Tetrahedron Vol 36, pp 2939 to 2943
© Pergamon Press Ltd 1980 Printed in Great Britain

0040 4020/80/1101 2939/$02.00/0

ALKYLATED TROPYLIUM IONS—III[1]

^{13}C NMR SPECTRA OF METHYLATED TROPYLIUM IONS, CORRELATIONS AMONG ^{1}H AND ^{13}C CHEMICAL SHIFTS, AND ELECTRON DENSITY BY THE HÜCKEL MO METHOD

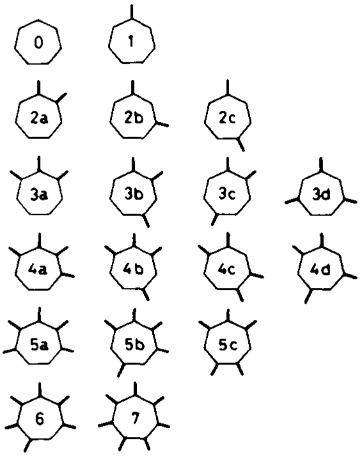
KEN'ICHI TAKEUCHI, YASUNORI YOKOMICHI, YASUHIRO KUBOTA and KUNIO OKAMOTO*
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

(*Received in Japan 7 December 1979*)

Abstract The ^{13}C NMR spectra for all seventeen methylated tropylium ions have been obtained in acetonitrile-d_3 and the chemical shifts of the Me- and the ring-carbons assigned. The plots of the ^{13}C shifts of ring-carbons against charge densities calculated by the simple Hückel MO method by the use of the inductive and the heteroatom models afford linear correlations. The ^{13}C shifts for the Me-carbons and the ^{1}H shifts for the Me- and the ring-hydrogens are linearly correlated with the ^{13}C shifts for the ring-carbons to which they are attached, provided the Me groups or the ring-hydrogens residing in similar steric environments are compared. From the slopes of the correlation lines the dependences of the ^{13}C shifts of Me-carbons and the ^{1}H shifts of ring- and Me-hydrogens on charge densities of ring-carbons have been estimated to be 35–50, 11 16, and 2.9 5.1 ppm, respectively, by assuming 160 ppm for the charge dependence of the ^{13}C shifts of the ring-carbons.

Since the discovery of the linear correlation between the ^{13}C NMR chemical shift and the electron density,[2a,b] various systems have been subjected to the examination of the correlation.[3] Although it is too premature at the present stage to regard the correlation as a general rule, it appears that the relationship is well established for various Hückeloid aromatic systems which exhibit ^{13}C chemical shifts over a wide range (*ca* 120 ppm),[3,4] and the proportionality constant of 160 ppm/electron[2b,4] is widely used.

The tropylium ion, which was first discovered among the Hückeloid carbocations, was included in the important work of Spiesecke and Schneider.[2b] However, this system has never been subjected to the examination of the dependence of ^{13}C chemical shifts of individual ring-carbons on the variation of charge density which is induced by the introduction of substituents. In the course of our work on the one-electron reduction of substituted tropylium ions[5] we succeeded in synthesizing all members of the methylated tropylium ions (Scheme 1).[1b] Consequently, we decided to examine whether such a correlation holds for the methylated tropylium system, where the spread in the ^{13}C shifts of the ring-carbons are limited to very narrow range (*ca* 27 ppm). In this paper we present assignment of ^{13}C chemical shifts of the Me- and the ring-carbons, and the linear correlations between the ^{13}C chemical shifts of the ring-carbons and their π-electron densities as calculated by the simple Hückel MO method.[6] In addition, the linear correlations of the ^{1}H shifts of the ring- and the Me-hydrogens and also the ^{13}C shifts of the Me-carbons with the ^{13}C shifts of the ring-carbons have been established. From these correlations the charge dependencies of the ^{13}C and ^{1}H chemical shifts for the ring and the Me groups have been estimated.



Scheme 1.

