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# ANODIC OXIDATION OF CYCLOHEPTATRIENE SYSTEMS AND ITS APPLICATION TO THE SYNTHESIS OF NON-BENZENOID AROMATIC COMPOUNDS[1,2]

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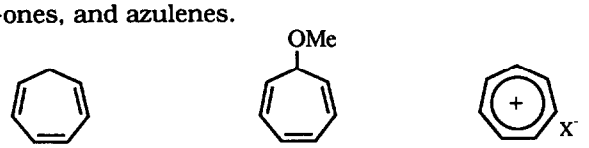
Summary: Anodic oxidation of cycloheptatrienes has been found to be one of the most powerful key tools for the preparation of a variety of non-benzenoid aromatic compounds such as tropylium salts, tropones, tropolones, 2H-cyclohepta[b]furan-2-ones, and azulenes.

In our continuing studies[5-8] on the anodic oxidation of olefinic systems such as monoolefins, dienes, and trienes, we have found that cycloheptatriene (**1**) was directly transformed to 7-methoxycycloheptatriene (**2**) by the anodic oxidation of **1** in MeOH.[9] The fact that **2** was formed directly from **1** by this very simple procedure is important on the basis of following two viewpoints.

One is that **2** is equivalent to tropylium salt (**3**) which is one of the key intermediates in the chemistry of non-benzenoid aromatic compounds[10] and has been prepared by a rather troublesome method.[11]

Another is that the rather easy formation of **2** from **1** strongly suggests usefulness of the anodic method in the synthesis of other seven membered non-benzenoid aromatic systems.

In the present study the anodic oxidation of cycloheptatriene systems has been applied as the key reaction to the synthesis of a variety of seven membered non-benzenoid aromatic compounds and their related compounds such as tropylium salts, tropones, tropolones, 2H-cyclohepta[b]furan-2-ones, and azulenes.



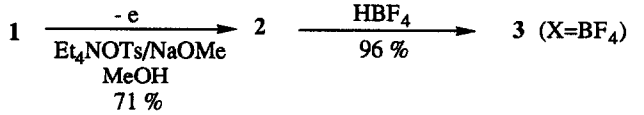

(1) (2) (3)

**Anodic Transformation of 1,3,5-Cycloheptatriene to Tropylium Salt, Tropone, and Tropolones**[2a]

In our previous preliminary study,[9] the anodic oxidation of 1,3,5-cycloheptatriene (**1**) had been carried out in MeOH using $Et_4NOTs$, NaOMe, $Bu_4NBF_4$ or $H_2SO_4$ as the supporting electrolytes and afforded 7-methoxy-1,3,5-cycloheptatriene (**2**) in rather low yield.[12] In this study, however, using a mixture of $Et_4NOTs$ and NaOMe as the supporting electrolyte was found to bring about a dramatical increase in the yield of **2** (scheme 1).[2a]

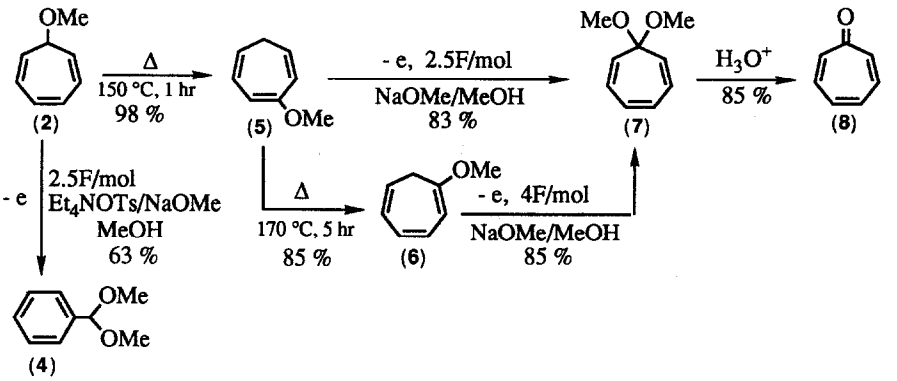
Furthermore, **2** was able to be transformed to the tropylium salt (**3**) in 96 % yield through its simple treatment with $HBF_4$.

Scheme 1.



