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Preparation of Polyacetoxytropones and Polyhydroxytropolones by Acetolysis and Hydrolysis of Halotroponoids by Acetyl Trifluoroacetate with Exhaustive Displacement of Halogens on the Tropone Ring. Predominant Formation of Reductive Acetolysates from Fully-Substituted Tropones

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Di-, tri-, and tetrahydroxytropolones were prepared in good yields by the acetolysis of corresponding halotropones or polyhalotropolones with acetyl trifluoroacetate followed by acetic acid hydrolysis. However, using the same treatment to obtain hexaacetoxytropone with fully substituted acetoxyhalotropones predominantly yielded fewer substituted acetoxytropones than expected; the mechanism of formation was shown to involve an acetic acid-mediated reduction of intermediary formed acetoxy-*p*-tropoquinone equivalents. A couple of 2,7-unsubstituted 3,4-diacetoxytropones were deduced to have cyclized 1,3-dioxole structures, 2-acetoxy-2-methyl-5*H*-cyclohepta-1,3-dioxol-5-ones. An acetolysis of the brominated 5-isopropyltropolones furnished an acetylated by-product, 2,3,7-triacetoxy-5-(1,1-dimethyl-2-oxopropyl)tropone, which might be formed by the acylation of an intermediate, 3,4,5,6-tetraacetoxy-8,8-dimethylheptafulvene.

It is well-known that polyhydroxytropolones are physiologically active; in the 1930's several carboxylic acid derivatives, stipitatic acid,[1] stipitatonic acid,[2] puberulic acid,[3] and puberulonic acid,[3] which all possessed additional hydroxyl groups, had already been isolated from microorganisms such as *Penicillium stipitatum Thom.* and *P. puberulum Bainier.* Even 3-hydroxytropolone (**1**) was recognized to be an antibiotic.[4]

Therefore, a systematic method for synthesizing polyhydroxylic tropolones is desirable; recently, we have demonstrated the facile preparation of **1** from 7-bromo-2-methoxytropone (**2**) by treatment with acetyl trifluoroacetate (ATA) prepared in situ from acetic anhydride and trifluoroacetic acid, with or without sodium acetate.[5]

In order to detemine its a versatility, we have extended this method to prepare 3- (**1**),[6] 4- (**3**),[7] and 5-hydroxytropolones (**4**),[8,9] along with several further hydroxylated tropolones, such as di-, tri-, tetra-, and pentahydroxytropolones. It is true that, to date, there has been no efficient method for the preparation of such fundamental derivatives, **1** and **3**; for the hydrochloric acid-hydrolysis of 3-bromotropolone (**5**) to **1** it was necessary to heat at 160—180 °C,[6] while an alkali fusion of **5** gave **3** instead of **1**. However, its yield was at most 17%.[7]

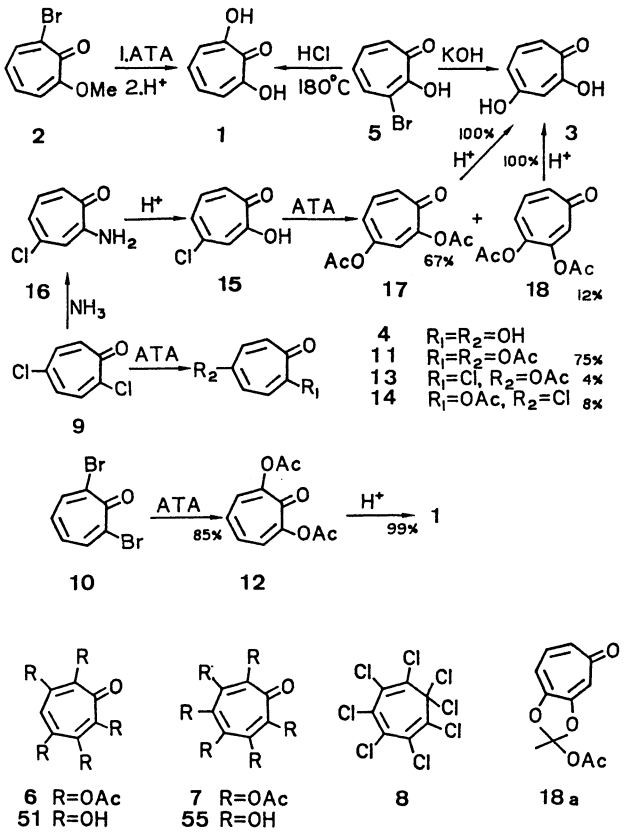
The attempted formation of pentaacetoxytropone (**6**) and hexaacetoxytropone (**7**) from corresponding halotroponoids by this method, however, yielded fewer substituted derivatives than predicted. After all, octachlorocycloheptatriene (**8**)[10] was converted to **7** in low yield together with some intermediary acetoxychlorotropones. Herein, we will show the results.

Results and Discussion

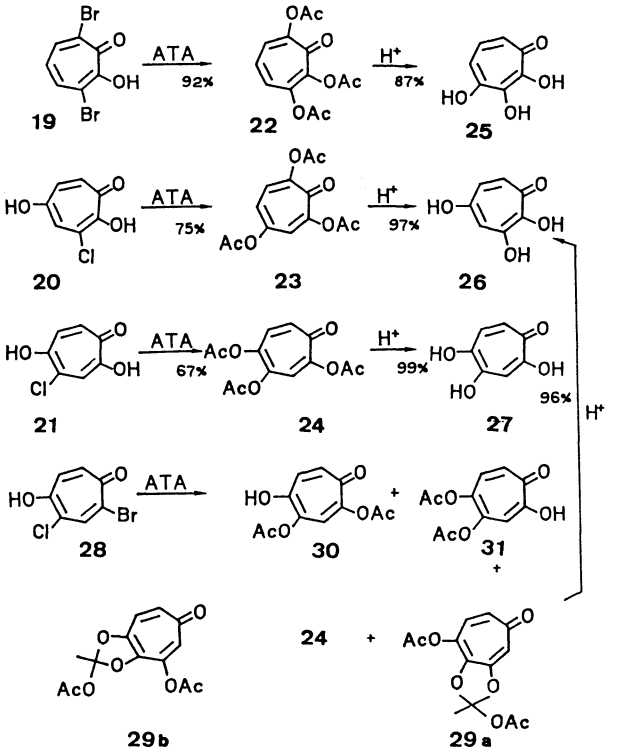
Acetolysis of Dihalotropones. First of all, in order to prepare fundamental hydroxytropolones, when 2,5-dichlorotropone (**9**)[11] and 2,7-dibromotropone (**10**)[12] were treated with ATA at 85 °C, a neat reaction occurred to form the halogen-free compounds, 2,5-diacetoxytropone (**11**)[8] and 2,7-diacetoxytropone (**12**),[8] 75 and 85%, respectively. Both **11** and **12** were identical with the authentic samples, as confirmed by direct comparisons. Under the conditions, **9** formed two intermediary chlorine-containing compounds, 5-acetoxy-2-chlorotropone (**13**)[13] and 2-acetoxy-5-chlorotropone (**14**), in 4 and 8% yields, respectively. Heating at a higher temperature, 100 °C, or for a prolonged period smoothly resulted in the replacement of all of the halogen atoms. In all cases, there was no ring-contracted benzene derivative. A mild hydrolysis of **11** and **12** with aqueous acetic acid gave, after evaporation of the solvent, **4** and **1** in nearly quantitative yields. Therefore, this may be applicable for preparing hydroxytropolones from corresponding halotropones.

Similarly, 4-chlorotropolone (**15**),[14] prepared from **9** via 2-amino-4-chlorotropone (**16**) by sequential reactions, was converted via 2,4-diacetoxytropone (**17**) and 3,4-diacetoxytropone (**18**) to 4-hydroxytropolone (**3**) as the sole product. An attempted hydrolysis of **15** with concentrated hydrochloric acid or acetolysis of **16** with the present reagent has been unsuccessful. Noteworthy was the structure of **18**. Namely, the ^{13}C NMR spectrum of **17** indicated an operating acetotropy[15,16] at room temperature, but that of **18** did not. In addition, its ^{1}H NMR showed another aspect of anomaly; the acetoxyl methyl signals on the troponoid rings generally appeared at δ=2.2 to 2.3; however, the acetoxyl signals of **18** were at a much higher region, i.e., one at 2.00, and the other at 2.08. These would not be ascribable to those on the aromatic ring. Moreover its ^{13}C NMR revealed a quarternary carbon signal at δ=124.3; this value has no analogy in any of the other

acetoxytropones that have been studied. Taking all these observations into account, **18** should be formulated as a cyclized 1,3-dioxole (**18a**) as depicted in Scheme 1. The formation of such a cyclized structure



Scheme 1.