RESULTS AND DISCUSSION

Assignment of ^{13}C chemical shifts. The ^{13}C NMR spectra of the methylated tropylium ions were measured in acetonitrile-d_3 at 25°. Unambiguous assignment of the Me ^{13}C chemical shifts of most of the ions was made based on the relative intensities or uniqueness of the signals and fully ^{1}H coupled spectra. Some of the Me ^{13}C signals of the ions **3b**, **4b**, **4c**, and **5c** could not be assigned by the use of the above methods. In such cases the simple additivity rule for the Me substituent effect on the chemical shift was successfully applied. In the case of **6** the above procedures could not necessarily be applied with success; therefore, 3-(deuteriomethyl)-1,2,4,5,6-pentamethyltropylium perchlorate was prepared and the ^{13}C signals for the 3- and 4-Me groups were unequivocally assigned. The results are tabulated in Table 1.

The ^{13}C chemical shifts of the ring-carbons were also assigned by utilizing the same technique as the

Table 1. ^{13}C NMR chemical shifts for methylated tropylium ions in CD_3CN at 25 $\left(\delta \frac{\mathrm{TMS}}{^{13}\mathrm{C}} = 0\,\mathrm{ppm}\right)$

	Methyl	Ring carbon							Methyl carbon						
Ion	position	1	2	3	4	5	6	7	1	2	3	4	5	6	7
0	—	156.2_3	156.2_3	156.2_3	156.2_3	156.2_3	156.2_3	156.2_3	—	—	—	—	—	—	—
1	1	174.1_3	156.6_4	153.5_9	153.9_9	153.9_9	153.5_9	156.6_4	29.3_0	—	—	—	—	—	—
2a	1,2	171.9_0	171.9_0	155.0_0	151.5_9	151.5_9	151.5_9	155.0_0	28.8_3	28.8_3	—	—	—	—	—
2b	1,3	170.9_0	157.1_7	170.9_0	154.7_6	151.3_0	151.3_0	154.7_6	29.3_6	—	29.3_6	—	—	—	—
2c	1,4	171.2_6	154.1_7	154.1_7	171.2_6	154.4_0	151.5_3	154.4_0	28.7_1	—	—	28.7_1	—	—	—
3a	1,2,3	168.9_6	170.7_3	168.9_6	153.4_7	149.4_0	149.4_0	153.4_7	30.2_9	25.4_2	30.2_9	—	—	—	—
3b	1,2,4	169.3_2	169.0_9	155.9_4	168.3_2	152.0_0	149.4_2	152.4_7	28.3_0	28.7_7	—	28.7_7	—	—	—
3c	1,2,5	168.9_6	168.9_6	153.1_7	152.1_8	168.0_8	152.1_8	153.1_7	28.1_2	28.1_2	—	—	27.6_5	—	—
3d	1,3,5	168.0_3	155.0_0	168.4_4	155.0_0	168.0_3	152.4_7	152.4_7	28.7_7	—	29.4_7	—	28.7_7	—	—
4a	1,2,3,4	165.9_7	168.6_7	168.6_7	165.9_7	150.9_4	146.7_2	150.9_4	29.6_5	26.5_4	26.5_4	29.6_5	—	—	—
4b	1,2,3,5	166.7_9	168.0_8	166.0_3	154.2_3	165.4_4	150.1_2	151.6_5	29.6_5	24.8_3	30.3_5	—	27.7_7	—	—
4c	1,2,4,5	166.2_0	166.5_0	155.0_0	166.5_0	166.2_0	151.0_0	151.0_0	27.3_0	28.3_0	—	28.3_0	27.3_0	—	—
4d	1,2,4,6	166.5_0	166.5_0	153.8_2	165.7_3	152.6_5	165.7_3	153.8_2	28.3_7	28.3_7	—	29.0_0	—	29.0_0	—
5a	1,2,3,4,5	162.8_6	165.3_3	167.7_9	165.3_3	162.8_6	148.7_1	148.7_1	28.4_7	25.7_7	28.0_0	25.7_7	28.4_7	—	—
5b	1,2,3,4,6	163.8_5	165.9_7	165.9_7	163.8_5	151.8_8	162.2_8	151.8_8	29.8_2	25.8_9	25.8_9	29.8_2	—	27.8_3	—
5c	1,2,3,5,6	164.0_9	164.9_7	164.0_9	153.2_9	163.7_4	163.7_4	153.2_9	29.8_2	24.0_7	29.8_2	—	27.3_6	27.3_6	—
6	1,2,3,4,5,6	160.6_3	162.1_0	164.3_9	164.3_9	162.1_0	160.6_3	150.5_3	28.4_7	24.5_4	26.8_9	26.8_9	24.5_4	28.4_7	—
7	1,2,3,4,5,6,7	160.2_8	160.2_8	160.2_8	160.2_8	160.2_8	160.2_8	160.2_8	24.4_8	24.4_8	24.4_8	24.4_8	24.4_8	24.4_8	24.4_8

