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DERIVATIVES OF 1-HYDROXYTETRAZOLE-5-CARBOXYLIC ACID

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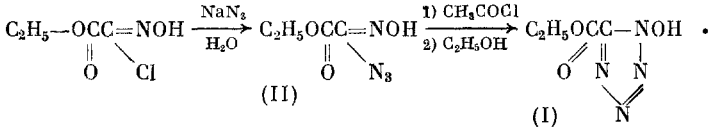
Among the many derivatives of tetrazole only individual examples of N-hydroxytetrazole derivatives are known.

The present work describes a method for obtaining ethyl 1-hydroxytetrazole-5-carboxylate (I) and a number of derivatives of 1-hydroxytetrazole-5-carboxylic acid on its hydroxyl and carboxyl groups



Ethoxycarbonylchloroaldoxime was treated with NaN_3 and the ethoxycarbonylazidoaldoxime (II) formed was allowed to stand with acetyl chloride by analogy with [1, 2]; and the mixture was then heated with ethanol to give the crystalline product (I) with a yield of more than 80%. The structure of (I) has been confirmed by the data of its elemental analysis and IR spectrum and also by chemical conversions.

By analogy with other 1-hydroxytetrazoles [3], when treated with bromoacetone in the presence of K_2CO_3 (I) is reduced to 5-ethoxycarbonyltetrazole, which is isolated as its Ag salt (III) (see scheme below).

As it is quite a strong OH acid, (I) readily forms stable salts with metals and nitrogenous bases. Because of its poor solubility in water Ag salt (IV) is conveniently obtained by mixing aqueous solutions of (I) with $AgNO_3$. In a similar manner the NH_4 salt (V) is formed when NH_3 is passed through a solution of (I) in low-polarity solvents such as ether. In polar solvents (V) reacts with NH_3 to give the NH_4 salt of 1-hydroxytetrazole-5-carboxamide (VI). Salts of ethyl 1-hydroxytetrazole-5-carboxylate and 1-hydroxytetrazole-5-carboxamide when acidified with mineral acids give the corresponding derivatives of 1-hydroxytetrazole-5-carboxylic acid.

The reaction of salts of (I) with primary or secondary alkyl iodides or bromides leads to ethyl 1-alkoxytetrazole-5-carboxylates [VIII, R = CH_3, IX, R = $CH(CH_3)_2$] with good yields. The Ag salt or tertiary amine salt can be used in the O-alkylation reaction with equal success.

The ethoxycarbonyl group in ethyl 1-alkoxytetrazole-5-carboxylates readily reacts with nucleophilic reagents. Interaction of (VIII) with NH_3 or $MeNH_2$ at 20°C results in the forma-