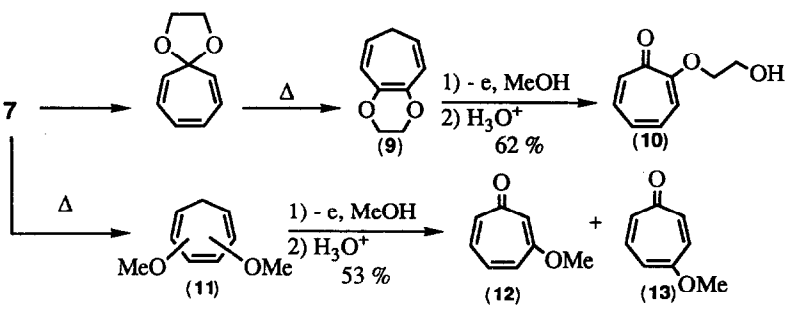

The anodic oxidation of **2** in MeOH resulted in the formation of benzaldehyde dimethyl acetal (**4**) through a ring contracting rearrangement (scheme 2),[14] whereas 3-methoxy-1,3,5-cycloheptatriene (**5**) and 1-methoxy-1,3,5-cycloheptatriene (**6**) prepared by a thermal rearrangement of **2** afforded 7,7-dimethoxy-1,3,5-cycloheptatriene (**7**) in 83 % and 85 % yield respectively upon the anodic oxidation. The hydrolysis of **7** in 5 % aqueous $H_2SO_4$ gave tropone (**8**) in 85 % yield. Thus, the excellent effectivity of this anodic method in the synthesis of **8** was clearly established.

Scheme 2.




The transformation of **7** to α–, β–, and γ-tropolones was achieved also by using the anodic oxidation in the key step (scheme 3). Namely, the thermal rearrangement of **7** yielding an isomeric mixture of dimethoxycycloheptatrienes (**11**)[16] and subsequent anodic oxidation of the mixture in MeOH gave a mixture of methyl ethers of β-tropolone (**12**) and γ-tropolone (**13**). On the other hand, the thermal rearrangement of ethylene acetal of tropone gave 3,4-dioxyethylenecycloheptatriene (**9**)[17] as a single product due to the difficulty of formation of other isomers, and the anodic oxidation of **9** gave the ether of α-tropolone (**10**).

Scheme 3



Furthermore, some substituted tropones, azulenes, and 2H-cyclohepta[b]furan-2-ones have been synthesized by using **5** and **7** as the key intermediates.

**Preparation of 2-Alkyl Tropones and Azulenes from 5.**

A simple and reliable method for the regioselective introduction of a variety of substituents to the 2-position of **5** has been found in this study and the usefulness of this method was shown in the preparation of some 2-substituted tropones, 2H-cyclohepta[b]furan-2-ones, and azulenes.

As shown in scheme 4, the addition of n-butyl lithium into a solution of **5** in THF gave an anionic species **14** regioselectively and its subsequent reaction with a variety of alkyl halides yielded 2-alkyl-3-methoxycycloheptatrienes (**15**). The transformation of **15** to 2-alkyltropones (**17**) has been achieved by the anodic oxidation of **15** followed by hydrolysis of the intermediate 1-alkyl-7,7-dimethoxycycloheptatriene (**16**). The other results of this transformation are shown in Table 1.

Scheme 4

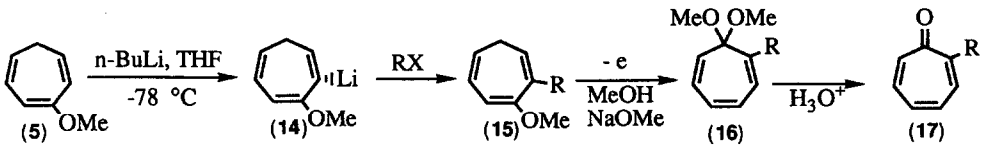
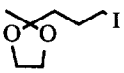