case of the Me-carbons. The assignment in the case of methyl-tropylium ion (**1**) was most important since the Me substituent-induced chemical shifts of the ring-carbons of **1** were often used to assign the signals of the ring-carbons of other ions. Therefore, methyltropylium-2,7-d_2 and methyltropylium-4-d perchlorates were prepared and the ring-carbon chemical shifts were unequivocally assigned. The results are also presented in Table 1.

Correlation of ^{13}C *chemical shifts with calculated charge densities.* The Me substituent-induced chemical shifts of the individual carbons of ionic π-systems were shown to linearly correlate with charge densities for methylated benzenium[3b,7] and naphthalenium[8] ions. However, no systematic study has been reported on the methylated tropylium ions. Therefore, we examined the correlation of the ^{13}C chemical shifts of all ring-carbons of all the methylated tropylium ions (Scheme 1) with charge densities calculated by the simple Huckel MO method by the use of the inductive and the heteroatom models.[6] The inductive parameter (h_{C_α}) for the Me-substituent was adjusted to -0.27, which was obtained by trial and error to afford reasonable values for the charge dependence of the ^{13}C chemical shifts of the ring-carbons (*vide infra*).

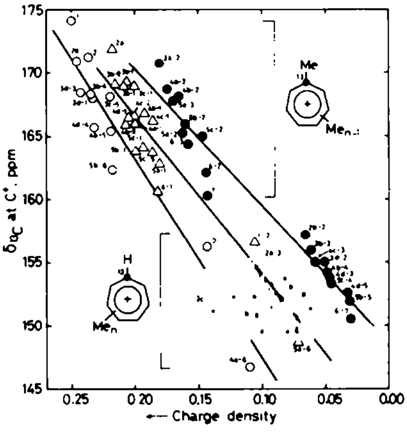


Fig. 1. Correlation for individual positions of the methylated tropylium ions of $\delta_{^{13}C}$ with charge density calculated by the inductive model. Open circle: ring-C with no *ortho* Me (ρ = 158, r = 0.9781). Triangle: ring-C with one *ortho* Me (ρ = 125; r = 0.9777). Solid circle: ring-C with two *ortho* Me's (ρ = 109, r = 0.9770). The numbers following the notations for the ions represent ring positions.

The plot of the ^{13}C shifts for the ring-carbons against their charge densities calculated by the use of the inductive model is shown in Fig. 1. Two characteristic features are apparent in the plot. First, both the Me-substituted and the hydrogen-carrying ring-carbons are divided into three categories, i.e. the ring-carbons possessing no, one, or two *ortho*† Me substituents. Conceivably, this stems from neglecting of the electron-withdrawing inductive effect[9] of the *ortho* Me substituents; if appropriate correction factors are introduced regarding such an inductive effect, the three categories might merge to give a single correlation line. Secondly, both the Me-substituted and the hydrogen-carrying ring-carbons are accommodated by a single straight line provided the ring-carbons belonging to one of the three categories mentioned above are selected. From the slopes of the correlation lines, the values for the charge dependence of the ^{13}C chemical shifts are calculated to be 158, 125,

---

†In this paper we use *ortho*, *meta*, and *para* to indicate the positions in the ring for convenience.

