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SYNTHESIS AND PROPERTIES OF ALL MEMBERS OF METHYLATED TROPYLIUM IONS

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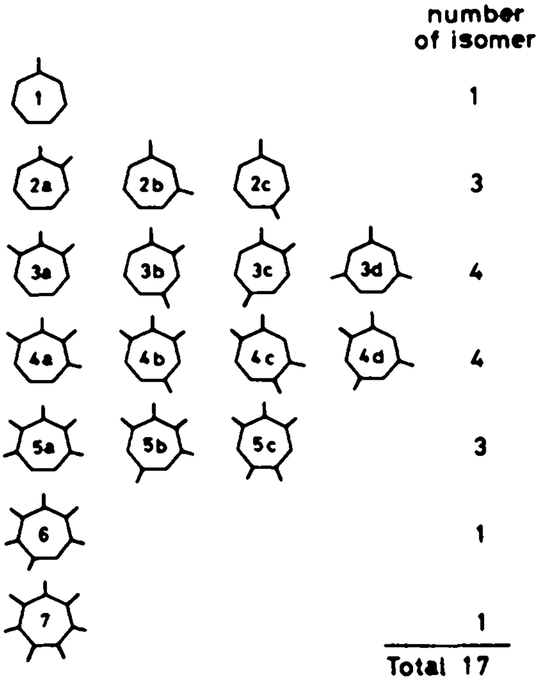
Abstract—All members of the methylated tropylium perchlorates have been synthesized and their properties (UV absorptions, ^{1}H NMR spectra, and charge-transfer spectra with pyrene) determined. The methylated tropylium ions other than the hexa- and hepta-methyl homologues have been prepared by abstracting a hydride ion with trityl perchlorate from the corresponding methylated tropilidenes. The preparation of the hexa- and hepta-methyltropylium ions has been effected by utilizing phosphorus pentachloride as the hydride-abstraction reagent. The methylated tropilidenes have been prepared via one of the three known routes, i.e. the ring expansion of methylated benzenes with diazomethane (Route 1) or with ethyl diazoacetate (Route 2), and the cycloaddition of cyclopropene or methylcyclopropenes with methylated thiophene 1,1-dioxides accompanied with the exclusion of sulfur dioxide (Route 3). The methyl ^{1}H NMR chemical-shift values have been assigned, partly with the aid of the Me ^{13}C NMR chemical-shift data for the tropylium ions containing the Me groups on contiguous ring-carbons (3a, 4a, 5a, 6 and 7). The transition energy for the charge-transfer band of the tropylium ions with pyrene increases with the increase in the number of the Me group, indicating that the more methylated the tropylium ion, the more stable is the ion.

Various mono-substituted tropylium ions are known and their properties[1] and reactivities in the one-electron reduction[2-4] have been extensively investigated. On the other hand, the tropylium ions containing more than one substituent hitherto reported are few, and therefore, the effects of the accumulated substituents on their properties and on various reactions have been little studied, except for the heptaphenyltropylium ion.[5,6] In the course of our studies on the one-electron reduction of carbonium ions we prepared several methylated tropylium ions[7,25] including the heptamethyl homologue,[8] and were interested in examining the effects of accumulated Me substituents on the properties and the one-electron reducibilities of the tropylium ions. This paper deals with the synthesis and physical properties of all members of the methylated tropylium ions (Scheme 1).



Scheme 1.

A direct synthesis of polymethyltropylium ions has been proposed by Peter-Katalinić *et al.*,[9] which involves the acid-catalyzed isomerization of methylated 6 - methylenetricyclo[3.2.1.0^{2,7}]oct - 3 - en - 8 - ones to form 1,2,4-trimethyl-, 1,2,3,4- and 1,2,4,6-tetramethyl-, 1,2,3,5,6-pentamethyl- and heptamethyl-tropylium ions as trifluoroacetate or hexachloroplatinates.† However, the method appeared to present difficulties in obtaining suitable starting compounds. Therefore, we adopted the conventional route which consists in the preparation of methylated tropilidenes followed by their conversion to the corresponding tropylium ions. As the practical preparative methods for the methylated tropilidenes we selected the ring-expansion of methylbenzenes with diazomethane[10] (Route 1) or with ethyl diazoacetate[11] (Route 2), and the cycloaddition of cyclopropenes with methylated thiophene 1,1-dioxides accompanied with the exclusion of sulfur dioxide[12] (Route 3) as illustrated in eqns (1), (2) and (3). Other reported methods, i.e. the ring-expansion of methylbenzenes with 1,1-diiodoethane and diethylzinc,[13] the methylation of tropylium ions,[14] the acid-catalyzed isomerization of 1,2,3 - trimethyl - 3 - allyl - 4 - methylene - 1 - cyclobutene to tetramethyltropilidene,[15] and the dehydration of cycloheptadienols,[16] were considered inadequate from the viewpoints of the availability of starting compounds and versatility of the methods.

RESULTS AND DISCUSSION

Abstraction of a hydride ion from methylated tropilidenes. The tropylium ions were successfully prepared by the abstraction of a hydride ion from the respective

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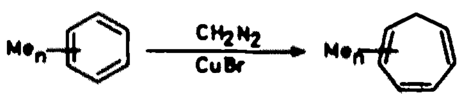
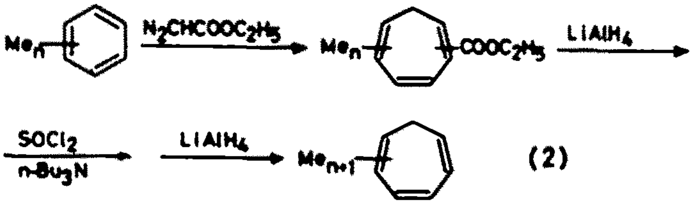
†The heptamethyltropylium ion was isolated as the hexachloroplatinate, but the purity could not be increased more than 60%.[9]

Route 1



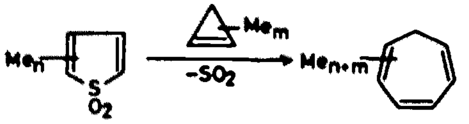
(1)

Route 2



(2)

