The Synthesis of 8-Hydroxy-1-oxaazulan-2-one and Its Derivatives by the Condensation of 3-Bromotropolones with Diethyl Malonate and Ethyl Acetoacetate

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During studies of the C-alkylation of tropolones by anionoid substitution reaction, it has been found that the reaction of 3-bromotropolones and diethyl malonate or ethyl acetoacetate afforded as condensation products 8-hydroxy-1-oxaazulan-2-one (8-hydroxy-2H-cyclohepta [b] furan - 2 - one) derivatives. The alkyl derivatives of these condensation products have also been obtained by the extension of this reaction to alkyl derivatives of 3-bromotropolone. Moreover, 8-hydroxy-1-oxaazulan-2-one itself and 3-carboxymethyltropolones have been derived from these condensation products. In this paper, the synthesis and some reactions of 8-hydroxy-1-oxaazulan-2 - ones will be described.

Hartley[1] reported that *o*-bromobenzoic acid reacted with diethyl malonate or ethyl acetoacetate, in the presence of a copper catalyst, to give condensation products. This reaction has now been extended to 3-bromotropolone (I). The heating of I with diethyl sodiomalonate, in the presence of copper acetate, gave an acidic compound (II), $C_{12}H_{10}O_5$ (one OC_2H_5), in a good yield. Under the same conditions, ethyl sodioacetoacetate also gave an acidic compound (III), $C_{11}H_8O_4$ (no OC_2H_5). These condensation products were soluble in alkalis, but they did not show any coloration with a ferric chloride solution. When heated in concentrated hydrobromic acid, II afforded an acidic compound IV while evolving carbon dioxide. The heating of II in a sodium hydroxide solution also gave IV. Acid IV is a dibasic acid with pK_a, 4.52 and 8.77,[2] and showed a green color with a ferric chloride solution. The heating of IV in pyridine gave 3-methyltropolone (V)[3] while carbon dioxide was evolved.

These results indicate that the acid IV is 3-carboxymethyltropolone and that, consequently, II is a condensation product possessing the malonic ester group at the 3-position of the tropolone nucleus. The lactone structure (A) may also be assumed for II from the analytical values and the negative ferric chloride test, which suggests that the hydroxyl group of tropolone is masked. However, II is a monobasic acid with pK_a, 3.57,[4] which value would be due to the enolic hydroxyl, not to the opening of the lactone ring. Furthermore, the acetylation of II with acetic anhydride gave a neutral monoacetate (VIa), and the methylation of II with diazomethane gave a neutral monomethyl derivative (VIIa). The ultraviolet absorption spectra of both VIa and VIIa are similar to those of 1-oxaazulan-2-ones,[5] as Fig. 2 shows. The ultraviolet absorption spectrum of II, as is shown in Fig. 1, is also similar to those of 1-oxaazulan-2-ones, although its maxima show a slight hypsochromic shift.

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[1] W. R. H. Hartley, *J. Chem. Soc.*, **1929**, 1870.

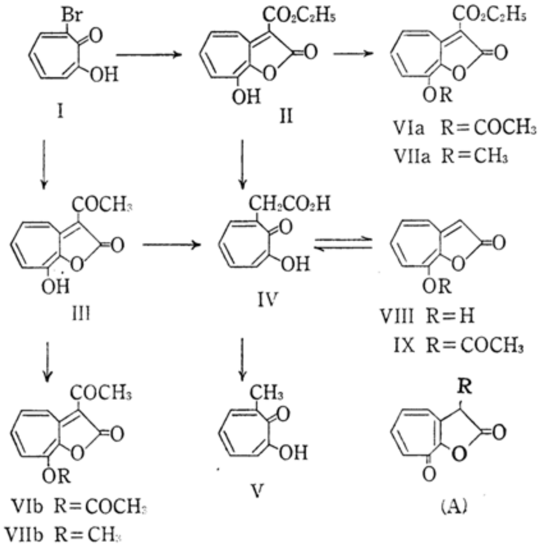
[2] N. Tanaka, I. T. Oiwa, T. Kurosawa and T. Nozoe, This Bulletin, **32**, 92 (1959).

