Facile Formations of *o*- and *p*-Tropoquinone Mono- and Bisacetals by Anodic Oxidations of 2,3-, 2,5-, 2,7-, and 4,5-Dimethoxytropones[1)]

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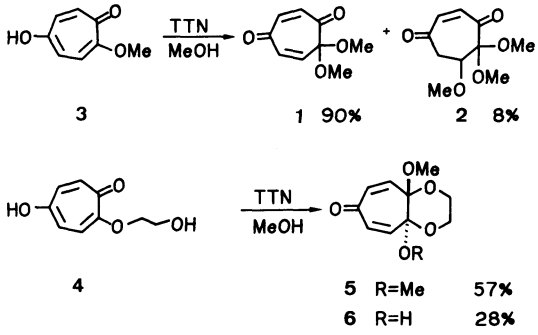
o- and *p*-Tropoquinone mono- and bisacetals (tetramethoxycycloheptadienones) were prepared from 2,3-, 2,5-, 2,7-, and 4,5-dimethoxytropones by means of anodic oxidations in practical yields. Cerium(IV) salt oxidations of dimethoxytropones afforded a mixture of products i.e., a hydrolysis product and/or a methanol adduct of tropoquinone bisacetals. By treating with sulfuric acid in a mixture of acetic acid and acetic anhydride, 4,4,7,7- and 2,2,7,7-tetramethoxycycloheptadienones gave the Thiele-type reaction products with a high positional selectivity. Similarly, 2-bromo-7-methoxytropone was anodically oxidized to 4,4,7,7-tetramethoxycycloheptadienone and its 2-bromo derivative. The mechanism of the reaction is also discussed in detail.

The facile acetal formation of *p*-tropoquinone (3,6-cycloheptadiene-1,2,5-trione) in methanol and the hydrate formation of *o*-tropoquinone (4,6-cycloheptadiene-1,2,3-trione) in water are well-known and repulsive dipole–dipole interactions of 1,2-dione and 1,2,3-trione moieties are attributable for the phenomena.[2,3)] Recently, we prepared tropoquinone acetals, which are useful for further transformations, toward functionalized troponoids: i.e., a) the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) oxidation of the ketol, derived from tropone via a photosensitized oxidation, an acetalization, and a bond cleavage of the endoperoxide with triethylamine[4)] and b) DDQ,[5)] thallium(III) nitrate (TTN),[6)] and cerium(IV) ammonium nitrate (CAN)[7)] oxidations of 2-alkoxy-5-hydroxytropones. We have now developed an improved preparation of bisacetals by the anodic oxidation of 2,3-, 2,5-, 2,7-, and 4,5-dimethoxytropones. This anodic oxidation was also applicable to tropone, 2-methoxytropone, and 2-bromo-7-methoxytropone.

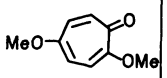
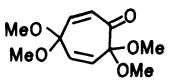
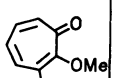
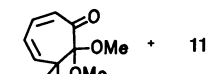
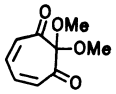
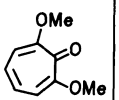
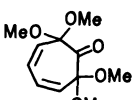
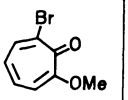
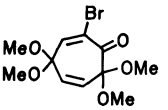


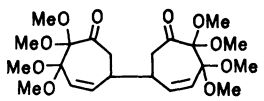
Scheme 1.

Results and Disccusion

2,5-Disubstituted Tropones. We have already shown that 7,7-dimethoxycyclohepta-2,5-diene-1,4-dione (**1**) can be prepared in good yield together with its methanol adduct (**2**) by the TTN-oxidation of 5-hydroxy-2-methoxytropone (**3**) in methanol.[6)] Similarly, 2-(2-hydroxyethoxy)-5-hydroxytropone (**4**) gave two bisacetals **5** and **6** in good combined yields.[6)] However, it is desirable to develop a selective formation of either of the two. Thus, when **3** was anodically oxidized in a singel-cell apparatus without accurate potential control in anhydrous methanol with lithium perchlorate, a single product **1** was obtained in 62% yield. In parallel, **4** gave **6** in 75% yield. Consequently, anodic oxidation is a practical method to obtain a single product selectively.

Table 1. Anodic and CAN Oxidations of Troponoids

Substrate	Anodic Oxidation	CAN Oxidation
3	1 62%	not tried
4	6 75%	not tried
 7	 8 97%	1 15% 2 77%
 9	 + 11* 10 57% 7%	 12 59%
 13	 14 94%	14 6%
 15	8 +  23% 16 67%	not reacted

*11 = 

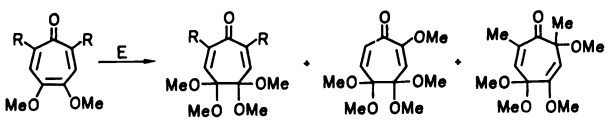
A similar electrolysis of 2,5-dimethoxytropone (**7**) also gave a single product (**8**) in quantitative yield. Its ^{1}H NMR spectrum showed two sets of an *AB*-quartet around δ 5.8—6.4, suggesting the structure to be 4,4,7,7-tetramethoxy-2,5-cycloheptadien-1-one. Again, the CAN-oxidation of **7** gave **1** and **2** in 15 and 77% yields. The difference in product distributions might depend on the reaction conditions, i.e., hydrolysis and Michael addition reactions must follow in an acidic medium under CAN-oxidation conditions, while the bisacetal **8** was stable under neutral electrolysis conditions.