Route 3



(3)

tropilidenes by the use of trityl perchlorate[17] except for the cases of hexa- and hepta-methyltropylium ions (6 and 7, respectively). When hexa- or hepta-methyltropilidene was treated with trityl perchlorate in acetonitrile, blue coloration of the solution occurred. Addition of ethyl acetate or ether to the solution afforded blue precipitates in both cases. Although hexamethyltropilidene afforded impure 6, heptamethyltropilidene failed to give even trace amounts of 7, as previously noted by Knoche.[11] On the contrary, the use of phosphorus pentachloride as a hydride abstraction reagent[18] under selected reaction conditions[8] enabled us to prepare pure 6 and 7 in the yields of 14 and 22%, respectively. The treatment of heptamethyltropilidene with phosphorus pentachloride in carbon tetrachloride under nitrogen for 1.5 hr at 0° afforded yellowish white precipitates, which were dissolved in acetic acid and then converted to the perchlorate by the addition of perchloric acid in 22% yield. The precipitates formed in the reaction with phosphorus pentachloride, presumably a double salt with a formula $(CH_3)_7C_7^+PCl_6^-\cdot(CH_3)_7C_7^+Cl^-$, are unstable and slowly decompose with evolution of hydrogen chloride consecutively as formed. The reaction of hexamethyltropilidene with phosphorus pentachloride at 0° for 1.8 hr, the optimum conditions so far investigated, followed by the treatment with perchloric acid in acetic acid afforded 6 in 14% yield.

Synthesis of 2a, 2b, 2c, 3a, 3d *and* 4c *via Route* 1.† These tropylium perchlorates, 2a, 2b, 2c, 3a, 3d and 4c, were prepared from methylated tropilidenes which were derived by the ring-expansion of *o*-xylene, *m*-xylene, *p*-xylene, hemimellitene, mesitylene and durene, respectively, with diazomethane in the presence of copper(I) bromide as catalyst.[10]

The solutions of di- or tri-methyltropilidenes in the starting aromatic hydrocarbons were concentrated by careful distillation to 50–90%. The ring-expansion of durene was conducted in heptane as solvent, and the product 1,2,4,5-tetramethyltropilidene was concentrated by precipitating durene by the addition of methanol. In all cases the desired methylated tropilidene was isolated as a mixture with the starting aromatic hydrocarbon, and then the mixture was subjected to the hydride-ion abstraction with trityl perchlorate.[17] In no case the methylene insertion occurred at the C–C bond in which each C atom bears a Me group. The physical properties and analytical data of the tropylium perchlorates are summarized in Tables 1 and 2.

Synthesis of 4d, 5e, 6 *and* 7 *via Route* 2. The Route 2 was applied to the preparation of the tropylium ions which were difficultly accessible with either of the Routes 1 and 3. The ring-expansion of mesitylene, durene, pentamethylbenzene and hexamethylbenzene with ethyl diazoacetate was conducted in the manner essentially similar to that reported by Knoche on hexamethylbenzene[11] (Scheme 2). The attack of the reagent to the benzene ring was found to occur at the least substituted C–C bond, as previously reported on the reaction of ethyl diazoacetate with 2 - isopropyl - 4,7 - dimethylindane[19] or with prehnitene.[20] Mesitylene and durene were found to react with ethyl diazoacetate to afford a single product in each case. However, pentamethylbenzene afforded a mixture of two isomeric esters, which on subsequent reactions afforded a mixture of two hexamethyltropilidenes as depicted in Scheme 2. The tetra- and penta-methyltropilidenes were converted to 4d and 5e, respectively, by the use of trityl perchlorate. The hexa- and hepta-methyltropilidenes were derived to 6 and 7, respectively, by using phosphorus pentachloride as a hydride-abstraction reagent[8,18] (*vide supra*). The physical properties and analytical data of the perchlorates are summarized in Tables 1 and 2.

Synthesis of 3b, 3c, 4a, 4b, 5a *and* 5b *via Route* 3. The cycloaddition of cyclopropenes to substituted thiophene 1,1-dioxides has been found to be a versatile method for the preparation of desired polysubstituted tropilidenes.[12] Because of its versatility, we decided to make the best use of this method in order to prepare tri-, tetra- and penta-methyltropilidenes. For this purpose, six methylated thiophene 1,1-dioxides (8–13) were selected as

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†For the notation of the perchlorates, see Scheme 1 and Table 1.

Table 1. UV spectral data and charge-transfer ν_{max} values (with pyrene) of the methylated tropylium ions

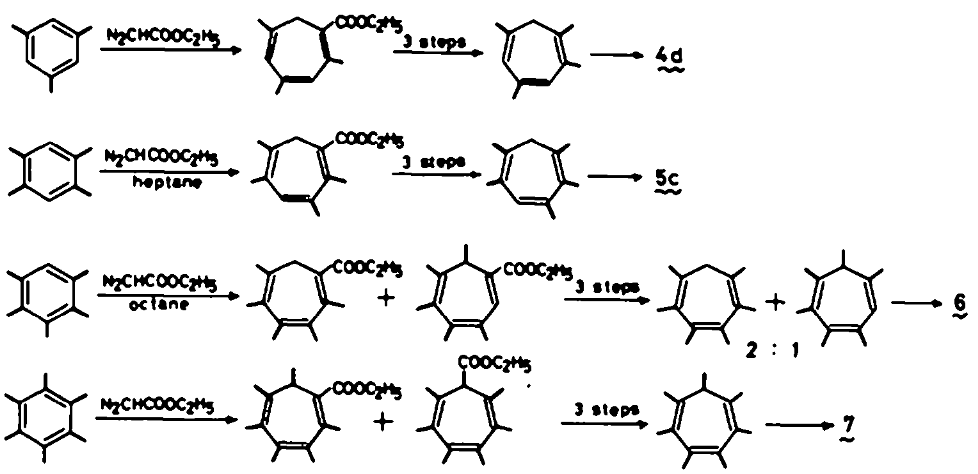
Perchlorate	Methyl position	UV $\lambda_{max}^{10\%HCl}$ nm, (c)	C. T. ν_{max} (a 10^4 cm^{-1}
1 (b	1	227.0(50600), 287.0(4760) 300(sh)	1.88
2a (c,d	1,2	232.0(46100), 296.5(5160)	1.98
2b (d	1,3	233.5(48300), 288.5(6150) 295(sh)	1.94
2c	1,4	230.5(42500), 302.0(6900)	1.94
3a (d	1,2,3	240.0(54100), 292.5(5660) 300(sh)	2.00
3b (e	1,2,4	238.5(51500), 293.0(5390) 297.5(5360), 309(sh)	2.01
3c	1,2,5	235.5(49900), 302(sh) 306.5(8430)	1.99
3d	1,3,5	238.5(53600), 289(sh) 296.0(6830), 305(sh)	1.99
4a (e	1,2,3,4	246.0(55100), 298.0(5680) 304(sh)	2.07
4b	1,2,3,5	243.0(58400), 302.5(5890) 307(sh)	2.07
4c	1,2,4,5	240.0(66000), 301(sh) 308.0(7470)	2.08
4d (e	1,2,4,6	242.0(71600), 298.0(7510) 310(sh)	2.04
5a	1,2,3,4,5	251.0(70000), 306.5(7200)	2.13
5b	1,2,3,4,6	248.0(67500), 303.5(6400) 312(sh)	2.11
5c (e	1,2,3,5,6	245.0(67100), 302.5(6180) 311.5(sh)	2.13
6	1,2,3,4,5,6	253.2(62600), 311.0(5750)	2.17
7 (e,f	1,2,3,4,5,6,7	260.0(49100), 345.0(6240)	(2.35) (g

