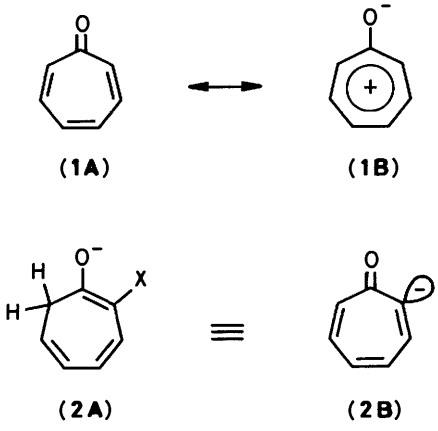
Umpolung of Tropone: The Reaction of 2-Halogenocycloheptadienone Enolates with Tropylium Cations and Several Other Cationic Electrophiles. Preparation of Novel 2-Substituted and 2,7-Disubstituted Tropones[1]

Hiroyuki Miyano and Makoto Nitta*
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169, Japan

The reactions of 2-halogenotropones (**3a–c**) with hydride reagents giving 2-halogenocycloheptadienone enolates (**4a–c**) have been studied to provide a reverse polarity (umpolung) of tropone. The structures of 2-chlorocycloheptadienone enolate (**4a**) and 2-chloro-7-deuteriocycloheptadienone enolate (**4D**) were confirmed by ^{1}H NMR spectral studies. The enolates were easily reacted with tropylium and substituted tropylium cations to give 2-(2,4,6-cycloheptatrienyl)tropone (**8**) and its derivatives, (**13b–d**) and (**14b–d**) in good yields. The other cationic electrophiles, such as benzo- and dibenzotropylium cations, di- and triphenylcyclopropenylium cations as well as tricarbonyl(cyclopentadienylium)iron and tricarbonyl(cyclohexadienylium)iron, were also reacted with the enolate to give the corresponding 2-substituted tropones (**21–27**) in good to modest yields. In a similar fashion, 2-halogeno-7-substituted cycloheptadienone enolates (**28a–e**) were generated through the reaction of 2-chlorotropone (**3a**) with Grignard and organolithium reagents as well as the reaction of 2-bromo-7-methoxytropone (**3d**) and 2,7-dibromotropone (**3e**) with hydride reagent. They reacted also with tropylium cation to give 2,7-disubstituted tropones (**29a–e**).

Cyclohepta-2,4,6-trienone (tropone) (**1**) is easily attacked by nucleophiles as can be seen from its resonance structure (**1B**). Fairly extensive studies have already been made on the reactions of (**1**) and its derivatives with various nucleophiles,[2–5]



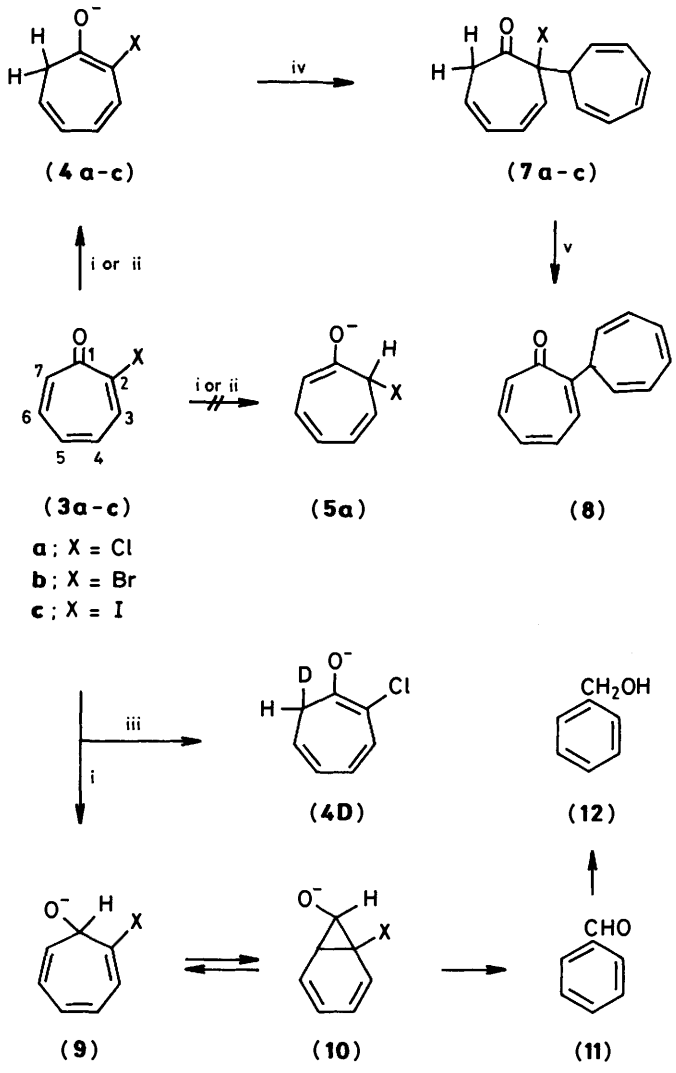
Scheme 1.

and we have studied the nucleophilic reaction of 2-halogenotropones with tricarbonyl(4-7-η-1*H*-1,2-diazepine)iron to provide three novel isomers of 1-(oxocycloheptatrienyl)-1*H*-1,2-diazepine.[6] Several examples of the C–C bond forming reactions of 2-halogenotropones with carbanions,[2] Grignard,[7,8] organolithium,[7,9] organocopper reagents,[10] and lithium enolates[11] have also been reported to give 2-substituted tropones. Since the resistance of the tropone nucleus to electrophilic attack is generally recognized,[2,3,12] the study of a reverse polarity (umpolung) strategy for realizing a formal electrophilic substitution of (**1**) could be fruitful in the synthesis of a variety of substituted troponoids. Our synthetic approach to (**2A**), which was expected to be an equivalent for 2-troponide ion (**2B**), involves 2-halogenocycloheptadienone enolates (**4a–c**) and (**28a–e**), generated *in situ* by the reaction of halogenotropones (**3a–e**) with hydride, Grignard, and organolithium reagents. This paper provides a full account for the reaction of 2-halogenocycloheptadienone enolates with a variety of cationic electrophiles.

Results and Discussion

Treatment of 2-halogenotropones (**3a–c**)[7,13] with $LiAlH_4$ at 0 °C or $LiAlH(OBu^t)_3$[14] at ambient temperature in tetrahydrofuran (THF) gave 2-halogenocycloheptadienone enolates (**4a–c**) (Scheme 2). The structural evidence for the enolates was provided by ^{1}H NMR spectral studies of (**4a**) and its deuteriated analogue (**4D**), both of which were generated by the reaction of (**3a**) with $LiAlH_4$ and $LiAl[^2H_4]$ in $[^2H_8]$THF, respectively. Both (**4a**) and (**4D**) are mixtures of two enolates, the counter cations of which are presumably different from each other though their exact nature is uncertain.