2,3-Disubstituted Tropones. The electrode oxidation of 2,3-dimethoxytropone (**9**)[8] gave two products **10** and **11** in 57 and 7% yields: the major product **10** was deduced to be 6,6,7,7-tetramethoxy-2,4-cycloheptadien-1-one from its ^{1}H NMR spectrum, showing four methoxyl and four olefinic proton signals. The by-product **11**, four methoxyl signals and two olefinic and three aliphatic proton signals, was suggested to be 4,4,4′,4′,5,5,5′,5′-octamethoxy-[bi-2-cyclohepten-1-yl]-6,6′-dione. The CAN-oxidation of **9** gave the symmetrical monoacetal **12** in 59% yield. Its structure was determined by spectral data.

2,7-Disubstituted Tropones. The anodic oxidation of 2,7-dimethoxytropone (**13**)[8] gave a single product **14** in 94%, whose NMR spectrum suggested it to be 2,2,7,7-tetramethoxy-3,5-cycloheptadien-1-one. On the other hand, **13** was slightly reactive to the CAN-oxidation to give **14** in only 6% yield with 9% conversion.

In the case of 2-bromo-7-methoxytropone (**15**), the CAN-oxidation gave no identifiable product at all. However, electrolysis afforded two products: one was **8** in 23% and the other, its relatively unstable bromo derivative **16**, in 67%. The oxidation occurred selectively at C-4, the para position to the methoxyl group and the bromine atom was removed to give **8** during electrolysis.

4,5-Dimethoxytropones. The anodic oxidation of 4,5-dimethoxytropone (**17**)[9] gave 4,4,5,5-tetramethoxy-2,6-cycloheptadien-1-one (**18**) in 41% and its methanol adduct **19** in 10% yields. The structure of **19** was unambiguously ascertained from the spectral data. The position of the methoxyl group in **19** was elucidated to be at C-2 from a consideration of the ^{13}C chemical shifts[10] i.e., C-2 at δ 152.6 and C-3 at δ 109.3 together with an absence of a long-range coupling between a singlet at δ 5.37 and a doublet at δ 6.13.



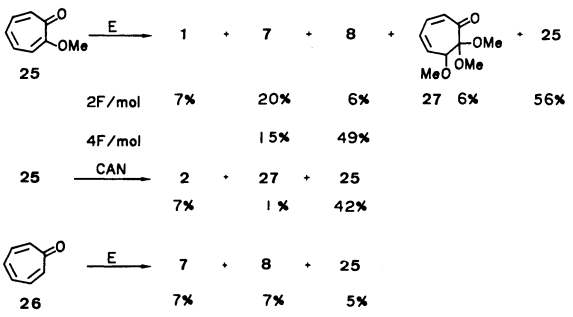
Scheme 2.

Therefore, the structure of **19** was determined to be 2,4,4,5,5-pentamethoxy-2,6-cycloheptadien-1-one.

Electrolysis of 4,5-dimethoxy-2,7-dimethyltropone (**20**)[5] gave 4,4,5,5-tetramethoxy-2,7-dimethyl-2,6-cycloheptadien-1-one (**21**) in 77% and its methanol adduct **22** in 8%. The structure of **22** was deduced from the ^{1}H chemical shifts of methyl signals at δ 1.37 and 1.92. No further transformation under anodic oxidation conditions occurred from **22** because of the presence of the methyl group, being different from the case of **19**.

Moreover, the oxidation of 4,5-dimethoxy-2,7-dipropyltropone (**23**) gave a single product **24** in 97%. The structure of **24** was determined to be 4,4,5,5-tetramethoxy-2,7-dipropyl-2,6-cycloheptadien-1-one from the same spectral criteria as **18** and **21**.

Other Troponoids. Since a further oxidation, **18** to **19**, took place in the anodic oxidation of **17**, other tropones, 2-methoxytropone (**25**) and tropone (**26**), should be examined: 2-Methoxytropone gave four products (**1**; 7%, **7**; 20%, **8**; 6%, and **27**; 6%) with a recovery of **25** in 56% after the consumption of 2 F mol^{-1} of electricity. By passing 4 F mol^{-1} of electricity, yields of **8** and **7** increased to 49 and 15%, respectively. Three (**1**, **7**, and **8**) of them were identical with authentic samples. The structure of a new product, **27**, was identified as 6,7,7-trimethoxy-2,4-cycloheptadien-1-one on the basis of the doublet methine proton at δ 4.09 and the carbonyl absorption at 1685 cm^{-1}. On the other hand, the CAN-oxidation of **25** afforded **2** in 7% and **27** in 1% yields. Tropone gave **7**, **8**, and **25** in 7, 7, and 5% yields, respectively.

