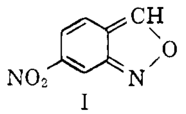
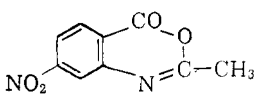
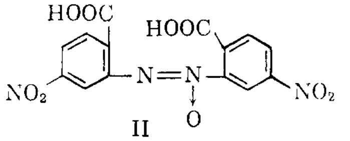


I



III



II

nitroanthranil. A mixed melting point determination with an authentic sample[5] showed no depression.

4-Nitroacetanthranil[6] (III) was obtained by heating I with acetic anhydride, which further confirmed its structure.

### Experimental[7]

2,4-Dinitrophenylacetic acid was obtained by the nitration of phenylacetic acid with fuming nitric acid.[8]

**6-Nitroanthranil** (I).—A solution of 4.0 g. of 2,4-dinitrophenylacetic acid in 30 ml. of concentrated sulfuric acid was heated for 2 hr. at 120–130° in an oil bath. The mixture was poured over crushed ice. A dirty white precipitate so obtained was washed with sodium bicarbonate solution. The residue was purified with activated charcoal and recrystallized from alcohol to give 1.0 g. of colorless solid, m.p. 133°. A mixed melting point with 6-nitroanthranil[5] showed no depression.

*Anal.* Calcd. for $C_7H_4N_2O_3$: C, 51.2; H, 2.4; N, 17.1. Found: C, 50.8; H, 2.5; N, 16.6.

**Hydrazine Salt of 6-Nitroanthranil.**—A solution of 0.25 g. of I in 10 ml. of alcohol and 1.5 ml. of hydrazine hydrate was allowed to reflux for 0.5 hr. On cooling, 0.20 g. of yellow needles separated, m.p. 175° (lit.,[5] m.p. 175°).

*Anal.* Calcd. for $C_7H_8N_4O_3$: N, 28.6. Found: N, 28.3.

**5,5′-Dinitroazoxybenzene-2,2′-dicarboxylic Acid** (II).—A solution of 3 g. of sodium dichromate in 8 ml. of water was added gradually to a boiling solution of 0.5 g. of I in 10 ml. of acetic acid, 6 ml. of water, and 2.5 ml. of concentrated sulfuric acid and the mixture was refluxed for 1 hr. The acid crystallized from the cold solution in lemon yellow cubes, m.p. 295° (lit.,[5] m.p. 285°).

*Anal.* Calcd. for $C_{14}H_8N_4O_9$: neut. equiv., 188. Found: neut. equiv., 190.5.

**2-Amino-4-nitrobenzoic Acid.**—A solution of 1.5 g. of sodium carbonate in 10 ml. of water was added to 0.5 g. of I and refluxed for 0.5 hr. The filtrate on acidification gave orange plates, m.p. 264°. Mixed melting point with an authentic sample[5] of 2-amino-4-nitrobenzoic acid was undepressed.

**4-Nitroacetanthranil** (III).—A solution of 0.5 g. of 6-nitroanthranil, 6 ml. of acetic anhydride, and 0.5 g. of zinc acetate in 2 ml. of glacial acetic acid was refluxed for 4 hr. On cooling, the crystals were separated and on recrystallization from acetic acid yielded pale yellow crystals, m.p. 138°.

*Anal.* Calcd. for $C_9H_6N_2O_4$: C, 52.4; H, 2.9. Found: C, 52.3; H, 2.6.

**Acknowledgment.**—The author's sincere thanks are due to Dr. S. S. Joshi, Research Director, School of Chemistry, Meerut College, Meerut, for his keen interest in the work and to the Ministry of Scientific Research and Cultural Affairs, Government of India, for the award of a research scholarship.

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## Synthesis of Polysubstituted Triptych-boroxazolidines[1,2]

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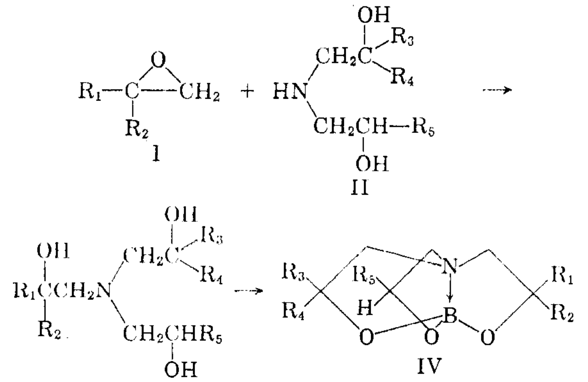
*Received March 12, 1962*