(a) Pyrene was used as an electron donor in 1,2-dichloroethane. Determined by drawing a smooth curve: accurate to $\pm 0.02 \times 10^4$ cm^{-1}. (b) The preparation of the perchlorate has been described in ref. 2. (c) The perchlorate has been described in ref. 10. (d) The perchlorate has been described in ref. 25. (e) The trifluoroacetate or hexachloroplatinate has been described in ref. 9. (f) The perchlorate has been described in ref. 8. (g) Inaccurate due to the weak intensity of the absorption.

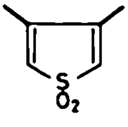
Table 2. The melting points and analytical data for the new methylated tropylium perchlorates

Perchlorate	M. p. (a °C	C% Calcd	C% Found	H% Calcd	H% Found
2c	61.0- 61.5	49.44	49.64	5.07	5.29
3b	72.0- 73.0	51.62	51.90	5.63	5.54
3c	98.0- 99.0	51.62	51.65	5.63	5.60
3d	137.0-138.0	51.62	51.38	5.63	5.35
4a	89.0- 89.5	53.56	53.52	6.13	6.19
4b	97.5- 98.0	53.56	53.26	6.13	6.16
4c	142.0-143.5	53.56	53.28	6.13	6.22
4d	78.5- 79.0	53.56	53.27	6.13	6.24
5a	54.0- 55.0	55.28	55.00	6.57	6.84
5b	116.5-117.0	55.28	54.69	6.57	6.53
5c	190.2-190.5	55.28	55.52	6.57	6.75
6	106.5-107.0	56.83	57.23	6.97	7.27
7 (b	180 -181(dec)	58.23	57.83	7.33	7.55

(a) Uncorrected. (b) Ref. 8.



Scheme 2.



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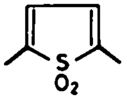

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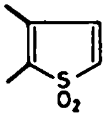

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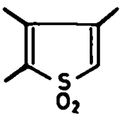

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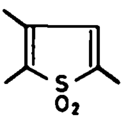

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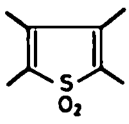

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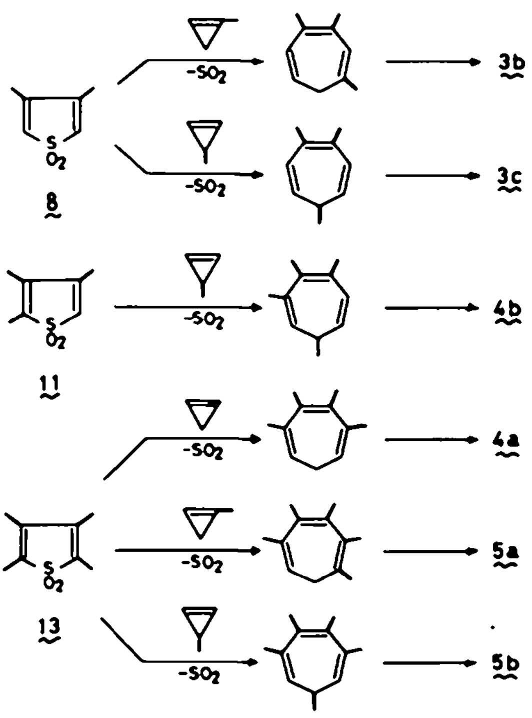
desirable starting compounds. However, 9,[21] 10 and 12 were obtained only in low yields by the perbenzoic acid oxidation of substituted thiophenes; eventually, we utilized 8, 11 and 13 which were prepared in practical yields (40–80%) by the perbenzoic acid oxidation of the corresponding methylated thiophenes.

The cycloaddition reaction for all the combinations examined (Scheme 3) proceeded in methylene chloride at room temperature with evolution of sulfur dioxide in the yields of *ca.* 70%. The perchlorates were prepared via the reaction with trityl perchlorate, and their properties and analytical data are listed in Tables 1 and 2.



Scheme 3.

^{1}H and ^{13}C NMR chemical-shift data. The ^{1}H NMR spectra were measured in trifluoroacetic acid for all the methylated tropylium ions and the chemical-shift values are listed in Table 3. Some of the ions (3a, 4a, 5a, 6 and 7) were also subjected to ^{13}C NMR measurement in acetonitrile-d$_3$, with a view to confirming the assignment of the methyl ^{1}H NMR chemical-shift values.

The chemical-shift data for the Me protons of 1, 2a, 2b, 2c, 3d, 4c and 7 were assigned based on the uniqueness of the signals. The values for 3a and 3c were assigned on the basis of the relative peak intensities. For other ions there has not been obtained such unambiguous evidence; therefore, somewhat empirical prediction was made. As the spectrum of 3a indicates, the 2-Me protons are more shielded than the 1- and 3-Me protons. Furthermore, the protons in the Me groups adjacent to each other are slightly more shielded than those of an isolated Me group as seen in 3c and in the comparison of 2a with 2b and 2c. These results made it possible to predict the assignment of the data for the Me protons of 3b, 4a, 4b, 4d and 5b.

