was obtained as a colorless, crystalline solid from water, yield 33.4 g. (91%), m.p. 211–211.5° with decomposition.[15]

Anal. Calcd. for $C_6H_5N_5$: C, 49.0; H, 3.4; N, 47.6. Found: C, 49.2; H, 3.7; N, 47.8.

5-(3'-Pyridyl)tetrazole was prepared from 3-cyanopyridine. Using the same quantities of reagents as in the foregoing example, the product was obtained as a colorless, crystalline solid from water, yield 33.3 g. (91%), m.p. 234–235° with decomposition.[15]

Anal. Calcd. for $C_6H_5N_5$: C, 49.0; H, 3.4; N, 47.6. Found: C, 49.2; H, 3.4; N, 47.7.

5-(4'-Pyridyl)tetrazole was prepared from 4-cyanopyridine in the same way with the same quantities of reagents. It crystallized from water as a colorless solid, yield 34.3 g. (93%), m.p. 253–254° with decomposition.[15]

Anal. Calcd. for $C_6H_5N_5$: C, 49.0; H, 3.4; N, 47.6. Found: C, 49.2; H, 3.6; N, 47.3.

2,6-Di(5'-tetrazolyl)pyridine. A solution of 27.5 g. (0.21 mole) of 2,6-dicyanopyridine in 100 ml. of *n*-butyl alcohol was refluxed for 2 days with 38.2 g. (0.59 mole) of sodium azide and 38 ml. of glacial acetic acid.[14] At this point another 10 g. of sodium azide and 20 ml. of glacial acetic acid were added. Refluxing continued for 2 days. The crude product, 45.6 g. (99%), was obtained by diluting the reaction mixture with water, distilling and acidifying as in the foregoing examples. The product was purified by dissolving it in aqueous sodium hydroxide and reprecipitating from the hot, colorless solution with acid. The analytical sample was recrystallized from hot water in which the product was only sparingly soluble, m.p. 290° with decomposition.

Anal. Calcd. for $C_7H_5N_9$: C, 39.1; H, 2.3; N, 58.6. Found: C, 39.2; H, 2.6; N, 58.6.

5-(2'-Piperidyl)tetrazole. A suspension of 11 g. of 5-(2'-pyridyl)tetrazole in 150 ml. of glacial acetic acid was shaken with 250 mg. of platinum oxide and hydrogen at an initial pressure of 50 p.s.i. Hydrogenation was complete in 24 hr. After removal of the catalyst by filtration the solution was evaporated to a small volume and diluted with ether to precipitate the product. Purification was effected by dissolving the colorless solid in the minimum amount of warm water, treating with Norit and reprecipitating with acetone, yield 10.5 g. (92%), m.p. 287° with decomposition.

Anal. Calcd. for $C_6H_{11}N_5$: C, 47.1; H, 7.2; N, 45.7. Found: C, 47.0; H, 7.1; N, 46.0.

The *acetyl* derivative was prepared by refluxing for 2 hrs. in glacial acetic acid with an equimolar amount of acetic anhydride. After removal of the solvent under reduced pressure, the residue of acetyl derivative was obtained as a colorless, crystalline solid from water, m.p. 135.5–136.5°.

Anal. Calcd. for $C_8H_{13}N_5O$: C, 49.2; H, 6.7; N, 35.9. Found: C, 49.1; H, 6.6; N, 35.6.

For preparative purposes it was advantageous to form the acetyl derivative directly by hydrogenation of the pyridyltetrazole as just described; after removal of the catalyst, acetic anhydride was added to the glacial acetic acid solution and acetylation was completed as just described. The over-all yield from the pyridyltetrazole was 84%.

5-(3'-Piperidyl)tetrazole was obtained in almost quantitative yield as a colorless, crystalline solid by hydrogenation of the pyridyltetrazole in a completely analogous manner, m.p. 296–297° with decomposition. The analytical sample was recrystallized from the minimum amount of water; the remainder of the product was precipitated from water with acetone.

Anal. Calcd. for $C_6H_{11}N_5$: C, 47.1; H, 7.2; N, 45.7. Found: C, 47.1; H, 7.3; N, 45.7.