[3] T. Nozoe, T. Mukai and K. Takase, *Proc. Japan Acad.*, **27**, 561 (1951); *Sci. Repts. Tohoku Univ.*, **I**, **36**, 40 (1952); T. Nozoe, T. Mukai and K. Matsui, *Proc. Japan Acad.*, **27**, 646 (1951); T. Nozoe, T. Mukai, M. Kunori, T. Muroi and K. Matsui, *Sci. Repts. Tohoku Univ.*, **I**, **35**, 242 (1952).

[4] The dissociation constants were measured by Mrs. Toshiko Kurosawa of the Chemical Laboratory, Faculty of Science, Tohoku University; to her the author's thanks are due.

[5] S. Seto, *Sci. Repts. Tohoku Univ.*, **I**, **37**, 367 (1953).

From this evidence, II is assumed to be 3-ethoxycarbonyl-8-hydroxy-1-oxaazulan-2-one, and VIa and VIIa, to be 3-ethoxycarbonyl-8-acetoxy- and 3-ethoxycarbonyl-8-methoxy-1-oxaazulan-2-one respectively.



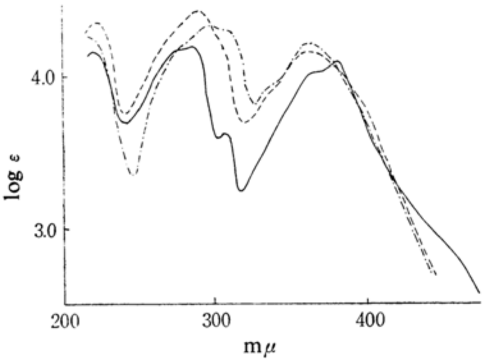


Fig. 1. UV spectra of II (------), III (-·-·-) and VIII (——) in methanol.

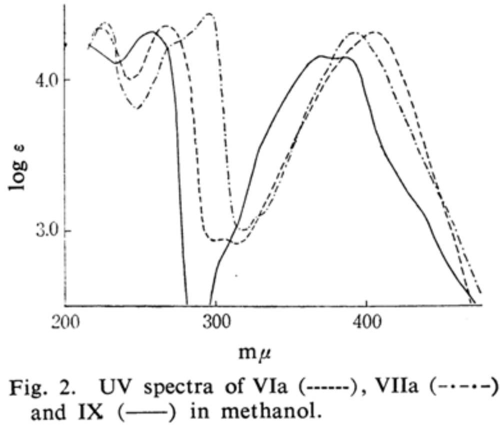


Fig. 2. UV spectra of VIa (------), VIIa (-·-·-) and IX (——) in methanol.

The condensation product (III) is assumed to be 3-acetyl-8-hydroxy-1-oxaazulan-2-one, similar to II, from the following evidence. This compound III is a monobasic acid with pK_a, 3.44,⁴⁾ and gave a neutral monoacetate VIb and a neutral monomethyl ether VIIb. The ultraviolet absorption spectra of III and of its acetate VIb and methyl ether VIIb are similar to those of II and of its derivatives, VIa and VIIa, respectively. The heating of III in concentrated hydrobromic acid afforded IV as well as liberated acetic acid.

The parent compound, 8-hydroxy-1-oxaazulan-2-one (VIII) was obtained as orange crystals by dissolving IV in concentrated sulfuric acid and then pouring the mixture into ice-water. Its ultraviolet absorption curve is similar to those of 1-oxaazulan-2-ones, as Fig. 1 shows. When heated in an aqueous solvent, VIII was easily hydrolized to IV. The acetylation of VIII gave an acetate IX, which was also obtained from IV by heating it with acetic anhydride. The ultraviolet absorption spectrum, as shown in Fig. 2, indicates that IX is 8-acetoxy-1-oxaazulan-2-one. The hydrolysis of IX by heating with acids gave IV.