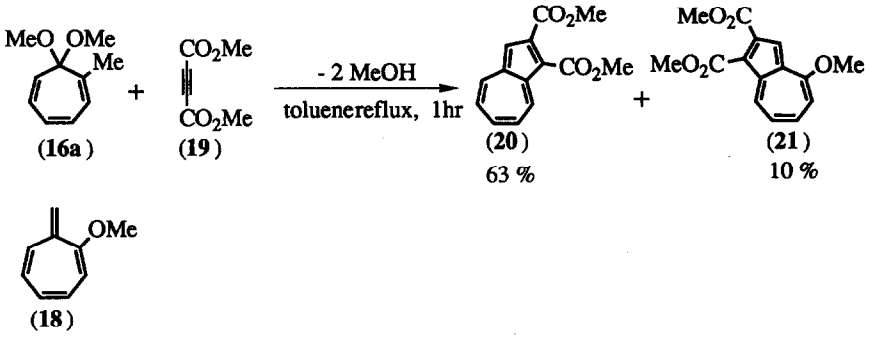

Table 1. Preparation of 2-Alkyltropones

| R-X | Yield (%) (15) | Supplied Electricity (F/mol) (15) ⟶ (16) | Yield(%) (17) |
|---|---|---|---|
| Me-I | 72 (**15a**) | 2.6 | 72 (**17a**) |
|  | 93 (**15b**) | 3.0 | 81 (**17b**) |
| $Br(CH_2)_3Cl$ | 65 (**15c**) | 3.0 | 75 (**17c**) |
|  | 70 (**15d**) | 4.5 | 67 (**17d**) |
| $Me_3SiCl$ | 92 (**15e**) | 3.5 | 96 (**17e**) |

The fact that 1-alkyl-tropone dimethylacetal **16** was formed by the anodic oxidation of **15** seems to be useful for the preparation of azulene skeleton since one molecule of methanol may be thermally eliminated from **16a** (R=Me), for instance, to generate 2-methoxy-heptafulven (**18**) *in situ*, and the [2+8] cycloaddition of **18** with dimethyl acetylecarboxylate (**19**) will give the corresponding azulene.

In fact, the reaction of **16a** with **19** in refluxing toluene gave the corresponding azulene (**20**) along with a small amount of methoxylated azulene (**21**) (scheme 5).

Scheme 5




**Preparation of 2-Hydroxyalkyltropones and 2H-Cyclohepta[b]furan-2-one**

The reaction of **14** with acetone (scheme 6) gave the corresponding 2-substituted-3-methoxycycloheptatriene (**22a**) in low yield (Table 2, run 1), while the same reaction carried out in the presence of a catalytic amount (10 mol. %) of CuI was found to result in a remarkable increase in the yield of **22a** (Table 2, run 2). Interestingly, the hydrolysis of **22a-c** with 20 % aqueous $H_2SO_4$ directly gave 2-alkyltropones (**23a-c**), whereas the anodic oxidation of **22a-e** gave the corresponding 2-substituted tropones (**24a-e**) in good yields.

Scheme 6

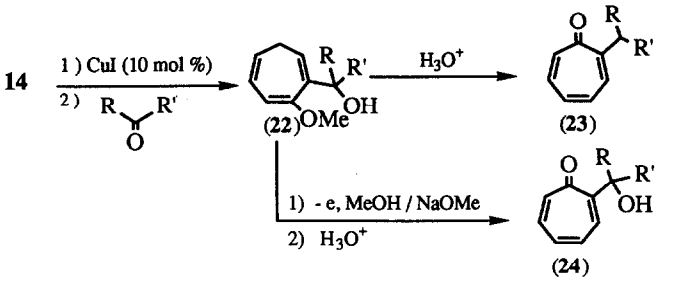


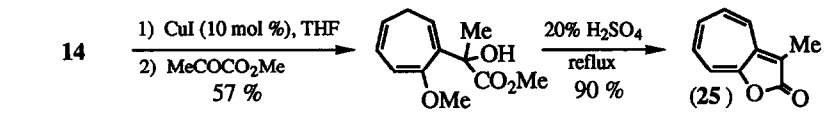

Table 2. The Reaction of **14** with Ketones.

| run | R = | R' = | Yield (%) (22) | Yield (%) (23) | Yield (%) (24) | Supplied electricity (F/mol) (22 → 24) |
|---|---|---|---|---|---|---|
| 1 | $CH_3$ | $CH_3$ | 35 (**22a**)[a] | 47 (**23a**) | 80 (**24a**) | 3.2 |
| 2 | $CH_3$ | $CH_3$ | 81 (**22a**) | | | |
| 3 | iso-Pr | H | 89 (**22b**) | 80 (**23b**) | 55 (**24b**) | 5.2 |
| 4 | -($CH_2$)$_5$- | | 95 (**22c**) | 45 (**23c**) | 33 (**24c**) | 10.8 |
| 5 | $CH_3$ | ▷ | 94 (**22d**) | | 68 (**24d**) | 5.5 |
| 6 | $CH_3$ | $CH_2$=CH | 44 (**22e**) | | 56 (**24e**) | 3.5 |
| 7 | n-Pr | H | 66 (**22f**) | | | |

a) The reaction was carried out without addition of CuI.

The versatility of this reaction has been shown by its application to the facile preparation of 3-methyl-2H-cyclohepta[b]furan-2-one (**25**) since **25** is a potential key intermediate for the synthesis of azulenes[18,19](scheme 7).