The *acetyl* derivative, prepared as described for the isomer, separated from isopropyl alcohol as a colorless, crystalline solid, m.p. 170–171°.

Anal. Calcd. for $C_8H_{13}N_5O$: C, 49.2; H, 6.7; N, 35.9. Found: C, 49.5; H, 6.7; N, 36.1.

5-(4'-Piperidyl)tetrazole was obtained in 86% yield by hydrogenation of the pyridyltetrazole in a completely analogous manner. The product crystallized from water as dense colorless prisms; it did not decompose below 370° but showed some shrinking and browning at 237°.

Anal. Calcd. for $C_6H_{11}N_5$: C, 47.1; H, 7.2; N, 45.7. Found: C, 47.0; H, 7.2; N, 46.0.

The *acetyl* derivative, obtained as described for the isomers, separated from isopropyl alcohol as a colorless, crystalline solid, m.p. 156.5–157.5°.

Anal. Calcd. for $C_8H_{13}N_5O$: C, 49.2; H, 6.7; N, 35.9. Found: C, 49.3; H, 6.8; N, 35.8.

East Lansing, Michigan

(15) B. Brouwer-van Straater, D. Solinger, C. van de Westeringh, and H. Veldstra, *Rec. trav. chim.*, **77**, 1129 (1958).

[Contribution from the Department of Chemistry, Michigan State University]

Tetrazole Analogs of Plant Auxins[1]

J. M. McMANUS[2,3] AND ROBERT M. HERBST

Received March 30, 1959

A group of chlorinated 5-phenoxymethyltetrazoles has been prepared as analogs of the corresponding substituted phenoxyacetic acids. Two methods of synthesis were used to corroborate the structure of the products. The tetrazole analog of the natural plant auxin, 3-indolylacetic acid, in which the carboxyl group is replaced by the acidic tetrazole moiety, has been prepared from the corresponding nitrile. An improved method for the synthesis of phenoxyacetonitriles is described.

The isolation and identification of 3-indolylacetic acid as a natural growth hormone in plants[4] initiated a search for other substances which could elicit this type of activity. Among those synthetic materials shown to stimulate growth was a group of chlorinated compounds derived from phenoxyacetic acid. Varying degrees of activity were demonstrated depending on the number and position of the chlorine atoms in the benzenoid portion of the structure; the most active are 2,4-dichloro-

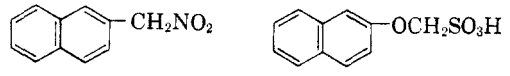
(1) Based on a doctoral thesis submitted to Michigan State University in 1958 by James M. McManus.

(2) White Laboratories Fellow, 1956–1958.

(3) Present address: Chas. Pfizer & Co., Inc., Brooklyn, N. Y.

(4) F. Kögl, A. J. Haagen-Smit and H. Erxleben, *Z. physiol. Chem.*, **228**, 90 (1934).

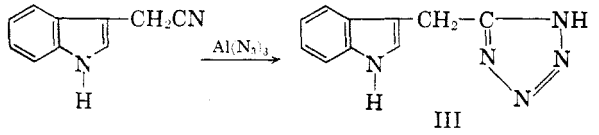
phenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T).[5] The requirement that there be a carboxyl group on the side chain[6] finds exception in that the corresponding aldehydes, nitriles, esters and amides also show, to a certain extent, hormonal activity. Exceptions to the carboxylic acid rule have been shown by active compounds in which the carboxyl group is replaced by a nitro group (I) or a sulfonic acid moiety (II).[7]



I II

Because of the acidic nature of 5-mono substituted tetrazoles,[8,9,10,11] it appeared of interest to incorporate a tetrazole nucleus into the chemical structure of an active plant auxin in place of the carboxyl group. In this study the tetrazole analogs of 3-indolylacetic acid and various chlorophenoxyacetic acids were synthesized.