The chemical-shift values for 5a of 2.93 ppm (three Me's) and 2.86 ppm (two Me's) cannot be fully explained on the basis of the above empirical rule. Since in 3a the 1- and 3-Me protons are less shielded than the 2-Me protons, it appears reasonable in 5a to assign the signal at 2.93 ppm to the 1- and 5-Me groups and that at 2.86 ppm to the 2- and 4-Me groups, and consequently the last Me signal at 2.93 ppm amounting to one Me group must be alloted to the 3-Me group. Therefore, it would be concluded that the signal of the 3-Me protons appears in a lower field than that of the 2- or 4-Me protons, although the 3-Me group is adjacent to the two Me groups and must be sterically most encumbered.

Hexamethyltropylium ion (6) exhibits a signal amounting to four Me groups at 2.84 ppm and that amounting to

Table 3. ^{1}H NMR chemical-shift data for the methylated tropylium ions

	δ ppm, CF_3COOH							
Perchlorate	1-Me	2-Me	3-Me	4-Me	5-Me	6-Me	7-Me	Ring protons
1[a]	3.25	—	—	—	—	—	—	9.12 (s, 6H)
2a	3.07	3.07	—	—	—	—	—	8.97 (m, 5H)
2b	3.15	—	3.15	—	—	—	—	8.90 (s, 4H), 9.00 (s, 1H)
2c	3.09	—	—	3.09	—	—	—	8.70 (s, 5H)
3a	3.10	2.90	3.10	—	—	—	—	8.5-9.0 (m, 4H)
3b	3.00	3.00	—	3.07	—	—	—	8.65-8.90 (m, 3H), 8.93 (br.s, 1H)
(3b)[b,c]	(3.00)[d]	(3.03)[d]	—	(3.10)	—	—	—	(8.65-8.90) (8.94)
3c	3.00	3.00	—	—	3.05	—	—	8.77 (br.s, 4H)
3d	3.05	—	3.05	—	3.05	—	—	8.68 (s, 2H), 8.75 (s, 2H)
4a	3.03	2.95	2.95	3.03	—	—	—	8.3-8.9 (m, 3H)
(4a)[b,c]	(3.05)	(2.96)	(2.96)	(3.05)	—	—	—	(8.4-8.9)
4b	3.04	2.87	3.04	—	3.04	—	—	8.57 (s, 1H), 8.63 (s, 1H), 8.73 (s, 1H)
4c	2.90	2.90	—	2.90	2.90	—	—	8.50 (s, 2H), 8.80 (s, 1H)
4d	2.92	2.92	—	3.00	—	3.00	—	8.60 (s, 1H), 8.67 (s, 2H)
(4d)[b,c]	(2.93)	(2.93)	—	(3.02)	—	(3.02)	—	(8.60) (8.72)
5a	2.93	2.86	2.93	2.86	2.93	—	—	8.46 (s, 2H)
5b	2.95	2.86	2.86	2.95	—	2.89	—	8.58 (s, 2H)
5c	2.96	2.80	2.96	—	2.87	2.87	—	8.71 (s, 2H)
(5c)[b,c]	(3.00)	(2.82)	(3.00)	—	(2.90)	(2.90)	—	(8.78)
6	2.84	2.73	2.84	2.84	2.73	2.84	—	8.56 (s, 1H)
7	2.77	2.77	2.77	2.77	2.77	2.77	2.77	——
(7)[c,e]	(2.82)	(2.82)	(2.82)	(2.82)	(2.82)	(2.82)	(2.82)	——

[a] Ref. 1. [b] Hexachloroplatinate. [c] Ref. 9. [d] These values are interchangeable. [e] Impure hexachloroplatinate.

two Me groups at 2.73 ppm. In analogy with the case of 5a, the signal at 2.84 ppm was assigned to the 1-, 3-, 4- and 6-Me groups and that at 2.73 ppm to the 2- and 5-Me groups.

The data for 5c were tentatively assigned by referring to those for 3a and 4b, in which the 2-Me protons are more shielded than the 1- and 3-Me protons by 0.17–0.20 ppm. On this basis the signals at 2.96 ppm, 2.87 ppm, and 2.80 ppm were assigned to the 1,3-Me groups, the 5,6-Me groups, and the 2-Me group, respectively.

For methylated benzenes it has been observed that there holds a parallel relation between ^{1}H and ^{13}C chemical-shift values for the Me groups contained in the same molecule.[20] Then it was anticipated that there would also hold such a relation for the Me groups of the methylated tropylium ions. The ^{13}C NMR spectra were measured for 3a, 4a, 5a, 6 and 7, and the Me chemical-shift data are listed in Table 4.

The spectra of 3a and 5a were unambiguously assigned on the basis of the relative intensities and the long range coupling data. The data for 4a were also assigned based on the long range coupling data. Apparently there is a parallel relation in 3a between the ^{1}H and the ^{13}C NMR chemical-shift data. Since it appears reasonable to assume that such a relation holds for 4a and 5a, the assignment of the ^{1}H NMR data listed in Table 3 for such ions are considered to be reliable.

The ^{13}C chemical-shift value of 28.5 ppm for 6 was unequivocally assigned to the 1- and 6-Me groups from the long range coupling spectra. Other Me ^{13}C signals for 6 were tentatively assigned in analogy with the case of 5 as listed in Table 4, although further confirmatory experiments are required to achieve unambiguous assignment.

The ring protons of most of the ions listed in Table 3 are unambiguously assigned on the basis of the uniqueness or the relative intensities of the signals; however, those of 3a,† 3b, 3d, 4a‡ and 4b are complex and unequivocal assignment is difficult at the present stage. The chemical-shift data for the ring carbons of the ions listed in Table 4 will be presented and discussed along with the ^{13}C NMR data for other methylated tropylium ions in a separate article.