Scheme 7




**Preparation of Acylcycloheptatrienes from 5.**

Although introduction of an acyl group into the cycloheptatriene ring is usually difficult,[20] the addition of a catalytic amount (10 mol. %) of $NiBr_2$ into the reaction system of **14** with amides (Table 3, runs 1 and 2) or an acid chloride (Table 3, run 3) gave 2-acyl-3-methoxycycloheptatrienes (**26**) in reasonable yields.

Scheme 8

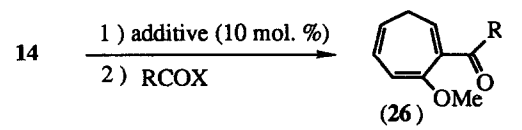



Table 3. Preparation of Acylcycloheptatriene.

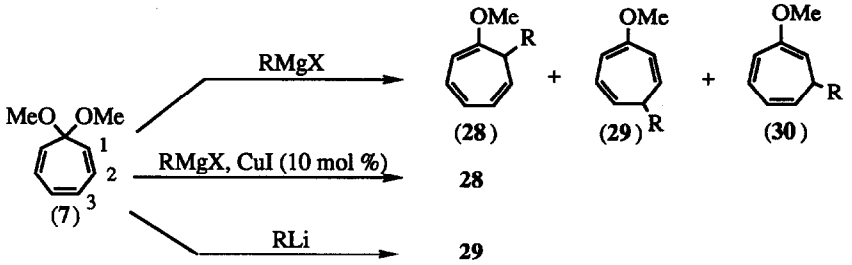
| run | R | X | Yield of **26** (%) | | |
|---|---|---|---|---|---|
| | | | Additive | $NiBr_2$ | CuI |
| 1 | H | $(CH_3)_2N$ | | 70 | 59 |
| 2 | $CH_3$ | $(CH_3)_2N$ | | 41 | 29 |
| 3 | $OCH_3$ | Cl | | 57 | 49 |

**Preparation of 2- and 4-Substituted Tropones from 7.**[2b]

The skeletons of 2- (**17**) and 4-alkyl tropones (**27**) are found widely in naturally occurring troponoids,[10] whereas the hitherto known syntheses[21,22] of **17** and **27**, especially preparation of the latter require many troublesome steps and a simple and reliable method for the regioselective introduction of a substituent R (R=alkyl or aryl group) to the 4-position of tropone ring has not yet been generally established. On the other hand, **7** prepared in this study by the anodic oxidation of **5** was found to be a potential key compound for the regioselective preparation of **17** and **27**.

As shown in scheme 9, the reaction of **7** with the Grignard reagent (RMgX) gave a mixture of alkylcycloheptatrienes (**28**), (**29**), and (**30**), whereas the addition of a catalytic amount (10 mol. %) of CuI to the reaction system gave surprisingly different selectivity and 1-methoxy-7-alkylcycloheptatriene (**28**) was obtained as the main product.[25] In addition, it has also been found that the reaction of **7** with alkyl lithium (RLi) took place at 3-position of **7** with high regioselectivity and formed 3-methoxy-7-alkylcycloheptatriene (**29**).

Scheme 9.




The anodic oxidation of **28** in MeOH gave 2-alkyl tropones (**17**) (scheme 10), while the thermal rearrangement of **29** to **31** followed by its anodic oxidation in MeOH afforded 4-alkyl tropones (**27**).[26] The results summarized in Table 4 indicate that this reaction is extensively applicable to the preparation of 2- and 4-substituted tropones. For instance, the anodic oxidation of 1-methoxy-4-isopropylcycloheptatriene (**31a**) (run 3, Table 4) afforded nezukone (**27a**) in a good yield.

Scheme 10

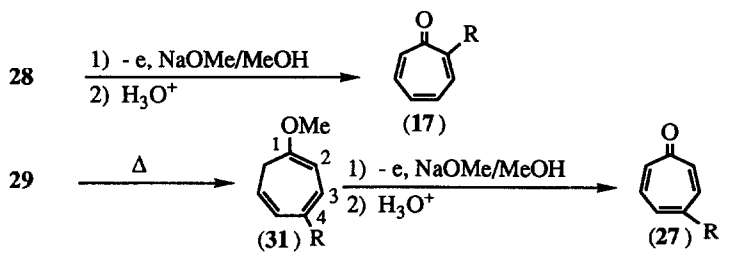
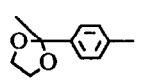



Table 4. Preparation of 2- and 4-Substituted Tropones.

