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The Bromination of 4-Acetyltropolone

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The bromination of 4-acetyltropolone was examined, and two kinds of monobromo compounds, 4-acetyl-3-bromo- and 4-acetyl-7-bromotropolones, two kinds of dibromo compounds, 4-acetyl-3,7-dibromo- and 7-bromo-4-(ω-bromoacetyl)tropolones, a tribromo compound, 4-acetyl-3,5,7-tribromotropolone, and a tetrabromo compound, 3,5,7-tribromo-4-(ω-bromoacetyl)tropolone, were obtained. The third isomer of the monobromo compounds, 4-acetyl-5-bromotropolone, was synthesized from 4-acetyltropolone through 4-acetyl-5-aminotropolone. Moreover, an isomeric dibromo compound, 4-acetyl-5,7-dibromotropolone, was obtained by the debromination of the tribromo compound.

4-Acetyltropolone (I)[1] may be expected to be one of the most important materials for synthetical studies in troponoid chemistry, and in a previous paper[2] we reported on the properties of I and its methyl ethers in reaction to several oxidizing and reducing reagents. This paper will describe the results of our studies of bromination of I as one of a series of investigations of acetyltropolones.

The bromination of I is interesting in comparison with those of the other 4-substituted tropolones, such as 4-methyl-,[3] 4-ethyl-[4] and 4-isopropyltorpolones,[5] which

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1) T. Nozoe, K. Takase, and M. Ogata, *Chem. Ind.*, **1957**, 1070.

2) T. Nozoe, K. Takase, K. Shimizu, and M. Yasunami, This Bulletin, **44**, 1951 (1971).

3) 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., Ser. I*, **35**, 242 (1952); R. D. Haworth and J. Hobson, *J. Chem. Soc.*, **1951**, 561.

4) T. Nozoe, K. Takase, and K. Umino, This Bulletin, **38**, 358 (1965).

5) T. Nozoe, T. Mukai, and K. Takase, *Proc. Japan Acad.*, **26**, 19 (1950); T. Nozoe, E. Sebe, S. Mayama, and S. Iwamoto, *Sci. Repts. Tohoku Univ., Ser. I*, **36**, 184 (1952); M. Yasunami, K. Takase, and T. Nozoe, *Tetrahedron Lett.*, **1970**, 4327.

have been studied well. Moreover, it seems to be important to prepare ω-bromoacetyl derivatives of I from the point of view of synthetical studies.

Results and Discussion

The bromination of 4-acetyltropolone was examined under the various reaction conditions listed in Table 1. In each experiment, the product was usually a complex mixture of several bromo compounds, and the separation into components was rather difficult. The major products and some minor products were eventually isolated by means of fractional recrystallization. The bromo compounds thus obtained were two kinds of monobromo (II) and (III), two kinds of dibromo (IV) and (V), and a tribromo compound (VI); their data are summarized in Table 1. The further bromination of the bromo compounds obtained here was also examined; some of these results are also listed in Table 1.

Table 1. Bromination of 4-acetyltropolone (I) and its monobromo derivatives (II) and (III)

Compound	Reaction conditions: Bromine mol. eq.	Medium	Bromination products: II	III	IV	V	VI
I	1—2	NaOAc-MeOH	++				
	1—2	MeOH	+			++	
	1	NaOAc-HOAc		++	+		+
	3	NaOAc-HOAc					++
	2	HOAc	+			++	
	1	$CHCl_3$	+			++	
	(NBS)	$CHCl_3$		+			
II	1	MeOH					++
	1—2	NaOAc-HOAc			+		++
III	1	NaOAc-MeOH			++		+
	1	MeOH				++	+
	1—2	NaOAc-HOAc					++