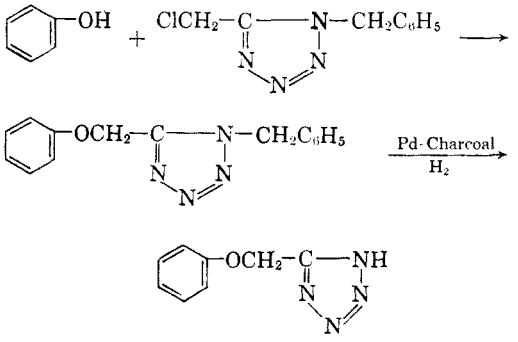
Behringer and Kohl[12] have shown that certain nitriles will react with aluminum azide in tetrahydrofuran to form 5-substituted tetrazoles. The preparation of 5-(3′-indolylmethyl)tetrazole (III) was accomplished by application of this general procedure to 3-indolylacetonitrile. It was found advantageous to modify the isolation technique recommended by these authors. Better results were obtained when the tetrahydrofuran was displaced from the reaction mixture by distillation while constant volume was maintained by simultaneous addition of water. The insoluble aluminum salt of the tetrazole which remained after all the tetrahydrofuran had been removed was decomposed with dilute hydrochloric acid, leaving an aqueous suspension of the tetrazole.



III

The substituted 5-phenoxymethyltetrazoles were synthesized by application of two general procedures: The first involved interaction of nitriles with sodium azide and acetic acid in *n*-butyl alcohol[10]; the second, interaction of nitriles with aluminum azide in tetrahydrofuran.[12] The first procedure was used successfully for the synthesis of 5-phenoxymethyltetrazole and the corresponding 2,4-dichloro- and 2,4,5-trichlorophenoxymethyl analogs from the appropriate nitriles. Attempts to prepare 5-(2′,4′,6′-trichlorophenoxymethyl)tetrazole in this way were not successful; the reaction mixture became very dark because of extensive decomposition, and no definite product was isolated. The interaction of 2-chloro-, 4-chloro-, and 2,4,6-trichlorophenoxyacetonitrile with aluminum azide in refluxing tetrahydrofuran resulted in good yields of the corresponding tetrazoles. After completion of this work an improved technique involving interaction of nitriles with lithium or an ammonium azide in dimethylformamide appeared.[13]

An alternate method used for the preparation of some of the phenoxymethyltetrazoles involved interaction of the appropriately substituted phenol with 1-benzyl-5-chloromethyltetrazole in an alkaline medium, followed by hydrogenolytic removal of the benzyl group with palladium on charcoal and hydrogen. In several instances, namely 5-(2,′4′-dichloro- and 2′,4′,6′-trichlorophenoxymethyl)-1-benzyltetrazole, debenzylation was accompanied by partial dehalogenation and possibly reduction. Isolation of pure compounds of unequivocal structure for comparison with the compounds prepared by other routes was not feasible in these two cases. In other instances compounds identical with those formed from the nitriles were obtained by this method.



The tetrazole analogs are similar to the phenoxyacetic acids in physical properties. All are solids with melting points in the same range as and similar solubilities to the corresponding carboxylic acids. No regular differences in melting points are noted, some are slightly higher some lower than those of the corresponding phenoxyacetic acids.

The nitriles used as intermediates for the phenoxymethyltetrazole syntheses were prepared from the phenol, chloroacetonitrile and potassium carbonate in refluxing acetone. This method of preparation offered a distinct advantage over methods which involved synthesis of the nitrile either from

(5) R. M. Muir, C. H. Hansch and A. H. Gallup, *Plant Physiol.*, **24**, 359 (1949).

(6) J. Koepfli, K. Thimann and F. Went, *J. Biol. Chem.*, 122, 763 (1937–38).

(7) R. Wain, *Ann. Appl. Biol.*, **36**, 558 (1949).

(8) E. Oliveri-Mandala, *Gazz. chim. ital.*, **44**, 175 (1914).

(9) J. S. Mihina and R. M. Herbst, *J. Org. Chem.*, 15, 1082 (1950).

(10) R. M. Herbst and K. R. Wilson, *J. Org. Chem.*, 22, 1142 (1957).