Alkyl derivatives of 8-hydroxy-1-oxaazulan-2-ones were obtained by the extension of this condensation reaction to alkyl derivatives of 3-bromotropolone. When heated with diethyl sodiomalonate or ethyl sodioacetoacetate, both 3-bromo-7-methyltropolone (X)⁶⁾ and 3-bromo-6-isopropyltropolone (XI)⁷⁾ gave corresponding condensation products, XIIa, b and XIIIa, b, respectively. All of these compounds are acidic and gave neutral monoacetate. The ultraviolet absorption spectra of these compounds and their acetates are closely similar to those of 8-hydroxy-1-oxaazulan-2-ones (II and III) and their acetates respectively. From this evidence, the condensation products, XIIa, b and XIIIa, b, are assumed to be 3-ethoxycarbonyl-7-methyl-, 3-ethoxycarbonyl-6-isopropyl-, 3-acetyl-7-methyl- and 3-acetyl-6-isopropyl-8-hydroxy-1-oxaazulan-2-one respectively. 3, 5-Dibromo-7-methyltropolone (XIV)⁶⁾ also reacted with diethyl sodiomalonate to give a condensation product XV. The structure of XV was established from the facts that its ultraviolet absorption spectrum is similar to those of 8-hydroxy-1-oxaazulan-2-ones and that its catalytic debromination gave XIIa.

When heated in concentrated hydrobromic acid, both XIIa and XIIIa afforded 3-carboxymethyl-7-methyltropolone (XVIa) and both

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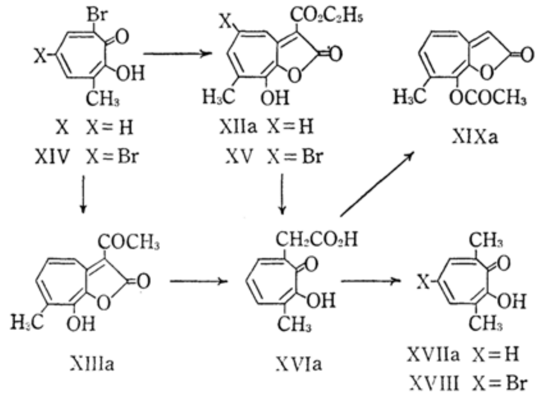
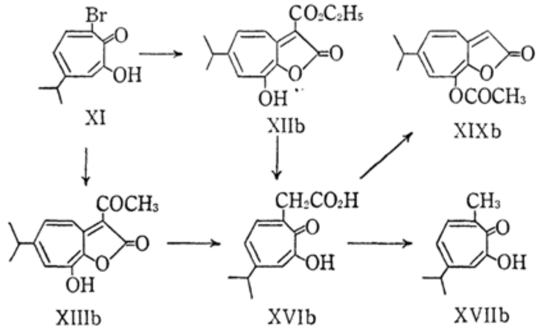
6) K. Takase, *Bull. Chem. Research Inst. Non-Aqueous Solns. Tohoku Univ.*, **13**, 169 (1964).

7) T. Nozoe, T. Mukai and K. Takase, *Proc. Japan Acad.*, **26** (8), 19 (1950); T. Nozoe, E. Sebe, S. Mayama and S. Iwamoto, *Sci. Repts. Tohoku Univ.*, **I**, **36**, 184 (1952).





XIIb and XIIIb afforded 3-carboxymethyl-6-isopropyltropolone (XVIb). The decarboxylation of XVIa and XVIb by heating in pyridine afforded 3, 7-dimethyltropolone (XVIIa)[3] and 6-isopropyl-3-methyltropolone (XVIIb)[3] respectively. The bromination of XVIIa gave 5-bromo-3, 7-dimethyltropolone (XVIII). When XVIa and XVIb were treated with acetic anhydride, they gave 7-methyl-8-acetoxy-(XIXa) and 6-isopropyl-8-acetoxy-1-oxaazulan-2-one (XIXb) respectively. The ultraviolet absorption spectra of XIXa and XIXb are similar to those of 1-oxaazulan-2-ones. Acetoxy derivatives XIXa, b were easily hydrolized by heating them in concentrated acid or dilute alkalis, affording carboxymethyltropolones (XVIa, b).