The synthesis of a series of monosubstituted triptych-boroxazolidines has been reported in a previous paper from this laboratory[3] in which the background for the undertaking is discussed. It was pointed out in that paper that Steinberg and Hunter[4] had detected a difference in rate of hydrolysis of *ca.* $10^5$ between triptych-boroxazolidine itself and the much more slowly hydrolyzed *sym*-trimethyltriptych-boroxazolidine. Thus, in the hope of obtaining a water stable triptych-boroxazolidine unit to which an amino acid moiety could be attached, the series of polysubstituted triptych-boroxazolidines reported in this paper was prepared.

The synthetic methods employed were similar to those discussed previously.[3] The appropriately substituted triethanolamine (III) was prepared



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(5) S. S. Joshi and I. R. Gambhir, *J. Am. Chem. Soc.*, **78**, 2222 (1956).

(6) I. R. Gambhir, Ph.D. thesis, University of Agra, 1956.

(7) Melting points are uncorrected.

(8) A. I. Vogal, "A Textbook of Practical Organic Chemistry," Longman Green and Co. Ltd., London, 1956, p. 758.

(1) This work was supported, in part, by Grant No. CY-3275 from the National Institutes of Health.

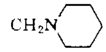
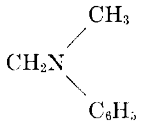
(2) The "triptych-boroxazolidine" nomenclature was proposed by H. K. Zimmerman [*Ann.*, **619**, 28 (1958); *ibid.*, **620**, 4 (1959)] based on an earlier suggestion of H. C. Brown [*J. Am. Chem. Soc.*, **73**, 2808 (1951)]. The Advisory Committee on Nomenclature of Organic Boron Compounds favors the designation of 2,8,9-trioxa-5-aza-1-borabicyclo[3.3.3]undecane (N-B) for the parent unsubstituted compound.

(3) A. A. Schleppnik and C. D. Gutsche, *J. Org. Chem.*, **25**, 1378 (1960).

(4) H. Steinberg and D. L. Hunter, *Ind. Eng. Chem.*, **49**, 174 (1957).

TABLE I

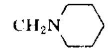
SUBSTITUTED TRIETHANOLAMINES (III)