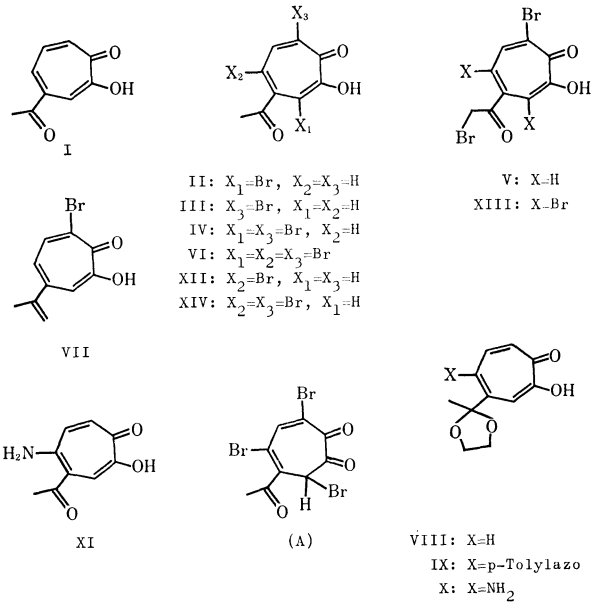
The bromination products isolated are shown by ++ for the major one, and + the minor one.

Table 2. The NMR spectra of the bromo derivatives of 4-acetyltropolone, δ ppm in $CDCl_3$ (intensity, signal pattern, coupling constant; Hz)

Compd.	Ring proton	Acetyl or bromoacetyl
II	6.70(1H, dd, J=7.8, 3.7) 7.38(1H, d, J=3.7) 7.42(1H, d, J=7.8)	2.59(3H, s)
III	7.47(1H, dd, J=10.4, 1.6) 7.92(1H, d, J=1.6) 8.37(1H, d, J=10.4)	2.68(3H, s)
V	7.47(1H, dd, J=10.3, 1.8) 7.89(1H, d, J=1.8) 8.41(1H, d, J=10.3)	4.43(2H, s)
VI	8.50(1H, s)	2.65(3H, s)
XII	6.97(1H, s) 7.10(1H, d, J=12.0) 7.77(1H, d, J=12.0)	2.57(3H, s)
XIII	8.52(1H, s)	4.49(2H, s)
XIV	6.99(1H, s) 7.25(1H, s)	2.58(3H, s)

a) s: singlet, d: doublet, dd: double doublet.

These bromo compounds showed the positive ferric chloride test characteristic of tropolones, and their ultraviolet absorption spectra indicated that all of them were tropolone derivatives. From the orientation in cationoid substitution at the tropolone nucleus[6] and from the reactivity of the acetyl group, it was expected that the bromo substituents of these bromo compounds should be present at the 3-, 5-, 7- and/or ω-positions. Moreover, it was assumed that the compound bearing the bromo substituents at the tropolone nucleus would be stable under a mild alkaline treatment, whereas ω-bromo compounds would be sensitive. On the basis of these considerations, as well as on that of the NMR data shown in Table 2 and the chemical evidence to be described below, the structures of the bromo compounds, II–VI, were determined as follows.



One of two monobromo compounds, II, was assigned the structure of 4-acetyl-3-bromotropolone on the basis of the NMR spectral data, which showed the presence of an acetyl group and three adjacent ring protons, as is shown in Table 2. The other monobromo compound, III, was identical to 4-acetyl-7-bromotropolone, which had been obtained from 7-bromo-4-isopropenyltropolone (VII)[7] by oxidation with hydrogen peroxide, followed by oxidation with metaperiodic acid, or by the Schmidt reaction. This structure was also revealed from the NMR spectral data shown in Table 2.

The dibromo compound, IV, was assigned the structure of 4-acetyl-3,7-dibromotropolone from the fact that IV was also obtained from both the monobromo compounds, II and III, on further bromination. The other dibromo compound, V, was assigned the structure of 7-bromo-4-(ω-bromoacetyl)tropolone, since it was also obtained from III by further bromination and gave

6) T. Nozoe, K. Takase, and H. Matsumura, "Dai Yuki Kagaku (Comprehensive Organic Chemistry)," Vol. 13, Chapter 5—9, Asakura-Shoten Tokyo (1960).

7) K. Takase, T. Kusunose, and T. Meguro, presented at the 12th Annual Meeting of the Chemical Society of Japan, Abstracts, (1959), p. 232.

a resinous material when treated with dilute alkali. This structure was also supported by the NMR spectral data, which showed the presence of the bromoacetyl group and three adjacent ring protons, as is shown in Table 2. The tribromo compound, VI, was assumed to be 4-acetyl-3,5,7-tribromotropolone, since it was obtained on the bromination of IV and gave a stable sodium salt when treated with a sodium hydroxide solution. The NMR spectral data shown in Table 2 also supported this assumption.