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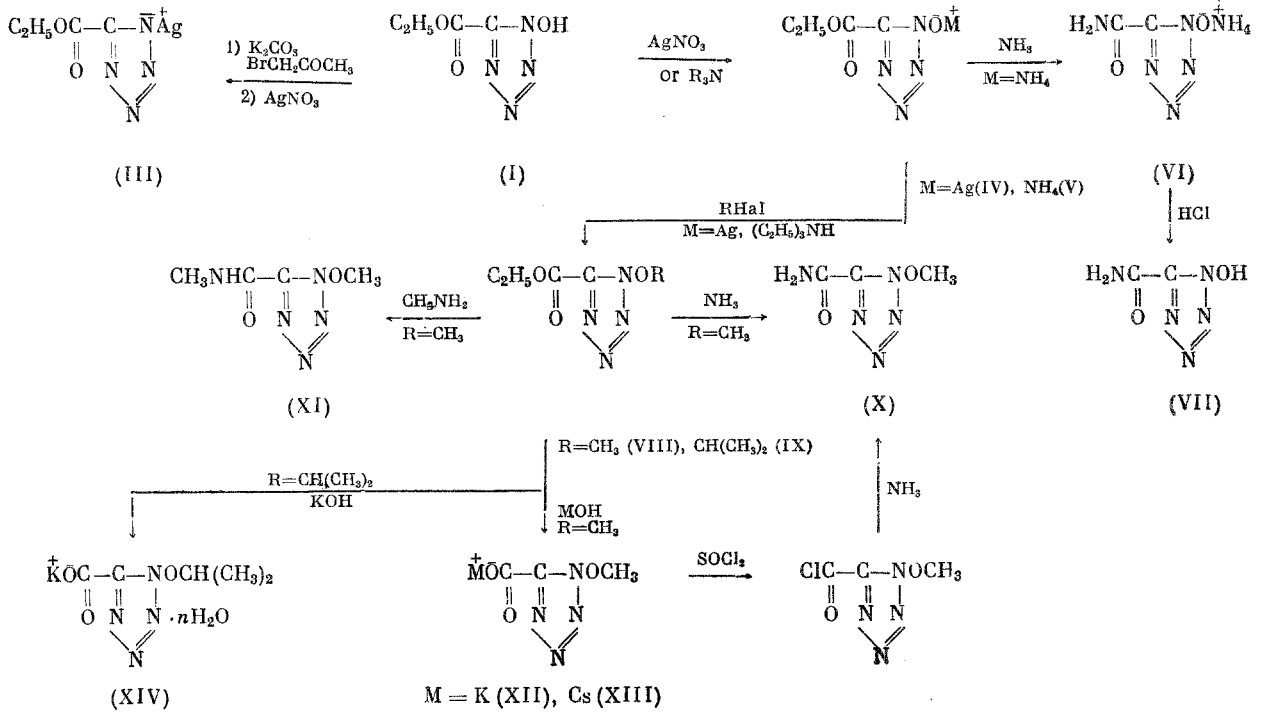
Scheme for conversions of ethyl 1-hydroxytetrazole-5-carboxylate



tion of the primary (X) or secondary (XI) amide of 1-methoxytetrazole-5-carboxylic acid with a yield of 76-83%. Treatment of ethyl 1-alkoxytetrazole-5-carboxylates with alkali metal hydroxides leads to salts of 1-alkoxytetrazole-5-carboxylic acids, which explode in the anhydrous state when subjected to weak mechanical stresses, so that they cannot be recommended for any syntheses.

This property of the salts of 1-alkoxytetrazole-5-carboxylic acids raises the question concerning their correct structure, and in particular whether they might be in the iminoazide form; in other words, that they might be salts of alkoxyiminoazidoacetic acid. However, in their IR spectra there is no absorption due to an azide group (2100-2300 cm^{-1}). Moreover, positive evidence for the assigned structure is given by the fact that careful treatment of the Cs salt of 1-methoxytetrazole-5-carboxylic acid (XIII) with $SOCl_2$ in benzene and subsequent saturation with ammonia gives amide (X) described above in 30% yield.

Attempts to obtain the free 1-methoxytetrazole-5-carboxylic acid by passing HCl through a suspension of its potassium salt (XII) in ether at 20°C gave a noncrystalline oil which, although it also had a carbonyl group absorption (1700-1750 cm^{-1}) in its IR spectrum, when treated with KOH did not afford the initial salt (XII).

EXPERIMENTAL

PMR spectra were recorded on a Perkin–Elmer R-12 (60 MHz) spectrometer; IR spectra were recorded on a UR-10 spectrometer.

Ethoxycarbonylazidoaldoxime (II). To a solution of 2.53 g of NaN_3 in 50 ml of H_2O was added 5.07 g of ethoxycarbonylchloroaldoxime, and the mixture was agitated at 20°C for 1 h and extracted with ether to give 4.82 g (91%) of (II), mp 96-99°C. IR spectrum (ν, cm^{-1}): 755 s, 860 s, 1025 sh, 1115 w, 1150 m, 1255 m, 1345 s, 1370 m, 1395 m, 1475 w, 1650 m, 1730-1745 s, 2155 v.s., 2990 w, 3265 s.br.