and 109 ppm/electron, corresponding to the ring-carbons possessing no, one, and two *ortho* Me substituents, respectively.†

Application of the heteroatom model[6] with the parameters $h_{C_x} = -0.1$, $h_X = 3.0$, and $k_{C-X} = 1.0$ also afforded three linear correlation lines, whose slopes are 171, 125, and 104 ppm/electron for the ring-carbons possessing no, one, and two *ortho* Me substituents, respectively (Fig. 2). In this case the linearity was slightly improved as compared with the inductive model. The calculations by the use of the hyperconjugative model[6] and the extended Huckel MO treatment[10] were attempted, but they resulted in poorer correlations.

Correlation of Me ^{13}C *chemical shifts with ring* ^{13}C *chemical shifts*. It has been suggested by Farnum that there would hold a linear correlation between the ^{13}C chemical shifts of Me groups in carbonium ions and those of the adjacent trigonal carbon atoms.[3a] He demonstrated this correlation[3a] by utilizing the data for limited number of the Me-substituted cycloalkenyl cations which had been reported by Olah and Liang.[11] When similar plot was attempted in the methylated tropylium system, the points appeared to scatter randomly. However, close observation of the plot revealed that there were linear correlations provided we selected a series of methylated tropylium ions in which the steric circumstance around the Me group of interest is highly similar to each other. As illustrated in Fig. 3, the introduction of Me groups *para* to the 3-Me of **4b**, 1-Me of **3a**, 3-Me of **3d**, 1-Me of **2b**, Me of **1**, 2-Me of **4a**, or 2-Me of **3a** affords a straight line in each case. Introduction of the single *ortho* Me group to **2b** and **1** also yields straight lines.‡ The slopes are in the range of 0.22 ~ 0.31, the average value being 0.27. If the Spiesecke-Schneider value of 160 ppm/electron[2b] is used for the linear charge dependence of the ^{13}C chemical shifts, the charge dependence of the ^{13}C shift for the Me-substituents attached to the carbonium carbons is calculated to be 35 ~ 50 (=0.22 × 160 ~ 0.31 × 160) ppm for the methylated tropylium ions.

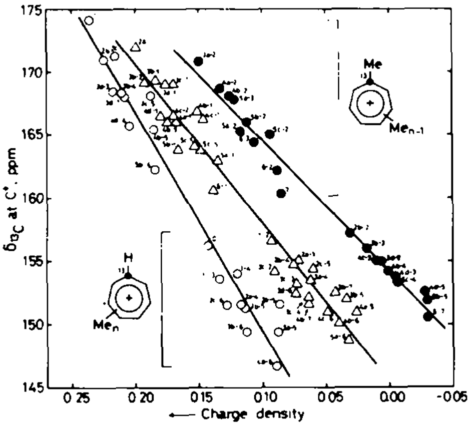


Fig. 2. Correlation for individual positions of the methylated tropylium ions of $\delta_{^{13}C}$ with charge density calculated by the heteroatom model. For notations, see the caption of Fig. 1. Open circles: $\rho = 171$; r = 0.9776. Triangles: $\rho = 125$; r = 0.9782. Solid circles: $\rho = 104$, r = 0.9893.

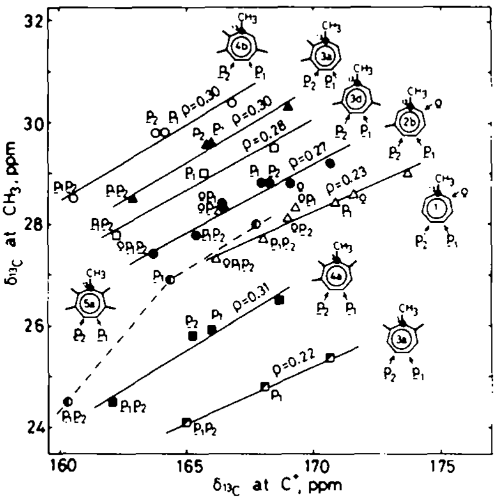


Fig. 3. Correlation of $\delta_{^{13}C}$ at Me with $\delta_{^{13}C}$ of the adjacent trigonal carbon atoms for the methylated tropylium ions. The arrow with a notation of o, p_1, or p_2 represents the introduction of a Me group to *ortho* or *para* positions

