Synthesis and Reactions of Halo-, Nitro-, and Arylazo-substituted 3-Aminotropolones. Formation of 8*H*-Cyclohept[*d*]oxazol-8-one Derivatives

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3-Acetamidotropolone (**1a**) reacted with bromine and fuming nitric acid to afford respectively 3-acetamido-7-bromo- (**1b**) and -5,7-dibromotropolone (**1c**) and 3-acetamido-5-nitrotropolone (**1d**). Azo-coupling reaction of **1a** gave 3-acetamido-5-(4-methylphenylazo)tropolone (**1f**). Bromination of **1d** and **1f** gave 7-bromo-substituted compounds **1e** and **1g**, respectively. The compounds **1b-g** were hydrolyzed to afford 3-aminotropolones **4b-g**, which reacted with triethyl orthoformate to give the corresponding 8*H*-cyclohept[*d*]oxazol-8-ones **5b-g**. Heating of 3-acetamidotropolones **1a-d** with polyphosphoric acid gave 2-methyl-8*H*-cyclohept[*d*]oxazol-8-ones **6a-d**.

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3-Aminotropolone, which has both a phenolic hydroxyl group and neighboring amino group, is important starting material for synthesis of heterocycle-fused troponoid compounds. In the chemistry of 3-aminotropolone, it is obtained from reduction of 3-nitrotropolone [1], nucleophilic substitution to 3-halotropolone [2], and Schmidt reaction of 3-acetyltropolone [3]. On the other hand, the tropolone nucleus is well-known to be susceptible to many electrophlic substitution reactions. However, electrophilic substitution reactions of 3- and 5-aminotropolones have been failed [4] in contrast to electrophilic substitution reactions of 4-aminotropolone [5]. These facts might be understood from the reverse electronic contribution of the amino and hydroxyl groups to the reactive 5- and 7- positions. Then, we introduced bromo-, nitro-, and arylazo groups to 3-aminotropolone *via* electrophilic substitution reactions of 3-acetamidotropolone followed by hydrolysis of acetamido group.

This paper deals with preparations of bromo-, nitro-, and arylazo-substituted 3-aminotropolones and their conversion to 8*H*-cyclohept[*d*]oxazol-8-one derivatives.

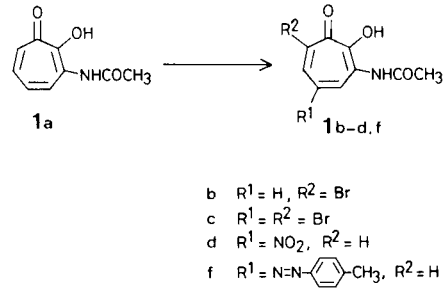
Results and Discussion.

Electrophilic Substitutions of 3-Acetamidotropolone (**1a**).

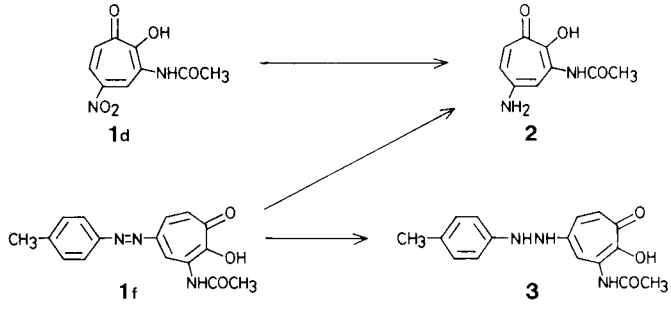
It is well known that tropolones are readily brominated at the 3-, 5- and 7-positions. When 3-acetamidotropolone (**1a**) [2,3] was treated with an equimolar amount of bromine in acetic acid in the presence of sodium acetate afforded 3-acetamido-7-bromo- (**1b**) and -5,7-dibromotropolone (**1c**) in 7.5 and 12% yields, respectively. The use of large excess of acetic acid gave the monobromo compound **1b** in 54% yield. Bromination with two molar equivalents of bromine gave the dibromo compound **1c** in 60% yield. The structures of these compounds **1b** and **1c** were confirmed from the elemental analyses and spectral data. The ^{1}H nmr spectrum of **1b** shows a singlet peak at δ 2.30 for CH_3, a broad peak at δ 9.15 for NH, and three peaks at δ 6.72 (dd, 1H, J = 10.6, 10.6 Hz, H-5), 7.69 (d, 1H, J = 10.6 Hz, H-6), and 9.19 (d, 1H, J = 10.6 Hz, H-4) for the three neighboring ring protons. Two ring proton of **1c** are observed at δ 8.03 (d, 1H, J = 2 Hz) for H-6 and 9.48 (d, 1H, J = 2 Hz) for H-4.

