Synthesis and Reactions of Halo-, Nitro-, and Arylazo-substituted 3-Acetyltropolones. Formation of Heterocycle-fused Troponoid Compounds

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Received November 5, 1986

3-Acetyltropolone (**1**) reacted with bromine, iodine, and nitric acid to afford respectively 3-acetyl-5,7-dibromotropolone (**2**), 3-acetyl-7-iodotropolone (**3**), and 3-acetyl-5-nitro- (**4**) and 3-acetyl-5,7-dinitrotropolone (**5**). Azo-coupling reactions of **1** gave 3-acetyl-5-arylazotropolones **7a-f**. The Schmidt reactions of **2** and **3** gave respectively 5,7-dibromo- (**9**) and 7-iodo-2-methyl-8*H*-cyclohept[*d*]oxazol-8-one (**10**), while **4** gave 3-acetamido-5-nitrotropolone (**11**). Compounds **2** and **4** reacted with hydroxylamine to give 3-methyl-8*H*-cyclohept[*d*]isoxazol-8-ones **12** and **13**. The reactions of **2**, **3**, and **4** with hydrazine gave 3-methyl-1,8-dihydrocycloheptapyrazol-8-ones **15**, **16**, and **17**.

J. Heterocyclic Chem., **24**, 779 (1987).

Recently, we reported many nucleophilic reactions of 3-acetyltropolone [1]. The reactions with nucleophiles having two reaction centers are very useful for the synthesis of heterocycle-fused troponoid compounds. On the other hand, tropolone nucleus is well-known to be susceptible to many electrophilic reactions [2]. There are many electrophilic reactions of alkyl-substituted tropolones, while the reactions of tropolones having carbonyl side-chains are little known except for 3-acetonyltropolone [3] and 4-acetyltropolone [4].

The present paper deals with the electrophilic substitution reactions of 3-acetyltropolone and the conversions of these products to heterocycle-fused troponoid compounds.

Results and Discussion.

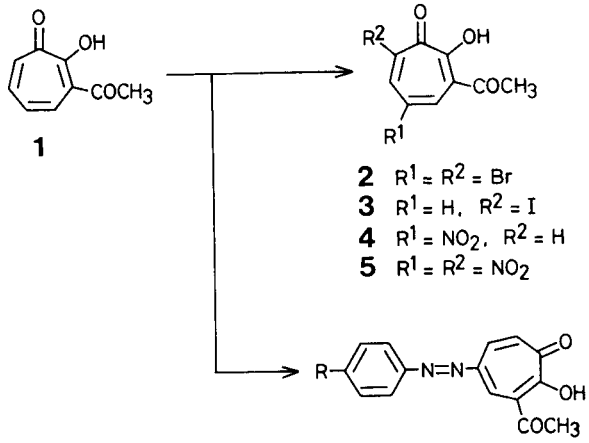
Electrophilic Substitutions of 3-Acetyltropolone (1).

It is well-known that tropolones are readily brominated at the 3-, 5-, and 7-positions, predominantly at the 3-position. When 3-acetyltropolone (**1**) was treated with an equimolar amount of bromine, dibromo-substituted compound **2** was obtained in 34% yield, the starting material **1** recovering in 20% yield. Compound **2** was shown to be 3-acetyl-5,7-dibromotropolone from its elemental analysis ($C_9H_6Br_2O_3$) and spectral data. The ^1H nmr spectrum shows only three peaks at δ 2.66 (s, 3H) for CH_3, 7.90 (d, 1H, J = 2.2 Hz) for H-6, and 8.46 (d, 1H, J = 2.2 Hz) for H-4. The reaction with two molar equivalents of bromine gave **2** in 50% yield.

Although the bromination of 4-acetyltropolone gave mono-, di-, and tri-substituted products according to the reaction conditions [4], the reactions of 3-acetyltropolone (**1**) gave only 5,7-dibromo-substituted compound. The reaction with *N*-bromosuccinimide (NBS) also afforded **2** in 21% yield as a sole product.