The average slope of 0.27 is somewhat smaller than the value (0.4) previously obtained in the plot for the Me-substituted cycloalkenyl cations.[3a] However, as Fig. 4 shows, when the ^{13}C chemical shift data for the three series of the systems, **3d**, **2b**, and **1**, in which the Me groups of interest are not flanked by adjacent Me groups, are plotted together with 1,4-dimethyl- and 1,3,5,7-tetramethylcyclooctatetraenyl dications,[12] toluene,[13] and xylenes,[13] all data are linearly correlated with a slope of 0.27. Therefore, the slope of 0.27 appears to be the one which is generally applicable

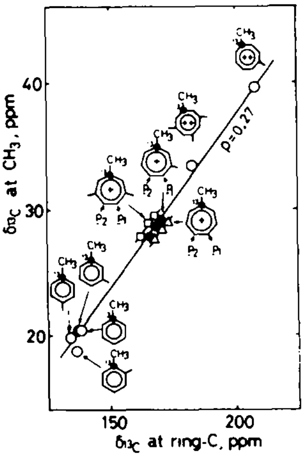


Fig. 4. Correlation of $\delta_{^{13}C}$ at Me with $\delta_{^{13}C}$ of the adjacent trigonal carbon atoms for various 6 π-electron Hückeloid aromatic systems.

---

†Actually, the inductive parameter ($h_{C_x} = -0.27$) was selected to afford the value of *ca* 160 ppm/electron[2b,4] as the charge dependence of the ^{13}C shifts of the ring-carbons possessing no *ortho* Me-substituent.

‡ The effect of introducing a Me group at the *meta* position is anomalous. It causes upfield shift of the methylated ring-carbon by *ca* 3 ppm, but almost no effect is found in the Me ^{13}C shift.

to 6 π-electron Huckeloid aromatic systems with 6-, 7-, or 8-membered ring.

The introduction of a Me group at the *para* position of 3-Me in **5a** fails to give a straight line as shown by a dashed line in Fig. 3. This appears to suggest severe steric crowding of the accumulated Me substituents. This aspect will be discussed in further detail in the following paper.[14]

Correlation of ring ^1H chemical shifts with ring ^{13}C chemical shifts. The dependence of the ^1H chemical shift upon charge density of the carbon to which the hydrogen of interest is attached has been investigated theoretically and experimentally.[15] Spiesecke and Schneider proposed a value of 10.6 ppm/electron for the dependence of ^1H chemical shifts on carbon charge.[2b] This correlation can also be tested by the plot of the chemical shifts of the hydrogens against those of the carbons to which they are attached.[3a] If we employ the charge dependencies, 160 for carbon and 10.6 ppm for hydrogen, the slope of the plot is expected to be 0.0663 ($=10.6/160$), which is the ratio of the charge dependence of ^1H chemical shifts to the charge dependence of ^{13}C chemical shifts. Farnum examined this sort of plot by utilizing corrected ^1H chemical shifts† for $C_3H_3^-$, $C_7H_7^+$, C_6H_6, $C_9H_9^-$, $C_5H_5^-$, and $C_8H_8^{2-}$, obtaining an excellent correlation with a slope of 0.0746, where the ^1H and the ^{13}C shifts ranged over 7 ppm and 92 ppm, respectively.[3a] A similar plot was tested for the hydrogens and the carbons of benzene perturbed by *para*-substituents, giving a line with a slope of 0.0581.[16] In the latter case, the ^1H and ^{13}C chemical shift ranges were much smaller, being 1.0 ppm and 20 ppm, respectively.