The ^{1}H NMR spectrum of (**4a**) exhibited a signal for methylene protons at δ 2.50–2.78 (2 H, m, 7-H), which is coupled with the signals for vinyl protons at δ 5.24 (0.56 H, br dt, *J* 9.7, 6.7 Hz, 6-H) and δ 5.59 (0.44 H, dt, *J* 10.8, 6.2 Hz, 6-H). On irradiation at δ 2.62, the 6-H signals became doublets. The remaining signals of the vinyl protons appear at δ 5.80–6.72 (3 H, m, 3,4,5-H). In contrast, the ^{1}H NMR spectrum of (**4D**) exhibited a signal for a methylene proton at δ 2.48–2.76 (1 H, m, 7-H), which is also coupled with the signals at δ 5.25 (0.7 H, br dd, *J* 7.9, 7.7 Hz, 6-H) and δ 5.59 (0.3 H, dd, *J* 9.7, 5.9 Hz, 6-H). The remaining signals appear at δ 5.80–6.72 (3 H, m). On irradiation at δ 2.58, the 6-H signals became doublets. Nucleophilic substitution onto a tropone nucleus carrying a mobile substituent is known to take place at C-2 (normal substitution) and/or C-7 (abnormal substitution) to give 2-substituted tropones.[15] The present hydride attack on (**3a**) was proved to take place at C-7 to give (**4a**), and not at C-2 to give (**5a**) (Scheme 2). The formation of (**4b, c**) is reasonably expected in the reaction of (**3b, c**).[3] Although a simple cycloheptadienone enolate,[16] which derives from the reduction of tropone (**1**) with $LiAlH_4$, has been postulated as the intermediate to give 3,5-



Scheme 2. *Reagents:* i, $LiAlH_4$; ii, $LiAlH(OBu^t)_3$; iii, $LiAl[^2H_4]$; iv, tropylium tetrafluoroborate, (**6a**); v, Et_3N.

Table 1. Results for the reactions of (**3a–c**) with hydride reagent and tropylium tetrafluoroborate.

Run	2-Halogeno-tropone	Hydride reagent	Product yield (%) (**8**)	(**12**)
1	(**3a**)	$LiAlH(OBu^t)_3$	87	0
2	(**3b**)	$LiAlH(OBu^t)_3$	83	0
3	(**3c**)	$LiAlH(OBu^t)_3$	74	0
4	(**3a**)	$LiAlH_4$	74	5
5	(**3b**)	$LiAlH_4$	59	8
6	(**3c**)	$LiAlH_4$	57	9
7	(**3a**)	$LiAl[^2H_4]$	70[a]	—

[a] A mixture of (**8**) and (**8D**) in a ratio of 27:73.

cycloheptadienone, no C–C bond forming process has been investigated.

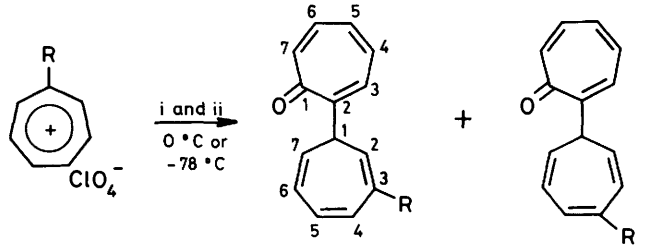
The solutions of (**4a–c**) generated *in situ* by the reaction of (**3a–c**) with $LiAlH_4$ and $LiAlH(OBu^t)_3$ were then treated with tropylium tetrafluoroborate (**6c**) and triethylamine in THF to result in the formation of 2-(2,4,6-cycloheptatrienyl)tropone (**8**), probably *via* the intermediate (**7a–c**) (Scheme 2). The results are summarized in Table 1. In the case of (**4D**), a mixture of (**8**), and 2-(2,4,6-cycloheptatrienyl)-7-deuteriotropone (**8D**) were obtained in 70% yield in a ratio of 27:73, which seems to reflect the isotope effect of the incorporated deuterium (Table 1, run 7). Since compound (**8**) is thermally unstable and is not purified by distillation, satisfactory analytical data were not obtained. The structure of (**8**) was assigned on the basis of the spectroscopic data. The ^1H- and ^{13}C-NMR spectra clearly show that (**8**) exists substantially as the cycloheptatriene form.

Table 2. Results for the reaction of (**4a**) with substituted tropylium perchlorates (**6b–d**).

Run	Tropylium perchlorate	Reaction temp. (°C)	Product yield (%) (**13**) + (**14**)	Ratio of (**13**):(**14**)
1	(**6b**)	24	82	35:65
2	(**6c**)	24	88	32:68
3	(**6d**)	24	75	35:65
4	(**6b**)	−78	84	29:71
5	(**6c**)	−78	96	28:72
6	(**6d**)	−78	78	33:67

The reaction of (**3a–c**) with $LiAlH(OBu^t)_3$ and subsequently with tropylium cation afforded (**8**) in good yield (Table 1, runs 1–3). However the reactions using $LiAlH_4$ gave (**8**) in relatively low yield along with a small amount of benzyl alcohol (**12**) (runs 4–6). The formation of (**12**) is best explained by hydride attack at C-1 of (**3a–c**) to give (**9**), which gives benzaldehyde (**11**) possibly *via* a norcaradiene (**10**). The aldehyde (**11**) is subsequently reduced with excess hydride to afford benzyl alcohol (**12**). The reaction of (**3a–c**) with $LiAlH_4$ exhibited lower site selectivity compared to that with $LiAlH(OBu^t)_3$ probably because of its stronger reactivity.[14]

Similarly, the enolate (**4a**) reacted with stable substituted tropylium perchlorates, such as t-butyltropylium (**6b**),[17] phenyltropylium (**6c**),[18] and chlorotropylium perchlorates (**6d**),[19] to give two products, 2-(3-substituted-2,4,6-cycloheptatrienyl)-tropones (**13b–d**) and 2-(4-substituted-2,4,6-cycloheptatrienyl)-tropones (**14b–d**), respectively, in good combined yields (Table 2, Scheme 3). Of four possible isomers, only (**13b–d**) and (**14b–d**)



Scheme 3. *Reagents:* i, (**3a**), $LiAlH(OBu^t)_3$; ii, Et_3N.

were obtained in each case. This fact implies that the steric hindrance of the substituent on the tropylium cation (**6b–d**) would be an important factor in the control of site selectivity. Furthermore, the selectivity seems to be increased at low temperatures (Table 2, runs 4–6). Compounds (**13b–d**) and (**14b–d**) decompose under distillation, and analytical data of these were not obtained. However, satisfactory high resolution mass spectral data were obtained for these compounds. The structures of (**13b–d**) and (**14b–d**) were determined on the basis of the ^1H and ^{13}C NMR spectral data, which are summarized in Table 3 and Table 4. The ^1H and ^{13}C signals of (**13b–d**) and (**14b–d**) were assigned by their COSY and H-C COSY spectra.

Table 3. ^{1}H Chemical shifts (ppm)[a] of the hydrogens on the cycloheptatriene ring of (**8**), (**13b–d**), and (**14b–d**).