| $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | Formula | B.p./mm.[a] | Nitrogen content Calcd. | Nitrogen content Found | Formula of triacetate | Nitrogen content Calcd. | Nitrogen content Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH(CH_3)_2$ | H | H | H | H | $C_9H_{21}NO_3$ | 130/0.03 | 7.32 | 7.47 | | | |
| $CH_2OCH_2CH_2CH_3$ | H | H | H | H | $C_{10}H_{23}NO_4$ | 174/0.01 | 6.39 | 6.34 | | | |
| $CH_2OCH(CH_3)_2$ | H | H | H | H | $C_{10}H_{23}NO_4$ | 190/0.04 | 6.39 | 6.57 | | | |
| $CH_3$ | H | $CH_3$ | H | H | $C_8H_{19}NO_3$ | 135/0.4 | 7.90 | 7.89 | $C_{14}H_{25}NO_6$ | 4.62 | 4.55 |
| $C_6H_5$ | H | $CH_3$ | H | H | $C_{13}H_{21}NO_3$ | 180/0.05 | 5.85 | 5.83 | $C_{19}H_{27}NO_6$ | 3.83 | 3.69 |
| $C_2H_5$ | H | $CH_3$ | H | $CH_3$ | $C_{10}H_{23}NO_3$ | 135/0.5 | 6.82 | 7.08 | $C_{16}H_{29}NO_6$ | 4.23 | 3.80 |
| $CH{=}CH_2$ | H | $CH_3$ | H | $CH_3$ | $C_{10}H_{21}NO_3$ | 135/0.05 | 6.89 | 7.02 | $C_{16}H_{27}NO_6$ | 4.25 | 4.25 |
| $CH(CH_3)_2$ | H | $CH_3$ | H | $CH_3$ | $C_{11}H_{25}NO_3$ | 130/0.02 | 6.39 | 6.42 | | | |
| $C_6H_5$ | H | $CH_3$ | H | $CH_3$ | $C_{14}H_{23}NO_3$ | 170/0.03 | 5.53 | 5.63 | $C_{20}H_{29}NO_6$ | 3.69 | 3.50 |
| $CH_2OCH_3$ | H | $CH_3$ | H | $CH_3$ | $C_{10}H_{23}NO_4$ | 175/0.05 | 6.33 | 6.57 | $C_{16}H_{29}NO_7$ | 4.03 | 3.77 |
| $CH_2OC_2H_5$ | H | $CH_3$ | H | $CH_3$ | $C_{11}H_{25}NO_4$ | 170/0.08 | 5.95 | 6.17 | $C_{17}H_{31}NO_7$ | 3.77 | 3.71 |
| $CH_2OCH_2CH_2CH_3$ | H | $CH_3$ | H | $CH_3$ | $C_{12}H_{27}NO_4$ | 140/0.02 | 5.66 | 5.84 | $C_{18}H_{33}NO_7$ | 3.73 | 3.57 |
| $CH_2OCH(CH_3)_2$ | H | $CH_3$ | H | $CH_3$ | $C_{10}H_{23}NO_4$ | 155/0.05 | 5.62 | 5.80 | | | |
| $CH_2N(CH_2CH_2CH_3)_2$ | H | $CH_3$ | H | $CH_3$ | $C_{15}H_{34}N_2O_3$ | 145/0.001 | 9.64 | 9.74 | $C_{21}H_{40}N_2O_6$ | 6.73 | 6.48 |
|  | H | $CH_3$ | H | $CH_3$ | $C_{14}H_{30}N_2O_3$ | 145/0.005 | 10.22 | 10.25 | $C_{20}H_{36}N_2O_6$ | 7.00 | 6.90 |
|  $CH_2N(CH_3)(C_6H_5)$ | H | $CH_3$ | H | $CH_3$ | $C_{16}H_{28}N_2O_3$ | 180/0.03 | 9.45 | 9.31 | $C_{22}H_{34}N_2O_6$ | 6.63 | 6.27 |
| $CH_3$ | $CH_3$ | $CH_3$ | H | H | $C_9H_{21}NO_3$ | 125/0.05 | 7.32 | 7.35 | | | |
| $CH_3$ | $CH_3$ | $CH_3$ | H | $CH_3$ | $C_{10}H_{23}NO_3$ | 130/0.5 | 6.82 | 6.96 | $C_{16}H_{29}NO_6$ | 4.23 | 4.24 |
| $CH_3$ | $CH_3$ | $CH_3$ | H | $CH_3$ | $C_{18}H_{23}NO_3$ | 165/0.8 | 6.82 | 6.87 | | | |

[a] The figures in this column refer to the temperature of an air bath necessary to promote distillation at the stated pressure in a two-bulb type apparatus.

TABLE II

SUBSTITUTED TRIPTYCH-BOROXAZOLIDINES (IV)

| $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | M.p. | Purification | Formula | Boron, % Calcd. | Boron, % Found | Nitrogen, % Calcd. | Nitrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH(CH_3)_2$ | H | H | H | H | 146–152 | [a] | $C_9H_{18}BNO_3$ | 5.44 | 5.77 | 7.04 | 7.33 |
| $CH_2OCH_2CH_2CH_3$ | H | H | H | H | 70 | [b] | $C_{10}H_{20}BNO_4$ | 4.73 | 5.06 | | |
| $CH_2OCH(CH_3)_2$ | H | H | H | H | 110 | [a] | $C_{10}H_{20}BNO_4$ | 4.73 | 4.98 | 6.12 | 6.29 |
| $CH_3$ | H | $CH_3$ | H | H | 140–148 | [a] | $C_8H_{16}BNO_3$ | 5.85 | 5.39 | 7.57 | 7.78 |
| $C_6H_5$ | H | $CH_3$ | H | H | 130–135 | [c] | $C_{13}H_{18}BNO_3$ | 4.38 | 4.76 | 5.54 | 5.46 |
| $C_2H_5$ | H | $CH_3$ | H | $CH_3$ | Oil | ... | $C_{10}H_{20}BNO_3$ | | | | |
| $CH{=}CH_2$ | H | $CH_3$ | H | $CH_3$ | 100–110 | [b] | $C_{10}H_{18}BNO_3$ | 6.64 | 6.47 | 5.13 | 4.98 |
| $C_6H_5$ | H | $CH_3$ | H | $CH_3$ | 155–158 | [a] | $C_{14}H_{20}BNO_3$ | 4.14 | 4.25 | 5.36 | 5.09 |
| $CH_2OCH_3$ | H | $CH_3$ | H | $CH_3$ | Glass | ... | $C_{10}H_{20}BNO_4$ | 4.72 | 4.77 | 6.11 | 6.39 |
| $CH_2OC_2H_5$ | H | $CH_3$ | H | $CH_3$ | Glass | ... | $C_{11}H_{22}BNO_4$ | 4.45 | 4.44 | 5.76 | 5.99 |
| $CH_2OCH_2CH_2CH_3$ | H | $CH_3$ | H | $CH_3$ | Waxy | [a] | $C_{12}H_{24}BNO_4$ | 4.21 | 4.34 | 5.81 | 5.98 |
| $CH_2OCH(CH_3)_2$ | H | $CH_3$ | H | $CH_3$ | Waxy | [a] | $C_{12}H_{24}BNO_4$ | 4.21 | 4.35 | 5.45 | 5.68 |
|  | H | $CH_3$ | H | $CH_3$ | 135–140 | [a] | $C_{14}H_{27}BN_2O_3$ | 3.83 | 3.81 | 9.92 | 9.81 |
| $CH_3$ | $CH_3$ | $CH_3$ | H | H | Waxy | [a] | $C_9H_{18}BNO_3$ | | | 7.04 | 7.11 |
| $CH_3$ | $CH_3$ | $CH_3$ | H | $CH_3$ | Waxy | [a] | $C_{10}H_{20}BNO_3$ | 5.08 | 4.81 | 6.56 | 6.54 |
| $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ | H | Waxy | [a] | $C_{10}H_{20}BNO_3$ | | | 6.57 | 6.45 |