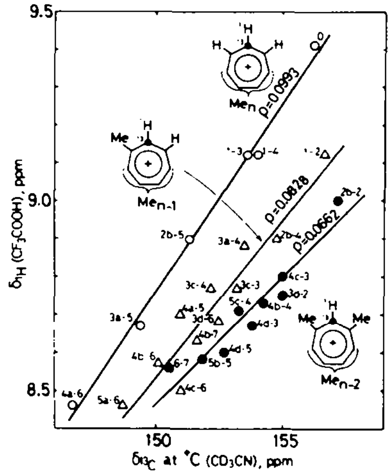


Fig. 5. Correlation of $\delta_{^1H}$ of ring hydrogens with $\delta_{^{13}C}$ of the adjacent trigonal carbon atoms for the methylated tropylium ions. The numbers following the notations for the ions represent ring positions.

When similar plot was tested on the methylated tropylium ions,‡ which show ^1H and ^{13}C chemical shifts over 1.0 and 10 ppm ranges, respectively, three linear correlation lines were obtained (Fig. 5), corresponding to the hydrogen flanked by no, one, or two *ortho* Me substituents; these lines afford the slopes 0.0993 (r: 0.9966), 0.0828 (r: 0.9481), and 0.0662 (r: 0.9501), respectively. The slopes are close to those previously determined in other systems mentioned above.§ However, the present results indicate that the sensitivity of ^1H chemical shifts toward carbon charge density depends on the degree of shielding of the hydrogen by adjacent Me-substituents. It appears that the more shielded hydrogens exhibit less charge dependence. By employing the Spiesecke–Schneider value of 160 ppm[2b] as the linear charge dependence of the ^{13}C chemical shifts, the charge dependence of the ring ^1H chemical shift becomes 11 ~ 16 ($=0.0662 \times 160$ ~ 0.0993×160) ppm.

Correlation of methyl ^1H chemical shifts with ring ^{13}C chemical shifts. The linear correlation between the ^1H chemical shifts of the Me groups in carbonium ions with charge density on adjacent carbonium carbons was demonstrated by MacLean and Mackor for the ^1H NMR spectra of a number of cyclohexadienyl cations.[2c] A similar correlation was also found to hold for the Huckeloid aromatic systems, i.e. hexamethylbenzene, trimethylcyclopropenium ion, and tetramethylcyclobutenium dication.[3a] However no systematic study on this sort of correlation for a single Huckeloid aromatic system has been carried out, presumably from lack of ^1H and ^{13}C chemical shift data.¶ Therefore, we examined the above correlation for the methylated tropylium ions.

As Fig. 6 shows, the points scatter over a wide range. However, close examination of the plot reveals that there are systematic correlations. In Fig. 6 solid circles represent outermost Me's in more than three Me's attached to contiguous ring-carbons; open circles represent isolated Me's; squares represent one of a pair of adjacent Me's; solid triangles represent Me's which are buried among three or more Me's; open triangles represent central Me's in three Me's attached to contiguous ring-carbons.|| (Here the notation, **3b**-4 for example, shows the Me group attached to 4-carbon of **3b**.) The slopes for a series of correlation lines are 0.032, 0.030, 0.027, 0.026, and 0.018 in the above mentioned order. In these cases also, the sensitivity of ^1H chemical shifts toward ring-carbon charge decreases as the hydrogen is more shielded, the trend being similar to the correlation of ring ^1H chemical shifts with ring-carbon charge (*vide supra*). If the Spiesecke–Schneider value of 160 ppm/electron is used for the charge dependence of the ^{13}C chemical shifts, then the charge dependence of the hydrogen of the Me group is calculated to be 2.9 ~ 5.1 ($=0.018 \times 160$ ~ 0.032×160) ppm.

In conclusion, the charge dependencies of the ^{13}C and the ^1H chemical shifts for the methylated tropylium ions may be summarized as in the following scheme. Although the sensitivity of the ^1H chemical

---

†Corrected for the ring-current effect.

‡For the ^1H chemical shift data in trifluoroacetic acid, see Ref 1*b*.

§Detailed discussion on the magnitude of the slopes may not be permitted since different solvents were used in ^1H and ^{13}C NMR measurements in this work.