Compound	1-H	2-H	3-H	4-H	5-H	6-H	7-H
(**8**)	3.47	5.37	6.25	6.60	6.60	6.25	5.37
(**13b**)	2.95	4.70	—	6.66	6.51	6.10	4.96
(**13c**)	3.25	5.13	—	6.81	6.69	6.28	5.03
(**13d**)	3.54	*ca.* 5.40[b]	—	6.49	6.55	*ca.* 6.16[c]	*ca.* 5.40[b]
(**14b**)	3.46	5.38	6.31	—	6.48	6.19	5.30
(**14c**)	3.58	5.55	6.43	—	6.92	6.34	5.46
(**14d**)	3.46	*ca.* 5.43[b]	6.22	—	6.77	6.16	*ca.* 5.43[b]

[a] In $CDCl_3$ using $SiMe_4$ as internal standard. [b] Overlapping with each other. [c] Overlapping with the signal of contaminated (**14d**).

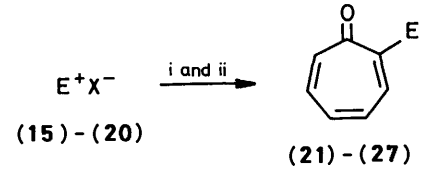
Table 4. ^{13}C Chemical shifts (ppm) of (**8**), (**13b–d**), and (**14b–d**)[a]

Compound	Tropone				Cycloheptatriene							Remaining absorption
	C-1	C-2	C-3 to C-6	C-7	C-1	C-2	C-3	C-4	C-5	C-6	C-7	
(**8**)	185.9	153.7	134.8 134.1 133.1 132.8	140.3	43.1	124.8	124.7	130.0	130.0	124.7	124.8	—
(**13b**)	186.3	156.2	134.8 133.4 133.1 132.5	140.2	40.3	104.9	145.7	128.2	128.8	124.3	112.1	Bu^t: 35.0 30.0 (3 C)
(**13c**)	186.3	154.9	135.0 133.5 133.4 132.8	140.3	40.7	108.5	137.4	129.2	130.0	125.1	112.4	Ph: 140.6 128.0 (2 C) 127.4 (2 C) 127.0
(**13d**)	185.9	152.8	135.1 134.4 133.4 132.2	140.8	42.2	119.5	129.1	129.8	131.0	124.8	124.8	—
(**14b**)	186.3	154.2	134.8 133.6 133.1 132.7	140.4	42.6	121.7	124.6	151.8	123.1	125.5	121.7	Bu^t: 35.7 30.3 (3 C)
(**14c**)	186.2	153.9	135.0 134.2 133.3 133.1	140.6	43.9	124.6	125.9	142.3[b]	127.6	125.3	124.9	Ph: 141.8[b] 128.2 (2 C) 127.1 126.7 (2 C)
(**14d**)	186.1	153.1	135.2 134.8 133.5 133.3	141.0	44.8	127.1	126.5	135.2	129.1	123.7	125.9	—

[a] Recorded in $CDCl_3$ using $SiMe_4$ as internal standard. [b] Interchangeable with each other.

It is characteristic that the ^{1}H NMR signals of 2-H, 7-H, and 1-H on the cycloheptatriene ring of (**13b, c**) were shifted to higher field as compared to those of (**8**), (**13d**), and (**14b–d**) [similar shifts occur in the ^{13}C NMR spectra of (**13b, c**)]. Generally, the 1-H and 6-H proton signals of the cycloheptatriene appear at δ 5.0–5.5 and those of norcaradiene appear at δ *ca.* 2.5.[20,21] Thus, in the compounds (**13b, c**), the equilibrium between cycloheptatriene and norcaradiene seems to be shifted appreciably towards the norcaradiene form. In the cases of (**13d**) and (**14b–d**), the equilibrium lies on the side of cycloheptatriene almost exclusively. It is reported that the equilibrium between cycloheptatriene and norcaradiene can be shifted to the norcaradiene side by the introduction of a t-butyl group into the C-1, C-2, or C-3 position of 7-alkyl-7-cyanocycloheptatriene[22,23] and into the C-2 or C-3 position of 7-cyanocycloheptatriene.[24] These findings have been ascribed to the steric effect, which destabilizes the cycloheptatriene form rather than the norcaradiene form.[23] The present result seems to be consistent with these facts.

Furthermore, several cationic electrophiles reacted conveniently with 2-chlorocycloheptadienone enolate (**4a**), which also derived from (**3a**) and $LiAlH(OBu^t)_3$, to give the corresponding 2-substituted tropones (**21**)–(**27**) in high to

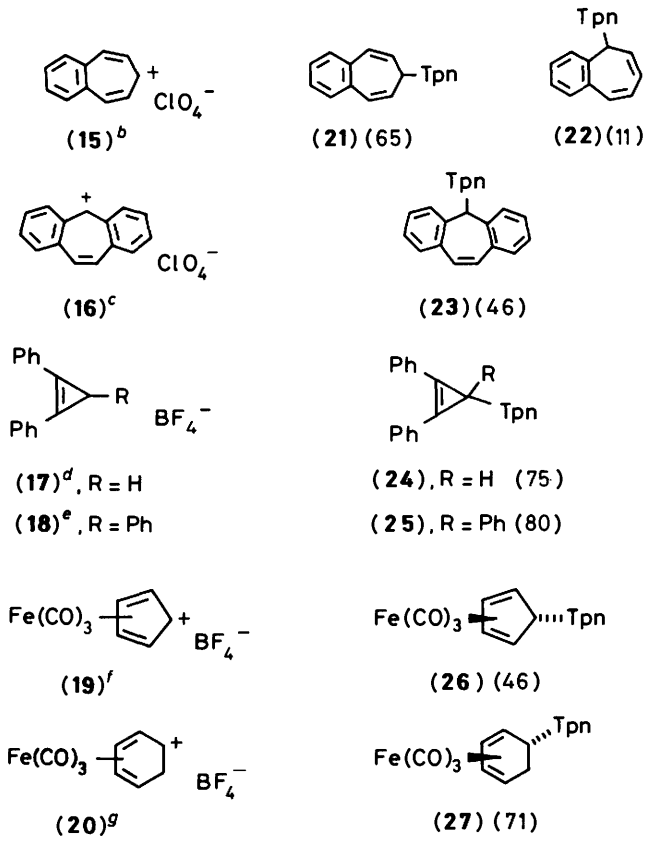


Scheme 4. *Reagents:* i, (**3a**), $LiAlH(OBu^t)_3$; ii, Et_3N.