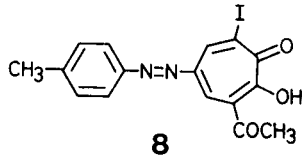
On the other hand, the iodination of tropolone requires the presence of carbonate. Then substitution takes place at the 3- and 7-positions. The reaction of **1** with an equimolar amount of iodine in the presence of potassium carbonate afforded only mono-substituted product **3** in 30% yield. Compound **3** was shown to be 3-acetyl-7-iodotropolone from its elemental analysis ($C_9H_7IO_3$) and spectral data. In the ^1H nmr spectrum, the three ring protons are observed at δ 6.73 (dd, 1H, J = 10.6 and 10.2 Hz) for H-5, 7.62 (d, 1H, J = 10.6 Hz) for H-6, and 8.42 (d, 1H, J = 10.2 Hz) for H-4, besides the acetyl peak at 2.68 (s, 3H). These signals support the existence of three neighboring ring protons.

Scheme 1



3-Acetyltropolone (**1**) treated with fuming nitric acid to give mononitro-substituted compound **4** in 21% yield in analogy with 4-acetyltropolone [5]. The structure was determined to be 3-acetyl-5-nitrotropolone from its elemental analysis ($C_9H_7NO_5$) and spectral data. The ^1H nmr spectrum shows three peaks at δ 7.35 (d, 1H, J = 11.5 Hz) for H-7, 8.64 (dd, 1H, J = 11.5 and 2.5 Hz) for H-6, and 8.95 (d, 1H, J = 2.5 Hz) for H-4, besides a singlet peak at δ 2.70 (s, 3H) for CH_3. The reaction of the compound **4** with sodium dithionate gave 3-acetyl-5-aminotropolone (**6**) in 42% yield. Further, the nitration of **1** with an excess of concentrated nitric acid gave dinitro-substituted compound **5** in 15% yield, which was 3-acetyl-5,7-dinitrotropolone. However, nitrosation of 3-acetyltropolone (**1**) failed and the starting material **1** was recovered.

Azo-coupling reaction of tropolone takes place at the 5-position to give crystalline dyes. The reactions of **1** with a various arenediazonium salts gave exclusively 5-arylazo-substituted 3-acetyltropolones **7a-f** in good yields. Their structures were confirmed by their elemental analysis and spectral data (see: Experimental part). Compound **3** also gave 3-acetyl-7-iodo-5-(4-methylphenylazo)tropolone (**8**) in 56% yield. In addition, the compound **7b** was converted into 3-acetyl-5-aminotropolone (**6**) in 32% yield by the reduction with sodium dithionate.



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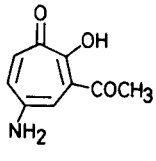

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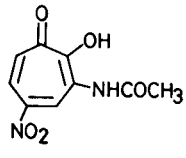

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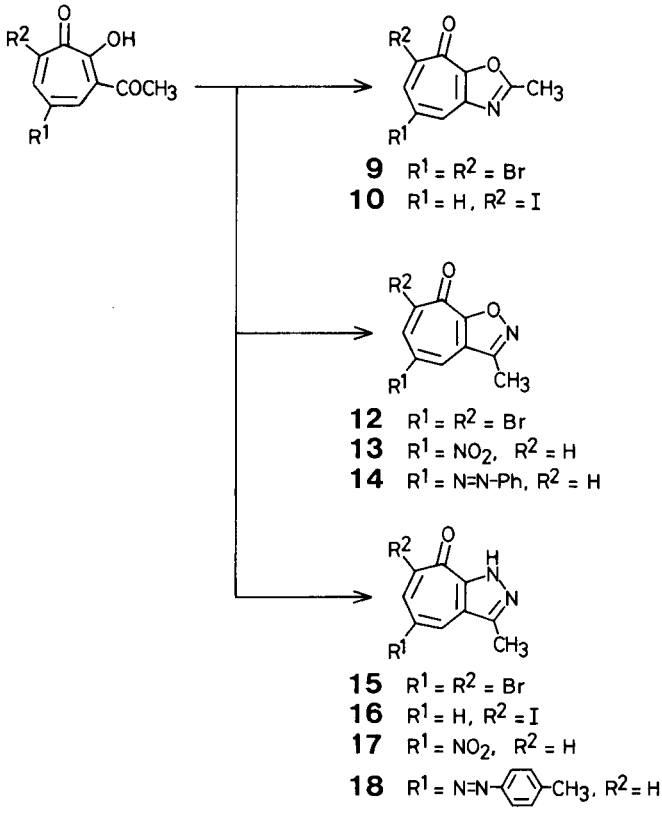
Figure 1