Ethyl 1-Hydroxytetrazole-5-carboxylate (I). To a solution of 3.23 ml of AcCl in a mixture of 98 ml of benzene and 15 ml of ether was added 4.82 g of (II) and the mixture was kept at 20°C for 18 h; the solvents were evaporated off and the residue was boiled for 0.5 h in 30 ml of ethanol. This gave 4.47 g (93%) of (I), mp 72-75°C (from benzene). Found, %: C 30.32, H 3.66. $C_4H_6N_4O_3$. Calculated, %: C 30.37, H 3.79. IR spectrum (ν, cm^{-1}): 770 w, 840 m, 1000 m, 1060 w, 1130 w, 1190 s, 1290 s, 1380 w, 1460 w, 1480 w, 1740 s, 2980 m. PMR spectrum (CH_2Cl_2, δ, ppm): 1.4 t (CH_3C), 4.5 q (CH_2).

Ag Salt of 5-Ethoxycarbonyltetrazole (III). A mixture of 0.2 g of (I), 0.1 ml of bromoacetone, and 0.31 g of K_2CO_3 in 5 ml of ethanol was boiled for 3 h, the alcohol was evaporated, and the residue was dissolved in water, acidified with 10% HCl, extracted with ether, and the extract was evaporated down and dissolved in water. The solution was mixed with a saturated solution of $AgNO_3$ and salt (III) was filtered off. Yield 0.1 g (59%). IR spectrum (ν, cm^{-1}): 1080 m, 1190 s, 1230 v.s, 1390 s, 1475 s, 1725 v.s, 2975 m. Its IR spectrum was identical to the IR spectrum of the Ag salt obtained from a known sample of 5-ethoxycarbonyltetrazole.

NH_4 Salt of 1-Hydroxytetrazole-5-carboxamide (VI). a) Ammonia was passed through a solution of 1.5 g of ethyl 1-hydroxytetrazole-5-carboxylate in ethyl acetate until there was no more precipitation of the NH_4 salt of ethyl 1-hydroxytetrazole-5-carboxylate (V). Yield 1.43 g (86%) of (V). IR spectrum (ν, cm^{-1}): 1030 s, 1090 s, 1190 v.s, 1235 s, 1310 s, 1420 s, 1460 s, 1495 s, 1745 s, 2850-3300 s.br. b) Ammonia was passed through a solution of 1.42 g of (V) in MeOH for 1.5 h and the mixture was diluted with ether. A precipitate of 0.87 g (73%) of (VI) was formed, mp 260-264°C (from MeOH). Found, %: C 16.86, H 4.05, N 57.73. $C_2H_6N_6O_2$. Calculated, %: C 16.43, H 4.1, N 57.5. IR spectrum (ν, cm^{-1}): 1255 s, 1420 s, 1670 s, 1720 m, 3050-3300 s.br.

1-Hydroxytetrazole-5-carboxamide (VII). Hydrogen chloride was passed through a suspension of 0.22 g of (VI) in MeOH for several minutes, and the mixture was filtered and evaporated to give 0.15 g (79%) of (VII), mp 248-251°C (with decomp.). IR spectrum (ν, cm^{-1}): 1080 m, 1380 s, 1600 m, 1650 s, 1690 m, 2780 w, 3020 s, 3120 s, 3310 m.