| run | R = | Yield (%) | | | | Supplied electricity (F / mol) | | Anode Potential (V vs. SCE) | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | (7 → 28) | (28 → 17) | (7 → 29) | (29 → 31) | (28 → 17) | (31 → 27) | (31 → 27) | (27) |
| 1 | Me | 94 (**28a**) | 44 (**17a**)[a] | | | 2.6 | | | |
| 2 | iso-Pr | 73 (**28b**) | 53 (**17b**)[a] | | | 3.7 | | | |
| 3 | iso-Pr | | | 95 (**29a**) | 99 (**31a**) | | 2.2 | | 70 (**27a**)[a] |
| 4 | n-Bu | | | 94 (**29b**) | 100 (**31b**) | | 3.0 | | 65 (**27b**)[a] |
| 5 | Ph | | | 94 (**29c**) | 75 (**31c**) | | 3.0 | 1.2 | 75 (**27c**) |
| 6 | p-$MeOC_6H_4$ | | | 90 (**29d**) | 73 (**31d**) | | 3.3 | 1.1 | 71 (**27d**) |
| 7 |  | | | 90 (**29e**) | 71 (**31e**) | | 2.7 | 1.2 | 89 (**27e**) |
| 8 | p-$BrC_6H_4$ | | | 61 (**29f**) | 78 (**31f**) | | 4.0 | 1.2 | 74 (**27f**) |
| 9 |  | | | 75 (**29g**) | 73 (**31g**) | | 2.4 | 1.3 | 49 (**27g**) |

a) Constant current electrolysis.

**A Novel Wittig Type Rearrangement of Alkoxycycloheptatrienes and Its application to the Synthesis of 2H-Cyclohepta[b]furan-2-ones.**

Furthermore, it was found that a novel Wittig-type rearrangement of alkoxycycloheptatriene (**32**) yielding hydroxyalkylcycloheptatriene (**33**) (scheme 11) took place by the treatment of **32** with LDA and this reaction was effective for the preparation of a variety of **33** (Table 5).

Scheme 11

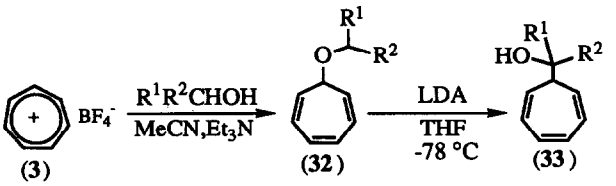
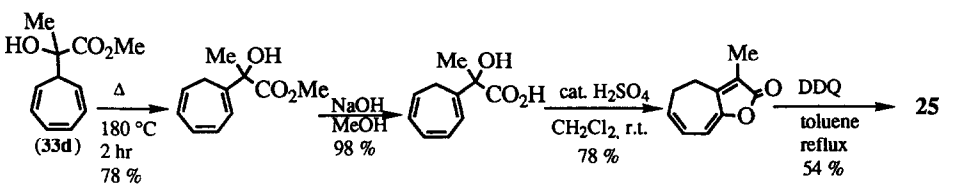



Table 5. Wittig Rearrangement of Alkoxycycloheptatriene.

| Run | $R^1$ | $R^2$ | yield (%) | |
|---|---|---|---|---|
| | | | (32) | (33) |
| 1 | p-$CNC_6H_4$ | H | 94 (**32a**) | 87 (**33a**) |
| 2 | $MeO_2C$ | $C_6H_5$ | 78 (**32b**) | 78 (**33b**) |
| 3 | $EtO_2C$ | H | 86 (**32c**) | 86 (**33c**) |
| 4 | $MeO_2C$ | Me | 91 (**32d**) | 91 (**33d**) |
| 5 | $CH_2$=CH | H | 90 (**32e**) | 98 (**33e**) |

This reaction was successfully applied to the synthesis of 3-methyl-2H-cyclohepta[b]-furan-2-one (**25**) by using **33d** as the starting material (scheme 12).

Scheme 12




The usefulness of the anodic oxidation of cycloheptatrienes as the powerful k tools for the preparation of a variety of non-benzenoid aromatic compounds such as tropylium salts, tropones, tropolones, 2H-cyclohepta[b]furan-2-ones, and azulenes has been clearly shown in this study.

Acknowledgement. The author (T.S and S.K) thank to the Ministry of Education, Science and Culture, Japan, for Grant-in Aid for Scientific Research (A) (No. 63430018).

## Experimental Section

$^1$H NMR spectra were recorded on Varian Gemini-200 spectrometer using TMS as an internal standard. IR spectra were obtained on Hitachi 260-10 spectrometer. High resolution mass spectra (HRMS) were measured by a JEOL JES-DX 300. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University. Because of the page limitation, spectroscopic data are shown for only some typical compounds.