¶Aryldimethylcarbonium ions, cycloalkenyl cations, and phenylmethylcarbonium ions have been subjected to the examination of this correlation by Farnum[3a] by utilizing the data available in the literature.

||The reason for the finding that the linear correlations hold only for a series of specific Me groups is considered to be ascribed to conformational effects[17] as will be discussed in the following paper.[14]

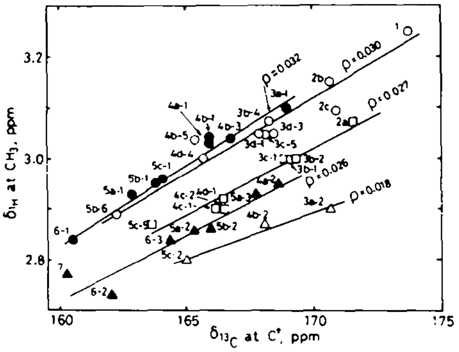
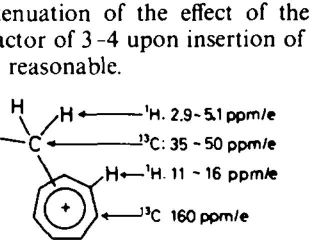


Fig. 6. Correlation of $\delta_{^1H}$ of Me hydrogens with $\delta_{^{13}C}$ of the adjacent trigonal carbon atoms for the methylated tropylium ions. The numbers following the notations for the ions represent ring positions.

shifts toward the charge densities of the ring-carbons was found to depend on the degree of shielding of the hydrogen, attenuation of the effect of the positive charge by a factor of 3-4 upon insertion of a carbon atom appears reasonable.



EXPERIMENTAL

Materials. All reagents were of reagent-grade quality except when otherwise noted.

3-(Deuteriomethyl)-1,2,4,5,6-pentamethyltropylium perchlorate. This compound was prepared by the hydride abstraction with trityl perchlorate[18] of deuteriomethylpentamethyltropilidene isomers, which was prepared *via* the ring expansion of 3-(deuteriomethyl)durene with ethyl diazoacetate as reported previously.[1b] 3-(Deuteriomethyl)-durene was prepared in the following manner. A soln of 3-(chloromethyl)durene (71.7 g, 0.392 mol), which was prepared following the method reported in the literature,[19] was added to LiAlD$_4$ (9.88 g, 0.235 mol) in THF (150 ml) under reflux with stirring over 1.5 hr and the mixture stirred under reflux for further 24 hr. The mixture was worked up in the usual manner to give 3-(deuteriomethyl)durene (57.1 g, 94.8%).

*Methyltropylium-*2,7-d$_2$ *perchlorate.* This was prepared by the hydride abstraction with trityl perchlorate[18] of 3-methyltropilidene-2,4-d_2, which was prepared from 2,6-cycloheptadienone-2,7-d_2 by the method reported previously.[20] 2,6-Cycloheptadienone-2,7-d_2 was prepared in the following manner. Cycloheptanone was converted to cycloheptanone-2,2,7,7-d_4 by the method reported,[21] which was then transformed into 2,6-cycloheptadienone-2,7-d_2 *via* the route of ethylene ketal formation, bromination, dehydrobromination, and hydrolysis.[22] During the ethylene ketal formation *ca* 75% of D was exchanged with H. However, the 2- and 7-deuterated carbons of the perchlorate were observable as a triplet on ^{13}C NMR measurement.

*Methyltropylium-*4-d *perchlorate.* This was prepared by the ring expansion of toluene-4-d with diazomethane[23] followed by hydride abstraction with trityl perchlorate.[18] Toluene-4-d containing 70% D was prepared by the treatment of *p*-tolylmagnesium bromide with D$_2$O.