As a result of the structural determination of the bromination products described above, it became clear that, on the bromination of 4-acetyltropolone (I), the positions at which bromination occurred predominantly were remarkably affected by the reaction conditions, such as the presence or absence of sodium acetate and the kind of solvent used. Thus, as is shown in Table 1, in the presence of acetate, bromination occurred only on the tropolone nucleus at the 3- and/or 7-position, whereas, in the absence of acetate, it occurred on the acetyl group as well as on the tropolone nucleus. This behavior of I is thought to be due to the dissociation of I, in the presence of sodium acetate, to its anion, in which the 3-, 5-, and 7-positions of the tropolone nucleus are more reactive toward the cationoid reagents. A similar tendency was also observed on the bromination of the monobromo compound, III.

It is interesting to find that, on the bromination of I in the presence of sodium acetate, the use of acetic acid as the solvent gave a 7-bromo compound, III, whereas the use of methanol gave a 3-bromo compound, II, predominantly. Moreover, it is noteworthy that the sterically-hindered 3-position was predominantly attacked with the reagents in the medium of methanol–sodium acetate, while no 3-bromo derivative is known to be obtained on the bromination of 4-alkyltropolones, except for the finding that the bromination of 4-isopropyltropolone in ethanol at −15°C afforded a small amount of the 3-bromo derivative, together with the other bromo derivatives.[5] The reason for the predominant formation of II is not yet apparent.

The third isomer of the monobromo derivative of I, that is, 4-acetyl-5-bromotropolone could not be obtained by the bromination of I, but it was derived from I as follows. Since the azo-coupling of I gave a cyclohepta[*c*]pyrazolone derivative,[8] the ethylene ketal (VIII)[9] of I was coupled with *p*-toluenediazonium chloride to give an azo compound (IX). The catalytic hydrogenation of IX in methanol over palladium on carbon gave an amino-ketal (X), which was then hydrolyzed to an amino-ketone (XI). The application of the Sandmeyer reaction to X or XI gave a bromo compound (XII). It is reasonable to assign the structure of 4-acetyl-5-bromotropolone to XII, since it has been known that the *p*-tolylazo group generally enters at the 5-position of the tropolone nucleus.[6] This structure was also supported by the finding that the bromination of XII gave VI in a good yield, as well as by its NMR spectral data, shown in Table 2.

The dibromo compound, IV, gave the tribromo compound, VI, when treated with bromine in the presence of sodium acetate. On the other hand, the similar treatment of the dibromo compound, V, gave a tetrabromo compound (XIII). The structure of XIII was identified as 4,5,7-tribromo-4-(ω-bromoacetyl) tropolone from the findings that it was derived from V and that its NMR spectrum showed two singlets at 4.49 (2H) and 8.52 ppm (1H).

Although the tribromo compound, VI, was stable under a mild alkaline treatment, giving only sodium salt, it gave a dibromo compound (XIV) when heated with sodium iodide in ethanol. This dibromo compound, different from IV, was assigned the structure of 4-acetyl-5,7-dibromotropolones on the basis of the finding that it gave the tribromo compound, VI, on bromination, as well as on the basis of its NMR spectral data, shown in Table 2. This debromination reaction is thought to take place through a diketone-type intermediate (A).

Experimental

All the melting points are uncorrected. The ultraviolet absorption spectra were measured on a Beckman DU spectrophotometer, while the infrared spectra were recorded on a Shimadzu IR-27 infracord apparatus. The NMR spectra were determined with a Varian A-60 spectrometer on samples dissolved in deuteriochloroform, containing tetramethylsilane as the internal standard.