**Anodic Oxidation of 1.**

Anodic oxidation of **1** (92 g, 1 mol) was carried out in an undivided cell equipped with carbon rod electrodes. Solvent was 300 ml of MeOH containing $Et_4NOTs$ (10 g) and NaOMe (5 g) as supporting electrolytes. After 3F /mol of electricity was passed with constant current of 5 A under the conditions of external cooling (-10-0 °C), the reaction mixture was poured into an aqueous solution of NaCl and extracted with ether. The product **2** was isolated by distillation under reduced pressure (62-65 °C/20 mmHg).[27]

**Alkylation of 5.**

A solution of n-BuLi (10 mmol) in hexane was added into the solution of **5** (10 mmol) in THF (50 ml) at -78 °C under nitrogen atmosphere. After the solution was stirred at 0°C for 30 minutes, alkylhalide (15 mmol) was added into this solution. The products (**15a-e**) were purified through silica gel column (Hexane:AcOEt=10:1).[28] **15b;** IR(neat) 3040, 2980, 2840, 1640, 1230 $cm^{-1}$. NMR($CDCl_3$) δ 2.23(t,2H,J=6.9Hz)), 3,03(d,2H,J=6.3Hz), 3.67(s,3H), 4.78-5.03(m,2H), 5.20-5.50(m,2H), 5.65-6.20(m,3H). HRMS. Calcd for $C_{11}H_{14}O$:162.1045; Found: 162.1044.**15c;** IR(neat) 3020, 2870, 2820, 1630, 1220 $cm^{-1}$. NMR($CDCl_3$) δ 1.85(m,2H), 2.24(t,2H,J= 6.9Hz) 2.48(t,2H,J=6.6Hz), 3,39(t,2H,J=6.6Hz), 3.67(s,3H), 5.25-5.53(m,2H), 5.81(d,1H,J=6.3Hz), 6.10(dd,1H,J=6.3 and 9.0Hz). HRMS. Calcd for $C_{11}H_{15}ClO$:198.0801; Found: 198.0803.

**Anodic Oxidation of 5, 6, 9, 11, 15, 22, and 28.**

The anodic oxidation of **5**, **6**, **9**, **11**, **15**, **22**, and **28** was performed in MeOH using NaOMe as the supporting electrolyte under similar reaction conditions to those of **1**.The structures of the products were determined by spectroscopic analysis and HRMS.[28]

The anodic oxidation of **11** gave a 1:1 mixture of **12** and **13**. **12;** IR(neat) 1650, 1560, 1470, 1230, 1210, 1170 $cm^{-1}$. NMR($CDCl_3$) δ 3.77(s,3H), 6.38-7.27(m,5H). HRMS. Calcd for $C_8H_8O_2$:136.0524; Found: 136.0517. **13;** IR(neat) 1650, 1580, 1530, 1240, 1210 $cm^{-1}$. NMR($CDCl_3$) δ 3.79(s,3H), 6.13-7.27(m,5H). HRMS. Calcd for $C_8H_8O_2$:136.0524; Found: 136.0516.

Compounds (**16a-e**) were not stable enough for HRMS and elemental analysis but the hydrolysis of **16a-e** with 5 % aqueous $H_2SO_4$ gave 2-alkyltropones (**17a-e**). **16a;** IR(neat) 3020, 2810, 1610, 1130, 1090 $cm^{-1}$. NMR($CDCl_3$) δ 2.06(s,3H), 3.16(s,6H), 5.62(d,1H,J=12Hz), 6.32-6.47(m,2H), 6.56-6.65(m,2H). **17b;** IR(neat) 2930, 1740, 1630, 1580, 1470, $cm^{-1}$. NMR($CDCl_3$) δ 3.40(d,2H,J=6.3Hz), 5.02-5.28(m,2H).5.72-6.20(m,1H), 6.87-7.27(m,5H). HRMS. Calcd for $C_{10}H_{10}O$:146.0732; Found:146.0730. **17c;** IR (neat) 2980, 1740, 1630, 1580, 920 $cm^{-1}$, NMR($CDCl_3$) δ 2.06(m,2H,), 2.80(t,2H,J=7.5Hz),

3.56(t,2H,J=6.3Hz), 6.87-7.40(m,5H). Anal Calcd for $C_{10}H_{11}ClO$: C,65.76; H,6.07; Cl,19.41, Found: C,65.60; H,5.79; Cl,19.62.