Reactions of 3-Acetyltropolone Derivatives with Hydrazoic Acid, Hydroxylamine, and Hydrazine.

The Schmidt reaction of 3- and 4-acetyltropolones gave 3-acetamidotropolone [6] and 4-aminotropolone [5], respectively. The former was hydrolyzed to afford 3-aminotropolone. This reaction was applied to 5,7-dibromo-substituted 3-acetyltropolone **2** to give cyclized product, 5,7-dibromo-2-methyl-8*H*-cyclohept[*d*]oxazol-8-one (**9**) [7] in 69% yield. Similarly, 3-acetyl-7-iodotropolone (**3**) reacted with hydrazoic acid to afford 7-iodo-2-methyl-8*H*-cyclohept[*d*]oxazol-8-one (**10**) in 39% yield, which was confirmed by its elemental analysis and spectral data. It is noteworthy that the Schmidt reaction of 3-acetyltropolone derivatives gave 8*H*-cyclohept[*d*]oxazol-8-ones. However, the reaction of 3-acetyl-5-nitrotropolone (**4**) gave 3-acetamido-5-nitrotropolone (**11**) in 47% yield by the Schmidt-type rearrangement, although we previously isolated 3-acetamidotropolone in the similar manner [6]. The ir spectrum of **11** shows four typical absorptions at 3450 (NH), 3250 (OH), 1690 (acetyl C=O), and 1610 cm^{-1} (tropone C=O).

Scheme 2



Previously, we found that 3-acetyltropolone (**1**) reacted with hydroxylamine and hydrazine to give respectively 3-methyl-8*H*-cyclohept[*d*]isoxazol-8-one [8] and 3-methyl-1,8-dihydrocycloheptapyrazol-8-one [9]. Then a mixture of 3-acetyl-5,7-dibromotropolone (**2**) and hydroxylamine in methanol was refluxed for 3 hours to give 5,7-dibromo-3-methyl-8*H*-cyclohept[*d*]isoxazol-8-one (**12**) in 29% yield. The structure was confirmed by its elemental analysis and spectral data. The ir spectrum shows a carbonyl absorption at 1620 cm^{-1}. In the ^1H nmr spectrum, a singlet peak for the methyl at δ 2.63 and two doublet peaks at δ 7.70 (J = 1.7 Hz) for H-6 and 8.62 (J = 1.7 Hz) for H-4. 5-Nitro- **4** and 5-phenylazo-substituted 3-acetyltropolone also reacted with hydroxylamine to give the corresponding 8*H*-cyclohept[*d*]isoxazol-8-ones **13** and **14** in 54 and 64% yields, respectively.

When a solution of 3-acetyl-5,7-dibromotropolone (**2**) and hydrazine hydrate in methanol was heated under

reflux for 1 hour, 5,7-dibromo-1,8-dihydrocycloheptapyrazol-8-one (**15**) in 64% yield, which was confirmed by its elemental analysis and spectral data. The ir spectrum shows absorptions for the NH and C=O groups at 3170 and 1620 cm^{-1}, respectively. Similarly, the reactions of 7-iodo- (**3**) and 5-nitro-3-acetyltropolone (**4**) gave 3-methyl-1,8-dihydrocycloheptapyrazol-8-ones **16** and **17** in 42 and 44% yields, respectively. 3-Methyl-5-(4-methylphenylazo)-1,8-dihydrocycloheptapyrazol-8-one (**18**) was also obtained in a similar manner.