Bromination of 4-Acetyltropolone (I). *a) Bromination in Methanol in the Presence of Sodium Acetate*: Into a suspension of I (3.20 g) and sodium acetate (2.40 g) in methanol (100 m*l*), a solution of bromine (3.50 g) in glacial acetic acid (6 m*l*) was stirred under cooling with ice water; the mixture was then stirred for 2 hr. After the addition of water (150 m*l*), the mixture was allowed to stand overnight in a refrigerator; the crystals thereby formed were collected by filtration. Yield, 4.35 g; mp 170—185°C. Recrystallization from methanol gave 4-acetyl-3-bromotropolone (II) (2.75 g) as pale yellow scales; mp 193—194°C.

Found: C, 44.67; H, 3.09%. Calcd for $C_9H_7O_3Br$: C, 44.47; H, 2.90%. UV (MeOH): λ_{max} nm (log ε); 260 (4.42), 340 (3.94), 385 (3.76), 410 (3.74). IR (KBr disk); $\nu_{C=O}$, 1712 cm^{-1}.

A similar treatment of I (320 mg) with two molar equivalents of bromine also gave II (220 mg); mp 193—194°C.

b) Bromination in Methanol in the Absence of Acetate: Into a suspension of I (960 mg) in methanol (15 m*l*), a solution of bromine (1.92 g) in the same solvent (5 m*l*) was stirred under cooling with ice water, after which the mixture was stirred for 2 hr. The solvent was then evaporated, and the residue was fractionally recrystallized from methanol. The less soluble part gave II (10 mg) as pale yellow scales; mp 193—194°C. The readily-soluble part gave 7-bromo-4-(ω-bromoacetyl)tropolone (V) (1.20 g) as yellow needles; mp 147—149°C. The melting point rose to 149—151°C upon further recrystallization from methanol.

Found: C, 33.58; H, 1.93%. Calcd for $C_9H_6O_3Br_2$: C, 33.57; H, 1.88%. UV (MeOH): λ_{max} nm (log ε); 260 (4.43), 335 (3.79), 385 (3.71). IR (KBr disk); $\nu_{C=O}$, 1702 cm^{-1}.

A similar treatment of I (320 mg) with an equimolar amount of bromine gave V (50 mg), mp 149—151°C, together with an oily material.

8) T. Nozoe, K. Takase, and K. Suzuki, to be published.
9) I. Murata, This Bulletin, **34**, 577 (1961).

c) Bromination in Acetic Acid in the Presence of Sodium Acetate: Into a solution of I (1.60 g) and sodium acetate (1.20 g) in glacial acetic acid (30 ml), a solution of bromine (1.80 g) in the same solvent (2 ml) was stirred under cooling with ice water. After being stirred for 3 hr, the mixture was diluted with water and the crystals thereby formed were collected by filtration. Yield, 2.30 g; mp 90—98°C. Repeated recrystallizations from methanol gave 4-acetyl-7-bromotropolone (III) (920 mg) as yellow needles; mp 132—133°C.

Found: C, 44.73; H, 2.58%. Calcd for $C_9H_7O_3Br$: C, 44.47; H, 2.90%. UV (MeOH): λ_{max} nm (log ε); 227 (4.38), 345 (3.97), 446 (3.92). IR (KBr disk); $\nu_{C=O}$, 1686 cm^{-1}.

All the filtrates of the recrystallization were combined, the solvent was evaporated, and the residue was fractionally recrystallized from methanol. The slightly-soluble part gave 4-acetyl-3,5,7-tribromotropolone (VI) (350 mg) as yellow needles; mp 158—159°C.

Found: C, 27.12; H, 1.27%. Calcd for $C_9H_5O_3Br_3$: C, 26.96; H, 1.26%. UV (MeOH): λ_{max} nm (log ε); 272 (4.47), 355 (4.14), 442 (4.13). IR (KBr disk); $\nu_{C=O}$, 1712 cm^{-1}.

The readily-soluble part gave further crops of III (110 mg); mp 132—133°C.

The first aqueous filtrate was extracted with chloroform; the subsequent evaporation of the solvent left an oily material, which was then solidified by the addition of methanol. Recrystallization from methanol gave 4-acetyl-3,7-dibromotropolone (IV) (70 mg) as pale yellow scales; mp 151—152°C.