**Preparation of Azulenes 20 and 21.**

The solution of **16a** (2.1 mmol) and **19** (1.4 mmol) in toluene (10 ml) was refluxed for 2 hr under ambient atmosphere. The products **20**[29] and **21** were separated through silica gel column (Hexane:AcOEt=2:1). IR (KBr) 2950, 1720, 1600, 1570, 1220 $cm^{-1}$, NMR($CDCl_3$) δ 3.94(s,3H,), 3.96(s,3H), 4.20(s,3H), 7.18(d,1H,J=10.6Hz), 7.31(t,J=10.6Hz,1H), 7.71(s,1H), 7.82(t,1H,J=10.6Hz), 9.32(d,1H,J=10.6Hz). Anal Calcd for $C_{15}H_{14}O_5$: C,65.69;H,5.15. Found: C,65.95; H,5.40.

**Preparation of 22, 23 and 24.**

Into a solution of **14** (10 mmol) in THF (50ml) was added CuI (1 mmol) at -78°C and the solution was stirred for 1 hr at 0 °C under nitrogen atmosphere, the solution of acetone (20 mmol) in 5 ml of THF was added and the reaction mixture was stirred for 1 hr at room temperature. The products (**22a-f**) were purified through silica gel column (Hexane:AcOEt= 5:1). **22a;** IR(neat) 3450, 2980, 1630, 1560, 1230, 1180 $cm^{-1}$. NMR($CDCl_3$) δ 1.37(s,6H), 2.21 (t,2H,J= 6.9Hz), 3.65(s,1H), 3.76(s,3H), 5.44(td,1H,J=6.9 and 9Hz), 5.61(t,1H,J=6.9Hz), 5.88 (d,1H,J=6.6Hz), 6.10(dd,1H,J=6.6 and 9Hz). HRMS. Calcd for $C_{11}H_{16}O_2$:180.1150; Found: 180.1150.

The hydrolysis of **22a-c** with 20 % aqueous $H_2SO_4$ directly gave 2-alkyltropones (**23a, b,** and **23c**) (Table 2). **23a;** IR(neat) 3040, 2970, 1670, 1640, 1590, 1470 $cm^{-1}$. NMR($CDCl_3$) δ 1.20 (d,6H, J=6.6 Hz), 3.48(m,1H), 6.87-7.27(m,5H). HRMS. Calcd for $C_{10}H_{12}O$: 140.0888; Found: 140.0882.

The anodic oxidation of **22a-e** (10 mmol) in MeOH (30 ml) using NaOMe (1 g) as a supporting electrolyte and the hydrolysis of the resulting products with 5 % aqueous $H_2SO_4$ gave 2-substituted tropones (**24a-e**). **24a;** IR(neat) 3420, 2980, 1700, 1630, 1230 $cm^{-1}$. NMR($CDCl_3$) δ 1.49(s,6H), 5.59(s,1H), 6.89-7.47(m,5H). HRMS.Calcd for $C_{10}H_{12}O_2$: 164.0837; Found: 164.0827.

**Preparation of 25.**

Into a solution of **14** (10 mmol) in THF (50ml) was added CuI (1 mmol) at -78°C and the solution was stirred for 1 hr at 0 °C under nitrogen atmosphere. Methyl pyruvate (20 mmol) was added into this solution and the reaction mixture was stirred for 3 hr at room temperature. The crude product was isolated by the extraction with ether and it was treated with 20 % aqueous $H_2SO_4$ (20 ml). The structure of **25** was determined by the comparison of its spectroscopic values with those of the authentic sample.[30]

**Preparation of 26.**

The synthesis of **26** was carried out using a catalytic amount of $NiBr_2$ (10 mol %) under otherwise similar reaction conditions to those of **22**. The spectroscopic values of 2-formyl-3-methoxycycloheptatriene (table 3, run 1) were as follows: IR(neat) 1710, 1615, 1240 $cm^{-1}$. NMR($CDCl_3$) δ 2.43(dd,2H,J=6 and 8Hz), 3.80(s,1H), 5.17-5.42(td,1H,J=6 and 8H), 5.97-6.54(m,3H), 9.82(s,1H). HRMS. Calcd for $C_9H_{10}O_2$: 150.0704; Found:150.0683.