[a] Purification by sublimation. [b] Purification by recrystallization from benzene–petroleum ether (b.p. 35–37°). [c] Purification by recrystallization from acetonitrile–ether.

by interaction of a 1-substituted or 1,1-disubstituted ethylene oxide (I) with a dialkanolamine of the general structure II. Treatment of III with tributyl borate then yielded the polysubstituted triptych-boroxazolidine (IV).

Not unexpectedly the polysubstituted triptych boroxazolidines proved to be more difficult to obtain as sharp-melting solids than did the monosubstituted counterparts, and in several instances only waxy materials could be isolated. This may be partly ascribed to the possibility for the existence of diastereoisomers in compounds of the general structure IV (whereas this is not true in the case of IV when $R_2 = R_3 = R_4 = R_5 = H$). The extreme hygroscopicity of many of the polysubstituted triptych-boroxazolidines, however, suggests that other factors might also be influencing the physical nature of the products. In particular, it appears possible that some of the polysubstituted triptych-boroxazolidines are not well represented by the structure IV in which intramolecular N-B interaction is depicted but rather by a structure in which such interaction is absent. Furthermore, molecular weight determinations on the polysubstituted compounds were 20–60% higher than those calculated for the monomer, indicating the 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.

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(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).

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# Reaction of Dichlorocarbene with Imines

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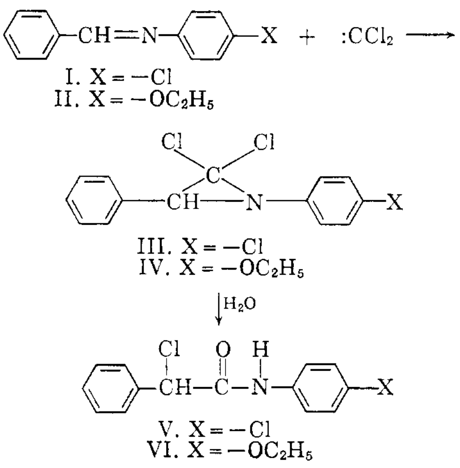
*Received March 15, 1962*

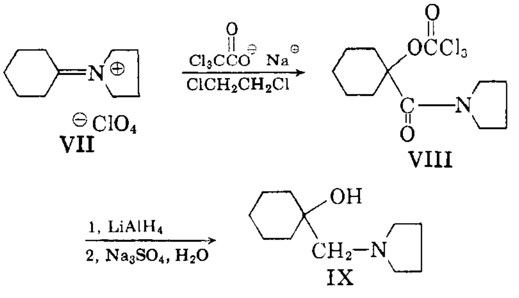
Addition of dichlorocarbene to the carbon-nitrogen double bond of benzalaniline has been described.[3] This reaction has been extended to other imines and an iminium salt.

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).