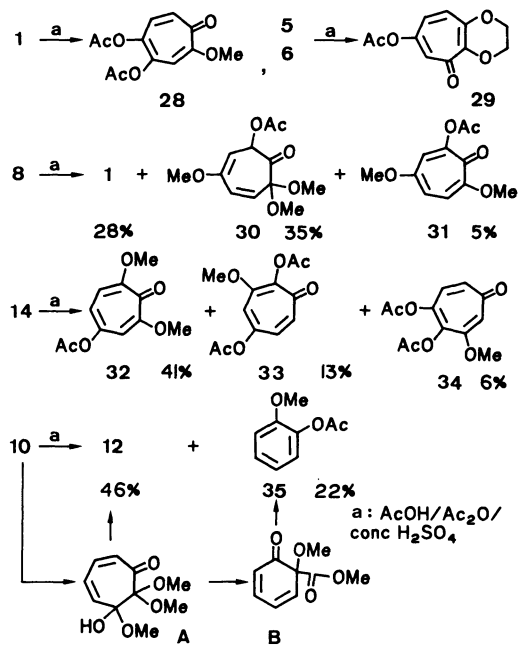


Scheme 3.

Thus, anodic oxidations of tropone and 2-methoxytropone were less satisfactory. Although the yields of products were not always high, a one-step formation of methoxylated troponoids is of practical value.

Thiele-Type Reactions of Bisacetals. As has been seen in CAN-oxidations of **7** and **25** and in anodic oxidations of **17** and **20**, methanol added to the C=O conjugated C=C double bond. It has been shown[6] that Thiele-type reactions of acetal **1** and bisacetals **5** and **6**, respectively, gave 4,5-diacetoxy-2-methoxytropone (**28**) and 6-acetoxy-2,3-(ethylenedioxy)tropone (**29**) with a high positional selectivity. The treatment of **8** with a 1:1-mixture of acetic acid and acetic anhydride with a catalytic amount of concd sulfuric acid gave three

products (**1**; 28%, **30**; 35%, **31**; 5%). The structures of **30** and **31** were determined by the spectral data. Since **31** showed a carbonyl carbon at δ 168.4 in the ^{13}C NMR spectrum, an acetotropy, which is common in 2-acetoxytropones,[11] is operative in **31**. Additionally, the decoupled ^1H NMR spectrum disclosed a long-range coupled ABX_3 system. Therefore, **31**, was 2-acetoxy-4,7-dimethoxytropone.



Scheme 4.

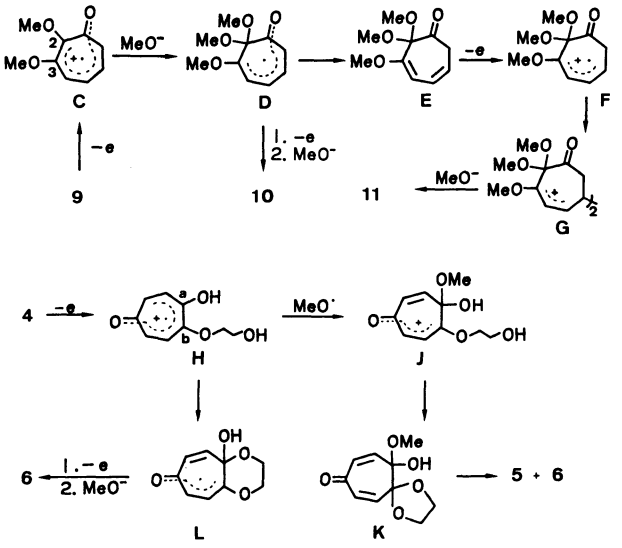
The ^1H NMR of the major product, **30**, showed an acetoxyl and three methoxyl signals together with three olefinic proton signals and a doublet methine proton signal at δ 5.65 (J=8.2 Hz). Taking the IR carbonyl absorption (1690 cm^{-1}) into account, the structure of **30** was assigned to be 2-acetoxy-4,7,7-trimethoxy-3,5-cycloheptadien-1-one.

Next, **14** furnished three troponoids (**32**; 41%, **33**; 13%, **34**; 6%) by a treatment under Thiele-type reaction conditions. All ^1H NMR spectral splittings of these compounds were suggested to be 5,7-disubstituted tropolone derivatives; i.e., two of three olefinic protons vicinally coupled (J=10.3—12.8 Hz) and the third proton appeared as a doublet with a small coupling constant (J≈2.5 Hz). From the presence of an acetoxyl and two methoxyl signals, the structure of **32** was deduced to be 4-acetoxy-2,7-dimethoxytropone. As **33** and **34** showed a methoxyl and two acetoxyl signals, the structures of **33** and **34** were 2,5-diacetoxy-3-methoxytropone[12] (J=10.3 Hz) and 4,5-diacetoxy-3-methoxytropone (J=12.8 Hz), respectively. On the contrary, **10** afforded only the hydrolysis product **12** in 46% and 2-acetoxyanisole (**35**) in 22% yields, but no Thiele-type product.

The formation of **35** from **10** could be explained in terms of a hydrolysis of one of the methoxyl groups at C-6 to give **A**, followed by a ring contraction and a decarbonylation via a six-membered dienone **B**.

Mechanistic Consideration of the Anodic Oxidation. According to mechanistic studies for anisoles[13] and 1,4-dimethoxybenzenes described in literature,[14] a sequence involving a methoxyl radical attack to the aryl radical cations (EECC sequence) in methanolic potassium hydroxide has been proposed. Under conditions without methoxide ion, the nucleophilic attack of methanol to anodically formed radical cations was predominant to give cations; further oxidation and methoxylation followed (ECEC sequence).