Table 4. Methyl ^{13}C NMR chemical-shift data for some methylated tropylium ions

	δ ppm,[a] CD_3CN						
Perchlorate	1-Me	2-Me	3-Me	4-Me	5-Me	6-Me	7-Me
3a	30.3	25.4	30.3	—	—	—	—
4a	29.6	26.5	26.5	29.6	—	—	—
5a	28.5	25.8	28.0	25.8	28.5	—	—
6	28.5	24.5	26.9	26.9	24.5	28.5	—
7	24.5	24.5	24.5	24.5	24.5	24.5	24.5

[a] The chemical-shift from TMS.

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†An A_2B_2 pattern was observed.

‡An AB_2 pattern was observed; see also Ref. 9.

Electronic and charge-transfer spectra. The UV spectra of all the methylated tropylium ions were measured in 10% hydrochloric acid and the data shown in Table 1 together with the reported values. All the ions exhibit absorptions at two wavelength regions, i.e. an intense absorption at 220–260 nm and a weaker one at 280–350 nm, being separated from each other by 50–80 nm as previously noted on various tropylium ions.[1] It is to be noted that the progressive introduction of the Me substituents gives rise to bathochromic shifts in the UV spectra. A similar effect of the Me substituent has been observed in the UV spectra of methylated benzenes.[24]

The charge-transfer spectra were measured on all the methylated tropylium ions by the use of pyrene as the standard electron donor in 1,2-dichloroethane. In all cases the longest wavelength absorption appears as a shoulder peak; therefore the absorption maximum was determined by assuming a smooth concave descent to the shorter wavelength absorption and by measuring the height of the shoulder peak. It is again noted that the ν_{max} value increases as the Me substituents are progressively introduced, indicating that the more methylated the tropylium ion, the more stable is the ion owing to the electron donating effect of the Me group.

EXPERIMENTAL

M.ps and b.ps are uncorrected. Elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto, Japan. UV and IR spectra were taken on a Hitachi model 200-10 and a Hitachi model 215 spectrophotometer, respectively. ^{1}H NMR spectra were recorded on a Hitachi R-24 (60 MHz). ^{13}C NMR spectra were recorded on a JEOL FX 100 (25.00 MHz) operating in the Fourier transform mode. Various physical properties are summarized in Tables 1–4.

Materials. 1,2-Dimethyl-,[10,25] 1,3-dimethyl-[25] and 1,2,3 - trimethyl - tropylium[25] perchlorates (2a, 2b and 3a, respectively) have been described previously. 3,4-Dimethylthiophene 1,1-dioxide (8) was prepared by the perbenzoic acid oxidation of 3,4-dimethylthiophene,[21] m.p. 110–112.5° (lit.[21] 114°). 2,3,4-Trimethylthiophene was prepared by the Wolff–Kishner reduction[26] of 3,4-dimethylthiophene 2-aldehyde, b.p. 158.0–164.0° (lit.[27] 160.0–163.0°). 2,3,4,5-Tetramethylthiophene was prepared by the chloromethylation of 2,5-dimethylthiophene followed by the reduction with $LiAlH_4$,[28] b.p. 101.0–102.5°/23 mmHg (lit.[28] 74–79°/15 mmHg). The soln of perbenzoic acid in $CHCl_3$ was prepared from equimolecular amounts of benzoyl chloride and sodium peroxide.[29] Ethyl diazoacetate was prepared following the procedure of Searle.[30] Dioxane and THF utilized in generating methylcyclopropenes were distilled from LAH just before use.

2,3,4-*Trimethylthiophene* 1,1-*dioxide* (11). To well stirred $CHCl_3$ (40 ml) were added a chilled soln (165 ml) of perbenzoic acid (0.0416 mol) in $CHCl_3$ and 2,3,4-trimethylthiophene (2.62 g, 0.0208 mol) from different necks at such a rate to maintain the mole ratio at 2:1 over a period of 10 min. The temp. rose from 17° to 28.5°. After stirring at room temp. for a further 50 min, the mixture was washed with four 30 ml portions 10% Na_2CO_3 aq, three 40 ml portions 10% NaCl aq and dried ($MgSO_4$). Evaporation of the solvent followed by a recrystallization of the residual solid from ligroin afforded 11 (1.45 g, 44.1%) as white crystals; m.p. 134.5–136.0°; ^{1}H NMR ($CDCl_3$) δ 2.00 (m, 9H), 6.29 (s, 1H); IR ($CHCl_3$): 3100 (w), 2990 (w), 2910, 1660 (w), 1580 (w), 1435, 1380, 1370, 1280 (s), 1170, 1100, 990 (w), 840 cm^{-1} (Found: C, 53.09; H, 6.36. $C_7H_{10}SO_2$ requires: C, 53.14; H, 6.37%).

2,3,4,5-*Tetramethylthiophene* 1,1-*dioxide* (13). To well stirred $CHCl_3$ (100 ml) were added a chilled soln (425 ml) of perbenzoic acid (0.129 mol) in $CHCl_3$ and 2,3,4,5-tetramethylthiophene (9.03 g, 0.0644 mol) from different necks at such a rate to maintain the mole ratio at 2:1, over a period of 32 min. The temp. of the mixture rose from 18° to 31°. After the completion of the addition, stirring was continued for a further 15 min. The mixture was washed with four 80 ml portions 10% Na_2CO_3 aq, three 100 ml portions 10% NaCl, and dried ($MgSO_4$). Evaporation of the solvent followed by addition of pentane (25 ml) afforded 13 (6.79 g, 61%) as greenish white crystals. Recrystallization from hexane afforded 5.6 g of pale greenish 13; m.p. 112.8–113.8°; ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 6H), 2.05 (s, 6H); IR (CCl_4): 3080 (w), 2960 (w), 2925, 2860 (w), 1670 (w), 1620 (w), 1440 (s), 1390 (w), 1380 (w), 1300 (s), 1170 (s), 1115, 1070, 1040 (w), 980 (w) cm^{-1} (Found: C, 55.62; H, 6.78. $C_8H_{12}SO_2$ requires: C, 55.78; H, 7.02%).