(11) R. M. Herbst, *Essays in Biochemistry*, S. Graff, Ed., John Wiley and Sons, Inc., New York, 1956, p. 141.

(12) H. Behringer and K. Kohl, *Chem. Ber.*, **89**, 2648 (1956).

(13) W. G. Finnegan, R. A. Henry and R. Lofquist, *J. Am. Chem. Soc.*, **80**, 3908 (1958).

TABLE I

PHENOXYACETONITRILES ARYL-OCH_2CN

Aryl	M.P.	Yield, %	Formula	Analyses Calcd. Cl	Calcd. N	Found Cl	Found N
C_6H_5	[a]	82					
2-ClC_6H_4	[b]	44	C_8H_6ClNO	21.2	8.4	21.1	8.1
4-ClC_6H_4	46.5–47.5	93	C_8H_6ClNO	21.2	8.4	21.2	8.2
2,4-$Cl_2C_6H_3$	48.5–49[c]	85	$C_8H_5Cl_2NO$	35.1	6.9	35.2	6.8
2,4,5-$Cl_3C_6H_2$	91.5–92.5	88	$C_8H_4Cl_3NO$	45.0	5.9	44.8	5.8
2,4,6-$Cl_3C_6H_2$	102–103[d]	98	$C_8H_4Cl_3NO$	45.0	5.9	44.9	5.7

[a] B.p. 73–76° at 1 mm., Powell and Adams[18] reported b.p. 132° at 30 mm. [b] B.p. 109° at 1 mm. [c] M.p. 44–46° previously reported.[14] [d] M.p. 103° previously reported.[19]

the acid by way of the acid chloride and amide or from phenoxymethyl chloride and sodium cyanide[14] as these latter methods involved a series of steps. The structure of the phenoxyacetonitriles was established by comparison of physical constants with those recorded in the literature, elemental analysis and, in several cases, by hydrolysis to the known phenoxyacetic acids.

5-(3′-Indolylmethyl)tetrazole appears to stimulate cell elongation in the *Avena* test at concentrations about 200 times as great as those of 3-indolylacetic acid required to produce the same effect. 5(2′,4′-Dichlorophenoxymethyl)tetrazole is inactive but appears to be a competitive antagonist for 2,4-dichlorophenoxyacetic acid in the *Avena* test. Details of these studies are to be published elsewhere.[15]

The preparation of both 5-(3′-indolylmethyl)- and 5-(2′,4′-dichlorophenoxymethyl)tetrazole by somewhat different techniques has just been reported by van de Westeringh and Veldstra.[16]

EXPERIMENTAL[17]

5-(3′-Indolylmethyl)tetrazole. Seven and eight-tenths g. (0.12 mole) of sodium azide and 5.3 g. (0.04 mole) of anhydrous aluminum chloride were refluxed together in 120 ml. of dry tetrahydrofuran for 1 hr. 5.8 g. (0.04 mole) of 3-indolylacetonitrile was added to the mixture and refluxing with stirring continued for 24 hrs. The tetrahydrofuran was then distilled from the reaction mixture while water was added slowly at such a rate that the volume remained constant. After the organic solvent had been removed, the suspended solid was filtered off, resuspended in 250 ml. of water, and treated with sufficient hydrochloric acid to bring the suspension to *p*H 2. After 10 min. stirring, the solid was filtered off and washed with water. Drying gave 6.5 g. of crude product which was recrystallized first from ethylene chloride and then from water, yield 4.5 g. (61%), m.p. 179–180° with decomposition.

Anal. Calcd. for $C_{10}H_9N_5$: C, 60.3; H, 4.6; N, 35.2. Found: C, 60.3; H, 4.8; N, 35.0.

The *monopicrate* crystallized from water, m.p. 131–132°.

Anal. Calcd. for $C_{16}H_{12}N_8O_6$: C, 44.9; H, 2.8; N, 26.2. Found: C, 45.5; H, 3.2; N, 25.8.