Since the present anodic oxidations of troponoids were performed in the presence of lithium perchlorate, methoxyl radicals would hardly exist under the reaction conditions. Therefore, the ECEC mechanism to **10** was assumed as shown in Scheme 5. An attack of a methoxide ion to the radical cation **C** occurred to give **D** at C-2 since the resultant radical could be more stabilized than the alternative from a C-3 attack of a methoxide ion in **C**. Further electrolysis and methoxylation should give **10**. The mechanism for the dimeric product **11** could be explained in terms of an intermediary formation of **E** from **D**. Successive oxidation, dimerization, and methoxylation gave product **11**. An attempted electrolysis of **10** gave no **11**. Additionally, the ECEC mechanism was also favored in the oxidation of **4**. If an EECC mechanism was operative, the attack of a methoxyl radical to **H** would be more preferable at C-a to give **J** than at C-b bacause of the steric hindrance. From **J**, a mixture of acetals **5** and **6** should be obtained via **K**. On the other hand, an internal attack of the hydroxyethoxy group in **H** led to radical **L**, which was further oxidized and a methoxylation followed to give **6**. Thus, an ECEC mechanism was favored.



Scheme 5.

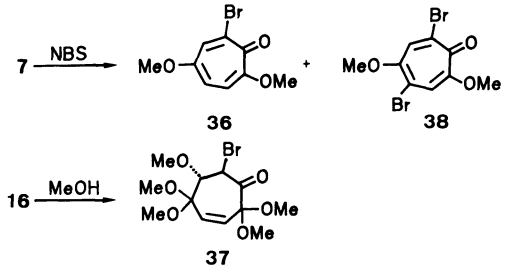
Next, for the formation of **8**, from **15**, a reduction process might be involved, since the reactions were

Table 2. Results of Controlled Anodic Oxidation of **15**

Electricity	Ratio of component				
F mol^{-1}	**15**	**36**	**16**	**8**	**37**
2.4	17	5	1	0	0
3.2	15	6	2	Trace	0
4.1	6	2	6	6	Trace
5.0	4	1	9	6	Trace
5.9	2	Trace	9	5	Trace
6.8	2	0	9	5	Trace
7.7	1.5	0	9	5.5	0.5
10.1	0	0	3	2.5	2.5
12.3	0	0	4	4	3
			(16)	(22)	(17)

Numbers in parentheses are yields isolated.

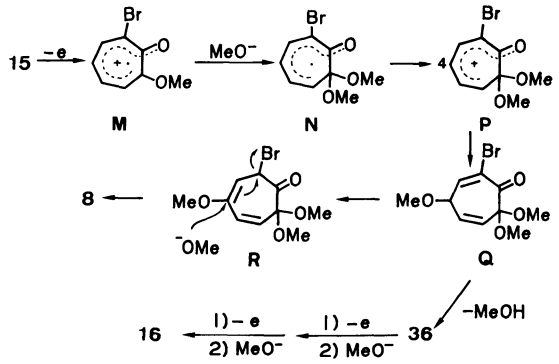
conducted in an undivided cell. In order to make the point clear, we investigated the reaction of **15** in some detail. When the reaction was traced by the ^{1}H NMR spectrum of the whole reaction mixture every hour, product distributions were obtained, as summarized in Table 2. After 3 h, a new product **36** was formed. After 5 h, the amount of **36** decreased with increasing amounts of **8** and **16**. Finally, another new product **37** was produced while **15** and **36** were consumed. Compound **36** was identical with the authentic 2-bromo-4,7-dimethoxytropone, which was prepared from the reaction of *N*-bromosuccinimide and **7** together with the dibromo derivative **38**.[15] Compound **37** was a methanol adduct of **16** from the spectral data.



Scheme 6.

An attempted oxidation of **16** gave only **37** but no **8** at all. The formation of **37** required no electricity since **37** was formed simply by standing in a methanol solution of **16**. On the other hand, an anodic oxidation of **36** gave **16** in quantitative yield.

Taking these evidences into account, the mechanism shown in Scheme 7 can be proposed. Compound **15** was electrolyzed to the cation radical **M**, where the attack of methanol, further oxidation, and methoxylation occurred to give **Q**. A subsequent elimination of methanol from **Q** led to **36**, which was again oxidized and methoxylated to **16**. On the other hand, a prototropy occurred from **Q** to **R** and a subsequent addition-elimination process led to give **8**. An exclusive attack of a methoxide ion to C-4 of **P** could be explained by a steric hindrance from the bromine and dimethyl acetal groups.



Scheme 7.

Conclusion

As has been described, the oxidation of twelve troponoids proceeded in practical yields. Interestingly, an electrode oxidation and a CAN-oxidation were complementary to some extent with each other. For instance, **13** having shown a better result regarding electrode oxidation, was inert to CAN-oxidation. Its conversion to **14** after 4.5 h was only 7%.

The reactivities of bisacetals to Thiele-type reactions were quite different and the site of the reaction with the acetate anion was selective in each case.

Experimental

The elemental analyses were performed by Miss S. Hirashima, of Institute of Advanced Material Study, Kyushu University. NMR spectra were measured by a JEOL 270H spectrometer in a $CDCl_3$ solution (unless otherwise specified); chemical shifts are expressed in the unit δ. Mass spectra were measured with a JEOL 01SG -2 spectrometer. IR spectra were taken as KBr disks or as a liquid film inserted between NaCl plates using a Jasco IR-A 102 spectrometer. UV spectra were measured by a Hitachi U-3200 spectrophotometer.

