclohexanecarboxylic acid in 92% yield] and 0.5 g. of red phosphorus at 85° was slowly added during an hour 32 g. of bromine. The reaction mixture was stirred at 85° for 3 days. The excess bromine was removed by dry nitrogen gas, and the residue was distilled to give 8.84 g. (46%) of 1-bromocyclohexanecarbonyl chloride, b.p. 129–131° (29 mm.), $n^{24}\text{D}$ 1.5193.

To a stirred cold solution of 8.8 g. (0.04 mole) of 1-bromocyclohexanecarbonyl chloride in 200 ml. of dry ether was slowly added 6 g. (0.084 mole) of pyrrolidine in 25 ml. of dry ether at −5° and 0°. After the addition was completed the reaction mixture was allowed to warm slowly to room temperature for 1 hr. The solution was filtered and the solvent was removed. The solid residue was washed with water and filtered. A total of 10.4 g. (100%) of N-(1-bromo-1-carboxycyclohexyl)pyrrolidine, colorless plates after sublimation, was obtained, m.p. 81–83°.

Anal. Calcd. for $C_{11}H_{18}BrNO$: C, 50.8; H, 7.0; Br, 30.7; N, 5.4. Found: C, 50.4; H, 7.4; Br, 30.4; N, 5.3.

Equimolar quantities of this bromo compound and sodium trichloroacetate were refluxed in ethylene dichloride for 24 hr. The bromo compound was recovered unchanged.

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(6) C. Philipp, *Ber.*, **25**, 3248 (1892).

(7) A. G. Cook, Ph.D. thesis: Univ. of Illinois, 1959.

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