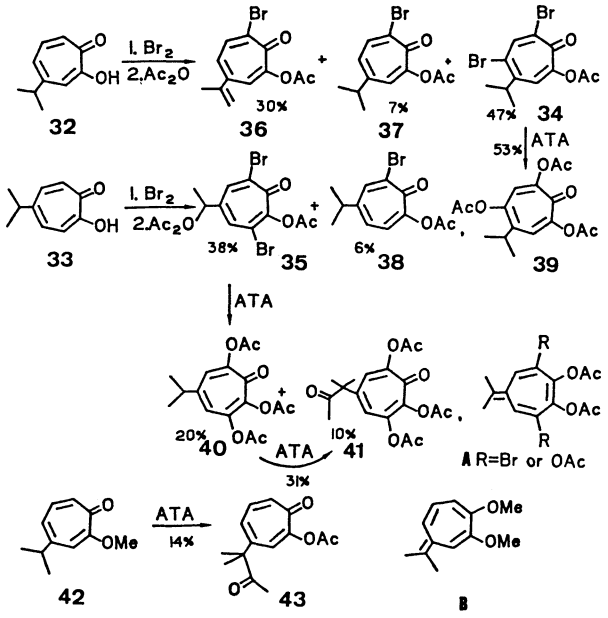


Scheme 2.

should be attributable to severe steric and repulsive non-bonding interactions of the *vic*-diacetoxyl groups on the seven-membered ring.[17]

Acetolysis of Dihalotropolones. By a similar acetolysis, 3,7-dibromotropolone (**19**),[18] 3-chloro-5-hydroxytropolone (**20**),[19] and 4-chloro-5-hydroxytropolone (**21**)[20] were respectively converted to triacetoxytropones, 2,3,7-triacetoxytropone (**22**), 2,4,7-triacetoxytropone (**23**),[21,22] and 2,4,5-triacetoxytropone (**24**), and further to dihydroxytropolones, 3,4-dihydroxytropolone (**25**),[3] 3,5-dihydroxytropolone (**26**),[19] and 4,5-dihydroxytropolone (**27**). From 2-bromo-4-chloro-5-hydroxytropone (**28**), four halogen-free products (**24**, **29**, **30**, and **31**) were isolated via silica-gel column chromatography; the major product obtained after elutions of **29** was the expected **24**. The ^{1}H NMR spectrum of **29** was identical with the "3,4,5-triacetoxytropone" already prepared by Itô et al., and its aqueous acetic acid hydrolysis indeed yielded **26**.[21,22] However, the ^{1}H NMR chemical shifts of the acetoxyl methyl signals again suggested a 1,3-dioxole derivative; the two methyl singlets at δ=2.01 and 2.08 were incompatible with the acetoxyl signals on the aromatic ring and were, therefore, tentatively assigned to be 2,8-diacetoxy-2-methyl-5*H*-cyclohepta-1,3-dioxol-5-one (**29a**), as depicted.[23,24] The formation of **29a** from **28** must involve a substitution at a remote position of the leaving group. More polar compounds, **30** and **31**, were partially-hydrolyzed diacetoxyhydroxytropones and the ^{1}H and ^{13}C NMR spectra distinguished the structures; **30**, showing a symmetry element, is therefore 2,4-diacetoxy-5-hydroxytropone.

Acetolysis of Bromo Derivatives Prepared from 4-, and 5-Isopropyltropolones. To extend the applicability of the reaction to alkyl derivatives, the acetolysis of dibromo derivatives of hinokitiol (**32**) and γ-



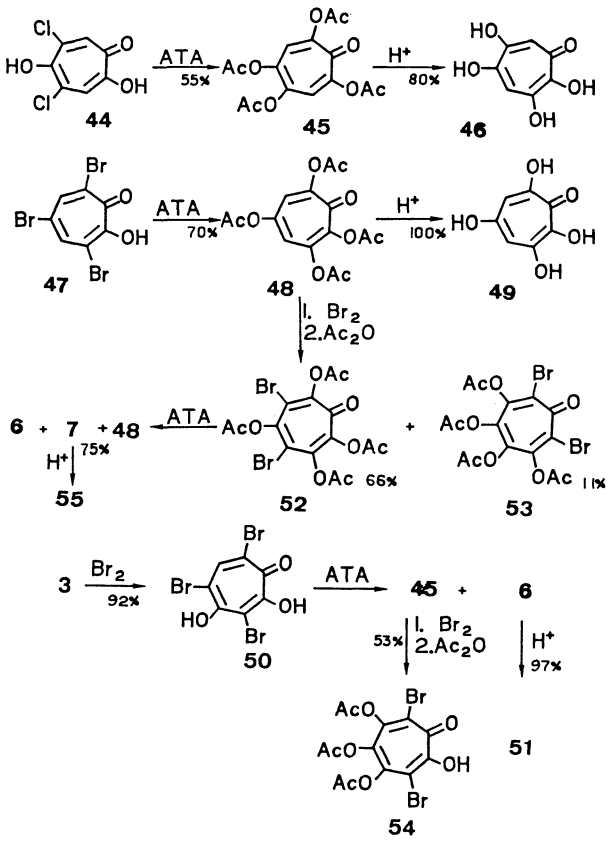
Scheme 3.

thujaplicin (**33**), 2-acetoxy-5,7-dibromo-4-isopropyltropone (**34**) and 2-acetoxy-3,7-dibromo-5-isopropyltropone (**35**),[25,26] was carried out. Through brominations, we have identified by-products, 2-acetoxy-7-bromo-4-isopropenyltropone (**36**) and 2-acetoxy-7-bromo-4-isopropyltropone (**37**) from **32** and 2-acetoxy-7-bromo-5-isopropyltropone (**38**) from **33**;[27] however, this is not further discussed.

The acetolysis of **34** and **35**, respectively, gave triacetoxytropones, 2,4,7-triacetoxy-5-isopropyltropone (**39**) and 2,3,7-triacetoxy-5-isopropyltropone (**40**) in good yields. A notable by-product in the acetolysis of **35** was the acylation product, 2,3,7-triacetoxy-5-(1,1-dimethyl-2-oxopropyl)tropone (**41**). An independent treatment of **40** gave **41** in a better yield, 31%. Evidently, **41** must be produced via a heptafulvene intermediate (**A**). The fact that such an acylated product from **34** did not appear might be due to the presence of an acetoxyl group at the vicinity of the isopropyl group, C-4. Indeed, acylation also occurred with a halogen-free heptafulvene (**B**) from 4-isopropyl-2-methoxytropone (**42**); a similar treatment of **42**, indeed, afforded 14% of the acylation product, 2-acetoxy-4-(1,1-dimethyl-2-oxopropyl)tropone (**43**). It has been emphasized that the Friedel-Crafts-type acylation and alkylation were not applicable to troponoids because of their insoluble metal chelate formation with the catalysts or easy protonation to form a delocalized stable cationic 6 π species by acid. The present example must constitute an overcoming of a deactivated reactivity towards the Friedel-Crafts acylation of the non-benzenoid aromatics. The electrophilic substitution of heptafulvenes has been successfully carried out only with some 8-monosubstituted heptafulvenes, such as 8-cyanoheptafulvene, showing that the reaction site is exclusively C-8.[28] The present examples are in that line.

Acetolysis of Polyhalo Troponoids: Occurrence of Reduction Process. Subsequently, when 4,6-dichloro-5-hydroxytropolone (**44**)[19] was treated with ATA, 2,4,5,7-tetraacetoxytropone (**45**) was obtained in 55% yield, and its mild hydrolysis gave 3,5,6-trihydroxytropolone (**46**) in 80% yield. On the other hand, 3,5,7-tribromotropolone (**47**) afforded 2,3,5,7-tetraacetoxytropone (**48**) and 3,4,6-trihydroxytropolone (**49**) in good yields.