EXPERIMENTAL

Measurements.

The ir spectra were taken on a Tiantsin Guangxue WFD-7G spectrophotometer. The ^1H nmr spectra were recorded with a JEOL FX-100 spectrometer.

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

(a) To a stirred solution of **1** (1.6 g, 10 mmoles) and sodium acetate (1.2 g, 15 mmoles) in acetic acid (30 ml) was added dropwise a solution of bromine (1.8 g, 11 mmoles) in acetic acid (2 ml) under cooling with an ice-water bath. After stirring for 3 hours, the mixture was diluted with water (30 ml). The precipitate was collected and recrystallized from methanol to afford 3-acetyl-5,7-dibromotropolone (**2**) as yellow needles, yield 1.1 g (34%), mp 173-174°; ir (potassium bromide): ν max 3180 (OH), 1700 (C=O), 1595 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.66 (s, 3H, CH_3), 7.90 (d, 1H, J = 2.2 Hz, H-6), 8.64 (d, 1H, J = 2.2 Hz, H-4).

Anal. Calcd. for $C_9H_6Br_2O_3$: C, 33.57; H, 1.88. Found: C, 33.80; H, 1.90.

(b) A solution of bromine (5.4 g, 40 mmoles) in acetic acid (8 ml) was added to an ice-cooled solution of **1** (3.28 g, 20 mmoles) in acetic acid (10 ml) with stirring. The mixture was stirred for 2 hours and worked up, as mentioned above, to give **2**, yield 3.2 g (50%).

(c) A mixture of **1** (500 mg, 3 mmoles) and NBS (534 mg, 3 mmoles) in dioxane (5 ml) was heated on a water bath for 5 minutes. After cooling, the mixture was poured into water to afford the crystals, which were collected, washed with a sodium sulfite solution, and recrystallized from methanol to give **2**, yield 200 mg (21%).

Iodination of 3-Acetyltropolone (**1**).

A stirred solution of iodine (2.24 g, 8.8 mmoles) and potassium iodide (2.24 g, 13.5 mmoles) in water (6 ml) was added dropwise into an ice-cooled solution of **1** (1.3 g, 8 mmoles) and potassium carbonate (2.44 g, 17.7 mmoles) in water (6 ml). After additional stirring for 1 hour, the mixture was washed with a sodium hydrogensulfite solution to remove an excess of iodine. The precipitate was collected and dissolved in hot water. The solution was acidified with 6*M* hydrochloric acid to give the crystals which were recrystallized from methanol to give 3-acetyl-7-iodotropolone (**3**) as greenish yellow needles, yield 700 mg (30%), mp 140-141°; ir (potassium bromide): ν ma 3120 (OH), 1700 (C=O), 1600 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.68 (s, 3H, CH_3), 6.73 (dd, 1H, J = 10.6, 10.2 Hz, H-5), 7.62 (d, 1H, J = 10.6 Hz, H-6), 8.42 (d, 1H, J = 10.2 Hz, H-4).

Anal. Calcd. for $C_9H_7IO_3$: C, 37.27; H, 2.43. Found: C, 37.06; H, 2.34.

Nitration of 3-Acetyltropolone (**1**).

(a) A mixture of fuming nitric acid (0.8 g, 12 mmoles) and acetic acid (2 ml) was added dropwise into a ice-cooled solution of **1** (1.6 g, 10 mmoles) in acetic acid (2 ml). After stirring for 1 hour, the precipitate was collected and recrystallized from methanol to give 3-acetyl-5-nitrotropolone (**4**) as yellow needles, yield 430 mg (21%), mp 138-139°; ir (potassium bromide): ν max 3200 (OH), 1700 (C=O), 1615 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.70 (s, 3H, CH_3), 7.35 (d, 1H, J = 11.5 Hz, H-7), 8.64 (dd, 1H, J = 11.5, 2.5 Hz, H-6), 8.95 (d, 1H, J = 2.5 Hz, H-4).