**Preparation of 29 and 31.**

A solution of **7** (10 mmol) in ether (10 ml) was added into a solution of alkyl lithium (25 mmol) in ether (60 ml) at room temperature. The reaction mixture was stirred for 3 hr under nitrogen atmosphere and poured into an aqueous solution of $NH_4Cl$. The product **29** was isolated by silica gel column (hexane:AcOEt=5:1). The thermal rearrangement of **29** to form **31** was carried out under nitrogen atmosphere (180 °C, 2hr). **29a**;IR(neat) 2970, 2840, 1630, 1560, 1180 $cm^{-1}$. NMR($CDCl_3$) δ 1.03(d,6H,J=6.9Hz), 1.43(m,1H), 1.88(m,1H), 3.73(s,3H), 5.17 (dd,1H,J=5.7 and 9Hz), 5.47(dd, 1H,J=6.3 and 10.5Hz), 5.89-6.34(m,3H). HRMS.Calcd for $C_{11}H_{16}O$: 164.1201; Found: 164.1214.

**31a;** IR (neat) 2960, 2830, 1630,1260,1160 $cm^{-1}$, NMR($CDCl_3$) δ 1.10(d,6H,J=7.2Hz), 1.91(m,1H), 2.48(d,2H,J=6.9Hz), 3.59(s,3H), 5.26(d,1H,J=9Hz), 5.40(td,1H,J=6.9 and 9Hz), 6.12(d,1H,J=9Hz), 6.25(d,1H,J=6.6Hz). HRMS. Calcd for $C_{11}H_{16}O$: 164.1201; Found:164.1184.

**Controlled Potential Electrolysis of 31.**

Oxidation potentials ($E_p$) of **29** and **31**(6.6 mmol/l) were measured with platinum electrodes (1 x 2 cm) in MeCN containing $Et_4NOTs$ (66 mmol/l) as a supporting electrolyte (scanning rate=200mV/sec). Controlled potential electrolysis of **31** was carried out in MeOH using NaOMe as a supporting electrolyte. The applied anode potentials were shown in Table 4. The anodic oxidation of **31a** in MeOH followed by hydrolysis (10 % $H_2SO_4$) afforded nezukone and its $C^{13}$-NMR was completely the same as that of authentic sample.[31]

**The Wittig Rearrangement of 32 and the Preparation of 25.**

A solution of **32** (10 mmol) in THF (10ml) was added into a solution of LDA (12 mmol) in 50 ml of THF at -78°C, and the reaction mixture was stirred for 1 hr at this temperature. The products (**33a-e**) were isolated by silica gel column (hexane:$Et_3N$=5:1). **32d;** IR(neat) 1750, 1140, 1120, 740, 700 $cm^{-1}$, NMR($CDCl_3$) δ 1.43(d,3H,J=6.6Hz), 3.50-3.70(m,1H), 3.72(s,3H), 4.20(q,1H,J=6.6Hz), 6.07-6.33(m,2H), 6.38-6.70(m,2H), 6.70(t,2H,J= 3.4Hz). HRMS. Calcd for $C_{11}H_{14}O_3$: 194.0943; Found:194.0946. **32e;** IR (neat) 3020, 2850, 1400, 1110, 925, 700 $cm^{-1}$, NMR($CDCl_3$) δ 3.90(d,2H,J=6Hz), 5.05-5.29(m,2H), 5.30-5.59(m,2H), 5.62-6.03(m,1H), 6.03-6.30(m,2H), 6.68 (m,2H). Anal Calcd for $C_{10}H_{12}O$: C,81.04;H,8.16. Found: C,80.29; H,8.18. **33d**;IR (neat) 3510, 1735, 1640 ,1730, 710$cm^{-1}$, NMR ($CDCl_3$) δ 1.52(s,3H), 1.60-1.92(m,1H), 3.45(bs,1H), 3.80(s,3H), 5.22(dd,1H,J=9.3 and 5.7Hz), 5.45(dd,1H,J=9.3 and 5.7Hz), 6.10-6.43(m,2H), 6.70(t,1H,J=3.1Hz). mass spectrum (relative intensity),m/e 194(0.6%),176(15%),91(100%). **33e;** IR (neat) 3370, 3020, 2850, 1400, 1140, 995, 925, 700 $cm^{-1}$, NMR($CDCl_3$) δ 1.60-2.06(m,2H), 4.25-4.55(m,1H), 5.15-5.55(m,4H), 5.79-6.20(m,1H), 6.20-6.44(m,2H), 6.70 (m,2H). Anal Calcd for $C_{10}H_{12}O$: C,81.04;H,8.16. Found: C,80.81; H,8.33.

The transformation of **33d** (Table 5, run 4) to **25** was accomplished by the procedures shown in scheme 12, and the structure of **25** was determined by the comparison of its spectroscopic values with those of the authentic sample.[30]

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