However, the same treatment of 3,5,7-tribromo-4-hydroxytropolone (**50**), obtained from the bromination of **3**, afforded a small amount of pentaacetoxytropone (**6**). The hydrolysis of **6** gave tetrahydroxytropolone (**51**). Even more surprising was the predominant formation of **6** from 2,3,5,7-tetraacetoxy-4,6-dibromotropone (**52**), which was prepared together with 3,4,5,6-tetraacetoxy-2,7-dibromotropone (**53**) by a further bromination and acetylation of **48**;[29] the yield of the expected **7** was around 0.5%. Several other attempts to make **7** from fully-substituted acetoxyhalotropones always resulted in the formation of **6**. Although the yields for the acetolysis products in the polysubstituted derivatives could be improved by the addition of sodium acetate to the mixture, yields of the reduction products became more predominant. For example, **50** gave the expected **6** in 11% yield together with **45** in 60% yield, whose bromination and acetylation afforded 4,5,6-triacetoxy-3,7-dibromotropolone (**54**). On the other hand, **52** yielded **48** in 48% and **6** in 12% yield. Particularly, the formation of **48** from **52** indicates an occurrence of two-fold reduction.[30] Thus, in the acetolysis of the polyhalotropones, the yields of the substitution product could not be improved by the addition of sodium acetate. The results are summarized in Table 1. As a whole, in spite of intensive attempts, the formation of **7** from fully substituted polyacetoxyhalotropones was not reproducible. A mild hydrolysis of **7** gave pentahydroxytropolone (**55**) in 75% yield.



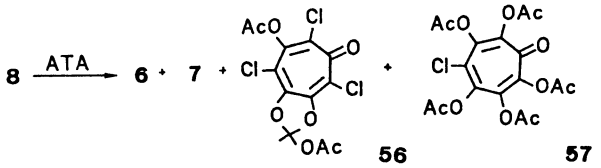
Scheme 4.

Table 1. Acetolysis of **50**, **52**, and **8** with ATA

Substrate	Condition	Addition	Yield/% of Product			
			6	**45**	**7**	**48**
50	85 °C, 9 h	—	11	—	—	—
50	125 °C, 2 d	NaOAc	11	60	—	—
52	110 °C, 5 d	—	2.6	—	0.5	—
52	110 °C, 5 d	NaOAc	12	—	—	48
8[a]	115 °C, 5 d[b]	NaOAc	3	—	0.6	—

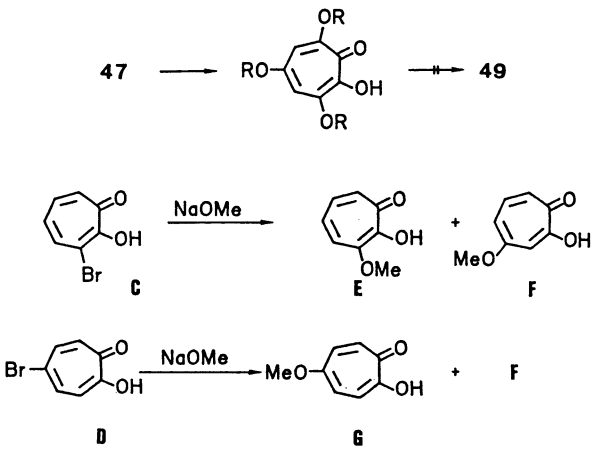
a) Acetolyses of **8** under other conditions were cited in Experimental. b) These were followed by further heating at 160 °C for 2 d.

Nevertheless, ATA-acetolysis of **8** always gave **6** and **7** in low yields together with a mixture of intermediary trichloro and monochloro derivatives (**56** and **57**). The structure of an intermediate product, **56**, was of interest. Its elemental analysis was compatible to triacetoxytrichlorotropone, and the ^{1}H and ^{13}CNMR spectra suggested 1,3-dioxole, since two of the three acetoxymethyl signals appeared at δ=2.09 and 2.12 together with a signal at 124.1. This signal is ascribable to the ortho-acetate carbon, being parallel to "3,4-diacetoxytropone" (**18a**) and "3,4,5-triacetoxytropone" (**29a**), which exist as a cyclized 1,3-dioxole form. These observations, together with a low-field signal at 2.38, an acetoxyl group between two chlorine atoms, indicated the structure to be 2,7-diacetoxy-4,6,8-trichloro-2-methyl-5*H*-cyclohepta-1,3-dioxol-5-one, a cyclisate from 3,4,6-triacetoxy-2,5,7-trichlorotropone.



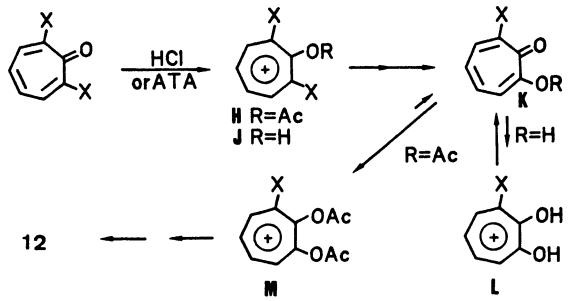
Scheme 5.

As far as we know, the previously known methods of hydrolyzing polyhalotropones have several limitations. Namely, an acid-hydrolysis of 2,7-dihalotropones to 3-halotropolones is rapid, but the second step of the substitution is very slow.[6] While 3,5,7-tribromotropolone (**47**) could be converted to 3,5,7-trialkoxytropolones together with several by-products, its hydrolysis to **49** was unsuccessful.[21] In addition to the above, a mechanistically-interesting elimination-addition reaction of 3- and 5-bromotropolones (**C** and **D**) with sodium methoxide is known to form, via benzyne-type intermediates, 3-, 4-, and 5-methoxytropolones (**E**, **F**, and **G**). However, this procedure should not be applicable to the displacement of *vic*-dihalo derivatives to alkoxyl groups.[31] Furthermore, the previously-studied sulfuric acid-hydrolysis of **8** gave structure-unidentified tetrachlorodihydroxytropones.[10] Thus, the utility of the present method for preparation of halogen-free derivatives is outstanding.



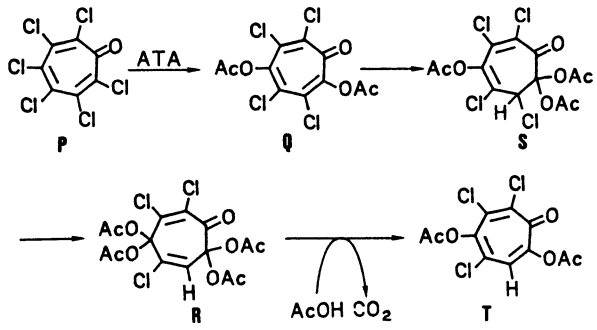
Scheme 6.

Since intermediates in the displacement of halogens, halogenated acetoxycycloheptatrienylium ions (**H**) should be formed, their further acetoxylation might be equally easy. To the contrary, the intermediate formed in the first step in an ordinary acid hydrolysis of polyhalotropones should be halogenated dihydroxycycloheptatrienylium salt (**L**), which can be deprotonated easily to tropolones (**K**). This is the reason why ordinary acid hydrolysis gives halogenated monohydroxylic tropones. In addition, this ATA acetolysis was inapplicable to the benzenoid compounds.[5] Therefore, this exhaustive displacement of acetoxyl group proceeded to the advantage of the formation of **H**.



Scheme 7.

Mechanism of Formation of Reduction Products. Now, the reaction mechanism leading to reduced products should be explained. In the later steps of the acetolysis in polysubstituted troponoids (**P**), the acetolysates may become halogenated 2,5-diacetoxytropone derivatives (**Q**). In case of sterically hindered **Q**, the base, sodium acetate, may facilitate an elimination of acetyl halide (or hydrogen halide) rather than a substitution to form the *p*-tropoquinone (**R**) via an intermediate (**S**). Under these conditions, *p*-tropoquinones should be reduced by acetic acid to 2,5-diacetoxytropone derivative (**T**), being parallel to the previously described parent *p*-tropoquinone and other derivatives.[19,32]

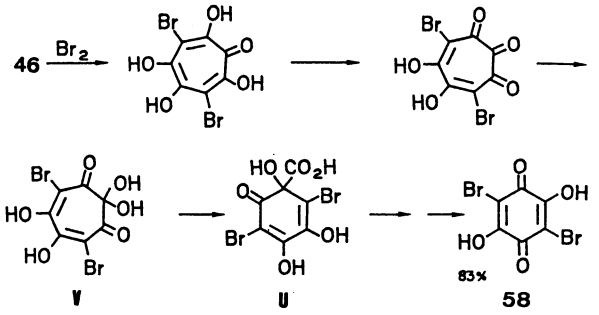


Scheme 8.