1,4-*Dimethyltropylium perchlorate* (2c). A soln of diazomethane in heptane (60 ml) was prepared from 10.3 g of nitrosomethylurea. The soln was added to *p*-xylene (30 ml) in the presence of copper(I) bromide (1.0 g) with stirring over 1 hr, maintaining the temp. at 115–130°. Rectification of the soln afforded a fraction (0.986 g) boiling at 65–79°/50 mmHg containing 83% dimethyltropilidene and 17% *p*-xylene as determined by glc (Carbowax 20 M). The hydride abstraction with trityl perchlorate (1.807 g, 5.27 mmol) in dry acetonitrile followed by the addition of dry ethyl acetate afforded 2c (1.02 g, 89%) as colorless crystals.

1,2,4-*Trimethyltropylium perchlorate* (3b). To a soln of 8 (2.28 g, 15.8 mmol) in CH_2Cl_2 (8 ml) was added a soln of 1-methylcyclopropene[31] (0.53 g) in CH_2Cl_2 (4 ml) which had been chilled at −78°. The soln was stirred at room temp. for 2 hr. Evaporation of the solvent followed by distillation afforded 1,3,4-trimethyltropilidene (1.39 g, 66%), b.p. 71.5–76.0°/13.5 mmHg; ^{1}H NMR ($CDCl_3$) δ 1.89 (s, 9H), 2.13 (d, 2H, J = 7.0 Hz), 4.98–5.90 (m, 3H). Treatment of 1,3,4-trimethyltropilidene (1.39 g, 10.4 mmol) with trityl perchlorate (3.56 g, 10.4 mmol) in dry acetonitrile afforded 1.98 g of crude 3b. A reprecipitation from acetonitrile with dry ethyl acetate afforded 3b (0.974 g, 40%) as colorless crystals.

1,2,5-*Trimethyltropylium perchlorate* (3c). 3-Methylcyclopropene was generated from 1-chloro-2-butene (3.8 g, 42 mmol) and $NaNH_2$ (2.3 g, 60 mmol) in dioxane[31] and introduced with a stream of N_2 to a soln of 8 (0.982 g, 6.82 mmol) in CH_2Cl_2 over 3 hr at 21°. Evaporation of the solvent followed by rectification afforded 3,4,7-trimethyltropilidene (0.682 g, 75%); b.p. 48–50°/6 mmHg; ^{1}H NMR (CCl_4) δ 1.23 (d, 3H, J = 6.0 Hz), 1.95 (s, 6H), 1.5–2.3 (m, 1H), 4.86 (dd, 2H, J = 9.0 and 5.0 Hz), 5.73 (d, 2H, J = 9.0 Hz). Treatment of 3,4,7-trimethyltropilidene (0.624 g, 4.65 mmol) with trityl perchlorate (1.59 g, 4.65 mmol) in dry acetonitrile afforded 0.87 g of crude 3c. After a reprecipitation from acetonitrile with dry ethyl acetate was obtained 3c in 72% yield.

1,3,5-*Trimethyltropylium perchlorate* (3d). Mesitylene was subjected to the ring-expansion with diazomethane in the presence of copper(I) bromide at 130–135°.[10] Rectification afforded a fraction containing 1,3,5-trimethyltropilidene and mesitylene in a ratio of 9:1 as determined with ^{1}H NMR; b.p. 73–77°/16 mmHg; ^{1}H NMR (CCl_4) δ 1.78 (s, 3H), 1.93 (s, 6H), 2.17 (d, 2H, J = 7.0 Hz), 4.97 (t, 1H, J = 7.0 Hz), 5.58 (s, 1H), 6.03 (s, 1H). Treatment of 1,3,5-trimethyltropilidene (1.44 g, 10.7 mmol) with trityl perchlorate (3.67 g, 10.7 mmol) in dry acetonitrile followed by the addition of dry ethyl acetate afforded 3d (2.03 g, 82%) as colorless crystals.

1,2,3,4-*Tetramethyltropylium perchlorate* (4a). Cyclopropene was generated from allyl chloride (13.5 g, 0.177 mol) and $NaNH_2$ (6.9 g, 0.18 mol) in heptane[31] and introduced with a stream of N_2 to a soln of 13 (1.47 g, 8.52 mmol) in CH_2Cl_2 at 18–20° over 4 hr. Evaporation of the solvent followed by the separation with an alumina column afforded 2,3,4,5-tetramethyltropilidene (liq) (0.925 g, 73%); ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 6H), 1.95 (s, 6H), 5.30 (t, 2H, J = 7.0 Hz). The C_7–H signals overlap with Me signals in ^{1}H NMR. Treatment of 2,3,4,5-tetramethyltropilidene (1.10 g, 7.40 mmol) with trityl perchlorate (2.41 g, 7.03 mmol) in dry acetonitrile followed by the addition of dry EtOAc afforded crude 4a (1.38 g, 76%). A reprecipitation from acetonitrile with dry EtOAc afforded 4a (1.18 g, 65%) as colorless crystals.

1,2,3,5-*Tetramethyltropylium perchlorate* (4b). To a soln of 11 (1.78 g, 11.3 mmol) in CH_2Cl_2 (7 ml) was added a soln of 3-methylcyclopropene[31] (1.05 g, 19.4 mmol) in CH_2Cl_2 (5 ml) which had been chilled at −78°. The flask was stoppered and the soln stirred at 20–25° for 1.5 hr, and then the solvent was evaporated and the residue subjected to distillation to give 2,3,4,7-tetramethyltropilidene (0.734 g, 44%); b.p. 74.0–75.0°/7 mmHg; ^{1}H NMR ($CDCl_3$) δ 1.18 (d, 3H, J = 7.0 Hz), 1.73 (s, 3H), 1.93 (s, 6H), 4.76 (br.d, 1H, J = 5.0 Hz), 5.00 (dd, 1H, J = 9.0 and 5.0 Hz), 5.73 (d, 1H, J = 9.0 Hz). 2,3,4,7-Tetramethyltropilidene (0.734 g, 4.95 mmol) was treated with trityl perchlorate (1.70 g, 4.97 mmol) in dry acetonitrile and then 4b was precipitated by the addition of dry EtOAc. A reprecipitation from acetonitrile with dry ether afforded 4b (0.716 g, 59%) as colorless crystals.