Phenoxyacetonitriles. The preparation of phenoxyacetonitrile will serve as a typical example. A mixture of 23.5 g. of phenol, 18.7 g. of chloroacetonitrile and 34.5 g. of anhydrous potassium carbonate in 75 ml. of dry acetone was heated under reflux for 8 hr. The mixture was then poured into 200 ml. of water containing 10 g. of sodium hydroxide and extracted with ether. The ether layer was separated and dried over sodium sulfate, and the ether was removed by distillation. Fractionation of the residual reddish oil gave the product as a colorless, oily liquid, yield 27.2 g. Physical properties, yields, and analytical data for the phenoxyacetonitriles prepared in this way are given in Table I. Except for 2,4,6-trichlorophenoxyacetonitrile, which was recrystallized from absolute ethanol, the solid chlorophenoxyacetonitriles were recrystallized from petroleum ether.

Phenoxyacetic acid. Phenoxyacetonitrile (5.3 g.) was refluxed in 100 ml. of 25% sodium hydroxide solution for 12 hr. The resulting solution was filtered and the filtrate was cooled and acidified with 6*N* hydrochloric acid. The yield of product after recrystallization from water was 4.9 g. (81%), m.p. 98–99°. Sabanejeff and Dworkowitsch[20] report m.p. 97°.

2,4-Dichlorophenoxyacetic acid, m.p. 138.5–139° was obtained from the nitrile in similar manner; previously reported[21] m.p. 138°.

2,4,5-Trichlorophenoxyacetic acid was obtained from the nitrile in similar manner and recrystallized from benzene, m.p. 150.5–152°. Porkorny[21] reported m.p. 153°.

Preparation of Phenoxymethyltetrazoles. 5-Phenoxymethyltetrazole. Procedure Ia. A mixture of 16.3 g. (0.125 mole) of phenoxyacetonitrile, 11 g. (0.165 mole) of sodium azide and 10 g. (0.165 mole) of glacial acetic acid in 60 ml. of *n*-butyl alcohol was heated under reflux for 4 days. Heating was continued for 2 days after addition of 2.5 g. of sodium azide and 5 g. of glacial acetic acid. The reaction mixture was diluted with 200 ml. of water, and the mixture was distilled until the alcohol was removed. Acidification of the residual aqueous solution with dilute sulfuric acid gave the product as a colorless solid, yield 22 g. Recrystallization from water gave the pure product, m.p. 127.5–129°.

(14) H. Barber, R. Fuller, M. Green and H. Zwartouw *J. Appl. Chem. (London)*, **3**, 266 (1953).

(15) We are indebted to Mr. R. H. Hamilton, Dr. A. Kivilaan and Dr. R. S. Bandurski of the Department of Botany at Michigan State University for their enthusiastic cooperation in these studies. Their results will be published separately in *Plant Physiology*.

(16) C. van de Westeringh and H. Veldstra, *Rec. trav. chim.*, **77**, 1107 (1958).

(17) Microanalyses were done on all compounds by Micro-Tech Laboratories, Skokie, Ill. Melting points were taken in open capillaries and are not corrected.

(18) S. Powell and R. Adams, *J. Am. Chem. Soc.*, **42**, 646 (1920).

(19) D. Drain, D. Peak, and F. Whitmont, *J. Chem. Soc.*, 2680 (1949).

(20) A. Sabanejeff and P. Dworkowitsch, *Ann.*, **216**, 284 (1883).

(21) R. Porkorny, *J. Am. Chem. Soc.*, **63**, 1768 (1941).

Anal. Calcd. for $C_8H_8N_4O$: C, 54.5; H, 4.6; N, 31.8. Found: C, 54.5; H, 4.7; N, 31.9.

5-(2'-Chlorophenoxymethyl)tetrazole. Procedure Ib. To a suspension of 16.7 g. (0.1 mole) of 2-chlorophenoxyacetonitrile and 19.5 g. (0.3 mole) of sodium azide in 50 ml. of dry tetrahydrofuran was added a solution of 13.3 g. (0.1 mole) of anhydrous aluminum chloride in 160 ml. of the same solvent. The mixture was refluxed with continuous stirring for 24 hr. The tetrahydrofuran was then distilled from the reaction mixture while water was added slowly at such a rate that the volume of the mixture remained constant. The solid which had separated was filtered off, resuspended in 250 ml. of water and treated with 30 ml. of concentrated hydrochloric acid. After being stirred for 1 hr. the solid was filtered off and dried, yield 18.8 g. of crude product which was recrystallized from toluene, m.p. 134.5–135.5°.