Conclusion

Before concluding, results of the bromination reac-

tion of polyhydroxytropolones must be mentioned. When **46** was treated with bromine in acetic acid at room temperature, a rapid decoloration of bromine was observed. The product after heating at 95 °C was, however, 2,5-dibromo-3,6-dihydroxy-*p*-benzoquinone (**58**);[33] evidently, a benzil-benzilic acid rearrangement product (**U**) of an intermediate, an *o*-tropoquinone hydrate derivative (**V**), was further decarboxylated to **58**, and a protection of free hydroxyl group must be essential to avoid the ring contraction.



Scheme 9.

Finally, up to pentaacetoxytropone, the present procedure is satisfactory; but for fully oxygenated hexaacetoxytropone, the reduction process was predominant. Still, no ring-contraction to the benzenoid derivative occurred. This is the scope and limitation of this method. The ^{1}H- and ^{13}C NMR spectra of hexaacetoxytropone, a potential C_7-oxo carbon precursor, has disclosed a degenerated acetyl migration operative at room temperature, and the kinetic features of this rearrangement will be a subject of an independent publication.[16]

Experimental

Elemental analyses were carried out by Miss S. Hirashima, of the Research Institute of Industrial Science, Kyushu University. The NMR spectra were measured by a JEOL FX 100 Spectrometer in $CDCl_3$ solution, unless otherwise specified, and the chemical shifts expressed were in δ unit. The mass spectra were measured with a JEOL OISG-2 Spectrometer. The IR spectra were taken as KBr disks or as a liquid film inserted between NaCl plates using a Jasco IR-A 102 Spectrometer. The UV spectra were measured by a Hitachi U-3200 Spectrophotometer.

Preparation of Acetyl Trifluoroacetate (ATA). Ac_2O (50 cm^3) was mixed with CF_3COOH (5 cm^3) and AcOH (2.5 cm^3) at room temperature. The whole operation should be carefully undertaken in a good ventilated hood. Each time, a portion of the solution was taken out by pipette.

Acetolysis of 2,5-Dichlorotropone (9). An ATA solution[34] (5.6 cm^3) of **9** (100 mg) was sealed in an autoclave and heated at 85 °C for 10 h. After removal of the solvent in vacuo, the residue was chromatographed on a silica-gel column to give **14** [colorless crystals, mp 70.5—73.5 °C, 9 mg; 8%. Found: C, 54.17; H, 3.58%; *m/z* 198.0068 and 200.0023 (M^+). Calcd for $C_9H_7O_3Cl$: C, 54.41; H, 3.53%; M, 198.0081 and 200.0053. ^{1}H NMR δ=2.33 (3H, s), 7.05 (2H, dd, J=11, 1.5 Hz), and 7.24 (2H, dd, J=11, 1.5 Hz). ^{13}C NMR δ=20.6, 132.4, 132.8, 134.0 (2C), 140.2, and 168.0 (3C). IR ν: 1765, 1630, 1580, 1200, 1075, and 860 cm^{-1}], **13** [colorless crystals, mp 102—103 °C (lit,[12] 101.5—102 °C), 4 mg; 4%. ^{1}H NMR δ=2.29 (3H, s), 6.68 (1H, ddd, J=10.5, 2.5, 0.5 Hz), 6.97 (1H, dd, J=13, 2.5 Hz), 7.21 (1H, dd, J=13, 0.5 Hz), and 7.71 (1H, d, J=10.5 Hz). ^{13}C NMR δ=20.9, 122.2, 133.9, 134.2, 138.2, 147.4, 154.5, 168.9, and 179.4], and **11** [pale yellow needles, mp 93—95 °C (lit,[8] 91—92 °C), 95 mg; 75%. ^{1}H NMR δ=2.26 (3H, s), 2.31 (3H, s), 6.88 (2H, dd, J=10.5, 1.5 Hz), and 7.17 (2H, dd, J=10.5, 1.5 Hz). ^{13}C NMR δ=20.6, 20.9, 128.2 (2C), 133.0 (2C), 153.5, 167.9 (2C), and 168.7 (2C). IR ν: 1755, 1585, 1365, 1140, and 920 cm^{-1}].

Acetolysis of 2,7-Dibromotropone (10). An ATA solution (8 cm^3) of **10** (64.2 mg) and NaOAc (101 mg) was heated in a sealed tube at 100 °C for 24 h. The mixture was then heated in vacuo, and the residue was chromatographed on a silica-gel column to give **12** [a colorless crystals, mp 90—91 °C (lit,[5] 86—87 °C), 45.6 mg; 85%].

Hydrolysis of 12 to 1. An aqueous AcOH (50%, 10 cm^3) of **12** (490 mg) was heated at 100 °C for 16 h to give **1** [orange needles, mp 179—181 °C, 248 mg; 99%].

Attempted Acetolysis of 2-Amino-4-chlorotropone (16). An ATA solution (2 cm^3) of **16** (40 mg) was heated in a sealed tube at 100 °C for 6 h. After evaporation of the solvent in vacuo, the residue was chromatographed on a silica-gel column, but no identifiable compound was obtained.

Acetolysis of 4-Chlorotropolone (15). An ATA solution (50 cm^3) of **15** (1.197 g) was heated in an autoclave at 100 °C for 14 h. The mixture was then heated in vacuo to remove the solvent, and the residue was chromatographed on a silica-gel column to give **17** [colorless crystals, mp 101—102.5 °C, 1.138 g; 67%. Found: C, 59.72; H, 4.48%. Calcd for $C_{11}H_{10}O_5$: C, 59.46; H, 4.54%. ^{1}H NMR δ=2.22 (3H, s), 2.28 (3H, s), 6.79 (1H, ddd, J=9, 3, 2 Hz), 6.96 (1H, d, J=2 Hz), 7.00 (1H, dd, J=10, 9 Hz), and 7.13 (1H, dd, J=10, 3 Hz). ^{13}C NMR δ=20.5, 20.8, 129.5, 129.7, 130.0, 131.9, 156.0, 164.2, 167.8, 168.5, and 170.9. IR ν: 2940, 1740, 1580, 1515, 1365, 1185, 1100, 1005, and 915 cm^{-1}] and **18** [pale yellow crystals, mp 89—91 °C, 212 mg; 12%. Found: C, 59.39; H, 4.53%. ^{1}H NMR δ=2.00 (3H, s), 2.08 (3H, s), 6.44 (1H, dd, J=8, 2 Hz), and 6.65—7.05 (3H, m). ^{13}C NMR δ=21.5, 24.0, 107.0, 115.6, 124.3, 133.4, 136.7, 154.2, 157.0, 167.3, and 184.7. IR ν: 1775, 1680, 1400, 1110, 955, and 880 cm^{-1}. UV λ_{max}^{MeOH}: 239 nm (ε=23200), 246 (22600, sh), 257 (18900, sh), 271 (5400, sh), 301 (6200, sh), and 312 (7100)].

Hydrolysis of 2,4-Diacetoxytropone (17). An aqueous AcOH solution (50%, 20 cm^3) of **17** (1.22 g) was heated at 100 °C for 5 h. After removal of the solvent in vacuo, the residue was washed with AcOEt, and recrystallized from MeOH to give **3** [colorless crystals, mp 229—230 °C (lit,[1] 230—231 °C), 761 mg; 100%. ^{1}H NMR (CD_3OD) δ=6.72 (1H, ddd, J=10.7, 2.5, 1 Hz), 6.87 (1H, d, J=2.5 Hz), 6.92 (1H, dd, J=10.3, 1 Hz), and 7.24 (1H, dd, J=10.7, 10.3 Hz). ^{13}C NMR (CD_3OD) δ=114.7, 115.8, 121.5, 138.1, 168.4, 169.8, and 174.7. IR ν: 3210, 2930, 1590, 1420, 1210, and 730 cm^{-1}].

Hydrolysis of 18 to 3. An aqueous AcOH solution (3 cm^3) of **18** (100 mg) was heated at 100 °C for 5 h. The same work up as above yielded **3** [62 mg; 100%].