These condensation reactions did not proceed without the use of copper acetate. 5-Bromotropolone did not react with diethyl malonate and ethyl acetoacetate under these conditions, while 3, 7-dibromotropolone afforded resinous substances.

Experimental[8]

3-Ethoxycarbonyl-8-hydroxy-1-oxaazulan-2-one (II).—To a solution of diethyl sodiomalonate prepared by dissolving sodium (12.0 g.) in a mixture of diethyl malonate (100 ml.) and dry dioxane (200 ml.), 3-bromotropolone (I) (20.0 g.) and copper acetate (200 mg.) were added; the mixture was then refluxed for 6 hr. After the addition of water (200 ml.), the mixture was shaken with ether (200 ml.) and the aqueous layer was acidified with 6 N hydrochloric acid and allowed to stand overnight. The crystals thereby formed were collected and washed with chloroform to give II (17.6 g.), m. p. 208°C (decomp.). Recrystallization from acetone afforded yellow needles, m. p. 225°C (decomp.).

λ_{max}^{MeOH} mμ (log ε); 222 (4.35), 290 (4.43), 357 (4.15).

Found: C, 61.60; H, 4.52; OC_2H_5, 19.22. Calcd. for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30; OC_2H_5, 19.20%.

3-Acetyl-8-hydroxy-1-oxaazulan-2-one (III).—To a solution of ethyl sodioacetoacetate prepared by dissolving sodium (12.0 g.) in a mixture of ethyl acetoacetate (90 g.) and dry dioxane (160 ml.), I (20.0 g.) and copper acetate (400 mg.) were added; the mixture was then refluxed for 18 hr. The reaction mixture was treated as described in the above experiment to give III (19.0 g.), m. p. 278°C (decomp.). Recrystallization from a large amount of acetone gave yellow silky needles, m. p. 285°C (decomp.).

λ_{max}^{MeOH} mμ (log ε); 294 (4.32), 361 (4.19).

Found: C, 64.82; H, 4.26. Calcd. for $C_{11}H_8O_4$: C, 64.70; H, 3.95%.

3-Carboxymethyltropolone (IV).—*a) From II.*—A mixture of II (3.95 g.) and concentrated hydrobromic acid (30 ml.) was heated at 130~140°C for 2 hr. The mixture was poured into ice-water (50 g.) and adjusted to pH 3 with a potassium hydroxide solution, the crystals thereby obtained were collected by filtration, affording IV (1.14 g.), m. p. 170°C (decomp.). From the mother liquor, further crops of IV (1.38 g.), m. p. 171°C (decomp.), were obtained by continuous extraction with ether for 20 hr. Recrystallization from dimethylformamide afforded pale yellow needles, m. p. 174°C (decomp.).

λ_{max}^{MeOH} mμ (log ε); 243 (4.26), 329 (3.94), 391 (3.91).

Found: C, 59.67; H, 4.66. Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.48%.

b) From III.—A mixture of III (4.0 g.) and concentrated hydrobromic acid (30 ml.) was treated as in a), affording IV (2.70 g.) as yellow needles, m. p. 170°C (decomp.).

c) The Heating of II in Alkali.—A solution of II (200 mg.) in a 2 N sodium hydroxide solution (3 ml.) was heated for 5 hr. The mixture was then acidified with 6 N hydrochloric acid and continuously extracted with ether for 5 hr., affording IV (100 mg.) as pale yellow needles, m. p. 170°C (decomp.).