Anal. Calcd. for $C_9H_7NO_5$: C, 51.68; H, 3.37; N, 6.70. Found: C, 51.53; H, 3.60; N, 6.69.

(b) To an ice-cooled solution of **1** (1.6 g, 10 mmoles) in acetic acid (5 ml) was added dropwise concentrated nitric acid (d = 1.4) (2.5 ml). After stirring for 2 hours, the mixture was diluted with water (25 ml). The precipitate was collected and recrystallized from methanol to give 3-acetyl-5,7-dinitrotropolone (**5**) as yellow needles, yield 380 mg (15%), mp 124-125°; ir (potassium bromide): ν max 3190 (OH), 1690 (C=O), 1600 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.75 (s, 3H, CH_3), 8.82 (d, 1H, J = 2.5 Hz, H-6), 8.90 (d, 1H, J = 2.5 Hz, H-4).

Anal. Calcd. for $C_9H_6N_2O_7$: C, 42.53; H, 2.38; N, 11.02. Found: C, 47.57; H, 2.66; N, 11.23.

3-Acetyl-5-aminotropolone (**6**).

A suspension of 3-acetyl-5-nitrotropolone (**4**) (420 mg, 2 mmoles) in 10% sodium hydroxide solution (10 ml) was stirred at 50° in the presence of sodium dithionate (3.5 g). After disappearance of the color of the solution, the mixture was cooled and filtered. The filtrate was neutralized with 6*M* hydrochloric acid to give the precipitate. The precipitate was dissolved in water and neutralized with a saturated sodium hydrogencarbonate solution to give 3-acetyl-5-aminotropolone (**6**) as greenish yellow needles, yield 150 mg (42%), mp 98-99°; ir (potassium bromide): ν max 3480 (NH), 3220 (OH), 1685 (C=O), 1610 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.58 (s, 3H, CH_3), 3.47 (br, 2H, NH_2), 6.8-7.0 (m, 3H), 11.72 (br, 1H, OH).

Anal. Calcd. for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.47; H, 5.29; N, 8.09.

Azo-coupling Reactions of 3-Acetyltropolone (**1**).

To an ice-cooled solution of **1** (820 mg, 5 mmoles) in pyridine (10 ml) was added dropwise arenediazonium chloride solution, prepared from anilines (5.5 mmoles), with stirring under cooling with an ice-water bath. After additional stirring for 2 hours, the mixture was diluted with water (10 ml) to precipitate 3-acetyl-5-arylazotropolone **7a-f** as red needles (from benzene).

3-Acetyl-5-phenylazotropolone (**7a**).

This compound was obtained in a yield of 385 mg (29%), mp 144-145°; ir (potassium bromide): ν max 3400 (OH), 1700 (C=O), 1600 cm^{-1} (C=O).

Anal. Calcd. for $C_{15}H_{12}N_2O_3$: C, 67.15; H, 4.51; N, 10.44. Found: C, 67.42; H, 4.36; N, 10.39.

3-Acetyl-5-(4-methylphenylazo)tropolone (**7b**).

This compound was obtained in a yield of 884 mg (63%), mp 167-168°; ir (potassium bromide): ν max 3400 (OH), 1700 (C=O), 1600 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.40 (s, 3H, Ar-CH_3), 2.66 (s, 3H, $COCH_3$), 7.20 (d, 2H, J = 8.0 Hz, H-3',5'), 7.43 (d, 1H, J = 11.0 Hz, H-7), 7.74 (d, 2H, J = 8.0 Hz, H-2',6'), 8.21 (dd, 1H, J = 11.0, 2.0 Hz, H-6), 8.40 (d, 1H, J = 2.0 Hz, H-4).

Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92. Found: C, 68.22; H, 4.98; N, 9.73.