Acetolysis of 3,7-Dibromotropolone (19) to 2,3,7-Triacetoxytropone (22). An ATA solution (10 cm^3) of **19** (117.4 mg) and NaOAc (168 mg) was similarly heated in a sealed tube at 100 °C for 4 d. The mixture was then heated in vacuo to

remove the volatile material and the residue was chromatographed on a silica-gel column to give **22** [a pale yellow oil, 107.9 mg; 92%. Found: m/z[35] 280.0551 (M^+). Calcd for $C_{13}H_{12}O_7$: M, 280.0581. ^{1}H NMR δ=2.30 (6H, s), 2.32 (3H, s), and 6.9—7.2 (3H, m). ^{13}C NMR δ=20.3, 20.5 (2C), 128.8, 129.2 (2C), 154.4 (2C), 166.9 (2C), and 167.8 (3C). IR ν: 1770, 1740, 1600, 1370, 1150, 1010, and 875 cm^{-1}].

Acetolysis of 3-Chloro-5-hydroxytropolone (20) to 2,4,7-Triacetoxytropone (23). An ATA solution (10 cm^3) of **20** (50 mg) was similarly heated in a sealed tube at 90 °C for 7 h. The mixture was then heated to remove the solvent and the residue was chromatographed on a silica-gel column to give **23** [colorless crystals, mp 110—111 °C (lit,[21,22] 111—112 °C), 61 mg; 75%. ^{1}H NMR δ=2.26 (3H, s), 2.31 (6H, s), 6.84 (1H, dd, J=10.5, 2.5 Hz), 7.12 (1H, d, J=2.5 Hz), and 7.21 (1H, d, J=10.5 Hz). ^{13}C NMR δ=20.4 (2C), 20.6, 122.8, 127.6, 127.8, 151.9, 155.8, 158.5, 167.3, 167.6 (2C), and 168.3].

Acetolysis of 4-Chloro-5-hydroxytropolone (21) to 2,4,5-Triacetoxytropone (24). An ATA solution (2 cm^3) of **21** (120 mg) was heated in a sealed tube at 80 °C for 4 h. The mixture was then heated to remove the solvent and the residue was chromatographed on a silica-gel column to give **24** [colorless needles, mp 126.5—128 °C, 130 mg; 67%. Found: C, 55.69; H, 4.31%. Calcd for $C_{13}H_{12}O_7$: C, 55.72; H, 4.32%. ^{1}H NMR δ=2.26 (6H, s), 2.32 (3H, s), 6.89 (1H, d, J=11.5 Hz), 7.06 (1H, s), and 7.11 (1H, d, J=11.5 Hz). ^{13}C NMR δ=20.4, 20.6, 20.8, 121.9, 123.5, 129.9, 146.5, 153.6, 153.8, 166.1, 167.2, 167.5, and 167.8. IR ν: 3050, 1770, 1595, 1370, 1070 and 910 cm^{-1}. UV λ_{max}^{MeOH}: 235 nm (ε=24400), 280 (6800), 318 (8400), and 384 (2000, sh)].

Hydrolysis of 22 to 3,4-Dihydroxytropolone (25). An aqueous AcOH solution (50%, 2 cm^3) of **22** (40.7 mg) was heated at 100 °C for 7 h. After cooling the solution to room temperature, the separated crystals were collected by filtration to give **25** [colorless plates, mp 230 °C (decomp) (lit,[3] mp 237—238 °C), 19.4 mg; 87%. ^{1}H NMR (CD_3OD) δ=7.04 (3H, s). ^{13}C NMR (CD_3OD) δ=119.3 (2C), 129.4, 158.4 (2C), and 159.1 (2C)].

Hydrolysis of 23 to 3,5-Dihydroxytropolone (26). An aqueous AcOH solution (50%, 6 cm^3) of **23** (61 mg) was heated at 100 °C for 24 h. After cooling, the mixture was heated in vacuo to remove the volatile material, and the residue was recrystallized from MeOH and AcOEt to give **26** [colorless crystals, mp 219—222 °C (lit,[20] 223—224 °C, 30 mg; 97%. ^{1}H NMR (CD_3OD) δ=6.93 (1H, s), 6.99 (1H, d, J=12 Hz), and 7.31 (1H, d, J=12 Hz). ^{13}C NMR (CD_3OD) δ=116.4, 116.7 (2C), 126.5, 127.9, 156.4, and 167.7.].

Hydrolysis of 24 to 4,5-Dihydroxytropolone (27). An aqueous AcOH solution (50%, 6 cm^3) of **24** (130 mg) was heated at 100 °C for 24 h. After evaporation of the mixture in vacuo, the residue was washed with AcOEt and recrystallized from MeOH and AcOEt to give **27** [pale yellow needles, mp 285—289 °C. 70 mg; 99%. Found: C, 54.48; H, 3.93%. Calcd for $C_7H_6O_4$: C, 54.54; H, 3.93%. ^{1}H NMR (CD_3OD) δ=6.92 (2H, s) and 7.04 (1H, s). ^{13}C NMR (CD_3OD) δ=116.2 (2C), 126.3, 156.0 (2C), and 167.5 (2C). IR ν: 3250, 2950, 1405, 1210, and 1090 cm^{-1}].

Acetolysis of 2-Bromo-4-chloro-5-hydroxytropone (28). a) An ATA solution (50 cm^3) of **28** (703 mg) was heated in a sealed tube at 85 °C for 15 h. The mixture was then heated in vacuo to remove the volatile material, and the residue was chromatographed on a silica-gel column to give [29] [colorless prisms, mp 127—128.5 °C, 86 mg; 10%. Found: C, 55.87; H, 4.32%. Calcd for $C_{13}H_{12}O_7$: C, 55.72; H, 4.32%. ^{1}H NMR δ=2.01 (3H, s), 2.08 (3H, s), 2.29 (3H, s), 6.42 (1H, d, J=10 Hz), 6.82 (1H, s), and 6.96 (1H, d, J=10 Hz). ^{13}C NMR δ=20.6, 21.5, 24.0, 103.8, 115.0, 124.4, 124.8, 152.9, 153.6, 156.8, 167.3, 168.6, and 176.0. IR ν: 1765, 1595, 1440, 1200, 1115, and 945 cm^{-1}. UV λ_{max}^{MeOH}: 240 nm (ε=26600), 258 (18100, sh), 310 (7500, sh), and 320 (8150)], **24** [380 mg; 45%], and **30** [colorless crystals, mp 131.5—132.5 °C, 37 mg; 5%. Found: C, 55.31; H, 4.31%. Calcd for $C_{11}H_{10}O_6$: C, 55.46; H, 4.23%. ^{1}H NMR δ=2.23 (6H, s), 6.93 (1H, s), and 7.02 (2H, s). ^{13}C NMR δ=20.6 (2C), 122.3, 124.6 (2C), 155.0 (2C), and 166—172 (4C). IR ν: 3600—3300, 1765, 1750, 1555, 1535, 1155 and 910 cm^{-1}. UV λ_{max}^{MeOH}: 252 nm (ε=30400), 263 (27000, sh), 332 (8200), and 367 (6700, sh)].

b) A similar treatment of **28** (50 mg) in an ATA solution (5 cm^3) at 85 °C for 10 h gave **24** [23 mg; 39%] and **31** [colorless crystals, mp 131—132.5 °C, 11 mg; 22%. Found: C, 55.18; H, 4.17%. Calcd for $C_{11}H_{10}O_6$: C, 55.46; H, 4.23%. ^{1}H NMR δ=2.27 (3H, s), 2.29 (3H, s), 6.88 (1H, d, J=11.2 Hz), 6.91 (1H, s), and 7.10 (1H, d, J=11.2 Hz). IR ν: 3050, 1770, 1560, 1370, 1155, and 915 cm^{-1}. UV λ_{max}^{MeOH}: 252 nm (ε=29100), 337 (7200), 358 (6700, sh), and 371 (5500, sh)].

Hydrolysis of 29 to 26. Similarly, an aqueous AcOH solution (6 cm^3) of **29** (86 mg) was heated at 100 °C for 4 h to yield **26** [45 mg; 96%], whose identity with the authentic **26** was confirmed by direct comparisons.