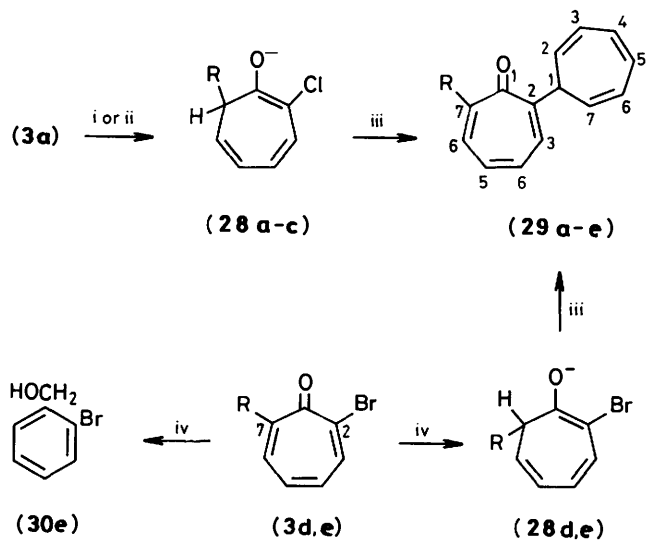
modest yields. The results are summarized in Scheme 4 and Table 5. Regarding the ratio of (**21**)/(**22**), (**21**) was formed preferentially over (**22**), for steric reasons as in the case of the reaction of (**4a**) with (**6b–d**). The structures of the products (**21**)–(**27**), all of which are new compounds, were assigned on the basis of their spectroscopic and analytical data except for thermally unstable high boiling oil (**22**). Each of the compounds (**26**) and (**27**) is a single stereoisomer. Thus, the 7-oxocyclohepta-1,3,5-trienyl (2-troponyl) group would be introduced from the less hindered exo side to the $Fe(CO)_3$ moiety, analogous to the reaction of 2-chlorotropone with tricarbonyl(1-4-η-cycloheptatrienide)iron.[31]

Interestingly, the present methodology is also applicable to

Table 5. Results for the reaction of (**4a**) with cationic electrophiles (**15**)–(**20**).[a] (Percentage yields given in brackets after compound number).



[a] Tpn denotes 7-oxocyclohepta-1,3,5-trienyl group. [b] Ref. 25. [c] Ref. 26. [d] Ref. 27. [e] Ref. 28. [f] Ref. 29. [g] Ref. 30.



a; R = Me, b; R = Bu, c; R = Ph, d; R = OMe, e; R = Br

Scheme 5. *Reagents:* i, RMgX (X = I, Br); ii, RLi; iii, tropylium tetrafluoroborate (**6a**), Et_3N; iv, $LiAlH(OBu^t)_3$.

Table 6. Results for the reaction of (**3a**, **d**, **e**) with nucleophiles and tropylium tetrafluoroborate.

Run	Halogenotropone	Nucleophile	Product yield/%
1	(**3a**)	MeMgI	(**29a**) 89
2	(**3a**)	MeLi	(**29a**) 88
3	(**3a**)	BuLi	(**29b**) 79
4	(**3a**)	PhMgBr	(**29c**) 90
5	(**3d**)	$LiAlH(OBu^t)_3$	(**29d**) 43, (**3d**) 24
6	(**3e**)	$LiAlH(OBu^t)_3$	(**29e**) 12, (**30e**) 38, (**3e**) 39

the synthesis of 2,7-disubstituted tropone derivatives (Scheme 5). The reaction of (**3a**) with Grignard or organolithium reagents instead of hydride reagent and subsequently with tropylium tetrafluoroborate (**6a**) in the presence of triethylamine gave disubstituted tropones (**29a–c**) in good yields. The results are summarized in Table 6 (runs 1–4). Since the nucleophilic attack of Grignard and organolithium reagent on (**3a**) and its related compounds have been reported to take place at C-7,[9,32] the intermediacy of (**28a–c**) is reasonably accepted.

Furthermore, the 2,7-disubstituted cycloheptadienone enolates (**28d, e**), which were generated by the reaction of 2-bromo-7-methoxytropone (**3d**)[33] and 2,7-dibromotropone (**3e**)[34] with $LiAlH(OBu^t)_3$, reacted with tropylium cation (**6a**) to give 2,7-disubstituted tropones (**29d, e**) in modest yields (Table 6, runs 5 and 6). Since the compounds (**29b–d**) are oily materials and decompose under distillation, satisfactory analytical data were not obtained. The structures of (**29a–e**) were assigned on the basis of the ^{13}C NMR spectra (Table 7) and other spectroscopic data. Hydride attack on (**3d, e**) occurred to give only (**29d, e**) *via* (**28d, e**). The low yield of (**29d, e**) and recovery of appreciable amounts of (**3d, e**) can be ascribed to the steric hindrance of the substituents on C-2 and C-7 toward hydride attack. In addition, the hydride attack on (**3e**) occurs at C-1 in appreciable amounts to give 2-bromobenzyl alcohol (**30e**) (see above). Nucleophilic attack at C-1 was also demonstrated in the reaction of (**3e**) with hydroxide ion to give 2-bromobenzoic acid.[35]

In conclusion, a number of 2-(2,4,6-cycloheptatrienyl)-tropones have become available through the methodology described here. The acid catalysed reaction of (**8**) and its related compounds will be described in the following paper.[36] Furthermore, (**8**) was reactive to organic base to give a dihydrodicyclohepta[*b,d*]furan system in good yield.[1] The details will be reported in a separate paper.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Hitachi R-24, a Hitachi R-90H, and a JEOL JNM-GSX400 spectrometers, chemical shifts are given in ppm (δ) relative to the internal $SiMe_4$ standard. IR spectra were recorded on a Shimadzu IR-400 spectrometer. The mass spectral studies and the high resolution mass spectral (HRMS) studies were conducted by using Shimadzu GCMS-QP1000 and JEOL DX-300 spectrometers. COSY and H-C COSY spectra were recorded on a JEOL JNM-GSX400 spectrometer. Microanalyses were performed at the Science and Engineering Research Laboratory of Waseda University. M.p.s were recorded on a Büchi apparatus and are uncorrected. All experimental procedures were performed under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was dried with sodium and distilled under nitrogen atmosphere prior to use.

^1H *NMR Spectral Studies of* 2-*Chlorocycloheptadienone Enolate* (**4a**) *and* 2-*Chloro*-7-*deuteriocycloheptadienone Enolate* (**4D**).—To a suspension of $LiAlH_4$ (23 mg, 0.6 mmol) or $LiAl[^2H_4]$ (25 mg, 0.6 mmol) in $[^2H_8]$THF (0.4 ml), 2-chlorotropone (**3a**)[13] (42 mg, 0.3 mmol) was added at ambient

Table 7. ^{13}C Chemical shifts (ppm) of (**29a–e**).[a]

Compound	Tropone				Cycloheptatriene			Remaining absorption
	C-1	C-2	C-3 to C-6	C-7	C-1	C-2,3,6,7	C-4,5	
(**29a**)	185.4	150.9[b]	133.9 133.6 132.0 131.0	150.0[b]	44.4	125.6 124.5	130.0	Me: 23.1
(**29b**)	185.4	153.5[b]	133.2 133.0 131.9 130.8	151.0[b]	44.5	125.6 124.3	129.9	Bu:35.8,31.1, 22.4, 13.6
(**29c**)	186.0	153.2	134.5 132.6 131.6 131.6	149.4	44.5	125.5 124.7	130.2	Ph: 140.3, 129.0 (2 C) 127.6 (3 C)
(**29d**)	178.8	148.3	135.3 131.4 126.5 111.8	164.1	45.2	126.2 124.7	130.2	MeO: 56.2
(**29e**)	179.8	149.9	138.4 133.7 133.3 130.3	141.7	45.2	125.4 124.8	130.3	—

[a] Recorded in $CDCl_3$ using $SiMe_4$ as internal standard; the numbering of carbons are employed in a way as depicted in Scheme 5. [b] Interchangeable with each other.

temperature. The suspension was filtered through quartz wool and the filtrate was introduced into a ^1H NMR tube. After adding tetramethylsilane, a ^1H NMR spectrum of the solution was recorded on a Hitachi R-90H spectrometer. For (**4a**): $\delta_H([^2H_8]THF)$ 2.50–2.78 (2 H, m, 7-H), 5.24 (0.56 H, br dt, *J* 9.7, 6.7 Hz, 6-H), 5.59 (0.44 H, dt, *J* 10.8, 6.2 Hz, 6-H), and 5.80–6.72 (3 H, m, 3,4,5-H).