1,2,4,5-*Tetramethyltropylium perchlorate* (4c). To a mixture of durene (50 g, 0.37 mol) and copper(I) bromide (1.5 g) in heptane (50 ml) was added a soln of diazomethane in heptane (180 ml), which had been prepared from 20.6 g of nitrosomethylurea, over 1.5 hr with stirring under reflux and N_2. After filtration of copper(I) bromide and subsequent distillation of a part of heptane (100 ml), the soln was cooled to 0° and most of unreacted durene was separated as ppts and washed with MeOH. The washings and the filtrate were combined, and then most of the solvent (heptane and MeOH) distilled off. The residue was again cooled and some more durene was recovered by filtration. Durene which was recovered amounted to 45 g. Evaporation of the solvent from the filtrate afforded a semisolid residue (3.1 g), which contained 1,2,4,5-tetramethyltropilidene and durene in a ratio 1.4:1 as determined by glc (Carbowax 20 M); ^{1}H NMR (CCl_4) δ 1.67–2.00 (s's, Me's), 5.25 (t, 1H, J = 8.0 Hz), 6.22 (br.s, 1H). Treatment of this mixture with trityl perchlorate (3.94 g, 11.5 mmol) in dry acetonitrile followed by the addition of dry EtOAc afforded crude 4c. A reprecipitation from acetonitrile with dry ether gave 4c (0.769 g, 27%) as colorless crystals.

1,2,4,6-*Tetramethyltropylium perchlorate* (4d). To mesitylene (200 g, 1.66 mol), which was stirred and refluxed under N_2, was added ethyl diazoacetate (35.9 g, 0.315 mol) over 1 hr, and then the mixture was refluxed for 30 min. After excess mesitylene had been removed from the dark brown mixture by distillation, the residue (50.4 g) was mixed with 10% KOH in MeOH (105 ml)–H_2O (25 ml) and refluxed with stirring for 4 hr in order to hydrolyze ethyl malonate and ethyl fumarate. Most of the MeOH was distilled off and the residue was treated in the usual manner to give 16.2 g of a mixture of ethoxycarbonyltrimethyltropilidene isomers (92%) and mesitylene (8%) as a light yellow liquid; b.p. 93–96°/1 mmHg. This was reduced with LAH (13.0 g, 0.343 mol) in dry ether to give hydroxymethyltrimethyltropilidene (viscous liquid) quantitatively. The crude alcohol (13.0 g, ca. 79 mmol) was dissolved in dry ether (170 ml) containing n-Bu_3N (14.6 g, 70 mmol) and to the resulting soln was added a soln of $SOCl_2$ (6.03 ml, 79 mmol) in dry ether (14 ml) over 30 min at −20° with stirring under N_2. After the addition the mixture was stirred for 2 hr at 0°. Two thirds of the ether was evaporated by bubbling N_2 at −10 to 0° and then pentane (100 ml) was added. The same procedure was repeated again, the lower layer (n-$Bu_3N \cdot HCl$) separated, and then finally the soln was concentrated to 30 ml by bubbling N_2 at 0°. The reddish brown residue was dissolved in dry ether (170 ml) and then the resulting soln was added to LAH (5.28 g, 0.139 mol) in dry ether (50 ml) at 0°. After stirring overnight at ambient temp., the mixture was refluxed for 3 hr, worked up in the usual manner, and then distilled to afford 7.43 g of light yellow liquid which contained 80–90% of 1,2,4,6-tetramethyltropilidene and 10–20% of mesitylene, as determined by ^{1}H NMR; b.p. 110–122°/32 mmHg; ^{1}H NMR (CCl_4) δ 1.87 (s, 12H), 2.10 (s, 2H), 5.58 (br.s, 2H). Treatment of 1,2,4,6-tetramethyltropilidene (1.00 g, 6.09 mmol) with trityl perchlorate (2.09 g, 6.09 mmol) in dry acetonitrile followed by the addition of dry EtOAc afforded crude 4d (1.16 g, 77%) as yellowish crystals. A reprecipitation from acetonitrile with dry ethyl acetate and dry ether gave 4d (1.11 g, 74%) as colorless crystals.

1,2,3,4,5-*Pentamethyltropylium perchlorate* (5a). To a soln of 13 (1.84 g, 10.7 mmol) in CH_2Cl_2 (10 ml) was added 1.3 g of 80% pure 1-methylcyclopropene which had been dissolved in CH_2Cl_2 (10 ml) and chilled to −78°. The flask was stoppered and then the mixture was stirred for 2.5 hr at 26°. The solvent was evaporated and the residue was chromatographed on an alumina column to give 1,2,3,4,5-pentamethyltropilidene (1.04 g, 55%); ^{1}H NMR (CCl_4) δ 1.63 (s, 3H), 1.75 (s, 3H), 1.83 (s, 3H), 1.87 (s, 6H), 5.20 (t, 1H, J = 6.5 Hz). The C_7–H signals were unable to be detected because of overlap with Me signals. In another run the product was purified by distillation; b.p. 72.0–73.0°/12 mmHg. Treatment of 1,2,3,4,5-pentamethyltropilidene (1.92 g, 10.9 mmol) with trityl perchlorate (3.73 g, 10.9 mmol) in dry acetonitrile followed by the addition of dry EtOAc afforded 5a (2.30 g, 76%) as pale brown crystals.

1,2,3,4,6-*Pentamethyltropylium perchlorate* (5b). 3-Methylcyclopropene was generated from 1-chloro-2-butene (4.6 g, 51 mmol) and $NaNH_2$ (2.2 g, 56 mmol) in dioxane[14] and introduced with a stream of N_2 to a soln of 13 (1.21 g, 7.03 mmol) in $CHCl_3$ (11 ml) at 20–25° over 2 hr and then the mixture was allowed to stand at ambient temp. overnight. The solvent was evaporated and the residue (1.97 g) subjected to rectification with a 30 cm spinning band column at 5–7 mmHg to give 2,3,4,5,7-pentamethyltropilidene (0.67 g, 59%). The measurement of the b.p. was impossible because of the small sample size. Treatment of 2,3,4,5,7-pentamethyltropilidene (0.538 g, 3.29 mmol) with trityl perchlorate (1.13 g, 3.29 mmol) in dry acetonitrile followed by the addition of dry EtOAc afforded crude 5b (0.82 g). A reprecipitation of the crude 5b from acetonitrile with dry EtOAc gave 5b (0.23 g, 27%) as colorless crystals.