Bromination of Hinokitiol (32).[25] An AcOH solution (50 cm^3) of **32** (1.20 g) was treated with Br_2 (3.2 g) dissolved in AcOH (32 cm^3) at 5 °C. The mixture was then heated at 95 °C for 3 h and kept for further 15 h at room temperature. After removal of the solvent in vacuo, the residue was acetylated with Ac_2O (2 cm^3) by heating at 100 °C for 4 h. After evaporation of the solvent, the residue was chromatographed on a silica-gel column to give **34** [a yellow oil, 1.25 g; 47%. Found: C, 39.40; H, 3.32%. Calcd for $C_{12}H_{12}O_3Br_2$: C, 39.59; H, 3.32%. ^{1}H NMR δ=1.21 (6H, d, J=7 Hz), 2.34 (3H, s), 3.53 (1H, sept, J=7 Hz), 7.13 (1H, s), and 8.59 (1H, s). ^{13}C NMR δ=20.6, 21.6 (2C), 38.4, 126.4, 137.0, 144.9 (2C), 150.8, 153.7, and 167.9 (2C). IR ν: 2980, 1780, 1630, 1470, 1370, 1175, 1115, and 755 cm^{-1}. UV λ_{max}^{MeOH}: 241 nm (ε=16600), 259 (24000), 264 (23400, sh), 340 (10600), and 416 (1450)], **36** [colorless crystals, mp 99—101.5 °C, 625 mg; 30%. Found: C, 50.94; H, 3.93%. Calcd for $C_{12}H_{11}O_3Br$: C, 50.91; H, 3.92%. ^{1}H NMR δ=2.13 (3H, dd, J=1.5, 0.5 Hz), 2.35 (3H, s), 5.33 (1H, q, J=1.5 Hz), 5.42 (1H, br s), 6.91 (1H, dd, J=10.5, 2 Hz), 7.45 (1H, d, J=2 Hz), and 8.12 (1H, d, J=10.5 Hz). ^{13}C NMR δ=20.6, 21.8, 118.7, 127.6, 128.0, 139.1, 139.9, 143.8, 146.0, 155.2, 168.3, and 171.7. IR ν: 3600—3300, 1770, 1610, 1500, 1375, 1200, 1090, 920, and 860 cm^{-1}. UV λ_{max}^{MeOH}: 241 nm (ε=12300), 247 (16300), 256 (15800, sh), 345 (12300), 358 (10500, sh), and 377 (4850, sh)], and **37** [a yellow oil, 149 mg; 7%. Found: m/z 284.0106 and 286.0071 (M^+). Calcd for $C_{12}H_{13}O_3Br$: M, 284.0048 and 286.0028. ^{1}H NMR δ=1.24 (6H, d, J=7 Hz), 2.36 (3H, s), 2.82 (1H, sept, J=7 Hz), 6.76 (1H, dd, J=10, 1.5 Hz), 7.19 (1H, d, J=1.5 Hz), 8.04 (1H, d, J=10 Hz). ^{13}C NMR δ=20.7, 22.9 (2C), 38.1, 128.2, 130.1, 138.3, 140.1, 154.4, 157.7, and 168.3 (2C). IR ν: 2930, 1775, 1605, 1365, 1190, 1160, and 1080 cm^{-1}. UV λ_{max}^{MeOH}: 226 nm (ε=14500), 248 (20200), 254 (18900, sh), and 331 (9100)].

Bromination of γ-Thujaplicin (33).[26] An AcOH solution (40 cm^3) of **33** (0.80 g) was similarly treated with Br_2 (2.2 g) in AcOH (22 cm^3) at 5 °C. The mixture was then heated at 95 °C for 3 h. After the removal of the volatile materials in

vacuo, the residue was treated with Ac_2O at 100 °C for 4 h. The mixture was then heated again in vacuo to remove the solvent, and the residue was chromatographed on a silica-gel column to give **35** [pale yellow crystals, mp 60—64 °C, 669 mg; 38%. Found: C, 39.80; H, 3.44%. Calcd for $C_{12}H_{12}O_3Br_2$: C, 39.59; H, 3.32%. ^{1}H NMR δ=1.25 (6H, d, J=7 Hz), 2.36 (3H, s), 2.79 (1H, sept, J=7 Hz), and 7.67 (2H, s). ^{13}C NMR δ=20.5, 22.9 (2C), 38.2, 135.2 (2C), 137.6 (2C), 149.9, and 167.0 (3C). IR ν: 3600—3300, 2960, 1770, 1610, 1590, 1175, 1130, 1090, and 810 cm^{-1}. UV λ_{max}^{MeOH}: 259 nm (ε=27000), 265 (26800), and 329 (7800)] and **38** [a yellow oil, 100 mg; 6%. Found: m/z 284.0137 and 286.0007 (M^+). Calcd for $C_{12}H_{13}O_3Br$: M, 284.0048 and 286.0028. ^{1}H NMR δ=1.25 (6H, d, J=7 Hz), 2.35 (3H, s), 2.83 (1H, sept, J=7 Hz), 6.92 (1H, d, J=10.5 Hz), 7.18 (1H, d, J=10.5 Hz), and 8.04 (1H, s). ^{13}C NMR δ=20.6, 23.1 (2C), 38.1, 129.1, 129.8, 135.8, 140.7, 152.8, and 168.4 (3C). IR ν: 2930, 1770, 1695, 1590, 1365, and 1175 cm^{-1}. UV λ_{max}^{MeOH}: 228 nm (ε=13000), 250 (21700), and 330 (8900)]. Several other products were detected on TLC, but no further fractionation was carried out.[27]

Acetolysis of 2-Acetoxy-5,7-dibromo-4-isopropyltropone (34). An ATA solution (50 cm^3) of **34** (1.157 g) was heated in an autoclave at 100 °C for 3 d. Then, the solvent was removed in vacuo, and the residue was chromatographed on a silica-gel column to give **39** [colorless crystals, mp 122—123 °C, 538 mg; 53%. Found: C, 59.71; H, 5.59%. Calcd for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63%. ^{1}H NMR δ=1.18 (6H, d, J=7 Hz), 2.31 (6H, s), 2.33 (3H, s), 3.14 (1H, sept, J=7 Hz), 7.07 (1H, s), and 7.25 (1H, s). ^{13}C NMR δ=20.5 (3C), 22.0 (2C), 29.8, 127.7, 128.5, 142.3, 147.6, I55.1, 155.8, 167.9, 168.2, and 169.0 (2C). IR ν: 1765, 1630, 1600, 1510, 1370, 1200, 1125, 1050 and 940 cm^{-1}. UV λ_{max}^{MeOH}: 236 nm (ε=27100), 325 (9750), and 396 (390)].

Acetolysis of 2-Acetoxy-3,7-dibromo-5-isopropyltropone (35). An ATA solution (30 cm^3) of **35** (413 mg) was heated in an autoclave at 100 °C for 3 d. The mixture was then heated in vacuo to remove the solvent and the residue was chromatographed on a silica-gel column to give **40** [colorless crystals, mp 91—93 °C, 73 mg; 20%. Found: C, 59.36; H, 5.61%. Calcd for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63%. MS m/z 322 (M^+). ^{1}H NMR δ=1.24 (6H, d, J=7 Hz), 2.30 (9H, s), 2.80 (1H, sept, J=7 Hz), and 6.97 (2H, s). ^{13}C NMR δ=20.4, 20.6 (2C), 22.8 (2C), 38.4, 128.0 (2C), 150.5, 154.1 (2C), 167.0 (2C), and 167.9 (3C). IR ν: 1780, 1610, 1375, 1200, 1165, and 1020 cm^{-1}. UV λ_{max}^{MeOH}: 238 nm (ε=26800), 322 (8400), and 391 (520, sh)] and **41** [colorless needles, mp 182—184 °C, 40 mg; 10%. Found: C, 59.35; H, 5.56%. Calcd for $C_{18}H_{20}O_8$: C, 59.33; H, 5.53%. ^{1}H NMR δ=1.45 (6H, s), 2.05 (3H, s), 2.31 (9H, s), and 6.92 (2H, s) ^{13}C NMR δ=20.4, 20.6 (2C), 24.7 (2C), 26.0, 55.5, 127.3 (2C), 145.5, 152.4, 153.5, 166.9 (2C), 167.8 (3C), and 208.8. IR ν: 3500—3300, 1775, 1710, 1605, 1365, 1200, 1160, and 1020 cm^{-1}. UV λ_{max}^{MeOH}: 240 nm (ε=26000), 321 (8000), and 400 (400)].

Acylation of 40 to 41. An ATA solution (3 cm^3) of **40** (50 mg) was heated at 100 °C for 3 d. After evaporation of the solvent in vacuo, the residue was chromatographed on a silica-gel column to give, after elution of the recovered **40** [19 mg; 38%], **41** [11 mg; 31%] whose identity with the authentic sample was confirmed by direct comparisons.