Ethyl 1-Methoxytetrazole-5-carboxylate (VIII). a) To a solution of 0.8 g of (I) in 10 ml of CH_3CN was added 0.7 ml of Et_3N and 0.94 ml of CH_3I and the mixture was kept at 20°C for 6 days; from the residue (0.59 g) by means of TLC on silica gel (benzene–ether, 10:1, as eluent) was isolated 0.4 g of (VIII), mp 34-36°C (from MeOH). Found, %: C 34.76, H 4.8, N 32.58. $C_5H_8N_4O_3$. Calculated, %: C 34.88, H 4.65, N 32.55. IR spectrum (ν, cm^{-1}): 640 m, 720 w, 780 m, 850 w, 950 m, 990 w, 1000 w, 1095 m, 1130 s, 1190 s, 1260 m, 1300 s, 1370 m, 1390 m, 1440 m, 1450 m, 1460 m, 1510 m, 1750 v.s, 2980 w, 3010 w. PMR spectrum (CCl_4, δ, ppm): 1.5 t, 4.45 q (CH_2), 4.37 s (CH_3O).

b) Saturated aqueous solutions of 5.5 g of (I) and 5.88 g of $AgNO_3$ were mixed and the precipitate was filtered off, washed with ethanol and ether, and dried over P_2O_5. This gave 8.7 g (87%) of the Ag salt of ethyl 1-hydroxytetrazole-5-carboxylate (IV). IR spectrum (ν, cm^{-1}): 995 m, 1010 s, 1060 s, 1130 s, 1170 v.s, 1205 s, 1300 s, 1380 s, 1470 s, 1710 v.s.

A suspension of 5.48 g of (IV) in a mixture of 40 ml of absolute CH_3CN and 2.58 ml of CH_3I was agitated at 20°C for 10 days; AgI was removed and from the residue (3.35 g) by means of TLC on silica gel (benzene–ether, 10:1, as eluant) was isolated 2.56 g (72%) of (VIII).

Ethyl 1-Isopropoxytetrazole-5-carboxylate (IX). A suspension of 1 g of (IV) in a mixture of 20 ml of absolute ether and 0.7 ml of i-PrBr was agitated at 20°C for 5 days; the precipitate of AgBr was separated, the solvent was removed, and from the residue by means of TLC on silica gel (benzene–ether, 5:1, as eluant) was isolated 0.54 g (72%) of (IX), mp 45-46°C (from hexane). Found, %: C 42.01, H 6.08, N 28.47. $C_7H_{12}N_4O_3$. Calculated, %: C 42, H 6, N 28. IR spectrum (ν, cm^{-1}): 810 w, 850 w, 895 w, 1010 m, 1050 w, 1100 m, 1110 w, 1190 m, 1280 s, 1385 w, 1740 s, 2990 w. PMR spectrum (C_6H_6, δ, ppm): 1.1 d [$(CH_3)_2C$], 1.05 t (CH_3C), 4.2 q (CH_2), 4.53 m (CH).

1-Methoxytetrazole-5-carboxamide (X). Ammonia was passed through a solution of 1.5 g of (VIII) in 40 ml of ether for 1.5 h with cooling by water; the precipitate was filtered off and 1.04 g (83%) of (X) was obtained, mp 166-167°C (from acetone). Found, %: C 24.47, H 3.48, N 48.72. $C_3H_5N_5O_2$. Calculated, %: C 25.17, H 3.49, N 48.95. IR spectrum (ν, cm^{-1}): 600 s, 950 s, 1380 m, 1720 v.s, 3200 m, 3345 s. PMR spectrum (acetone, δ, ppm): 4.3 s (CH_3O).

1-Methoxytetrazole-5-carboxylic Acid Methylamide (XI). Dry CH_3NH_2 was passed through an ether solution of (VIII) for 1 h. This gave a precipitate of 0.34 g (76%) of (XI), mp 148-149°C (from C_6H_6). Found, %: C 31.40, H 4.36. $C_4H_7N_5O_2$. Calculated, %: C 30.57, H 4.45. IR spectrum (ν, cm^{-1}): 950 s, 1130 m, 1290 m, 1410 m, 1570 s, 1690 v.s, 3333 s.