Found: C, 34.16; H, 2.12%. Calcd for $C_9H_6O_3Br_2$: C, 33.57; H, 1.88%. UV (MeOH): λ_{max} nm (log ε); 268 (4.41), 345 (3.95), 425 (4.06). IR (KBr disk); $\nu_{C=O}$, 1703 cm^{-1}.

d) Bromination in Acetic Acid in the Absence of Acetate: To a solution of I (320 mg) in glacial acetic acid (6 ml), a solution of bromine (650 mg) in the same solvent (0.5 ml) was added; the mixture was then stirred for 2 hr under cooling with ice water. Water was added to this mixture, the product was extracted with chloroform, and the solvent was evaporated, leaving crystals. Recrystallization from methanol gave V (310 mg) as yellow needles; mp 149—151°C.

e) Bromination in Chloroform: To a solution of I (320 mg) in chloroform (5 ml), a solution of bromine (320 mg) in the same solvent (1 ml) was added under cooling with ice water, after which the mixture was stirred for 3 hr. The crystals thereby formed were collected by filtration and recrystallized from methanol, giving II (50 mg) as pale yellow scales; mp 193—194°C.

All the filtrates were combined in a chloroform solution and washed with water. The evaporation of the solvent left an oily material, which was then crystallized by the addition of methanol, giving yellow crystals (250 mg); mp 144—146°C. Recrystallization from methanol gave V (80 mg) as yellow needles; mp 149—151°C.

f) Bromination with N-*Bromosuccinimide*: To a solution of I (800 mg) in chloroform, *N*-bromosuccinimide (800 mg) was added, after which the mixture was stirred for 5 hr at room temperature. The solvent was then evaporated, and the residue was recrystallized from methanol, giving III (240 mg) as yellow needles; mp 132—133°C.

Bromination of 4-Acetyl-3-bromotropolone (II). a) Bromination in Methanol: To a suspension of II (240 mg) in methanol (5 ml), a solution of bromine (160 mg) in the same solvent (1 ml) was added, after which the mixture was stirred for 2 hr under cooling with ice water. The subsequent evaporation of the solvent left crystals, which were then fractionally recrystallized from methanol to give VI (60 mg) as pale yellow needles; mp 158—159°C; II (50 mg) was also recovered.

b) Bromination in Acetic Acid in the Presence of Sodium Acetate: To a solution of II (240 mg) and sodium acetate (130 mg) in glacial acetic acid (8 ml) a solution of bromine (160 mg) in the same solvent (1 ml) was added, after which the mixture was stirred for 2 hr under cooling with ice water. Water was added to this mixture, and the crystals thereby formed were collected and fractionally recrystallized from methanol, thus giving VI (90 mg) as yellow needles, mp 158—159°C, and IV (40 mg) as pale yellow scales, mp 151—152°C.

A similar treatment of II (240 mg) with two molar equivalents of bromine gave VI (240 mg); mp 158—159°C.

Bromination of 4-Acetyl-7-bromotropolone (III). a) Bromination in Methanol in the Presence of Sodium Acetate: To a suspension of III (720 mg) and sodium acetate (300 mg) in methanol (15 ml), a solution of bromine (480 mg) in the same solvent (1 ml) was added, after which the mixture was stirred for 3 hr under cooling with ice water. The reaction mixture was diluted with water, and the product was extracted with chloroform. The evaporation of the solvent left an oily material, which was solidified by the addition of methanol. Fractional recrystallization from methanol gave IV (420 mg) as pale yellow scales, mp 151—152°C, and VI (50 mg) as yellow needles, mp 158—159°C.

b) Bromination in Methanol in the Absence of Acetate: To a suspension of III (240 mg) in methanol (5 ml), a solution of bromine (160 mg) in the same solvent (1 ml) was added, after which the mixture was stirred for 3 hr under cooling with ice water. The solvent was then evaporated, and the residue was fractionally recrystallized from methanol to give V (90 mg) as yellow needles mp 149—151°C, and VI (50 mg) as yellow needles, mp 158—159°C.

c) Bromination in Acetic Acid: To a suspension of III (240 mg) and sodium acetate (100 mg) in glacial acetic acid (8 ml), a solution of bromine (160 mg) in the same solvent (1 ml) was added, after which the mixture was stirred for 2 hr under cooling with ice water. Water was then added to the mixture, and the crystals thereby formed were collected and fractionally recrystallized from methanol to give VI (80 mg) as yellow needles, mp 158—159°C, III (80 mg) was also recovered.