For (**4D**): $\delta_H([^2H_8]THF)$ 2.48–2.76 (1 H, m, 7-H), 5.25 (0.7 H, br dd, *J* 7.9, 7.7 Hz, 6-H), 5.59 (0.3 H, dd, *J* 9.7, 5.9 Hz, 6-H), and 5.80–6.72 (3 H, m, 3,4,5-H).

General Procedure for the Reaction of 2-*Halogenocycloheptadienone Enolate* (**4a–c**) *with Tropylium Tetrafluoroborate* (**6a**).—*Method A.* To a stirred suspension of $LiAlH(OBu^t)_3$ (1.66 g, 6.5 mmol) in THF (15 ml), 2-halogenotropone (**3a–c**)[7,13] (5 mmol) was added and the mixture was stirred for 30 min at ambient temperature. The solution was then added dropwise to a stirred mixture of tropylium tetrafluoroborate (1.16 g, 6.5 mmol) and triethylamine (658 mg, 6.5 mmol) in THF (10 ml) at 0 °C, and stirred for another 10 min at ambient temperature. After the reaction mixture was quenched with H_2O (20 ml), the mixture was extracted with ethyl acetate and the extract was dried (Na_2SO_4). The solvent was evaporated and the resulting residue was separated by column chromatography on silica gel. The fractions eluted with hexane–ethyl acetate (5:1) afforded (**8**). The results are summarized in Table 1 (runs 1–3).

Method B. To a stirred suspension of $LiAlH_4$ (137 mg, 3.6 mmol) in THF (10 ml), 2-halogenotropones (**3a–c**) (10 mmol) were added at 0 °C and the mixture was stirred for 10 min. The solution was then added dropwise to a stirred mixture of tropylium tetrafluoroborate (2.31 g, 13 mmol) and triethylamine (1.32 g, 13 mmol) in THF (10 ml) at 0 °C, and the mixture was stirred for another 10 min at ambient temperature. After the usual workup described above, the product was chromatographed on alumina using hexane–ethyl acetate (10:1) as eluant to give (**8**) and (**12**). The results are summarized in Table 1 (runs 4–6).

(**8**), a pale yellow oil; $\delta_H(CDCl_3)$ 3.47 (1 H, br t, *J* 6.0 Hz), 5.37 (2 H, dddd, *J* 8.9, 6.0, 0.9, 0.7 Hz), 6.25 (2 H, dddd, *J* 8.9, 3.9, 2.7, 0.9 Hz), 6.60 (2 H, dddd, *J* 3.9, 2.7, 0.9, 0.7 Hz), 6.89–7.21 (4 H, m), and 7.25–7.42 (1 H, m); $\nu_{max}(CHCl_3)$ 1 627 and 1 577 cm^{-1}; λ_{max}(EtOH) 229 and 307 nm (log ε 4.29 and 3.86); *m/z* 196 (M^+, 100%) [(HRMS) M^+, 196.0882. $C_{14}H_{12}O$ requires *M*, 196.0889].

Reaction of 2-*Chloro*-7-*deuteriocycloheptadienone Enolate* (**4D**) *with Tropylium Tetrafluoroborate* (**6a**).—To a stirred suspension of $LiAl[^2H_4]$ (25.2 mg, 0.6 mmol) in THF (4 ml), 2-chlorotropone (**3a**) (141 mg, 1 mmol) was added at 0 °C and the mixture was stirred for 10 min. The solution was then added dropwise to a stirred mixture of tropylium tetrafluoroborate (231 mg, 1.3 mmol) and triethylamine (132 mg, 1.3 mmol) in THF (5 ml) at 0 °C, and the mixture was stirred for another 10 min at ambient temperature. After the usual workup described above, the product was chromatographed on alumina using hexane–ethyl acetate (10:1) as eluant to give a mixture of (**8**) and (**8D**) (138 mg, 70%) in a ratio of 27:73 as a pale yellow oil; $\delta_H(CDCl_3)$ 3.45 (1 H, br t, *J* 6.0 Hz), 5.36 (2 H, br dd, *J* 8.8, 6.0 Hz), 6.23 (2 H, br t, *J* 8.8, 3.0 Hz), 6.59 (2 H, br t, *J* 3.0 Hz), 6.84–7.15 (3.27 H, m), and 7.18–7.42 (1 H, m); $\delta_C(CDCl_3)$ 186.2 (s), 154.0 (s), 140.6 (d, weak), 134.8 (d), 134.2 (d), 133.3 (d), 132.9 (d), 130.2 (2 C, d), 125.0 (4 C, d), and 43.9 (d); $\nu_{max}(CHCl_3)$ 1 624 and 1 577 cm^{-1}; *m/z* 197 (M^+, 87%), 196 (100), [(HRMS) M^+, 197.0949. $C_{14}H_{11}DO$ requires *M*, 197.0951].

General Procedure for the Reaction of 2-*Chlorocycloheptadienone Enolate* (**4a**) *with Tropylium Perchlorate* (**6b–d**).—To a stirred suspension of $LiAlH(OBu^t)_3$ (178 mg, 0.7 mmol) in THF (4 ml), 2-chlorotropone (70 mg, 0.5 mmol) and triethylamine (71 mg, 0.7 mmol) was added and the mixture was stirred for 20 min at ambient temperature. The solution was then added dropwise to a stirred suspension of tropylium perchlorate (**6b–d**)[17–19] (0.7 mmol) in THF (4 ml) at 24 °C or at −78 °C, then stirred for 30 min or 2 h, respectively. After the reaction mixture was quenched with H_2O, the mixture was extracted with ethyl acetate and the extract was dried (Na_2SO_4). After evaporation of the solvent, the residue was purified by TLC on silica gel using hexane–ethyl acetate (5:1) as a developer to give a mixture of (**13b–d**) and (**14b–d**). The results

are summarized in Table 2. The mixture could be separated by MPLC on silica gel using hexane–ethyl acetate (5:1) to give almost pure samples of (**13b**, **c**) and (**14b**, **c**). In the case of a mixture of (**13d**) and (**14d**), a pure sample of (**14d**) was obtained. Although (**13d**) was contaminated with (**14d**), satisfactory ^1H and ^{13}C NMR, IR, and HRMS spectral data were obtained.