Anodic Oxidation of 5-Hydroxy-2-methoxytropone (3). An anhydrous MeOH solution (90 cm^3) of **3** (51.4 mg) and $LiClO_4$ (41 mg) was electrolyzed in an undivided cell fitted with a circular Pt-gauze (10 mm in diameter×20 mm in height) anode and a Pt cathode under a constant current (10 mA). After 2.2 F mol^{-1} of electricity were passed at room temperature under an N_2 atmosphere, the solvent was evaporated in vacuo. The residue was diluted with water and extracted with $CHCl_3$. The solvent was evaporated and the residue was chromatographed on a silica-gel column to give 37.9 mg (62%) of **1**: a pale-yellow oil, which was identical with the authentic sample.[6]

Anodic Oxidation of 5-Hydroxy-2-(2-hydroxyethoxy)-tropone (4). An anhydrous MeOH solution (90 cm^3) of **4** (100 mg) and $LiClO_4$ (40 mg) was oxidized anodically to give 87.7 mg (75%) of **6**: colorless crystals, mp 123—124 °C, which was identical with the authentic sample.[6]

Anodic Oxidation of 2,5-Dimethoxytropone (7). An anhydrous MeOH solution (80 cm^3) of **7** (101.6 mg) and $LiClO_4$ (44 mg) was electrolyzed (2 F mol^{-1}) to give 135 mg (97%) of **8**: a colorless oil; ^1H NMR δ=3.29 (6H, s), 3.30 (6H, s), 5.82 (1H, d, J=12.5 Hz), 6.01 (1H, d, J=12.5 Hz), 6.09 (1H, dd, J=12.5, 2.0 Hz), and 6.34 (1H, dd, J=12.5, 2.0 Hz); ^{13}C NMR δ=49.7 (2C), 50.4 (2C), 98.5, 101.9, 127.4, 131.2, 135.9, 139.8, and 193.0; IR 1705, 1460, 1440, 1390, 1300, and 1210 cm^{-1}; UV (MeOH) 202 (ε 6000), 229 (sh 2900), and 336 nm (140).

Found: C, 57.62; H, 7.12%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

CAN-Oxidation of 7. An anhydrous MeOH solution (1.5 cm^3) of **7** (60 mg) and CAN (396 mg) was stirred at 0 °C and the mixture was kept at room temperature for 4.5 h with stirring. Silica-gel chromatography of the mixture afforded 9.7 mg (15%) of **1** and 59.4 mg (77%) of **2**: a colorless oil. The latter was identical with the authentic sample.[6]

Anodic Oxidation of 2,3-Dimethoxytropone (9). An anhydrous MeOH solution (100 cm^3) of **9** (122 mg) and $LiClO_4$ (104 mg) was electrolyzed (2.8 F mol^{-1}) to give 95.4 mg (57%) of **10** and 11.6 mg (7%) of **11**.

10: Colorless crystals, mp 107—108 °C; ^1H NMR δ=3.36 (6H, br s), 3.42 (6H, s), 5.86 (1H, dd, J=12.0, 1.0 Hz), 6.06 (2H, m), and 6.40 (1H, ddd, J=12.0, 6.0, 2.0 Hz); ^{13}C NMR δ=51.3 (2C), 52.9 (2C), 101.2, 103.5, 126.2, 128.1, 133.4, 137.9, and 194.5; IR 1670, 1420, 1140, and 1120—980 cm^{-1}; UV (MeOH) 201 (ε 3800), 231 (2400), and 293 nm (4700).

Found: C, 57.99; H, 6.88%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

11: Colorless crystals, mp 150—152 °C; ^1H NMR δ=2.26 (2H, d, J=11.0 Hz), 2.62 (2H, m), 2.96 (2H, t, J=11.0 Hz), 3.17 (6H, s), 3.35 (6H, s), 3.38 (6H, s), 3.47 (6H, s), 5.73 (2H, dd, J=11.7, 2.2 Hz), and 5.93 (2H, dd, J=11.7, 3.7 Hz); ^{13}C NMR δ=39.1 (2C), 44.8 (2C), 50.6 (2C), 51.1 (2C), 51.2 (2C), 51.5 (2C), 101.6 (2C), 106.2 (2C), 132.1 (2C), 134.3 (2C), and 202.7 (2C); IR 1720, 1440, 1170, and 1100 cm^{-1}; UV (MeOH) 297 nm (ε 130).

Found: C, 56.49; H, 7.39%. Calcd for $C_{22}H_{34}O_{10}\cdot 1/2H_2O$: C, 56.53; H, 7.49%.

CAN-Oxidation of 9. An anhydrous MeOH solution (2 cm^3) of **9** (31.6 mg) was treated with CAN (115 mg) to give 20.3 mg (59%) of **12** and 11.3 mg of unreacted **9**.

12: Pale-yellow crystals, mp 69—70 °C; ^1H NMR δ=3.38 (6H, s), 6.0—6.1 (2H, m), and 6.5—6.6 (2H, m); ^{13}C NMR δ=52.7 (2C), 104.6, 129.5 (2C), 133.0 (2C), and 195.1 (2C); IR 1700, 1450, 1420, and 1220 cm^{-1}; UV (MeOH) 313 nm (ε 3500).

Found: C, 59.42; H, 5.61%. Calcd for $C_9H_{10}O_4$: C, 59.33; H, 5.53%.