Heating of 3-acetamidotropolone (**1a**) with fuming nitric acid gave 3-acetamido-5-nitrotropolone (**1d**) [6], which was

Scheme 1



Scheme 2

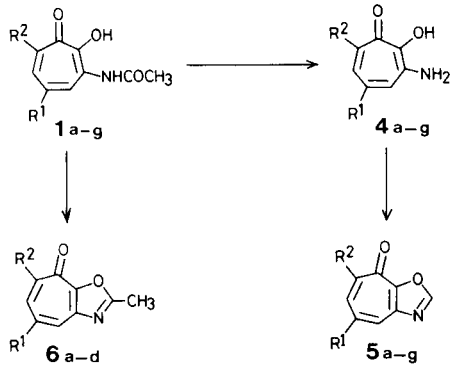


previously obtained by Schmidt reaction of 3-acetyl-5-nitrotropolone. The compound **1d** was brominated to afford 3-acetamido-7-bromo-5-nitrotropolone (**1e**), whose ^{1}H nmr spectrum shows four peaks at δ 2.24 (s, 3H) for CH_3, 8.73 (d, 1H, J = 2 Hz) for H-6, 9.82 (d, 1H, J = 2 Hz) for H-4, and 9.66 (br, 1H) for NH proton. Furthermore, catalytic hydrogenation of the nitro compound **1d** on 5% palladium-charcoal afforded 3-acetamido-5-aminotropolone (**2**) [7].

In general, treatment of tropolones with nitrous acid gave 5-nitrosotropolones. Nitrosation of 3-acetamidotropolone (**1a**) did not give expected 5-nitroso compound but gave 5-nitrotropolone **1d** even under nitrogen atmosphere.

Azo-coupling reaction of 3-acetamidotropolone (**1a**) gave 3-acetamido-5-(4-methylphenylazo)tropolone (**1f**), whose bromination gave 3-acetamido-7-bromo-5-(4-methylphenylazo)tropolone (**1g**). These structures were confirmed by the elemental analyses and spectral data. Catalytic reduction of the compound **1f** on 5% palladium-charcoal gave the 5-amino compound **2** in acetic acid and **3** in ethyl acetate. The structure of the compound **3** was determined to be 3-acetamido-5-[2-(4-methylphenyl)hydrazino]-tropolone by its elemental analysis and spectral data. In the ^{1}H nmr spectrum, two broad peaks at δ 7.72 (1H) for α-NH and 8.65 (1H) for β-NH proton, besides peaks at δ 2.14 (s, 3H) for 4′-CH_3, 2.20 (s, 3H) for $COCH_3$, 6.52-7.08 (m, 5H) for H-2′,3′,5′,6′,6, 7.27 (d, 1H, J = 10.5 Hz) for H-7, 8.88 (d, 1H, J = 2.2 Hz) for H-4, and 9.68 (br, 1H) for 3-NH. This 5-arylhydrazinotropolone **3** is a new type of tropolone.

Scheme 3



a $R^1 = R^2 = H$
b $R^1 = H$, $R^2 = Br$
c $R^1 = R^2 = Br$
d $R^1 = NO_2$, $R^2 = H$
e $R^1 = NO_2$, $R^2 = Br$
f $R^1 = N{=}N{-}C_6H_4{-}CH_3$, $R^2 = H$
g $R^1 = N{=}N{-}C_6H_4{-}CH_3$, $R^2 = Br$

Hydrolysis of 3-Acetamidotropolones.

Previously, we reported that 3-acetamidotropolone (**1a**) was readily hydrolyzed with sulfuric acid to afford 3-aminotropolone (**4a**) [3]. Accordingly, the substituted 3-acetamidotropolones **1b-g** were refluxed for 0.5-2 hours in the presence of 50% sulfuric acid to give the corresponding 3-aminotropolones **4b-g**, respectively, in good yields. It is found that this method is more simple and gave 3-aminotropolones in higher yields than nucleophilic substitution to 3-halotropolones [2].