(**13b**), pale yellow oil; $\delta_H(CDCl_3)$ 1.12 (9 H, s), 2.95 (1 H, br t, *J* 5.7 Hz), 4.70 (1 H, br d, *J* 5.8 Hz), 4.96 (1 H, br ddd, *J* 8.7, 5.6, 1.9 Hz), 6.10 (1 H, dddd, *J* 8.7, 5.8, 1.0, 0.8 Hz), 6.51 (1 H, br dd, *J* 10.7, 5.8 Hz), 6.66 (1 H, br d, *J* 10.7 Hz), 6.84–7.13 (4 H, m), and 7.13–7.35 (1 H, m); $\nu_{max}(CHCl_3)$ 1 632 and 1 577 cm^{-1}; *m/z* 252 (M^+, 63%) and 195 (100) [(HRMS) M^+, 252.1515. $C_{18}H_{20}O$ requires *M*, 252.1514].

(**14b**), yellow oil; $\delta_H(CDCl_3)$ 1.16 (9 H, s), 3.46 (1 H, br t, *J* 6.4 Hz), 5.30 (1 H, br dd, *J* 9.2, 6.4 Hz), 5.38 (1 H, br ddd, *J* 9.2, 6.4, 0.8 Hz), 6.19 (1 H, br dd, *J* 9.2, 6.2 Hz), 6.31 (1 H, br d, *J* 9.2 Hz), 6.48 (1 H, br d, *J* 6.2 Hz), 6.80–7.18 (4 H, m), and 7.20–7.38 (1 H, m); $\nu_{max}(CHCl_3)$ 1 631 and 1 577 cm^{-1}; *m/z* 252 (M^+, 71%) and 195 (100) [(HRMS) M^+, 252.1499. $C_{18}H_{20}O$ requires *M*, 252.1514].

(**13c**), pale yellow oil; $\delta_H(CDCl_3)$ 3.25 (1 H, br t, *J* 5.8 Hz), 5.03 (1 H, br ddd, *J* 8.7, 5.5, 1.6 Hz), 5.13 (1 H, br dd, *J* 5.9, 1.6 Hz), 6.28 (1 H, dddd, *J* 8.7, 5.8, 1.0, 0.8 Hz), 6.69 (1 H, br dd, *J* 11.0, 5.8 Hz), 6.81 (1 H, br d, *J* 11.0 Hz), and 6.90–7.45 (10 H, m); $\nu_{max}(CHCl_3)$ 1 629 and 1 578 cm^{-1}; *m/z* 272 (M^+, 100%) [(HRMS) M^+, 272.1212. $C_{20}H_{16}O$ requires *M*, 272.1201].

(**14c**), yellow crystals, m.p. 52.3–54.2 °C (from hexane–ether, 1:1; $\delta_H(CDCl_3)$ 3.58 (1 H, br t, *J* 6.1 Hz), 5.46 (1 H, br dd, *J* 8.5, 6.1 Hz), 5.55 (1 H, br dd, *J* 8.0, 6.1 Hz), 6.34 (1 H, br dd, *J* 8.0, 6.2 Hz), 6.43 (1 H, br d, *J* 8.5 Hz), 6.92 (1 H, br d, *J* 6.2 Hz), 6.77–7.14 (4 H, m), and 7.15–7.56 (6 H, m); $\nu_{max}(CHCl_3)$ 1 618 and 1 575 cm^{-1}; *m/z* 272 (M^+, 100%) (Found: C, 88.2; H, 6.1. $C_{20}H_{16}O$ requires C, 88.20; H, 5.92%) [(HRMS) M^+, 272.1191. $C_{20}H_{16}O$ requires *M*, 272.1201].

(**13d**), pale yellow oil; $\delta_H(CDCl_3)$ 3.54 (1 H, br t, *J* 6.4 Hz), 5.38–5.43 (2 H, m), 6.14–6.20 (1 H, m), 6.49 (1 H, ddd, *J* 11.3, 1.3, 0.8 Hz), 6.55 (1 H, dd, *J* 11.3, 5.5 Hz), 6.97–7.03 (2 H, m), 7.07–7.18 (2 H, m), and 7.27–7.31 (1 H, m); $\nu_{max}(CHCl_3)$ 1 633 and 1 578 cm^{-1}; *m/z* 232 (M^+, 8%), 230 (M^+, 22), and 165 (100).

(**14d**), yellow oil; $\delta_H(CDCl_3)$ 3.46 (1 H, br t, *J* 6.1 Hz), 5.39–5.46 (2 H, m), 6.16 (1 H, br dd, *J* 9.2, 6.4 Hz), 6.22 (1 H, br d, *J* 9.3 Hz), 6.77 (1 H, dd, *J* 6.4, 1.5 Hz), 6.97–7.03 (2 H, m), 7.07–7.18 (2 H, m), and 7.29–7.32 (1 H, m); $\nu_{max}(CHCl_3)$ 1 633 and 1 578 cm^{-1}; *m/z* 232 (M^+, 10%), 230 (M^+, 30), and 165 (100) [(HRMS) M^+, 230.0476. $C_{14}H_{11}ClO$ requires *M*, 230.0498].

General Procedure for the Reaction of 2-*Chlorocycloheptadienone Enolate* (**4a**) *with Cationic Electrophiles* (**15–20**).—To a stirred suspension of $LiAlH(OBu^t)_3$ (1.3 mmol) in THF (5 ml), 2-chlorotropone (**3a**) (1 mmol) and triethylamine (1.3 mmol) were added, and the mixture was stirred for 20 min at ambient temperature. The solution was then added dropwise to a stirred suspension of the cationic electrophiles (**15–20**)[25–30] (1.3 mmol) in THF (5 ml), and it was stirred for another 10 to 30 min. After the reaction mixture was quenched by H_2O (10 ml), the mixture was extracted with ethyl acetate and the extract was dried (Na_2SO_4). After evaporation of the solvent, the residue was separated by TLC on silica gel using hexane–ethyl acetate (3:1–8:1) as a developer to give the products (**21–27**). The results are summarized in Table 5.

2-(1*H*-4,5-Benzocycloheptatrienyl)tropone (**21**), yellow crystals; m.p. 126–127 °C (from ethanol); $\delta_H(CDCl_3)$ 4.35 (1 H, br t, *J* 6.3 Hz), 5.81 (2 H, dd, *J* 10.6, 6.3 Hz), 6.58 (2 H, dd, *J* 10.6, 0.9 Hz), 6.73–7.12 (4 H, m), 7.21 (4 H, s), and 7.12–7.30 (1 H, m); $\delta_C(CDCl_3)$ 185.8 (s), 154.7 (s), 141.0 (d), 135.8 (2 C, s), 135.1 (d), 135.0 (d), 133.5 (d), 132.9 (d), 131.9 (2 C, d), 130.5 (2 C, d), 130.1 (2 C, d), 126.9 (2 C, d), and 43.0 (d); $\nu_{max}(CHCl_3)$ 1 633 and 1 588 cm^{-1}; λ_{max}(EtOH) 232 and 309 nm (log ε 4.51 and 3.97); *m/z* 246 (M^+, 100%) (Found: C, 87.6; H, 5.85. $C_{18}H_{14}O$ requires C, 87.78; H, 5.73%) [(HRMS) M^+, 246.1047. $C_{18}H_{14}O$ requires *M*, 246.1045].