3-Methyltropolone (V).—A mixture of IV (5.00 g.) and pyridine (15 ml.) was heated under reflux for 3 hr. After the addition of water, the mixture was acidified with 6 N hydrochloric acid and extracted with chloroform. The solvent was evaporated, the residue was sublimed at 110~120°C under reduced pressure, and the sublimate was recrystallized from cyclohexane to give V (3.32 g.) as colorless plates, m. p. 49~50°C, which showed

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[8] All melting points are uncorrected.

no depression of melting point on admixture with an authentic specimen.[3]

3-Ethoxycarbonyl-8-acetoxy-1-oxaazulan-2-one (VIa).—A mixture of II (1.00 g.) and acetic anhydride (2.5 ml.) was heated at 140°C for 1 hr. Water was added, and the crystals thereby formed were collected and recrystallized from ethanol to give VIa (1.00 g.) as yellow needles, m. p. 135~136°C.

λ_{max}^{MeOH} mμ (log ε); 223 (4.33), 265 (4.34), 402 (4.29).

Found: C, 60.91; H, 4.71. Calcd. for $C_{14}H_{12}O_6$: C, 60.87; H, 4.38%.

The heating of VIa in concentrated hydrobromic acid at 140°C for 1 hr. gave IV.

3-Acetyl-8-acetoxy-1-oxaazulan-2-one (VIb).—A mixture of III (1.00 g.) and acetic anhydride (1 ml.) was treated as described in the above experiment, affording VIb (1.00 g.) as orangish yellow needles, m. p. 168~169°C, after recrystallization from ethanol.

λ_{max}^{MeOH} mμ (log ε); 225 (4.47), 277 (4.41), 416 (4.38).

Found: C, 63.67; H, 4.05. Calcd. for $C_{13}H_{10}O_5$: C, 63.41; H, 4.09%.

3-Ethoxycarbonyl-8-methoxy-1-oxaazulan-2-one (VIIa).—Into a suspension of II (460 mg.) in ethyl acetate (10 ml.), an ethereal solution of diazomethane (3.5 ml.) was stirred while it was being cooled. The mixture was then stirred for 10 hr., and the crystals thereby formed were collected and recrystallized from ethanol to give VIIa (310 mg.) as yellow needles, m. p. 142~143°C.

λ_{max}^{MeOH} mμ (log ε); 225 (4.38), 295 (4.43), 392 (4.31).

Found: C, 62.83; H, 4.87. Calcd. for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87%.

The heating of VIIa in concentrated hydrobromic acid at 140°C for 1 hr. gave V.

3-Acetyl-8-methoxy-1-oxaazulan-2-one (VIIb).—III (410 mg.) was treated with diazomethane as described in the above experiment, affording VIIb (320 mg.) as orangish yellow needles, m. p. 231~232°C (decomp.) after recrystallization from ethanol.

λ_{max}^{MeOH} mμ (log ε); 228 (4.39), 258 (4.08), 300 (4.47), 404 (4.35).

Found: C, 66.02; H, 4.68; OCH_3, 14.21. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62; OCH_3, 14.05%.

8-Hydroxy-1-oxaazulan-2-one (VIII).—A solution of IV (400 mg.) in concentrated sulfuric acid (1 ml.) was poured into ice-water to give VIII (220 mg.), m. p. 220°C (decomp.). Recrystallization from a mixture of dioxane and dimethylformamide gave orangish yellow prisms, m. p. 223°C (decomp.).

λ_{max}^{MeOH} mμ (log ε); 220 (4.16), 275 (4.17), 285 (4.18), 305 (3.62), 380 (4.09).

Found: C, 66.41; H, 3.87. Calcd. for $C_9H_6O_3$: C, 66.67; H, 3.73%.

8-Acetoxy-1-oxaazulan-2-one (IX).—*a) From IV.*—A mixture of IV (1.00 g.) and acetic anhydride (2 ml.) was heated at 140°C for 2 hr. After the addition of water (30 ml.), the mixture was extracted with benzene and the benzene solution was passed through a short column of silica gel, affording IX (930 mg.), m. p. 140~150°C. Recrystallization from methanol gave orange prisms or needles, m. p. 151~152°C.