Cyclization of 3-Aminotropolones with Orthoester.

It is known that 3-aminotropolone reacted with acetic anhydride [2], formamide [8], or *p*-nitrobenzaldehyde [8]. Recently, we also reported cyclization of 3-aminotropolone (**4a**) by using orthoesters [3] and acyl halides [9]. Thus, the orthoester cyclization reaction was applied to the substituted 3-aminotropolones **1b-g** to give the corresponding 8*H*-cyclohept[*d*]oxazol-8-one derivatives **5b-g** in good yields. The structures were confirmed by the elemental analyses and spectral data.

Cyclization of 3-Acetamidotropolones with Polyphosphoric Acid.

In the reaction of 3-aminotropolone with acyl halides, we found that 3-(phenylacetamido)tropolone was cyclized by heating in polyphosphoric acid [9].

A mixture of each 3-acetamidotropolone **1a-d** and polyphosphoric acid was heated at 170° for 4 hours to afford the corresponding 2-methyl-8*H*-cyclohept[d]oxazol-8-ones **6a-d**. On the other hand, the heating of 5-arylazo-substituted compound with polyphosphoric acid did not give 8*H*-cyclohept[*d*]oxazol-8-one but gave tarry material.

EXPERIMENTAL

Measurements.

The ir spectra were taken on a Tiantsin Guangxue WFD-7G spectrophotometer. The ^{1}H nmr spectra were recorded with a JEOL JNM-PMX60 spectrometer.

Bromination of 3-Acetamidotropolone (**1**).

(a) To a stirred solution of **1a** (230 mg, 1.3 mmoles) in acetic acid (5 ml) containing sodium acetate (125 mg) was added dropwise a solution of bromine (200 mg, 1.3 mmoles) in acetic acid (1.5 ml) at room temperature. After additional stirring for 2 hours, the precipitate was collected and recrystallized from ethanol to give 3-acetamido-5,7-dibromotropolone (**1c**) as pale yellow needles, yield 50 mg (12%), mp 210°; ir (potassium bromide): ν max 3350 (NH), 3200 (OH), 1696 (amide C=O), 1591 cm^{-1} (tropone C=O); ^{1}H nmr (deuteriochloroform): δ 2.29 (s, 3H, CH_3), 8.03 (d, 1H, J = 2 Hz, H-6), 9.00 (br, 1H, NH), 9.48 (d, 1H, J = 2 Hz, H-4).

Anal. Calcd. for $C_9H_7Br_2NO_3$: C, 32.08; H, 2.10; N, 4.18. Found: C, 32.22; H, 2.11; N, 4.01.

The filtrate was extracted with ethyl acetate. After drying over sodium sulfate and removal of the solvent, the residue was recrystallized from methanol to give 3-acetamido-7-bromotropolone (**1b**) as pale yellow needles, yield 25 mg (7.5%); mp 178-179°; ir (potassium bromide): ν max 3360 (NH), 3210 (OH), 1694 (amide C=O), 1590 cm^{-1} (tropone C=O); ^{1}H

nmr (deuteriochloroform): δ 2.30 (s, 3H, CH_3), 6.72 (dd, 1H, J = 10.6, 10.6 Hz, H-5), 7.69 (d, 1H, J = 10.6 Hz, H-6), 9.15 (br, 1H, NH), 9.19 (d, 1H, J = 10.6 Hz, H-4).

Anal. Calcd. for $C_9H_8BrNO_3$: C, 42.00; H, 3.13; N, 5.48. Found: C, 41.81; H, 2.98; N, 5.54.

(b) Bromine (200 mg, 1.3 mmoles) was added to a solution of **1a** (230 mg, 1.3 mmoles) in acetic acid (50 ml) in the presence of sodium acetate (125 mg). The mixture was stirred for 2 hours at room temperature. After removal of the solvent under reduced pressure, the residue was diluted with water to give precipitate, which was recrystallized from methanol to afford **1b**, yield 180 mg (54%).