A similar treatment of III (120 mg) with two molar equivalents of bromine gave VI (160 mg); mp 158—159°C.

4-Acetyl-7-bromotropolone (III) from 7-Bromo-4-isopropenyltropolone (VII).[7] a) To a solution of VII (960 mg) in formic acid (7 ml), a 30% hydrogen peroxide solution (0.5 ml) was dropped in at 40—55°C; the mixture was then kept at this temperature for 3 hr. The solvent was evaporated, and the oily residue was dissolved in an N sodium hydroxide solution (10 ml). This solution was warmed at 50—60°C for 5 hr, and then acidified with 2N sulfuric acid and shaken with chloroform. To the aqueous layer potassium periodate (460 mg) was added, after which the mixture was stirred for an hour at room temperature. The crystals thereby formed were collected and recrystallized from methanol to give III (250 mg) as yellow needles; mp 132—133°C.

b) A solution of VII (480 mg) in chloroform (1 ml) was stirred to a mixture of sodium azide (400 mg), chloroform (2 ml), and concentrated sulfuric acid (2 ml) at about 20°C. After being stirred for 3 hr, the mixture was allowed to stand overnight; then it was poured into ice water and extracted with chloroform. The solvent was evaporated, and the residue was recrystallized from methanol to give III (150 mg) as yellow needles; mp 132—133°C.

4-(1,1-Ethylenedioxyethyl)tropolone (VIII). A mixture of I (2.20 g), ethyleneglycol (4.10 g), and benzene (15 ml) was refluxed for 5 hr in the presence of *p*-toluenesulfonic acid (10 mg). The benzene-soluble part was collected by decantation; the subsequent evaporation of the solvent gave VIII (2.68 g), mp 90—93°C. Recrystallization from petroleum ether af-

forded colorless needles; mp 98—99°C. The melting point previously reported[9] was 97—98°C.

Found: C, 63.95; H, 5.44%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%. UV (MeOH): λ_{max} nm (log ε); 238 (4.45), 320 (3.89), 350 (3.78).

4-(1,1-Ethylenedioxyethyl)-5-(p-tolylazo)tropolone (IX). Into a solution of VIII (600 mg) in pyridine (2 ml), we stirred a solution of *p*-toluenediazonium chloride which had been prepared by the diazotization of a solution of *p*-toluidine (330 mg) in 2N hydrochloric acid with a solution of sodium nitrite (240 mg) in water (1.5 ml); we did this under cooling with ice water. After additional stirring for 2 hr, water was added to this mixture and the crystals thereby formed were collected and recrystallized from benzene to give IX (470 mg) as red micro-prisms; mp 176—178°C.

Found: C, 65.95; H, 5.38; N, 8.42%. Calcd for $C_{18}H_{18}O_4N_2$: C, 66.24; H, 5.56; N, 9.58%. UV (MeOH): λ_{max} nm (log ε); 230 (4.39), 293 (4.00), 385 (4.35).

5-Amino-4-(1,1-ethylenedioxyethyl)tropolone (X). A suspension of IX (660 mg) in methanol (12 ml) was shaken under a hydrogen atmosphere in the presence of 5% palladium-carbon (80 mg); 100 ml of hydrogen gas was consumed during a period of 7 hr. After the subsequent removal of the catalyst, the solution was concentrated to a small volume and allowed to cool, thus giving X (270 mg); mp 164—166°C. Recrystallization from methanol afforded yellow plates; mp 166—167°C.

Found: C, 59.04; H, 5.65; N, 6.30%. Calcd for $C_{11}H_{13}O_4N$: C, 59.18; H, 5.87; N, 6.28%. UV (MeOH): λ_{max} nm (log ε); 238 (4.38), 360 (4.12), 387 (4.08).

4-Acetyl-5-aminotropolone (XI). A solution of X (200 mg) in methanol (5 ml) containing N hydrochloric acid (0.5 ml) was refluxed for an hour. The subsequent concentration of the solution gave XI (150 mg) as reddish-orange needles; mp 180—181°C.