Anodic Oxidation of 2,7-Dimethoxytropone (13). An anhydrous MeOH solution (50 cm^3) of **13** (48.2 mg) and $LiClO_4$ (54 mg) was electrolyzed (3.1 F mol^{-1}) to give 62.1 mg (94%) of **14**: a colorless oil; ^1H NMR δ=3.26 (12H, s), 5.5—5.7 (2H, m), and 6.1—6.3 (2H, m); ^{13}C NMR δ=50.5 (4C), 101.0 (2C), 127.4 (2C), 130.2 (2C), and 192.5; IR 1740, 1175, 1140, 1080, and 1050 cm^{-1}; UV (MeOH) 206 (ε 7600) and 259.6 nm (2900).

Found: C, 57.74; H, 7.07%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

CAN-Oxidation of 13. a) An anhydrous MeOH solution (2 cm^3) of **13** (43.4 mg) was oxidized with CAN (145 mg) to give 3.4 mg (6%) of **14** and 39.3 mg of unreacted **13**.

b) An anhydrous MeOH solution (4 cm^3) of **13** (12.1 mg) was oxidized with CAN (130 mg) to give a complex mixture.

Anodic Oxidation of 2-Bromo-7-methoxytropone (15). a) An anhydrous MeOH solution (50 cm^3) of **15** (98 mg) and $LiClO_4$ (57 mg) was electrolyzed (8.1 F mol^{-1}) to give 23.6 mg (23%) of **8** and 94.7 mg (67%) of **16**: a pale-yellow oil; ^1H NMR δ=3.24 (6H, s), 3.27 (6H, s), 5.82 (1H, d, J=12.0 Hz), 6.07 (1H, dd, J=12.0, 2.0 Hz), and 6.84 (1H, d, J=2.0 Hz); ^{13}C NMR δ=49.8 (2C), 50.6 (2C), 99.4, 101.0, 121.2, 131.0, 135.5, 140.1, and 188.3; IR 1720, 1620, 1460—1440, 1380, and 1100—1020 cm^{-1}.

Found: m/z 306.0074 and 308.0041. Calcd for $C_{11}H_{15}O_5Br$: M, 306.0101 and 308.0081.

b) An anhydrous MeOH solution (50 cm^3) of **15** (98 mg) and $LiClO_4$ (58 mg) was electrolyzed. Every 1 cm^3 of the mixture was taken out, evaporated, and filtered by a silica cartridge (Sep-pak) in order to monitor by ^1H NMR spectroscopy. After 3 h, the work-up gave the crude **36**, whose ^1H NMR spectrum was identical with that of an authentic sample. After 11 h, the whole mixture was evaporated and the residue was chromatographed to give 19.3 mg (16%) of **16**, 19.2 mg (22%) of **8**, and 22 mg (17%) of **37**: pale-yellow crystals, mp 76—78 °C; ^1H NMR δ=3.08 (3H, s), 3.13 (3H, s), 3.29 (3H, s), 3.38 (3H, s), 3.67 (3H, s), 3.95 (1H, d, J=6.2 Hz), 4.80 (1H, d, J=6.2 Hz), 5.86 (1H, d, J=11.8 Hz), and 6.01 (1H, d, J=11.8 Hz); ^{13}C NMR δ=48.9, 49.1, 49.6, 50.3, 54.8, 60.0, 87.5, 97.8, 101.0, 130.0, 133.5, and 188.3; IR 1750, 1460, and 1390 cm^{-1}; UV (MeOH) 201.8 (ε 2600) and 290 nm (170).

Found: C, 42.31; H, 5.57%. Calcd for $C_{12}H_{19}O_6Br$: C, 42.49; H, 5.65%.

NBS-Bromination of 2,5-Dimethoxytropone (7). Preparation of 2-Bromo-4,7-dimethoxytropone (36). A CCl_4 solution (4 cm^3) of **7** (222 mg) and NBS (248 mg) was refluxed for 2 h. After cooling the mixture to room temperature, the precipitate was filtered. The solvent was evaporated and the residue was chromatographed on a silica-gel column to give 38 mg (12%) of **36**, 28 mg (6%) of **38**, and 90 mg of recovered **7**.

36: Pale-yellow crystals, mp 146—147 °C; ^1H NMR δ=3.78 (3H, s), 3.88 (3H, s), 6.43 (1H, dd, J=11.0, 3.0 Hz), 6.79 (1H, d, J=11.0 Hz), and 8.07 (1H, d, J=3.0 Hz); ^{13}C NMR δ=55.9, 56.6, 108.3, 113.7, 135.9, 138.5, 156.6, 157.3, and 173.6; IR 1580, 1495, 1390, 1340, 1245, 1210, 1185, and 1120 cm^{-1}.

Found: C, 43.86; H, 3.76%. Calcd for $C_9H_9O_3Br$: C, 44.11; H, 3.70%.

38: Pale-yellow crystals, mp 139—142 °C (lit,[15] mp 140—142 °C).

Anodic Oxidation of 36. An anhydrous MeOH solution (50 cm^3) of **36** (30 mg) and $LiClO_4$ (51 mg) was electrolyzed (5.6 F mol^{-1}) to give 37 mg (99%) of **16**, which was identical with the authentic sample.

CAN-Oxidation of 15. An anhydrous MeOH solution (2 cm^3) of **15** (59 mg) was treated with CAN (301 mg). The starting material was completely recovered.