(c) To a stirred solution of **1a** (450 mg, 2.5 mmoles) in acetic acid (10 ml) containing sodium acetate (500 mg) was added dropwise a solution of bromine (800 mg, 5.0 mmoles) in acetic acid (5 ml) at room temperature. The mixture precipitated yellow crystals and was stirred for an additional 1 hour. After removal of the acetic acid under reduced pressure, the residue was diluted with water to give precipitate, which was recrystallized from ethanol to give **1c**, yield 510 mg (60%).

Nitration of 3-Acetamidotropolone (**1a**).

A mixture of fuming nitric acid (200 ml) and acetic acid (0.5 ml) was added dropwise to a cold solution of **1a** (650 mg, 3.6 mmoles) in acetic acid (2 ml) with stirring. After stirring for an additional 2 hours, the precipitate was collected and recrystallized from acetic acid-ethanol to give 3-acetamido-5-nitrotropolone (**1d**) as yellow needles, yield 190 mg (23%), mp 233-234° (lit [6], mp 239-240°).

3-Acetamido-7-bromo-5-nitrotropolone (**1e**).

To a solution of **1d** (220 mg, 1 mmole) in acetic acid (10 ml) containing sodium acetate (200 mg) was added dropwise a solution of bromine (0.1 ml) in acetic acid (1 ml) at room temperature. After stirring for 1 hour, the precipitate was collected and recrystallized from ethanol to afford 3-acetamido-7-bromo-5-nitrotropolone (**1e**) as yellow needles, yield 200 mg (67%), mp 210-211°; ir (potassium bromide): ν max 3300 (NH), 3070 (OH), 1692 (amide C=O), 1591 cm^{-1} (tropone C=O); ^1H nmr (deuteriodimethyl sulfoxide): δ 2.24 (s, 3H, CH_3), 8.73 (d, 1H, J = 2 Hz, H-6), 9.66 (br, 1H, NH), 9.82 (d, 1H, J = 2 Hz, H-4).

Anal. Calcd. for $C_9H_7BrN_2O_5$: C, 35.76; H, 2.34; N, 9.27. Found: C, 35.65; H, 2.15; N, 8.97.

Reduction of 3-Acetamido-5-nitrotropolone (**1d**).

A suspended solution of **1d** (200 mg, 0.9 mmole) and 5% palladium-charcoal (100 mg) in acetic acid (30 ml) was stirred for 3 days at room temperature under hydrogen atmosphere. The catalyst was filterd off and the filtrate was brought to dryness by evaporation of the acetic acid under reduced pressure. The residue was diluted with water, neutralized with saturated sodium hydrogencarbonate solution, and extracted with chloroform. After removal of the solvent, the residue was recrystallized from benzene to give 3-acetamido-5-aminotropolone (**2**), yield 100 mg (58%), mp 270° (lit [7], mp 270°).

Azo-coupling Reaction of 3-Acetamidotropolone (**1a**).

To an ice-cooled solution of **1a** (450 mg, 2.5 mmoles) in pyridine (5 ml) was added dropwise *p*-methylbenzenediazonium chloride solution, prepared from toluidine (300 mg), with stirring under cooling with an ice-water bath. After additional stirring for 2 hours, the mixture was diluted with water to give precipitate, which was collected and recrystallized from ethanol to afford 3-acetamido-5-(4-methylphenylazo)tropolone (**1f**) as red needles, yield 600 mg (80%), mp 184-185°: ir (potassium bromide): ν max 3350 (NH), 3290 (OH), 1680 (amide C=O), 1600 cm^{-1} (tropone C=O); ^1H nmr (deuteriochloroform): δ 2.30 (s, 3H, $COCH_3$), 2.41 (s, 3H, 4′-CH_3), 7.26 (d, 2H, J = 8 Hz, H-3′,5′), 7.54 (d, 1H, J = 11 Hz, H-7), 7.83 (d, 2H, J = 8 Hz, H-2′,6′), 7.91 (dd, 1H, J = 11, 2 Hz, H-6), 9.17 (br, 1H, NH), 9.95 (d, 1H, J = 2 Hz, H-4).

Anal. Calcd. for $C_{16}H_{15}N_3O_3$: C, 64.63; H, 5.09; N, 14.14. Found: C, 64.51; H, 5.08; N, 13.97.

3-Acetamido-7-bromo-5-(4-methylphenylazo)tropolone (**1g**).