2-(1*H*-2,3-Benzocycloheptatrienyl)tropone (**22**), a yellow oil; $\delta_H(CDCl_3)$ 4.91 (1 H, d, *J* 7.0 Hz), 5.86–6.40 (3 H, m), 6.60–7.12 (7 H, m), and 7.12–7.45 (3 H, m); $\delta_C(CDCl_3)$ 185.9 (s), 151.9 (s), 140.2 (d), 136.6 (s), 136.0 (s), 134.6 (d), 134.2 (d), 133.0 (d), 132.5 (2 C, d), 131.3 (d), 129.2 (d), 129.1 (d), 127.9 (d), 127.3 (d), 125.9 (d), 124.8 (d), and 48.0 (d); ν_{max} 1 632 and 1 576 cm^{-1}; λ_{max}(EtOH) 225, 292, and 309 nm (log ε 4.33, 3.93, and 3.87sh); *m/z* 246 (M^+, 49%), 105 (100) [(HRMS) M^+, 246.1062. $C_{18}H_{14}O$ requires *M*, 246.1045].

2-(1*H*-2,3,6,7-Dibenzocycloheptatrienyl)tropone (**23**), pale yellow crystals; m.p. 152–153 °C (from ethanol); $\delta_H(CDCl_3)$ 5.92 (1 H, s), 6.58–6.75 (7 H, m), and 7.17–7.70 (8 H, m); $\delta_C(CDCl_3)$ 186.1 (s), 149.9 (s), 138.9 (d), 137.6 (2 C, s), 134.7 (2 C, s), 133.9 (d), 133.0 (d), 132.1 (d), 131.9 (d), 131.7 (2 C, d), 130.7 (2 C, d), 129.5 (2 C, d), 128.6 (2 C, d), 126.6 (2 C, d), and 55.6 (d); $\nu_{max}(CHCl_3)$ 1 623 and 1 581 cm^{-1}; λ_{max}(EtOH) 212, and 293 nm (log ε 4.66 and 4.26); *m/z* 296 (M^+, 100%) (Found: C, 89.3; H, 5.6. $C_{22}H_{16}O$ requires C, 89.16; H, 5.44%) [(HRMS) M^+, 296.1205. $C_{22}H_{16}O$ requires *M*, 296.1202].

2-(1*H*-2,3-Diphenylcyclopropenyl)tropone (**24**), yellow crystals, m.p. 110–111 °C (from ethanol); $\delta_H(CDCl_3)$ 3.72 (1 H, s), 6.65–6.97 (3 H, m), 7.00–7.17 (2 H, m), 7.20–7.55 (6 H, m), and 7.57–8.81 (4 H, m); $\delta_C(CDCl_3)$ 188.0 (s), 157.4 (s), 139.1 (d), 135.0 (d), 133.6 (d), 131.5 (d), 130.3 (d), 129.7 (2 C, d), 128.6 (3 C, d), 127.6 (s), 112.3 (2 C, d), and 22.5 (d); $\nu_{max}(CHCl_3)$ 1 831, 1 628, 1 600, and 1 566 cm^{-1}; λ_{max}(EtOH) 227, 247, 312, and 327 (log ε 4.52, 4.28sh, 4.53, and 4.45sh); *m/z* 296 (M^+, 100%) (Found: C, 89.0; H, 5.45. $C_{22}H_{16}O$ requires C, 89.16; H, 5.44%) [(HRMS) M^+, 296.1216. $C_{22}H_{16}O$ requires *M*, 296.1202].

2-(1,2,3-Triphenylcyclopropenyl)tropone (**25**), pale yellow crystals, m.p. 177–178 °C (from benzene–hexane); $\delta_H(CDCl_3)$ 6.67–7.64 (16 H, m), and 7.77–8.00 (4 H, m); $\delta_C(CDCl_3)$ 187.0 (s), 158.1 (s), 144.1 (s). 140.7 (d), 134.5 (d), 134.4 (d), 133.4 (d), 132.7 (d), 129.7 (4 C, d), 128.8 (6 C, d), 127.9 (2 C, s), 127.8 (2 C, d), 126.1 (2 C, d), 125.4 (d), 118.4 (2 C, s), and 39.3 (s); $\nu_{max}(CHCl_3)$ 1 817, 1 631, and 1 582 cm^{-1}; λ_{max}(EtOH) 227, 306, and 325 nm (log ε 4.55, 4.34, and 4.24sh); *m/z* 372 (M^+, 100%) (Found: C, 90.45; H, 5.55. $C_{28}H_{20}O$ requires C, 90.29; H, 5.29%) [(HRMS) M^+, 372.1507. $C_{28}H_{20}O$ requires *M*, 372.1514].

Tricarbonyl[1-4-η-5*H*-5-(7-oxocyclohepta-1,3,5-trienyl)-cyclopentadiene]iron (**26**), yellow crystals, m.p. 146–147 °C (from ethanol); $\delta_H(CDCl_3)$ 3.37 (2 H, ddd, *J* 2.4, 2.2, 2.0 Hz), 4.06 (1 H, br s), 5.55 (2 H, ddd, *J* 2.4, 2.2, 0.7 Hz), and 6.70–7.10 (5 H, m); $\delta_C(CDCl_3)$ 211.1 (3 C, s), 185.8 (s), 156.3 (s), 141.4 (d), 135.1 (d), 133.3 (d), 132.3 (d), 132.1 (d), 83.6 (2 C, d), 57.3 (d), and 56.3 (2 C, d); $\nu_{max}(CHCl_3)$ 2 053, 1 935, 1 632, and 1 571 cm^{-1}; λ_{max}(EtOH) 226 and 307 nm (log ε 4.66 and 4.06); *m/z* 254 ($M^+ - 56$, 36%), 226 (100) (Found: C, 58.2; H, 3.3. $C_{15}H_{10}FeO_4$ requires C, 58.10; H, 3.25%).

Tricarbonyl[1-4-η-5-(7-oxocyclohepta-1,3,5-trienyl)cyclohexa-1,3-diene]iron (**27**), colourless crystals; m.p. 145–146 °C (from benzene–hexane); $\delta_H(CDCl_3)$ 1.36 (1 H, br d, *J* 15.8 Hz), 2.49 (1 H, ddd, *J* 15.8, 11.0, 3.8 Hz), 2.98–3.33 (2 H, m), 3.77 (1 H, ddd, *J* 11.0, 3.8, 3.7 Hz), 5.35–5.67 (2 H, m), 6.83–7.16 (4 H, m), and 7.20–7.42 (1 H, m); $\delta_C(CDCl_3)$ 211.3 (3 C, s), 186.6 (s), 159.6 (s), 140.1 (d), 134.9 (d), 133.4 (d), 132.5 (d), 132.0 (d), 85.9 (d), 84.5 (d), 64.2 (d), 60.7 (d), 40.7 (d), and 32.4 (t); $\nu_{max}(CDCl_3)$ 2 168, 1 980, 1 630, and 1 574 cm^{-1}; *m/z* 324 (M^+, 5%), 240 (100) (Found: C, 59.3; H, 3.8. $C_{16}H_{12}FeO_4$ requires C, 90.29; H, 5.29%) [(HRMS) $M^+ - CO$, 296.0152. $C_{15}H_{12}FeO_3$ requires *M*, 296.0136].