λ_{max}^{MeOH} mμ (log ε); 257 (4.30), 369 (4.14), 387 (4.14).

Found: C, 64.63; H, 4.00. Calcd. for $C_{11}H_8O_4$: C, 64.70; H, 3.95%.

The heating of IX in concentrated hydrobromic acid at 140°C for 1 hr. gave IV.

b) From VIII.—A mixture of VIII (100 mg.) and acetic anhydride (0.5 ml.) was treated as in a), affording IX (100 mg.), m. p. 151~152°C.

3-Ethoxycarbonyl-7-methyl-8-hydroxy-1-oxaazulan-2-one (XIIa).—To a solution of diethyl sodiomalonate prepared by dissolving sodium (600 mg.) in a mixture of dioxane (10 ml.) and diethyl malonate (6 ml.), 3-bromo-7-methyltropolone (X) (1.07 g.) and copper acetate (50 mg.) were added; the mixture was then heated under refluxing for 15 hr. The reaction mixture was diluted with water and acidified with 6 N hydrochloric acid. The crystals thereby formed were collected and recrystallized from acetone to give XIIa (1.02 g.) as yellow silky needles, m. p. 201°C (decomp.).

λ_{max}^{MeOH} mμ (log ε); 227 (4.29), 295 (4.46), 355 (4.13).

Found: C, 63.08; H, 4.88. Calcd. for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87%.

Acetate: m. p. 146~147°C, yellow needles (from methanol).

λ_{max}^{MeOH} mμ (log ε); 230 (4.43), 267 (4.40), 408 (4.40).

Found: C, 62.12; H, 4.83. Calcd. for $C_{15}H_{14}O_6$: C, 62.06; H, 4.86%.

3-Ethoxycarbonyl-6-isopropyl-8-hydroxy-1-oxaazulan-2-one (XIIb).—To a solution of diethyl sodiomalonate prepared by dissolving sodium (3.0 g.) in a mixture of dioxane (40 ml.) and diethyl malonate (25 ml.), 3-bromo-6-isopropyltropolone (XI) (6.0 g.) and copper acetate (100 mg.) were added; the mixture was then heated under refluxing for 15 hr. The reaction mixture was treated as described in the above experiment to give XIIb (5.28 g.) as yellow needles, m. p. 214~215°C, after recrystallization from acetone.

λ_{max}^{MeOH} mμ (log ε); 230 (4.46), 290 (4.50), 355 (4.26).

Found: C, 65.47; H, 5.72. Calcd. for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84%.

Acetate: m. p. 116~117°C, yellow needles (from methanol).

λ_{max}^{MeOH} mμ (log ε); 230 (4.43), 270 (4.34), 410 (4.38).

Found: C, 64.26; H, 5.61. Calcd. for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70%.

3-Acetyl-7-methyl-8-hydroxy-1-oxaazulan-2-one (XIIIa).—To a solution of ethyl sodioacetoacetate prepared by dissolving sodium (600 mg.) in a mixture of dioxane (10 ml.) and ethyl acetoacetate (5 ml.), X (1.07 g.) and copper acetate (50 mg.) were added; the mixture was then heated under refluxing for 20 hr. The reaction mixture was treated as described in the above experiment to give XIIIa (980 mg.) as yellow silky needles, m. p.

265°C (decomp.), after recrystallization from acetone.

$\lambda_{max}^{\text{MeOH}}$ mμ (log ε); 225 (4.25), 295 (4.41), 362 (4.12).

Found: C, 66.19; H, 5.12. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62%.

Acetate: m. p. 200~201°C, orange prisms (from methanol).

$\lambda_{max}^{\text{MeOH}}$ mμ (log ε); 230 (4.37), 275 (4.25), 421 (4.30).

Found: C, 64.74; H, 4.56. Calcd. for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65%.