1,2,3,5,6-*Pentamethyltropylium perchlorate* (5c). The ring-expansion of durene with ethyl diazoacetate was conducted in the manner essentially similar to that described for the same reaction of mesitylene leading to 4d except for the following. The soln of ethyl diazoacetate (26.7 g, 0.234 mol) in heptane (54 ml) was added dropwise to a soln of durene (100 g, 0.745 mol) in heptane (300 ml) in the presence of copper(I) bromide (1.74 g) over 1 hr under reflux. After the copper(I) bromide had been filtered off, most of heptane was distilled and the residue was cooled to crystallize out durene. This was filtered and washed with MeOH in order to extract ethoxycarbonyltetramethyltropilidene. The crude ester was treated with 10% KOH in MeOH (105 ml)–H_2O (25 ml), isolated by distillation (b.p. 85–95°/1 mmHg) and then subjected to the subsequent reactions as described for 4d. The yield of hydroxymethyltetramethyltropilidene and that of 1,2,3,5,6-pentamethyltropilidene based on ethyl diazoacetate were 8.1 and 3.8%, respectively. When the crude pentamethyltropilidene was subjected to purification by means of preparative tlc (SiO_2, hexane), 1,2,3,5,6-pentamethyltropilidene was obtained, being contaminated with 50% of durene; ^{1}H NMR (CCl_4) δ 1.68 (br.s, 6H), 1.80 (br.s, 6H), 1.93 (br.s, 3H), 5.97 (s, 1H). No ^{1}H NMR signals ascribable to the positional isomers of pentamethyltropilidenes were observed. Treatment of 1.24 g of a mixture of 1,2,3,5,6-pentamethyltropilidene and durene (1:1 in mol) with trityl perchlorate (1.31 g, 3.83 mmol) in dry acetonitrile followed by the addition of dry EtOAc afforded 5c (0.549 g, 55%) as colorless crystals.

1,2,3,4,5,6-*Hexamethyltropylium perchlorate* (6). A soln of ethyl diazoacetate (48.2 g, 0.424 mol) in octane (100 ml) was added dropwise to a soln of pentamethylbenzene (200 g, 1.35 mol) in octane (500 ml) over 4 hr under reflux. Most of the solvent was distilled and the residue was cooled to crystallize out pentamethylbenzene. This was filtered and washed with MeOH to extract resulting ethoxycarbonylpentamethyltropilidene. Evaporation of most of the solvent (octane and MeOH) from the combined filtrates afforded a semisolid, which was again filtered. Evaporation of the solvent from the filtrate gave a dark red liquid (69 g). The above ring expansion was repeated and the combined crude products (185 g) were heated in 10% KOH in MeOH (212 ml)–H_2O (49 ml) under reflux for 5 hr in order to hydrolyze ethyl malonate and ethyl fumarate. The mixture was worked up in the usual manner and the product distilling at 137–140°/1 mmHg (21.7 g) was collected. The fraction exhibited a weak ^{1}H NMR signal at δ 7.2 which is assigned to the signal of the C_7–H of 6-ethoxycarbonyl-1,2,3,4,7-pentamethyltropilidene, no other olefinic proton being observed. The mixture of the esters was subjected to the subsequent three steps (LAH, $SOCl_2$ and LAH) leading to hexamethyltropilidene in the manner as described for 4d. The yields of hydroxymethylpentamethyltropilidene and hexamethyltropilidene were 10.9 and 4.7% based on starting ethyl diazoacetate, respectively. Crude hexamethyltropilidene isolated was contaminated with 21% of pentamethylbenzene as determined by glc; therefore this was purified by means of column chromatography (SiO_2, hexane). In this way the purity was raised to 84%: ^{1}H NMR (CCl_4) for the mixture of 1,2,3,4,5,6- and 1,2,3,4,6,7-hexamethyltropilidenes, δ 6.11 (s, C_5-H of 1,2,3,4,6,7-hexamethyltropilidene) and 1.20 (d, J = 6 Hz, C_7-Me of 1,2,3,4,6,7-hexamethyltropilidene). The assignment of other methyl-proton signals were difficult. To a suspension of PCl_5 (4.34 g, 20.8 mmol) in dry CCl_4 (20 ml) was added a soln of 84% pure hexamethyltropilidene (2.19 g, 10.4 mmol) in dry CCl_4 (20 ml) over 7 min at 0° under N_2. After stirring for 2 hr at 0° under a slow stream of N_2, the resulting white ppts were filtered off with a glass filter under N_2 and then dissolved in AcOH (25 ml)–Ac_2O (7.4 ml) cooled to 17°. To the soln was added 60% $HClO_4$ (2.00 ml, 18.5 mmol) to give a reddish purple soln. Addition of dry ether to the soln under cooling in an ice bath afforded 6 (0.463 g, 16%) as pale pink precipitates. A reprecipitation of the ppts from acetonitrile with dry ether afforded 6 as colorless crystals.

Heptamethyltropylium perchlorate (7).[8] 1,2,3,4,5,6,7-Heptamethyltropilidene was prepared from hexamethylbenzene via the ring-expansion with ethyl diazoacetate according to the procedure of Knoche.[11] The treatment of the heptamethyltropilidene (0.678 g, 3.56 mmol) with PCl_5 (1.48 g, 7.12 mmol) in dry CCl_4 (10 ml) under N_2 for 1.5 hr at 0° afforded yellowish ppts. The ppts were collected on a glass filter under N_2 and then immediately dissolved in AcOH (5 ml)–Ac_2O (0.27 ml) to give a dark red soln. Addition of 60% $HClO_4$ (0.65 ml, 6.02 mmol) followed by precipitation with dry ether (100 ml) afforded 7 (0.224 g, 22%) as colorless crystals.

Charge-transfer spectra. To approximately 5 mg of a perchlorate was added 5 ml of 0.1 M soln of pyrene in 1,2-dichloroethane in the dark and thoroughly shaken. The soln was transferred to a 10 mm quartz cell and the spectrum was measured. In most of the perchlorates the longest wave length absorption appeared as a shoulder peak. Therefore the wave number for the maximum absorption was determined by drawing a smooth curve and by analyzing the shoulder peak. The wave number determined in this manner was accurate to ±0.02 × 10^4 cm^{-1}.

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