To a solution of **1f** (370 mg, 1.2 mmoles) and sodium acetate (200 mg) in acetic acid (20 ml) was added dropwise a solution of bromine (0.1 ml) in acetic acid (1 ml) at room temperature. After stirring for 1 hour, the precipitate was collected and recrystallized from ethanol to afford 3-acetamido-7-bromo-5-(4-methylphenylazo)tropolone (**1g**) as red crystals, yield 300 mg (64%), mp 234°; ir (potassium bromide): ν max 3350 (NH), 3210 (OH), 1718 (amide C=O), 1600 cm^{-1} (tropone C=O); ^1H nmr (deuteriodimethyl sulfoxide): δ 2.26 (s, 3H, $COCH_3$), 2.42 (s, 3H, 4′-CH_3), 7.41 (d, 2H, J = 8 Hz, H-3′,5′), 7.80 (d, 2H, J = 8 Hz, H-2′,6′), 8.35 (s, 1H, H-6), 9.53 (br, 1H, NH), 9.74 (s, 1H, H-4).

Anal. Calcd. for $C_{16}H_{14}BrN_3O_3$: C, 51.19; H, 3.76; N, 11.19. Found: C, 50.94; H, 3.51; N, 10.93.

Reduction of 3-Acetamido-5-(4-methylphenylazo)tropolone (**1f**).

(a) A suspended mixture of **1f** (350 mg, 1.2 mmoles) and 5% palldium-charcoal (100 mg) in acetic acid (30 ml) was stirred for 3 days under hydrogen atmosphere. The catalyst was filtered off and the residue was brought to dryness by evaporation of the acetic acid under reduced pressure. The residue was diluted with water, neutralized with saturated sodium hydrogencarbonate solution, and extracted with chloroform. After removal of the solvent, the residue was recrystallized from benzene to give, **2**, yield 110 mg (48%).

(b) A suspended solution of **1f** (35 mg, 1.2 mmoles) and 5% palladium-charcoal (100 mg) in ethyl acetate (25 ml) was stirred for 3 days under hydrogen atmosphere. After removal of the catalyst and evaporation of the solvent, the residue was recrystallized from benzene to give 3-acetamido-5-[2-(4-methylphenyl)hydrazino]tropolone (**3**), yield 300 mg (85%), mp 160°; ir (potassium bromide): ν max 3325 (NH), 3270 (NH), 3050 (OH), 1690 (amide C=O), 1600 cm^{-1} (tropone C=O); ^1H nmr (deuteriochloroform-deuteriodimethyl sulfoxide): δ 2.14 (s, 3H, $COCH_3$), 2.20 (s, 3H, 4′-CH_3), 6.52-7.08 (m, 5H), 7.27 (d, 1H, J = 10.4 Hz, H-7), 7.72 (br, 1H, NH), 8.65 (br, 1H, NH), 8.88 (d, 1H, J = 2.2 Hz, H-4), 9.68 (br, 1H, NHCO).

Anal. Calcd. for $C_{16}H_{17}N_3O_3$: C, 64.20; H, 5.72; N, 14.04. Found: C, 64.50; H, 5.75; N, 13.80.

Hydrolysis of 3-Acetamidotropolones **1b-g**.

A mixture of one of 3-acetamidotropolone derivatives **1b-g** (0.36 mmole) and 50% sulfuric acid (3 ml) in methanol (10 ml) was refluxed. After removal of the solvent, the residue was neutralized with saturated sodium hydrogencarbonate solution and made again slightly acidic with 30% acetic acid. The precipitate was collected and recrytallized to give 3-aminotropolones **4b-g**, respectively.

3-Amino-7-bromotropolone (**4b**).

Hydrolysis of **1b** (5 mg, 0.36 mmole) for 0.5 hour gave 3-amino-7-bromotropolone (**4b**) as greenish yellow crystals (from benzene-hexane), yield 68 mg (87%), mp 189° (lit [2], mp 196°).

3-Amino-5,7-dibromotropolone (**4c**).

Hydrolysis of **1c** (120 mg, 0.36 mmole) for 1 hour gave 3-amino-5,7-dibromotropolone (**4c**) as yellow crystals (from benzene), yield 100 mg (95%), mp 234° (lit [2], mp 237°).

3-Amino-5-nitrotropolone (**4d**).