3-Acetyl-5-(4-methoxyphenylazo)tropolone (**7c**).

This compound was obtained in a yield of 1.12 g (75%), mp 182-183°; ir (potassium bromide): ν max 3240 (OH), 1710 (C=O), 1610 cm^{-1} (C=O).

Anal. Calcd. for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.19; H, 4.69; N, 9.42.

3-Acetyl-5-(4-chlorophenylazo)tropolone (**7d**).

This compound was obtained in a yield of 992 mg (65%), mp 168-169°; ir (potassium bromide): ν max 3400 (OH), 1700 (C=O), 1610 cm^{-1} (C=O).

Anal. Calcd. for $C_{15}H_{11}ClN_2O_3$: C, 59.31; H, 3.65; N, 9.26. Found: C, 59.33; H, 3.80; N, 9.26.

3-Acetyl-5-(4-bromophenylazo)tropolone (**7e**).

This compound was obtained in a yield of 1.46 g (84%), mp 153-154°; ir (potassium bromide): ν max 3445 (OH), 1700 (C=O), 1610 cm^{-1} (C=O).

Anal. Calcd. for $C_{15}H_{11}BrN_2O_3$: C, 51.89; H, 3.19; N, 8.07. Found: C, 51.65; H, 3.27; N, 7.89.

3-Acetyl-5-(4-nitrophenylazo)tropolone (**7f**).

This compound was obtained in a yield of 1.0 g (64%), mp 164-165°, ir (potassium bromide): ν max 3350 (OH), 1700 (C=O), 1610 cm^{-1} (C=O).

Anal. Calcd. for $C_{15}H_{11}N_2O_5$: C, 57.51; H, 3.54; N, 13.42. Found: C, 57.42; H, 3.45; N, 13.47.

3-Acetyl-7-iodo-5-(4-methylphenylazo)tropolone (**8**).

3-Acetyl-7-iodotropolone (**3**) (500 mg, 2 mmoles) was treated with 4-methylbenzenediazonium chloride, prepared from *p*-toluidine (235 mg, 2.2 mmoles), and worked up, as mentioned above, to give 3-acetyl-7-iodo-5-(4-methylphenylazo)tropolone (**8**) as red needles (from benzene), yield 454 mg (56%), mp 201-202°; ir (potassium bromide): ν max 3420 (OH), 1705 (C=O), 1600 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.46 (s, 3H, Ar-CH_3), 2.73 (s, 3H, $COCH_3$), 7.37 (d, 2H, J = 8.0 Hz, H-3′,5′), 7.84 (d, 2H, J = 8.0 Hz, H-2′,6′), 8.40 (d, 1H, J = 2.2 Hz, H-6), 9.20 (d, 1H, J = 2.2 Hz, H-4).

Anal. Calcd. for $C_{16}H_{13}IN_2O_3$: C, 47.08; H, 3.21; N, 6.86. Found: C, 47.23; H, 3.15; N, 6.71.

Reduction of 3-Acetyl-5-(4-methylphenylazo)tropolone (**7b**).

A suspension of **7b** (1.0 g, 3.5 mmoles) in 10% sodium hydroxide solution (25 ml) was treated with sodium dithionate (6 g) and worked up, as mentioned above, to give **6**, yield 200 mg (32%).

2-Methyl-8*H*-cyclohept[*d*]oxazol-8-ones.

To a suspension of 3-acetyltropolone derivative **2** or **3** (1.5 mmoles) and sodium azide (200 mg) in chloroform (6 ml) was added dropwise concentrated sulfuric acid (1 ml) with stirring at room temperature. After additional stirring for 2 hours, the chloroform was removed by decantation. The residue was diluted with water (5 ml) to precipitate the crystals which were recrystallized from acetone to give 2-methyl-8*H*-cyclohept[*d*]oxazol-8-one **9** or **10**, respectively.

5,7-Dibromo-2-methyl-8*H*-cyclohept[*d*]oxazol-8-one (**9**).