Anodic Oxidation of 4,5-Dimethoxytropone (17). An anhydrous MeOH solution (40 cm^3) of **17** (53 mg) and $LiClO_4$ (54 mg) was electrolyzed (5.2 F mol^{-1}) to give 29.6 mg (41%) of **18** and 8.5 mg (10%) of **19**.

18: A colorless oil; ^1H NMR δ=3.31 (6H, br s), 3.48 (6H, br s), 6.10 (2H, dm, J=12.5 Hz), and 6.42 (2H, dm, J=12.5 Hz); ^{13}C NMR δ=50.4 (2C, br), 51.7 (2C, br), 102.2 (2C), 131.0 (2C), 141.2 (2C), and 190.8; IR 1665, 1620, 1460,

and 1390 cm^{-1}; UV (MeOH) 209 nm (ε 9000).

Found: C, 57.83; H, 6.90%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

19: A colorless oil; ^1H NMR δ=3.30 (6H, br s), 3.51 (6H, br s), 3.67 (3H, s), 5.37 (1H, s), 6.13 (1H, d, J=12.6 Hz), and 6.41 (1H, d, J=12.6 Hz); ^{13}C NMR δ=50.4 (2C, br), 51.6 (2C, br), 55.4, 101.6, 103.3, 109.3, 130.0, 140.7, 152.6, and 186.4; IR 1720, 1670, 1640, and 1460 cm^{-1}.

Found: m/z 258.1103. Calcd for $C_{12}H_{18}O_5$: M, 258.1108.

Anodic Oxidation of 4,5-Dimethoxy-2,7-dimethyltropone (20). An anhydrous MeOH solution (120 cm^3) of **20** (186 mg) and $LiClO_4$ (116 mg) was electrolyzed (3.7 F mol^{-1}) to give 188 mg (77%) of **21** and 20.3 mg (8%) of **22**.

21: Colorless crystals, mp 98—100 °C; ^1H NMR δ=1.93 (6H, d, J=1.4 Hz), 3.27 (6H, br s), 3.45 (6H, br s), and 6.14 (2H, d, J=1.4 Hz); ^{13}C NMR δ=20.4 (2C), 50.2 (2C, br), 51.5 (2C, br), 102.0 (2C), 134.1 (2C), 138.1 (2C), and 194.9; IR 1635, 1440, and 1385 cm^{-1}; UV (MeOH) 240 nm (ε 6400).

Found: C, 60.80; H, 7.92%. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87%.

22: A colorless oil; ^1H NMR δ=1.37 (3H, s), 1.92 (3H, d, J=1.4 Hz), 3.15 (3H, s), 3.26 (3H, s), 3.28 (3H, s), 3.63 (3H, s), 4.46 (1H, s), and 6.06 (1H, d, J=1.4 Hz); ^{13}C NMR δ=19.3, 25.8, 49.6, 50.3, 52.4, 55.1, 81.9, 99.6, 101.3, 134.8, 139.2, 158.6, and 203.8; IR 1710, 1650, 1450, and 1350 cm^{-1}.

Found: m/z 256.1307. Calcd for $C_{13}H_{20}O_5$: M, 256.1308.

Anodic Oxidation of 4,5-Dimethoxy-2,7-dipropyltropone (23). An anhydrous MeOH solution (50 cm^3) of **23** (26 mg) and $LiClO_4$ (52 mg) was electrolyzed (6.7 F mol^{-1}) to give 31.6 mg (97%) of **24**: a colorless oil; ^1H NMR δ=0.90 (6H, t, J=7.3 Hz), 1.41 (4H, m), 2.29 (4H, m), 3.25 (6H, br s), 3.45 (6H, br s), and 6.01 (1H, t, J=1.1 Hz); ^{13}C NMR δ=13.6 (2C), 21.8 (2C), 36.0 (2C), 50.4 (2C, br), 51.4 (2C, br), 102.1 (2C), 133.1 (2C), 143.0 (2C), and 196.3; IR 1670, 1650, 1460, 1430, 1380, and 1360 cm^{-1}; UV (MeOH) 243 nm (ε 6300).

Found: C, 65.27; H, 8.91%. Calcd for $C_{17}H_{28}O_5$: C, 65.36; H, 9.03%.

Anodic Oxidation of 2-Methoxytropone (25). a) An anhydrous MeOH solution (50 cm^3) of **25** (427.4 mg) and $LiClO_4$ (53 mg) was electrolyzed (2.0 F mol^{-1}) to give 103.5 mg (20%) of **7**, 44.5 mg (6%) of **8**, 37.5 mg (7%) of **1**, 37 mg (6%) of **27**, and 237.8 mg of unreacted **25**.

27: A pale-yellow oil; ^1H NMR δ=3.28 (3H, s), 3.40 (3H, s), 3.41 (3H, s), 4.09 (1H, d, J=6.0 Hz), 5.90 (1H, d, J=12.0 Hz), 6.10 (1H, dd, J=11.5, 6.5 Hz), 6.33 (1H, ddd, J=11.5, 6.0, 1.0 Hz), and 6.48 (1H, ddd, J=12.0, 6.5, 1.0 Hz); ^{13}C NMR δ=51.2, 51.4, 58.7, 76.8, 102.0, 127.4, 127.5, 134.3, 135.0, and 195.0; IR 1685, 1595, 1450, and 1425 cm^{-1}.