Anal. Calcd. for $C_8H_7ClN_4O$: C, 45.6; H, 3.4; Cl, 16.8; N, 26.6. Found: C, 45.9; H, 3.6; Cl, 16.9; N, 26.6.

5-(4'-Chlorophenoxymethyl)tetrazole. Following *Procedure Ib* a mixture of 16.7 g. (0.1 mole) of 4-chlorophenoxyacetonitrile, 19.5 g. (0.3 mole) of sodium azide, and 13.3 g. (0.1 mole) of anhydrous aluminum chloride in 210 ml. of dry tetrahydrofuran gave 20.6 g. of crude product. Recrystallization from aqueous ethanol gave 13.9 g. (66%) of pure product, m.p. 165–166°.

Anal. Calcd. for $C_8H_7ClN_4O$: C, 45.6; H, 3.4; Cl, 16.8; N, 26.6. Found: C, 45.7; H, 3.6; Cl, 16.8; N, 26.5.

5-(2' 4'-Dichlorophenoxymethyl)tetrazole. Using *Procedure Ia* a mixture of 25.2 g. (0.125 mole) of 2,4-dichlorophenoxyacetonitrile, 11 g. (0.165 mole) of sodium azide, and 10 g. of glacial acetic acid in 60 ml. of *n*-butyl alcohol gave 25.6 g. of crude product which was purified by recrystallization from toluene, m.p. 124.5–125.5°.

Anal. Calcd. for $C_8H_6Cl_2N_4O$: C, 39.2; H, 2.5; Cl, 28.9; N, 22.9. Found: C, 39.4; H, 2.6; Cl, 29.0; N, 23.0.

5-(2',4',5'-Trichlorophenoxymethyl)tetrazole. Following *Procedure Ia* a mixture of 29.6 g. (0.125 mole) of 2,4,5-trichlorophenoxyacetonitrile, 11 g. (0.165 mole) of sodium azide, and 10 g. of glacial acetic acid in 60 ml. of *n*-butyl alcohol gave 25.4 g. of crude product that was purified by recrystallization from toluene, m.p. 163.5–165°.

Anal. Calcd. for $C_8H_5Cl_3N_4O$: C, 34.4; H, 1.8; Cl, 38.1; N, 20.1. Found: C, 34.7; H, 1.8; Cl, 38.3; N, 20.1.

5-(2',4',6'-Trichlorophenoxymethyl)tetrazole. Using *Procedure Ib* 5.8 g. (0.025 mole) of 2,4,6-trichlorophenoxyacetonitrile, 4.8 g. (0.074 mole) of sodium azide, and 2.98 g. (0.025 mole) of anhydrous aluminum chloride in 90 ml. of dry tetrahydrofuran gave 6.6 g. of crude product which was recrystallized first from toluene and then from ethanol, m.p. 164–165°.

Anal. Calcd.: for $C_8H_5Cl_3N_4O$: C, 34.4; H, 1.8; Cl, 38.1; N, 20.1. Found: C, 34.6; H, 2.1; Cl, 37.9; N, 20.0.

Several attempts to prepare this compound using *Procedure Ia* were accompanied by extensive decomposition; no definite product was isolated from the reaction mixtures.

1-Benzyl-5-phenoxymethyltetrazole. A mixture of 8.3 g. (0.04 mole) of 1-benzyl-5-chloromethyltetrazole,[22] 4.7 g. (0.05 mole) of phenol, and 2.7 g. (0.05 mole) of sodium methoxide in 75 ml. of absolute methanol was heated under reflux with stirring for 10 hr. The contents of the flask were then poured into 150 ml. of water, the precipitate was filtered off and recrystallized from aqueous methanol to give 3.8 g. (36%) of the desired product, m.p. 66.5–67°.