This compound was obtained as colorless needles in a yield of 220 mg (69%), mp 202° (lit [7] 198-199°); ir (potassium bromide): ν max 1630 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.71 (s, 3H, CH_3), 8.00 (d, 1H, J = 1.7 Hz, H-6), 8.57 (d, 1H, J = 1.7 Hz, H-4).

7-Iodo-2-methyl-8*H*-cyclohept[*d*]oxazol-8-one (**10**).

This compound was obtained as colorless needles in a yield of 166 mg (39%), mp 181-182°; ir (potassium bromide): ν max 1635 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.72 (s, 3H, CH_3), 6.83 (dd, 1H, J = 10.7, 9.8 Hz, H-5), 7.65 (dd, 1H, J = 10.7, 0.7 Hz, H-6), 8.69 (dd, 1H, J = 9.8, 0.7 Hz, H-4).

Anal. Calcd. for $C_9H_6INO_2$: C, 36.66; H, 2.11; N, 4.88. Found: C, 36.84; H, 1.95; N, 4.78.

3-Acetamido-5-nitrotropolone (**11**).

A suspension of 3-acetyl-5-nitrotropolone (**4**) (100 mg, 0.5 mmole) and sodium azide (100 mg) in chloroform (3 ml) was treated with concentrated sulfuric acid (0.5 ml) and worked up, as mentioned above, to give 3-acetamido-5-nitrotropolone (**11**) as yellow needles (from methanol), yield 50 mg (47%), mp 239-240°; ir (potassium bromide): ν max 3450 (NH), 3250 (OH), 1690 (C=O), 1610 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.35 (s, 3H, CH_3), 7.50 (d, 1H, J = 11.0, H-7), 8.45 (dd, 1H, J = 11.0, 1.8 Hz, H-6), 9.18 (br, 1H, NH), 10.38 (d, 1H, J = 1.8 Hz, H-4).

Anal. Calcd. for $C_9H_8N_2O_5$: C, 48.22; H, 3.60; N, 12.50. Found: C, 48.01; H, 3.60; N, 12.22.

3-Methyl-8*H*-cyclohept[*d*]isoxazol-8-ones.

A mixture of 3-acetyltropolone derivative **2**, **4**, or **7a** (2 mmoles) and hydroxylamine hydrochloride (279 mg, 4 mmoles) in methanol (20 ml) was refluxed for 3 hours. After cooling, the precipitate was collected and recrystallized from ethanol to give 3-methyl-8*H*-cyclohept[*d*]isoxazol-8-one **12**, **13**, or **14**, respectively.

5,7-Dibromo-3-methyl-8*H*-cyclohept[*d*]isoxazol-8-one (**12**).

This compound was obtained as colorless needles in a yield of 184 mg (29%), mp 198-199°; ir (potassium bromide): ν max 1620 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.63 (s, 3H, CH_3), 7.70 (d, 1H, J = 1.7 Hz, H-6), 8.62 (d, 1H, J = 1.7 Hz, H-4).

Anal. Calcd. for $C_9H_5Br_2NO_2$: C, 33.89; H, 1.58; N, 4.39. Found: C, 33.63; H, 1.44; N, 4.37.

3-Methyl-5-nitro-8*H*-cyclohept[*d*]isoxazol-8-one (**13**).

This compound was obtained as yellow needles in a yield of 221 mg (54%), mp 160-161°; ir (potassium bromide): ν max 1645 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.71 (s, 3H, CH_3), 7.38 (d, 1H, J = 13.4 Hz, H-7), 8.38 (dd, 1H, J = 13.4, 2.2 Hz, H-6), 8.61 (d, 1H, J = 2.2 Hz, H-4).

Anal. Calcd. for $C_9H_6N_2O_4$: C, 52.43; H, 2.93; N, 13.39. Found: C, 52.54; H, 2.89; N, 13.28.

3-Methyl-5-phenylazo-8*H*-cyclohept[*d*]isoxazol-8-one (**14**).