General Procedure for the Reaction of 7-*Substituted* 2-*Chlorocycloheptadienone Enolates* (**28a–c**) *with Tropylium Tetrafluoroborate* (**6a**).—To a stirred solution of Grignard reagent (1.2 mmol) or organolithium reagent (1.2 mmol) in

THF (5 ml), 2-chlorotropone (**3a**) (141 mg, 1 mmol) in THF (2 ml) was added over 1 min at 0 °C, and the mixture was stirred for 10 min. The solution was then added dropwise to a stirred mixture of tropylium tetrafluoroborate (**6a**) (267 mg, 1.5 mmol) and triethylamine (152 mg, 1.5 mmol) in THF (5 ml) at 0 °C, and stirred for another 10 min at ambient temperature. The solution was quenched by aqueous NH_4Cl (10 ml), and extracted with ethyl acetate and the extract was dried (Na_2SO_4). Evaporation of the solvent followed by purification by TLC on silica gel using hexane–ethyl acetate (20:1–7:1) as a developer gave the following products; [reaction details and product yields are summarized in Table 6 (runs 1–4)].

2-(2,4,6-Cycloheptatrienyl)-7-methyltropone (**29a**), pale yellow crystals; m.p. 52–53 °C (from benzene–hexane, 1:10); $\delta_H(CDCl_3)$ 2.31 (3 H, s), 3.47 (1 H, br t, *J* 5.9 Hz), 5.37 (2 H, ddd, *J* 8.9, 5.9, 0.7 Hz), 6.23 (2 H, dddd, *J* 8.9, 3.7, 2.5, 0.9 Hz), 6.60 (2 H, ddd, *J* 3.7, 2.5, 0.7 Hz), 6.80–7.05 (2 H, m), and 7.20–7.45 (2 H, m); $\nu_{max}(CHCl_3)$ 1 623 and 1 571 cm^{-1}; *m/z* 210 (M^+, 62%) and 165 (100) (Found: C, 85.5; H, 6.9. $C_{15}H_{14}O$ requires C, 85.68; H, 6.71%) [(HRMS) M^+, 210.1054. $C_{15}H_{14}O$ requires *M*, 210.1045].

2-Butyl-7-(2,4,6-cycloheptatrienyl)tropone (**29b**), pale yellow oil; $\delta_H(CDCl_3)$ 0.92 (3 H, br t, *J* 6.2 Hz), 1.10–1.75 (4 H, m), 2.70 (2 H, br t, *J* 7.3 Hz), 3.43 (1 H, br t, *J* 5.9 Hz), 5.38 (2 H, dd, *J* 8.9, 5.9 Hz), 6.23 (2 H, dddd, *J* 8.9, 3.5, 2.9, 0.8 Hz), 6.61 (2 H, dd, *J* 3.5, 2.9 Hz), 6.82–6.96 (2 H, m), and 7.13–7.39 (2 H, m); $\nu_{max}(CHCl_3)$ 1 623 and 1 575 cm^{-1}; *m/z* 252 (M^+, 16%) and 91 (100) [(HRMS) M^+, 252.1506. $C_{18}H_{20}O$ requires *M*, 252.1515].

2-(2,4,6-Cycloheptatrienyl)-7-phenyltropone (**29c**) as a pale yellow oil; $\delta_H(CDCl_3)$ 3.51 (1 H, br t, *J* 6.3 Hz), 5.43 (2 H, dd, *J* 9.3, 6.3 Hz), 6.11–6.36 (2 H, m), 6.51–6.67 (2 H, m), 6.83–7.12 (2 H, m), and 7.15–7.60 (7 H, m); $\nu_{max}(CHCl_3)$ 1 623 and 1 591 cm^{-1}; λ_{max}(EtOH) 229, 265sh, and 324 nm (log ε 4.38, 4.04, and 4.00); *m/z* 272 (M^+, 100%) [(HRMS) M^+, 272.1218. $C_{20}H_{16}O$ requires *M*, 272.1201].

General Procedure for the Reaction of 7-Substituted 2-Chlorocycloheptadienone Enolate (**28d, e**) *with Tropylium Tetrafluoroborate* (**6a**).—To a suspension of $LiAlH(OBu^t)_3$ (330 mg, 1.3 mmol) in THF (6 ml), 2-bromo-7-methoxytropone (**3d**)[33] (215 mg, 1 mmol) or 2,7-dibromotropone (**3e**)[34] (264 mg, 1 mmol) was added at 0 °C and the mixture was stirred for 20 min at ambient temperature. The solution was then added dropwise to a stirred mixture of tropylium tetrafluoroborate (**6a**) (231 mg, 1.3 mmol) and triethylamine (132 mg, 1.3 mmol) in THF (5 ml) at 0 °C, and the mixture was stirred for another 10 min at ambient temperature. After the solution was diluted with H_2O (5 ml), the mixture was extracted with ethyl acetate and dried (Na_2SO_4). Evaporation of the solvent followed by separation by TLC on silica gel using hexane–ethyl acetate (1:1) as a developer gave the following products; [the results are summarized in Table 6 (runs 5 and 6)].

2-(2,4,6-Cycloheptatrienyl)-7-methoxytropone (**29d**), as a pale yellow oil; $\delta_H(CDCl_3)$ 3.54 (1 H, br t, *J* 5.9 Hz), 3.89 (3 H, s), 5.39 (2 H, dd, *J* 9.4, 5.9 Hz), 6.05–6.28 (2 H, m), 6.46–6.60 (2 H, m), 6.60–7.15 (3 H, m), and 7.41 (1 H, dd, *J* 8.2, 1.3 Hz); $\nu_{max}(CHCl_3)$ 1 599 and 1 575 cm^{-1}; *m/z* 226 (100%) [(HRMS) M^+, 226.0998. $C_{15}H_{14}O_2$ requires *M*, 226.0994].

2-Bromo-7-(2,4,6-cycloheptatrienyl)tropone (**29e**), yellow crystals, m.p. 51–52 °C (from hexane–ether); $\delta_H(CDCl_3)$ 3.58 (1 H, br t, *J* 6.2 Hz), 5.38 (2 H, dd, *J* 8.9, 6.2 Hz), 6.10–6.35 (2 H, m), 6.48–6.63 (2 H, m), 6.77 (1 H, ddd, *J* 10.6, 8.9, 1.4 Hz), 7.07 (1 H, td, *J* 10.6, 1.2 Hz), 7.36 (1 H, ddd, *J* 10.6, 1.4, 0.4 Hz), and 8.08 (1 H, dd, *J* 8.9, 1.2 Hz); $\nu_{max}(CHCl_3)$ 1 622 and 1 593 cm^{-1}; λ_{max}(EtOH) 247 and 322 nm (log ε 4.09 and 3.72); *m/z* 276 (M^+, 39%), 274 (M^+, 40), and 165 (100) (Found: C, 61.05; H, 4.0. $C_{14}H_{11}BrO$ requires C, 61.11; H, 4.03%) [(HRMS) M^+, 274.0008. $C_{14}H_{11}BrO$ requires *M*, 273.9994].

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