Hydrolysis of **1d** (80 mg, 0.36 mmole) for 1 hour gave 3-amino-5-nitrotropolone (**4d**) as red needles (from ethanol-water), yield 27 mg (41%), mp 202° (lit [7], mp 204° dec).

3-Amino-7-bromo-5-nitrotropolone (**4e**).

Hydrolysis of **1e** (110 mg, 0.36 mmole) for 1 hour gave 3-amino-7-bromo-5-nitrotropolone (**4e**) as red needles (from benzene-hexane), yield 85 mg (90%), mp 198-199°; ir (potassium bromide): ν max 3775 (NH), 3475 (NH), 3225 (OH), 1630 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 7.10 (br, 2H, NH_2), 8.20 (d, 1H, J = 2 Hz, H-4), 8.38 (d, 1H, J = 2 Hz, H-6).

Anal. Calcd. for $C_7H_5BrN_2O_4$: C, 32.31; H, 1.94; N, 10.77. Found: C, 32.05; H, 1.90; N, 10.50.

3-Amino-5-(4-methylphenylazo)tropolone (**4f**).

Hydrolysis of **1f** (110 mg, 0.36 mmole) for 2 hours gave 3-amino-5-(4-methylphenylazo)tropolone (**4f**) as red needles (from ethanol), yield 75 mg (80%), mp 224°; ir (potassium bromide): ν max 3440 (NH), 3370 (NH), 3200 (OH), 1630 cm^{-1} (C=O); ^1H nmr (deuteriodimethyl sulfoxide): δ 2.55 (s, 3H, CH_3), 7.16-7.86 (m, 9H).

Anal. Calcd. for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.60; H, 5.00; N, 16.48.

3-Amino-7-bromo-5-(4-methylphenylazo)tropolone (**4g**).

Hydrolysis of **1g** (135 mg, 0.36 mmole) for 2 hours gave 3-amino-7-bromo-5-(4-methylphenylazo)tropolone (**4g**) as red needles (from ethanol), yield 91 mg (76%), mp 210°; ir (potassium bromide): ν max 3475 (NH), 3350 (NH), 3220 (OH), 1610 cm^{-1} (C=O); ^1H nmr (deuteriodimethyl sulfoxide): δ 2.47 (s, 3H, CH_3), 7.33 (br, 2H, NH_2), 7.35-7.90 (m, 5H), 8.11 (d, 1H, J = 2 Hz, H-6).

Anal. Calcd. for $C_{14}H_{12}BrN_3O_2$: C, 50.32; H, 3.62; N, 12.58. Found: C, 50.27; H, 3.66; N, 12.25.

Reaction of 3-Aminotropolones (**4b-g**) with Triethyl Orthoformate.

A mixture of one of 3-aminotropolone derivatives **4b-g** (1 mmoles) and triethyl orthoformate (3 ml) was refluxed for 2 hours. After removal of the excess of triethyl orthoformate under reduced pressure, the residue was recrystallized to give 8*H*-cyclohept[*d*]oxazolo-8-ones **5b-g**, respectively.

7-Bromo-8*H*-cyclohept[*d*]oxazol-8-one (**5b**).

This compound was obtained in a yield of 199 mg (88%), mp 214° (from chloroform-hexane); ir (potassium bromide): ν max 1635 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 6.97 (dd, 1H, J = 10, 10 Hz, H-5), 7.72 (d, 1H, J = 10 Hz, H-6), 8.24 (s, 1H, H-2), 8.32 (d, 1H, J = 2 Hz, H-4).

Anal. Calcd. for $C_8H_4BrNO_2$: C, 42.64; H, 1.79; N, 6.26. Found: C, 42.52; H, 1.50; N, 6.00.

5,7-Dibromo-8*H*-cyclohept[*d*]oxazol-8-one (**5c**).

This compound was obtained in a yield of 275 mg (90%), mp 236° (from ethanol-acetic acid); ir (potassium bromide): ν max 1629 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 8.29 (d, 1H, J = 2 Hz, H-6), 8.68 (d, 1H, J = 2 Hz, H-4), 9.04 (s, 1H, H-2).

Anal. Calcd. for $C_8H_3Br_2NO_2$: C, 31.50; H, 0.99; N, 4.62. Found: C, 31.27; H, 0.86; N, 4.49.

5-Nitro-8*H*-cyclohept[*d*]oxazol-8-one (**5d**).