This compound was obtained as orange needles in a yield of 341 mg (64%), mp 212-213°; ir (potassium bromide): ν max 1630 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.72 (s, 3H, CH_3), 7.2-8.4 (m, 8H).

Anal. Calcd. for $C_{15}H_{11}N_3O_2$: C, 67.91; H, 4.18; N, 15.84. Found: C, 67.69; H, 4.02; N, 15.79.

3-Methyl-1,8-dihydrocycloheptapyrazol-8-ones.

A solution of 3-acetyltropolone derivative **2**, **3**, **4**, or **7b** (1.5 mmoles) and 80% hydrazine hydrate (193 mg, 3 mmoles) in methanol (10 ml) was refluxed for 1 hour. After cooling, the precipitate was collected and recrystallized from methanol to give 3-methyl-1,8-dihydrocycloheptapyrazol-8-one **15**, **16**, **17**, or **18**, respectively.

5,7-Dibromo-3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**15**).

This compound was obtained as yellow needles in a yield of 232 mg (49%), mp 274° dec; ir (potassium bromide): ν max 3170 (NH), 1620 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.58 (s, 3H, CH_3), 7.95 (d, 1H, J = 1.5 Hz, H-6), 8.61 (d, 1H, J = 1.5 Hz, H-4), 11.21 (br, 1H, NH).

Anal. Calcd. for $C_9H_6Br_2N_2O$: C, 33.99; H, 1.90; N, 8.81. Found: C, 33.83; H, 1.67; N, 8.57.

7-Iodo-3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**16**).

This compound was obtained as yellow needles in a yield of 182 mg (42%), mp 223-224°; ir (potassium bromide): ν max 3220 (NH), 1610 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.61 (s, 3H, CH_3), 6.54 (dd, 1H, J = 10.0, 9.8 Hz, H-5), 7.58 (d, 1H, J = 10.0 Hz, H-6), 8.63 (d, 1H, J = 9.8 Hz, H-4).

Anal. Calcd. for $C_9H_7IN_2O$: C, 37.78; H, 2.47; N, 9.79. Found: C, 37.66; H, 2.35; N, 9.76.

3-Methyl-5-nitro-1,8-dihydrocycloheptapyrazol-8-one (**17**).

This compound was obtained as yellow needles in a yield of 135 mg (44%), mp 242°; ir (potassium bromide): ν max 3220 (NH), 1645 cm^{-1} (C=O); ^1H nmr (deuteriodimethyl sulfoxide): δ 2.69 (s, 3H, CH_3), 7.10 (d, 1H, J = 13.4 Hz, H-7), 8.38 (dd, 1H, J = 13.4, 2.4 Hz, H-6), 8.92 (d, 1H, J = 2.4 Hz, H-4), 14.6 (br, 1H, NH).

Anal. Calcd. for $C_9H_7N_3O_3$: C, 52.68; H, 3.44; N, 20.48. Found: C, 52.42; H, 3.67; N, 20.19.

3-Methyl-5-(4-methylphenylazo)-1,8-dihydrocycloheptapyrazol-8-one (**18**).

This compound was obtained as orange needles in a yield of 270 mg (65%), mp 259°; ir (potassium bromide): ν max 3170 (NH), 1625 cm^{-1} (C=O); ^1H nmr (deuteriodimethyl sulfoxide): δ 2.42 (s, 3H, Ar-CH_3), 2.63 (s, 3H, 3-CH_3), 7.11 (d, 1H, J = 13.0 Hz, H-7), 7.41 (d, 2H, J = 8.4 Hz, H-3′,5′), 7.83 (d, 2H, J = 8.4 Hz, H-2′,6′), 8.24 (dd, 1H, J = 13.0, 1.1 Hz, H-6), 8.42 (d, 1H, J = 1.1 Hz, H-4).

Anal. Calcd. for $C_{16}H_{16}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found: C, 69.12; H, 4.97; N, 20.21.

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