Found: m/z 198.0890. Calcd for $C_{10}H_{14}O_4$: M, 198.0859.

b) An anhydrous MeOH solution (65 cm^3) of **25** (101 mg) and $LiClO_4$ (40 mg) was electrolyzed (4.0 F mol^{-1}) to give 18.4 mg (15%) of **7** and 82.5 mg (49%) of **8**.

CAN-Oxidation of 25. An anhydrous MeOH solution (2 cm^3) of **25** (48 mg) was treated with CAN (437 mg) to give 5.6 mg (7%) of **2**, 1 mg (1%) of **27**, and 20 mg of unreacted **25**.

Anodic Oxidation of Tropone (26). An anhydrous MeOH solution (50 cm^3) of **26** (84 mg) and $LiClO_4$ (58 mg) was electrolyzed (2.5 F mol^{-1}) to give 5.3 mg (5%) of **25**, 9.8 mg (7%) of **7**, 11.8 mg (7%) of **8**, and 40 mg of unreacted **26**.

Thiele-Type Reaction of 8. A 1:1-mixture (3 cm^3) of AcOH and Ac_2O, and **8** (177.5 mg) was stirred with a catalytic amount of concd H_2SO_4 at room temperature for 2 h. The mixture was diluted with water and extracted with $CHCl_3$. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column to give 39.5 mg (28%) of **1**, 67 mg (35%) of **30**, and 8.7 mg (5%) of **31**.

30: A pale-yellow oil; ^1H NMR δ=2.01 (3H, s), 3.25 (3H, s), 3.37 (3H, s), 3.60 (3H, s), 5.25 (1H, dd J=8.2, 2.2 Hz), 5.65 (1H, d, J=8.2 Hz), 5.98 (1H, d, J=13.2 Hz), and 6.41 (1H, dd, J=13.2, 2.2 Hz); ^{13}C NMR δ=21.0, 49.9, 52.0, 54.9, 69.4, 97.5, 100.4, 126.7, 136.4, 156.6, 169.9, and 193.2; IR 1750, 1690, 1650, 1405, 1370, and 1230 cm^{-1}.

Found: m/z 256.0945. Calcd for $C_{12}H_{16}O_6$: M, 256.0945.

31: Colorless crystals, mp 131—133 °C; ^1H NMR δ=2.37 (3H, s), 3.78 (3H, s), 3.89 (3H, s), 6.65 (1H, dd, J=12.1, 2.9 Hz), 6.84 (1H, d, J=2.9 Hz), and 6.90 (1H, d, J=12.1 Hz); ^{13}C NMR δ=20.7, 55.8, 57.4, 120.0, 120.4 (2C), 156.9, 160.6, and 168.4 (3C); IR 1770, 1590, 1510, 1460, 1250, and 1170 cm^{-1}.

Found: m/z 224.0684. Calcd for $C_{11}H_{12}O_5$: M, 224.0684.

Thiele-Type Reaction of 10. A 1:1-mixture of AcOH and Ac_2O (1 cm^3) of **10** (97 mg) was stirred in the presence with a catalytic amount of concd H_2SO_4 to give 35.9 mg (46%) of **12** and 15.5 mg (22%) of **35**. The latter was identical with an authentic sample.

Thiele-Type Reaction of 14. A 1:1-mixture of AcOH and Ac_2O (0.4 cm^3) and **14** (31.6 mg) was stirred with a catalytic amount of concd H_2SO_4 to give 12.6 mg (41%) of **32**, 4.5 mg (13%) of **33**, and 2.1 mg (6%) of **34**.

32: A pale-yellow oil; ^1H NMR δ=2.32 (3H, s), 3.93 (6H, s), 6.62 (1H, d, J=2.6 Hz), 6.65 (1H, dd, J=10.3, 2.6 Hz), and 6.80 (1H, d, J=10.3 Hz); ^{13}C NMR δ=21.1, 56.6 (2C), 111.6, 112.2, 117.3, 147.8, 160.6, 161.2, 169.5, and 173.1; IR 1760, 1595, 1500, 1450, 1380, and 1360 cm^{-1}.

Found: m/z 224.0685. Calcd for $C_{11}H_{12}O_5$: M, 224.0685.

33: A colorless oil; ^1H NMR δ=2.33 (3H, s), 2.36 (3H, s), 3.94 (3H, s), 6.59 (1H, d, J=2.2 Hz), 6.62 (1H, dd, J=10.3, 2.2 Hz), and 7.24 (1H, d, J=10.3 Hz); ^{13}C NMR δ=20.6, 21.1, 56.7, 111.3, 116.4, 127.1, 152.9, 163.9, 168.4 (2C), and 168.8 (2C); IR 1785, 1600, 1500, and 1370 cm^{-1}.

Found: m/z 252.0631. Calcd for $C_{12}H_{12}O_6$: M, 252.0631.

34: A colorless oil; ^1H NMR δ=2.29 (6H, s), 3.80 (3H, s), 6.51 (1H, d, J=2.2 Hz), 6.78 (1H, d, J=12.8 Hz), and 6.91 (1H, dd, J=12.8, 2.2 Hz).

Found: m/z 252.0633. Calcd for $C_{12}H_{12}O_6$: M, 252.0631.

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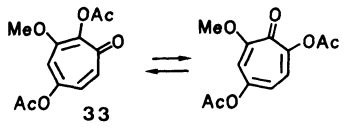

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