Acylation of 2-Methoxy-4-isopropyltropone (42). An ATA solution (7 cm^3) of **42** (57 mg) was heated in an autoclave at 95 °C for 2 d. A similar workup afforded **43** [a yellow oil, 11 mg; 14%. Found: m/z 248.1005 (M^+). Calcd for $C_{14}H_{16}O_4$: M, 248.1048. ^{1}H NMR δ=1.83 (6H, s), 2.01 (3H, s), 2.33 (3H, s), 6.7—7.2 (3H, m), and 7.13 (1H, d, J=0.5 Hz). ^{13}C NMR δ=20.7, 24.8 (2C), 25.9, 55.8, 131.7, 132.5 (2C), 133.4, 151.0, 168.4 (3C), and 209.5. IR ν: 2950, 1770, 1715, 1605, 1365, 1195, and 1145 cm^{-1}. UV λ_{max}^{MeOH}: 233 nm (ε=19000), 316 (6660), and 442 (790)].

Acetolysis of 4,6-Dichloro-5-hydroxytropolone (44) to 45 with ATA. An ATA solution (4 cm^3) of **44** (152 mg) was heated in a sealed tube at 80 °C for 2 d. After removal of the solvent in vacuo, the residue was chromatographed on a silica-gel column to give **45** [colorless needles, mp 166—167 °C, 136 mg; 55%. Found: C, 53.43; H, 4.11%. Calcd for $C_{15}H_{14}O_9$: C, 53.26; H, 4.17%. ^{1}H NMR δ=2.27 (6H, s), 2.32 (6H, s), and 7.16 (2H, s). ^{13}C NMR δ=20.5 (4C), 126.4 (2C), 142.5 (2C), 155.2 (2C), 167.1 (2C), and 167.3 (3C). IR ν: 1775, 1600, 1500, 1360, 1135, 1100, and 935 cm^{-1}].

Acid Hydrolysis of 45 to 46. An aqueous AcOH solution (33%, 9 cm^3) of **45** (150 mg) was heated at 100 °C for 4 h. The mixture was then heated in vacuo to remove the solvent, and the residue was washed with AcOEt to obtain insoluble product, **46** [pale yellow needles, mp 269—271 °C (decomp), 60 mg; 80%. Found: C, 49.12; H, 3.59%. Calcd for $C_7H_6O_5$: C, 49.42; H, 3.56%. ^{1}H NMR (CD_3OD) δ=6.98 (2H, s). ^{13}C NMR (CD_3OD) δ=112.0 (2C), 158.1 (2C), and 158.4 (3C). IR ν: 3600—3200, 1395, 1365, 1190, and 900 cm^{-1}. UV λ_{max}^{MeOH}: 256 nm (ε=25600), 281 (3700, sh), 332 (5400, sh), 353 (6500), and 329 (2900, sh)].

Acetolysis of 3,5,7-Tribromotropolone (47) to 48. a) An ATA solution (4 cm^3) of **47** (500 mg) was sealed in a pressure bottle and heated at 100 °C for 2 d. After cooling the mixture to room temperature, volatile materials were evaporated in vacuo, and the residue was chromatographed on a silica-gel column to give **48** [colorless needles, mp 133—134 °C, 326 mg; 70%. Found: C, 52.99; H, 4.13%. Calcd for $C_{15}H_{14}O_9$: C, 53.25; H, 4.18%. ^{1}H NMR δ=2.28 (3H, s), 2.31 (6H, s), 2.32 (3H, s), and 6.95 (2H, s). ^{13}C NMR δ=20.2, 20.5 (2C), 20.8, 124.0 (2C), 150.0, 153.4 (2C), 166.5, 167.2 (3C), and 168.2 (2C). IR ν: 3050, 1770, 1605, 1515, 1375, 1360, and 1020 cm^{-1}. UV λ_{max}^{MeOH}: 222 nm (ε=19500), 238 (29100), 280 (4600), and 322 (8500)].

b) Similarly, an ATA solution (16 cm^3) of **47** (500 mg) and NaOAc (330 mg) was heated at 110 °C for 2 d. The mixture was then heated in vacuo to remove the solvent and the residue was chromatographed on a silica-gel column to give **48** [356 mg; 76%].

Acid Hydrolysis of 2,3,5,7-Tetraacetoxytropone (48) to 49. An aqueous AcOH solution (50%, 5 cm^3) of **48** (326 mg) was heated at 100 °C for 24 h. After evaporation in vacuo, the mixture was washed with AcOEt, and the residue was collected by filtration to give **49** [pale yellow crystals, mp 263—266 °C (decomp), 164 mg; 100%. Found: C, 49.13; H, 3.55%. Calcd for $C_7H_6O_5$: C, 49.42; H, 3.56%. ^{1}H NMR (CD_3OD) δ=6.63 (2H, s). ^{13}C NMR (CD_3OD) δ=107.8 (2C), 151.5, 161.9 (2C), and 163.0 (2C). IR ν: 3370, 3300, 1580, 1480, 1400, 1010, and 850 cm^{-1}].

Bromination of 4-Hydroxytropolone (3) to 3,5,7-Tribromo-4-hydroxytropolone (50). An AcOH solution (13 cm^3) of **3** (440 mg), NaOAc (780 mg) was treated with bromine (1550 mg) in AcOH (15.5 cm^3) at 5 °C. The mixture was then heated at 95 °C for 1.5 h, and the mixture was heated in vacuo to remove the solvent. The residue was extracted with $CHCl_3$ and the organic extract was evaporated in vacuo to leave a crude product which was purified by recrystalliza-

tions from MeOH to yield **50** [pale green needles, mp 149—151 °C (lit,[7] 151 °C), 1.102 g; 92%. ^{1}H NMR (CD_3OD) δ=8.39 (1H, s). ^{13}C NMR (CD_3OD) δ=112.6, 113.8, 118.6, 142.9, 160.4, 161.5, and 167.3. IR ν: 3330, 1600, 1350, 1260, 1170, 1110, and 795 cm^{-1}].

Acetolysis of 3,5,7-Tribromo-4-hydroxytropolone (50) to 6. An ATA solution (50 cm^3) of **50** (343 mg) was heated in an autoclave at 85 °C for 9 h. The mixture was evaporated in vacuo to remove the solvent and the residue was chromatographed on a silica-gel column to give **6** [colorless crystals, mp 183.5—185 °C, 39 mg; 11%. Found: C, 51.28; H, 3.95%. Calcd for $C_{17}H_{16}O_{11}$: C, 51.52; H, 4.07%. ^{1}H NMR δ=2.28 (6H, s), 2.30 (9H, s), and 6.95 (1H, s). ^{13}C NMR (DMF-d_7) δ=20.1, 20.4, 123.5, 123.8, 147.4, 167.5, 167.7, and 168.6. IR ν: 1780, 1600, 1365, 1180, and 995 cm^{-1}. UV λ_{max}^{MeOH}: 218 nm (ε=18000), 240 (29900), 292 (6500), and 319 (7800)] together with a mixture of 2,4-diacetoxy-3,5,7-tribromotropone and a tetraacetoxybromotropone [283 mg].

Acetolysis of 50 to 45 and 6 in the Presence of NaOAc. An ATA solution (15 cm^3) of **50** (150 mg) and NaOAc (99 mg) was heated in an autoclave at 125 °C for 2 d. The solvent was then removed by heating the mixture in vacuo and the residue was chromatographed on a silica-gel column to give, from hexane-AcOEt (1 : 1), **45** [81 mg; 60%], identical with the authentic sample, and **6** [18 mg; 11%].

Acid Hydrolysis of 6. An aqueous AcOH solution (60%, 5 cm^3) of **6** (129 mg) was heated at 100 °C for 5 h. After removal of the solvent, the residue was recrystallized from MeOH-AcOEt to give **51** [brown crystals, mp>300 °C (decomp), 59 mg; 97%. Found: C, 44.78; H, 3.32%; m/z, 186.0158 (M^+). Calcd for $C_7H_6O_6$: C, 45.17; H, 3.25%; M, 186.0163. ^{1}H NMR (DMF-d_7) δ=6.77 (1H, s). ^{13}C NMR (DMF-d_7) δ=104.9, 142.0 (2C), 150.3 (2C), and 154.3 (2C). IR ν: 3510, 3400—3000, 1600, 1380, 1305, 1205, and 1030 cm^{-1}. UV λ_{max}^{MeOH}: 268 nm (ε=31500), 317 (2800, sh), 332 (3500, sh), 340 (3600, sh), and 360 (3000, sh)].