Anal. Calcd. for $C_{15}H_{14}N_4O$: C, 67.7; H, 5.3; N, 21.0. Found: C, 67.4; H, 5.4; N, 21.1.

1-Benzyl-5-(2',4'-dichlorophenoxymethyl)tetrazole. Under similar conditions 8.3 g. of 1-benzyl-5-chloromethyltetrazole, 8.15 g. of 2,4-dichlorophenol, and 2.7 g. of sodium methoxide in 75 ml. of absolute methanol gave 12.4 g. of crude product from which, after recrystallization from methanol, 8.6 g. of pure product, m.p. 107.5–108°, was obtained.

Anal. Calcd. for $C_{15}H_{12}Cl_2N_4O$: C, 53.8; H, 3.6; Cl, 21.2; N, 16.7. Found: C, 53.8; H, 3.9; Cl, 21.0; N, 16.8.

1-Benzyl-5-(2',4',6'-trichlorophenoxymethyl)tetrazole. In similar manner 6.9 g. of 1-benzyl-5-chloromethyltetrazole, 8.2 g. of 2,4,5-trichlorophenol, and 2.2 g. of sodium methoxide in 75 ml. of absolute methanol gave 10.6 g. of crude product which on recrystallization from methanol gave 6.4 g. of pure product, m.p. 113.5–114.5°.

Anal. Calcd. for $C_{15}H_{11}Cl_3N_4O$: C, 48.7; H, 3.0; Cl, 28.8; N, 15.2. Found: C, 48.6; H, 3.1; Cl, 28.7; N, 15.3.

1-Benzyl-5-(2',4',6'-trichlorophenoxymethyl)tetrazole. Similarly 6.9 g. of 1-benzyl-5-chloromethyltetrazole, 8.15 g. of 2,4,6-trichlorophenol, and 2.2 g. of sodium methoxide in 75 ml. of absolute methanol gave 12.3 g. of crude product and after recrystallization from methanol, 9.1 g. of pure material, m.p. 112–113°.

Anal. Calcd. for $C_{15}H_{11}Cl_3N_4O$: C, 48.7; H, 3.0; Cl, 28.8; N, 15.2. Found: C, 48.8; H, 3.0; Cl, 28.9; N, 15.0.

Debenzylation of 1-Benzyl-5-phenoxymethyltetrazole. A solution of 2.7 g. (0.01 mole) of 1-benzyl-5-phenoxymethyltetrazole in 100 ml. of absolute ethanol was shaken for 12 hr. with 1 g. of 5% palladium on charcoal at an initial hydrogen pressure of 50 p.s.i. The catalyst was filtered off and the solvent was removed from the filtrate in a vacuum. The residue was treated with dilute sodium hydroxide and filtered. From the alkali insoluble solid, 1.3 g. (49%) of the starting material was recovered. Acidification of the alkaline solution with dilute hydrochloric acid gave a precipitate of 5-phenoxymethyltetrazole, 400 mg. (43%), which was recrystallized from water, m.p. and mixture m.p. 127.5–128.5°.

Debenzylation of 1-benzyl-5-(2',4',5'-trichlorophenoxymethyl)tetrazole. A mixture of 1.8 g. of 1-benzyl-5-(2',4',5'-trichlorophenoxymethyl)tetrazole and 1 g. of palladium on charcoal in 75 ml. of absolute ethanol was shaken for 12 hr. at an initial hydrogen pressure of 50 p.s.i. The catalyst was filtered and washed with warm ethanol. Removal of the solvent from the combined filtrate and washings in a vaccum left a residue which after repeated crystallization from toluene gave 5-(2',4',5'-trichlorophenoxymethyl)tetrazole, m.p. and mixture m.p. 160–162°.

Both 1-benzyl-5-(2',4'-dichloro- and 2',4',6'-trichlorophenoxymethyl)tetrazole were debenzylated in a similar manner, but in neither case was a pure product isolated from the resulting mixture of products. Apparently debenzylation was accompanied by dehalogenation and possibly reduction in varying degrees which would have vitiated this approach as an unequivocal synthesis.

EAST LANSING, MICH.

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