K Salt of 1-Methoxytetrazole-5-carboxylic Acid (XII). Methanol solutions of 0.51 g of (VIII) and 0.16 g of KOH were combined and the mixture was allowed to stand for 0.5 h. The mixture was diluted with ether and a precipitate of (XII) separated out. Yield 0.38 g (70%) of salt, mp 276-280°C. IR spectrum (ν, cm^{-1}): 790 m, 950 m, 1330 s, 1670 v.s.

Cesium Salt of 1-Methoxytetrazole-5-carboxylic Acid (XIII). Saturated methanol solutions of 0.3 g of (VIII) and 0.24 g of CsOH were combined and the mixture was allowed to stand for 2 h and the salt was precipitated out with ether. Yield 0.36 g (75%) of (XIII), did not melt on heating to 250°C. IR spectrum (ν, cm^{-1}): 795 s, 950 s, 1340 v.s, 1660 v.s.

K Salt of 1-Isopropoxytetrazole-5-carboxylic Acid (XIV). Methanol solutions of 0.52 g of (IX) and 0.15 g of KOH were combined and the mixture was agitated at 20°C for 1 h, evaporated, and the residue was washed with ether to give 0.52 g (95%) of (XIV). Judging by the IR spectrum, (XIV) contained water of crystallization. At 148-151°C water was given off, but the salt did not melt up to 250°C. IR spectrum (ν, cm^{-1}): 805 m, 897 m, 1100 m, 1350 s, 1620 s, 1670 v.s, 3000 m, 3350 m, 3470 s.

Reaction of Cs Salt of 1-Methoxytetrazole-5-carboxylic Acid with $SOCl_2$. To a suspension of 0.35 g of (XIII) in benzene was added dropwise 0.09 ml of $SOCl_2$; the mixture was agitated at 20°C for 1 h, the precipitate was filtered off, the solvent was distilled off, and 0.22 g of an oil was obtained, which contained 1-methoxytetrazole-5-carboxylic acid chloride. Ammonia was passed through an ether solution of the oil obtained and the ether was distilled off; the residue was extracted with acetone and the acetone was evaporated to give 0.05 g (28%) of (X).

CONCLUSIONS

We have developed a method for obtaining ethyl 1-hydroxytetrazole-5-carboxylate from ethoxycarbonylchloroaldoxime. Various derivatives of 1-hydroxytetrazole-5-carboxylic acid have been obtained.

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ACYL DERIVATIVES OF N,N'-DIAMINODIBENZO-18-CROWN-6 ETHER, THEIR COMPLEXING AND CATALYTIC PROPERTIES

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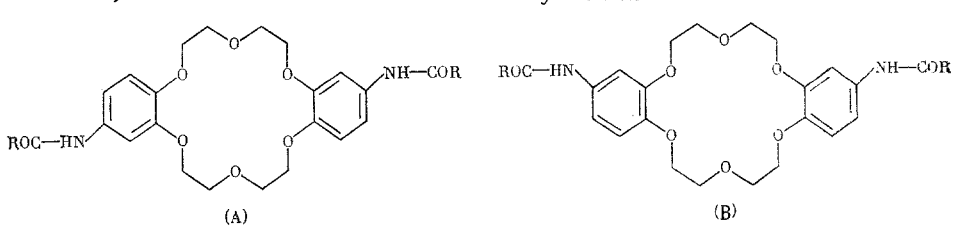
It has already been shown that the complexing ability of dibenzo-18-crown-6 ether (DBC) changes when substituents are introduced into the benzene rings [1]. In the present work, bis-acylamino derivatives of DBC were synthesized, and their complexing ability and catalytic activity in transesterification and polycondensation reactions in the synthesis of poly(ethylene terephthalate) were studied [2, 3]. Derivatives (I)-(V) were obtained by the reactions of 4,4'- or 4,5'-diamino-DBC with acid anhydrides



(A) (B)

R = Me (I); o-$HOOCC_6H_4$ (II); $HOOC(CH_2)_2$ (III); Ph (IV), HCF_2CF_2 (V).

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