Bromination of 2,4,5,7-Tetraacetoxytropone (45) to 4,5,6-Triacetoxy-3,7-dibromotropolone (54). A $CHCl_3$ solution of **45** (90 mg) was treated with Br_2 (100 mg) in $CHCl_3$ (1 cm^3) at room temperature. Then, the mixture was heated at 60 °C for 4 h, and the mixture was heated in vacuo to remove the solvent, and the residue was acetylated with Ac_2O (2 cm^3) at 110 °C for 6 h. After removal of the solvent in vacuo, the residue was chromatographed on a silica-gel column to give **54** [a yellow oil, 28 mg; 53%. Found: C, 34.23; H, 2.34%; Calcd for $C_{13}H_{10}O_8Br_2$: C, 34.39; H, 2.22%. ^{1}H NMR δ=2.33 (9H, s). ^{13}C NMR δ=20.4 (2C), 166.0, and 166.2. IR ν: 3600—3300, 1790, 1610, 1375, 1165, 1010, and 960 cm^{-1}. UV λ_{max}^{MeOH}: 212 nm (ε=9900), 250 (20200, sh), 259 (23200, sh), 266 (22800, sh), 341 (6700), and 419 (800)] together with the recovered **45** [51 mg; 57%].

Bromination of 2,3,5,7-Tetraacetoxytropone (48) to 2,3,5,7-Tetraacetoxy-4,6-dibromotropone (52) and 3,4,5,6-Tetraacetoxy-2,7-dibromotropone (53). A $CHCl_3$ solution (25 cm^3) of **48** (356 mg) was treated with Br_2 (400 mg) in $CHCl_3$ (4 cm^3) at room temperature. The mixture was then heated to 60 °C for 4 h, and evaporated to remove the solvent. The residue was acetylated by Ac_2O (2 cm^3) at 95 °C for 6 h, and again evaporated in vacuo. The residue was chromatographed on a silica-gel column to give **52** [colorless needles, mp 140.5—142.5 °C, 342 mg; 66%. Found: C, 36.55; H, 2.55%. Calcd for $C_{15}H_{12}O_9Br_2$: C, 36.32; H, 2.44%. MS m/z 495 (M^++1), 410, 368, 330, 328, 326 (1 : 2 : 1), 298. ^{1}H NMR δ=2.30 (3H, s), 2.32 (6H, s), and 2.37 (3H, s). ^{13}C NMR δ=20.2, 20.3 (2C), 20.7, 166.1, and 166.3. IR ν: 3600—3300, 1795, 1625, 1375, 1285, 1170, 1035, and 900 cm^{-1}. UV λ_{max}^{MeOH}: 257 nm (ε=25800) and 335 (7700)], and **53** [colorless crystals, mp 145—147 °C, 60 mg; 11%. Found: C, 36.18; H, 2.57%. ^{1}H NMR δ=2.27 (6H, s) and 2.33 (6H, s). ^{13}C NMR δ=20.0 (2C), 20.5 (2C), 130.6 (2C), 149.1 (4C), 165.8 (2C), and 166.1 (3C). IR ν: 1790, 1625, 1380, 1285, 1165, 1015, and 840 cm^{-1}. UV λ_{max}^{MeOH}: 232 nm (ε=16100), 268 (19300), and 332 (6900)].

Acetolysis of 2,3,5,7-Tetraacetoxy-4,6-dibromotropone (52). An ATA solution (15 cm^3) of **52** (311 mg) was sealed in an autoclave and heated at 100 °C for 5 d. After removal of the solvent in vacuo, the residue was chromatographed on a silica-gel column to give **6** [6.4 mg; 2.6%] and **7** [colorless crystals, mp 173—175 °C, 1.3 mg; 0.5%. Found: C, 50.16; H, 4.06%. Calcd for $C_{19}H_{18}O_{13}$: C, 50.23; H, 3.99%. (Calcd for $C_{17}H_{16}O_{12}$, as a pentaacetoxytropolone: C, 49.52; H, 3.91%). ^{1}H NMR δ=2.29 (18H, s). ^{13}C NMR δ=20.1 (6C) and 165.9 (6C). IR ν: 3600—3300, 1800, 1785, 1615, 1370, and 1175 cm^{-1}. MS m/z 412 (M^+−42), 370, 328, 286, 244, 202, and 176. UV λ_{max}^{MeOH}: 243 nm (ε=29700) and 320 (7300)].

Acetolysis of 52 in the Presence of NaOAc. Formation of 2,3,5,7-Tetraacetoxytropone (48) and Pentaacetoxytropone (6). An ATA solution (16 cm^3) of **52** (513 mg) and NaOAc (180 mg) was heated at 110 °C for 5 d. The mixture was then heated in vacuo to remove the solvent, and the residue was chromatographed on a silica-gel column to give **48** [168 mg; 48%] and **6** [49 mg; 12%].

Acetolysis of Octachlorocycloheptatriene (8). a) An ATA solution (15 cm^3) of NaOAc (200 mg) and **8** (200 mg) was sealed in a pressure bottle, and heated at 85 °C in an autoclave for 12 d. The solvent was then removed in vacuo, and the residue was chromatographed on a silica-gel column to give **56** [green needles, mp 128.5—130.5 °C, 20 mg; 10%. Found: C, 40.95; H, 2.64%. Calcd for $C_{13}H_9O_7Cl_3$: C, 40.71; H, 2.36%. ^{1}H NMR δ=2.09 (3H, s), 2.12 (3H, s), and 2.38 (3H, s). ^{13}C NMR δ=20.3, 21.6, 24.6, 111.9, 124.1 (2C), 134.8, 147.4, 148.9, 151.8, 166.1, 166.7, and 170.0. IR ν: 1780, 1595, 1360, 1170, 1120, and 995 cm^{-1}. UV λ_{max}^{MeOH}: 245 nm (ε=22100), 262 (31600), 271 (25500, sh), 328 (7200, sh), 340 (7800), 353 (6700, sh), and 372 (3500, sh)]. The rest of fractions were complex mixture of products, and no further fractionation was carried out.

b) An ATA solution (100 cm^3) of **8** (950 mg) and NaOAc (1.6 g) was sealed in a pressure bottle and heated in an autoclave at 130 °C for 5 d. The solvent was then removed in vacuo, and the residue was chromatographed on a silica-gel column to give **57** [20 mg; 2%. MS m/z 431 (M^++1). ^{1}H NMR δ=2.31 (3H, s), 2.32 (6H, s), and 2.36 (6H, s). ^{13}C NMR δ=20.1 (5C) and 165.9 (5C). UV λ_{max}^{MeOH}: 248 nm (ε=22600), 278 (5400, sh), 295 (4900), and 325 (6100)], and a mixture consisted of pentaacetoxychlorotropone, triacetoxytrichlorotropones, and diacetoxytetrachlorotropones (ca. 70%).

c) An ATA solution (41 cm^3) of NaOAc (1.3 g) and **8** (750 mg) was heated similarly in an autoclave at 115 °C for 5 d, then 160 °C for 2 d. After removal of the solvent in vacuo, the residue was chromatographed on a silica-gel column to give **6** [23 mg; 3%], which was identical with the sample prepared from **50**, and **7** [colorless crystals, mp 173—175 °C, 6 mg; 0.6%.].

Acid Hydrolysis of Hexaacetoxytropone (7). An aqueous AcOH solution (50%, 4 cm^3) of **7** (3 mg) was heated at 95 °C

for 10 h. Removal of the volatile material left **55** [pale brown crystals, mp >300 °C, 1 mg; 75%. UV λ_{max}^{MeOH}: 226, 272, and 292 nm].

Bromination of 46 in AcOH. An AcOH solution (5 cm^3) of **46** (11 mg) and NaOAc (9 mg) was treated with Br_2 (20 mg) at room temperature. The mixture was then heated at 95 °C for 2 h, and evaporated the solvent in vacuo. The residue was extracted with $CHCl_3$, and again evaporated to give **58** [orange crystals, mp 222 °C (decomp) (lit,[33] mp 270 °C (decomp)), 16 mg; 83%. ^{13}C NMR (CD_3OD) δ=102.5 (2C) and 167.1 (4C). MS *m/z* 300, 298, 296 (M^+, 1 : 2 : 1)].

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29) Chlorination of **48** gave 2,3,5,7-tetraacetoxy-4,6-dichlorotropone [^1H NMR δ=2.31 (3H, s), 2.34 (6H, s), and 2.39 (3H, s). ^{13}C NMR δ=20.2 (4C) and 166.3 (4C)], but its yield was only 14%.

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