3-Acetyl-6-isopropyl-8-hydroxy-1-oxaazulan-2-one (XIIIb).—To a solution of ethyl sodioacetoacetate prepared by dissolving sodium (3.0 g.) in a mixture of dioxane (40 ml.) and ethyl acetoacetate (22 ml.), XI (6.0 g.) and copper acetate (100 mg.) were added; the mixture was then heated under refluxing for 15 hr. The reaction mixture was treated as described in the above experiment to give XIIIb (5.60 g.) as yellow needles, m. p. 253°C (decomp.), after recrystallization from acetone.

$\lambda_{max}^{\text{MeOH}}$ mμ (log ε); 230 (4.30), 293 (4.38), 367 (4.16).

Found: C, 68.31; H, 5.72. Calcd. for $C_{14}H_{14}O_4$: C, 68.20; H, 5.73%.

Acetate: m. p. 105~106°C, yellow needles (from methanol).

$\lambda_{max}^{\text{MeOH}}$ mμ (log ε); 230 (4.43), 278 (4.33), 420 (4.39).

Found: C, 66.85; H, 5.39. Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59%.

5-Bromo-3-ethoxycarbonyl-7-methyl-8-hydroxy-1-oxaazulan-2-one (XV).—To a solution of diethyl sodiomalonate prepared from sodium (100 mg.), dioxane (4 ml.) and diethyl malonate (0.9 ml.), 5,7-dibromo-3-methyltropolone (XIV) (400 mg.) and copper acetate (50 mg.) were added; the mixture was then heated under refluxing for 20 hr. After the addition of water (5 ml.), the sodium salt thereby formed was collected, dissolved in hot water and acidified with 6 N hydrochloric acid to give XV (310 mg.) as yellow needles, m. p. 275°C (decomp.), after recrystallization from dioxane.

$\lambda_{max}^{\text{MeOH}}$ mμ (log ε); 240 (4.36), 300 (4.49), 363 (4.14).

Found: C, 48.05; H, 3.54. Calcd. for $C_{13}H_{11}O_5Br$: C, 47.73; H, 3.39%.

The Debromination of XV.—When a solution of XV (160 mg.) and sodium acetate (100 mg.) in water (5 ml.), in the presence of palladium-carbon (10 mg.), was shaken with hydrogen, 13.3 ml. of hydrogen was absorbed during a 3.5 hr. period. The catalyst was then filtered off and the filtrate acidified with 6 N hydrochloric acid to give XIIa as yellow needles, m. p. 201°C (decomp.), after recrystallization from acetone.

3-Carboxymethyl-7-methyltropolone (XVIa).—*a) From XIIa.*—A mixture of XIIa (490 mg.) and concentrated hydrobromic acid (3 ml.) was heated at 130~140°C for 45 min. The reaction mixture was then diluted with water and adjusted to pH 3 with a potassium hydroxide solution, and the crystals thereby formed were collected and recrystallized from glacial acetic acid to give XVIa (360 mg.) as pale yellow needles, m. p. 177°C (decomp.).

$\lambda_{max}^{\text{MeOH}}$ mμ (log ε); 242 (4.49), 320 (3.81), 355 (3.78), 370 (3.81).

Found: C, 61.97; H, 5.20. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19%.

b) From XIIIa.—A mixture of XIIIa (320 mg.) and concentrated hydrobromic acid (3 ml.) was heated at 130~140°C for 2 hr.; the crystals thereby formed were collected by filtration to give dark green needles, m. p. over 300°C (110 mg.).

$\lambda_{max}^{\text{MeOH}}$ mμ; 227, 312, 355, 450.

Found: C, 57.91; H, 3.76%.

The filtrate was adjusted to pH 3 with a potassium hydroxide solution, affording XVIa (160 mg.) as yellow needles, m. p. 177°C (decomp.), after recrystallization from glacial acetic acid.