Found: C, 60.39; H, 4.76; N, 7.47%. Calcd for $C_9H_9O_3N$: C, 60.33; H, 5.06; N, 7.82%. UV (MeOH): λ_{max} nm (log ε); 247 (4.47), 365 (4.12), 465 (3.93).

4-Acetyl-5-bromotropolone (XII). Into a solution of X (220 mg) in 50% aqueous dioxane (2.5 ml) containing 6N sulfuric acid (0.9 ml), a solution of sodium nitrite (75 mg) in water (0.2 ml) was added at 0—5°C. After stirring for an additional 30 min, this mixture was added to a solution of cuprous bromide (350 mg) in concentrated hydrobromic acid (1.9 ml), after which the mixture was stirred for 3 hr under cooling with ice water. The mixture was diluted with water, and the copper chelate compound thus precipitated was collected by filtration. Through a suspension of this copper chelate in chloroform, hydrogen sulfide gas was passed, after which the copper sulfide thereby formed was filtered off. The subsequent evaporation of the solvent from the filtrate left some crystals (170 mg); mp 105—125°C. Recrystallization from methanol gave XII (90 mg) as pale yellow needles; mp 142—143°C.

Found: C, 44.09; H, 2.80%. Calcd for $C_9H_7O_3Br$: C, 44.47; H, 2.90%. UV (MeOH): λ_{max} nm (log ε); 235 (4.29), 248 (4.30), 335 (4.04), 4.10 (3.54). IR (KBr disk); $\nu_{C=O}$, 1709 cm^{-1}.

A similar treatment of XI (70 mg) gave XII (30 mg); mp 142—143°C.

Bromination of 4-Acetyl-5-bromotropolone (XII). To a solution of XII (50 mg) and sodium acetate (40 mg) in glacial acetic acid (1 ml), a solution of bromine (65 mg) in the same solvent (0.5 ml) was added, after which the mixture was stirred for 2 hr under cooling with ice water. Water was then added to this mixture, and the crystals thereby formed were collected and recrystallized from methanol to give VI (70 mg) as yellow needles; mp 158—159°C.

Bromination of 4-Acetyl-3,7-dibromotropolone (IV). To a solution of IV (110 mg) and sodium acetate (30 mg) in glacial acetic acid (2 ml), a solution of bromine (60 mg) in the same solvent (0.5 ml) was added, after which the mixture was stirred for 2 hr. Water was then added to this mixture, and the crystals thereby formed were collected and recrystallized from methanol to give VI (110 mg) as yellow needles; mp 158—159°C.

3,5,7-Tribromo-4-(ω-bromoacetyl)tropolone (XIII). To a solution of V (640 mg) and sodium acetate (200 mg) in glacial acetic acid (20 ml), a solution of bromine (320 mg) in the same solvent (1 ml) was added, after which the mixture was stirred for 2 hr under cooling with ice water. Water was then added to this mixture, and the crystals thereby formed were collected and recrystallized from methanol to give XIII (490 mg); mp 161—162°C. Further recrystallization from the same solvent afforded yellow needles; mp 164—165°C.

Found: C, 22.23; H, 1.09%. Calcd for $C_9H_4O_3Br_4$: C, 22.53; H, 0.84%. UV (MeOH): λ_{max} nm (log ε); 273 (4.48), 360 (4.14), 450 (4.18). IR (KBr disk); $\nu_{C=O}$, 1730 cm^{-1}.

4-Acetyl-5,7-dibromotropolone (XIV). A solution of VI (400 mg) and sodium iodide (300 mg) in ethanol (10 ml) was refluxed for 3 hr. To this solution we then added water (30 ml) containing a small amount of sodium hydrogen sulfite, and the mixture was stirred for 30 min. The crystals thereby formed were collected and recrystallized from methanol to give XIV (90 mg) as yellow, silky needles; mp 191—192°C.

Found: C, 33.73; H, 1.94%. Calcd for $C_9H_6O_3Br_2$: C, 33.57; H, 1.88%. UV (MeOH): λ_{max} nm (log ε); 265 (4.40), 353 (4.15), 430 (4.00). IR (KBr disk); $\nu_{C=O}$, 1700 cm^{-1}.

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