This compound was obtained in a yield of 172 mg (89%), mp 220° (from benzene-hexane); ir (potassium bromide): ν max 1640 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 7.41 (d, 1H, J = 14 Hz, H-7), 8.31 (dd, 1H, J = 14, 2.2 Hz, H-6), 8.35 (s, 1H, H-2), 8.86 (d, 1H, J = 2.2 Hz, H-4).

Anal. Calcd. for $C_8H_4N_2O_4$: C, 50.01; H, 2.10; N, 14.58. Found: C, 50.24; H, 1.83; N, 14.40.

7-Bromo-5-nitro-8*H*-cyclohept[*d*]oxazol-8-one (**5e**).

This compound was obtained in a yield of 163 mg (60%), mp 152° (from benzene-hexane); ir (potassium bromide): ν max 1643 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 8.44 (s, 1H, H-2), 8.98 (d, 1H, J = 2 Hz, H-6), 9.27 (d, 1H, J = 2 Hz, H-4).

Anal. Calcd. for $C_8H_3BrN_2O_4$: C, 35.56; H, 1.11; N, 10.37. Found: C, 35.39; H, 0.89; N, 10.50.

5-(4-Methylphenylazo)-8*H*-cyclohept[*d*]oxazol-8-one (**5f**).

This compound was obtained in a yield of 213 mg (80%), mp 210-211° (from benzene-hexane); ir (potassium bromide): ν max 1635 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.43 (s, 3H, CH_3), 7.30 (d, 2H, J = 8 Hz, H-3',5'), 7.41 (d, 1H, J = 14 Hz, H-7), 7.83 (d, 2H, J = 8 Hz, H-2',6'), 8.25 (dd, 1H, J = 14, 2 Hz, H-6), 8.26 (s, 1H, H-2), 8.31 (d, 1H, J = 2 Hz, H-4).

Anal. Calcd. for $C_{15}H_{11}N_3O_2$: C, 67.91; H, 4.18; N, 15.84. Found: C, 67.66; H, 4.03; N, 15.57.

7-Bromo-5-(4-methylphenylazo)-8*H*-cyclohept[*d*]oxazol-8-one (**5g**).

This compound was obtained in a yield of 138 mg (40%), mp 220° (from benzene-hexane); ir (potassium bromide): ν max 1939 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.48 (s, 3H, CH_3), 7.36 (d, 2H, J = 8 Hz, H-3',5'), 7.90 (d, 2H, J = 8 Hz, H-2',6'), 8.36 (s, 1H, H-2), 8.46 (d, 1H, J = 2 Hz, H-6), 9.21 (d, 1H, J = 2 Hz, H-4).

Anal. Calcd. for $C_{15}H_{10}BrN_3O_2$: C, 52.47; H, 2.94; N, 12.24. Found: C, 52.30; H, 2.73; N, 11.95.

Cyclization of 3-Acetamidotropolones **1a-d** with Polyphosphoric Acid.

A mixture of 3-acetamidotropolone derivative **1a-d** (2.4 mmoles) and polyphosphoric acid (3 ml) was heated for 4 hours at 170°. The reaction mixture was cooled, diluted with water, and extracted with chloroform. The extract was washed twice with saturated sodium hydrogencarbonate solution and twice with water and dried over sodium sulfate. After removal of the solvent, the residue was recrystallized from benzene-hexane to give 2-methyl-8*H*-cyclohept[*d*]oxazol-8-ones **6a-d**.

2-Methyl-8*H*-cyclohept[*d*]oxazol-8-one (**6a**).

This compound was obtained in a yield of 250 mg (65%), mp 150° (lit [2], mp 150-151°).

7-Bromo-2-methyl-8*H*-cyclohept[*d*]oxazol-8-one (**6b**).

This compound was obtained in a yield of 400 mg (70%), mp 169° (lit [2], mp 163-164°).

5,7-Dibromo-2-methyl-8*H*-cyclohept[*d*]oxazol-8-one (**6c**).

This compound was obtained in a yield of 540 mg (71%), mp 202° (lit [2], mp 198-199°).

2-Methyl-5-nitro-8*H*-cyclohept[*d*]oxazol-8-one (**6d**).

This compound was obtained in a yield of 200 mg (40%), mp 202° (lit [7], mp 202° dec).

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