3-Carboxymethyl-6-isopropyltropolone (XVIb).—*a) From XIIb.*—A mixture of XIIb (500 mg.) and concentrated hydrobromic acid (6 ml.) was heated at 130~140°C for 2 hr. After it had cooled, the mixture was poured into water (20 ml,) to give XVIb (360 mg.), m. p. 158°C (decomp.). Recrystallization from chloroform afforded colorless needles, m. p. 160°C (decomp.).

$\lambda_{max}^{\text{MeOH}}$ mμ (log ε); 245 (4.47), 335 (3.84), 368 (3.81).

Found: C, 64.50; H, 6.23. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%.

b) From XIIIb.—A mixture of XIIIb (500 mg.) and concentrated hydrobromic acid (6 ml.) was treated as in a), affording XVIb (340 mg.) as colorless needles, m. p. 160°C (decomp.), after recrystallization from chloroform.

3,7-Dimethyltropolone (XVIIa).—A mixture of XVIa (200 mg.) and pyridine (2 ml.) was heated under refluxing for 6 hr. After the addition of water (5 ml.), the mixture was acidified with 6 N hydrochloric acid and extracted with chloroform. The solvent was evaporated, the residue was sublimed at about 100°C under reduced pressure, and the sublimate was recrystallized from petroleum ether to give XVIIa (80 mg.) as colorless plates, m. p. 68~70°C, which was undepressed on admixture with an authentic specimen.[3]

$\lambda_{max}^{\text{MeOH}}$ mμ (log ε); 243 (4.53), 320 (3.79), 355 (3.77), 370 (3.81).

6-Isopropyl-3-methyltropolone (XVIIb).—A mixture of XVIb (500 mg.) and pyridine (1 ml.) was heated under refluxing for 5 hr. After the addition of water (5 ml.), the mixture was acidified with 6 N hydrochloric acid and extracted with chloroform. The removal of the solvent left an oil, which was then distilled under reduced pressure to give XVIIb (330 mg.) as a pale yellow oil. The *p*-tolylazo derivative of this oil showed no depression of melting point on admixture with the known 5-(*p*-tolylazo)-6-isopropyl-3-methyltropolone.[3]

5-Bromo-3,7-dimethyltropolone (XVIII).—To a solution of XVIIa (30 mg.) in methanol (2 ml.), bromine (30 mg.) was added; the mixture was then stirred for 2 hr. Water was added, and the crystals thereby formed were recrystallized from methanol to give XVIII (40 mg.) as colorless plates, m. p. 136~137°C.

λ_{max}^{MeOH} mμ (log ε) ; 245 (4.48), 330 (3.97), 368 (3.64), 387 (3.64).

Found : C, 47.51 ; H, 4.14. Calcd. for $C_9H_9O_2Br$: C, 47.19 ; H, 3.96%.

7-Methyl-8-acetoxy-1-oxaazulan-2-one (**XIXa**).—A mixture of XVIa (120 mg.) and acetic anhydride (0.4 ml.) was heated at 140°C for 2 hr. Water was added, and the crystals thereby formed were recrystallized from methanol to give XIXa (120 mg.) as orange prisms, m. p. 127~128°C.

λ_{max}^{MeOH} mμ (log ε) ; 228 (4.31), 257 (4.35), 392 (4.22).

Found : C, 66.00 ; H, 5.08. Calcd. for $C_{12}H_{10}O_4$: C, 66.05 ; H, 4.62%.

6-Isopropyl-8-acetoxy-1-oxaazulan-2-one (XIXb).—A mixture of XVIb (1.00 g.) and acetic anhydride (2 ml.) was treated as described in the above experiment to give XIXb (880 mg.) as orange prisms, m. p. 101~102°C, after recrystallization from methanol.

λ_{max}^{MeHO} mμ (log ε) ; 228 (4.23), 255 (4.29), 373 (4.22), 388 (4.23).

Found : C, 68.47 ; H, 5.56. Calcd. for $C_{14}H_{14}O_4$: C, 68.27 ; H, 5.73%.

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