^{13}C NMR measurement. ^{13}C NMR spectra were recorded on a JNM-FX100 operating in the Fourier transform mode with 10 mm tubes at 25.00 MHz with proton noise decoupling for the solns of the perchlorates (50-100 mg) dissolved in CD$_3$CN (1.0 ml) at 25°. Chemical shifts in ppm were determined relative to the CD$_3$ group of CD$_3$CN and converted to the TMS scale using δ_{CD_3} 1.35 for CD$_3$CN. Generally the spectra were obtained employing a 6024 Hz width in 8192 data points. The chemical shifts were reproducible to ±0.05 ppm. When necessary fully ^{1}H coupled spectra were obtained for unambiguous assignments of the signals.

REFERENCES

[1a] Part I. K. Takeuchi, Y. Yokomichi and K. Okamoto, *Chem. Lett.* 1177 (1977). [b] Part II. K. Takeuchi, Y. Yokomichi, T. Kurosaki, Y. Kimura and K. Okamoto, *Tetrahedron* **35**, 949 (1979).

[2a] P. C. Lauterbur, *Tetrahedron Letters* 274 (1961); [b] H. Spiesecke and W. G. Schneider, *Ibid.* 468 (1961); [c] C. MacLean and E. L. Mackor, *Mol. Phys.* **4**, 241 (1961).

[3] For leading refs, see; [a] D. G. Farnum, *Advances in Physical Organic Chemistry* (Edited by V. Gold and D. Bethell), Vol. 11. Academic Press, New York (1975); [b] G. L. Nelson and E. A. Williams, *Progress in Physical Organic Chemistry* Edited by R. W. Taft), Vol. 12. J. Wiley, New York (1976).

[4] G. A. Olah and G. D. Mateescu, *J. Am. Chem. Soc.* **92**, 1430 (1970).

[5] K. Takeuchi, K. Komatsu, K. Yasuda, F. Mikuchi and K. Okamoto, *J. Chem. Soc.* Perkin II, 1005 (1979), and previous work.

[6] A Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*. J. Wiley, New York (1961).

[7a] G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly and G. D. Mateescu, *J. Am. Chem. Soc.* **94**, 2034 (1972); [b] V. Koptyug, A. Rezvukhin, E. Lippmaa and T. Pehk, *Tetrahedron Letters* 4009 (1968).

[8] K. Lammertsma and H. Cerfontain, *J. Am. Chem. Soc.* **101**, 3618 (1979).

[9] References cited in G. A. Olah and D. A. Forsyth, *Ibid.* **97**, 3137 (1975).

[10] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).

[11] G. A. Olah and G. Liang, *J. Am. Chem. Soc.* **94**, 6434 (1972)

[12] G. A. Olah, J. S. Staral, G. Liang, L. A. Paquette, W. P. Melega and M. J. Carmody, *Ibid.* **99**, 3349 (1977).

[13a] W. R. Woolfenden and D. M. Grant, *Ibid.* **88**, 1496 (1966); [b] D. K. Dalling, K. H. Ladner, D. M. Grant and W. R. Woolfenden, *Ibid.* **99**, 7142 (1977).

[14] K. Takeuchi, Y. Yokomichi and K. Okamoto, *Tetrahedron* **36**, 0000 (1980).

[15] For a leading Ref., see Ref. 3*a*.

[16] J. B. Stothers, *Carbon-13 Nuclear Magnetic Resonance Spectroscopy* Chap. 5. Academic Press, New York (1972).

[17] D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.* **89**, 5315 (1967).

[18] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *Ibid.* **79**, 4557 (1957).

[19] R. R. Aitken, G. M. Badger and J. W. Cook, *J. Chem. Soc.* **1950**, 331.

[20] K. Takeuchi, T. Maeda and K. Okamoto, *Bull. Chem. Soc. Jpn.* **50**, 2817 (1977).

[21] L. K. Montgomery, A. O. Clouse, A. M. Crelier and L. E. Applegate, *J. Am. Chem. Soc.* **89**, 3453 (1967).

[22] E. W. Garbisch, Jr., *J. Org. Chem.* **30**, 2109 (1965).

[23] E. Muller, H. Kessler, H. Fricke and W. Kiedaisch, *Liebigs Ann. Chem.* **675**, 63 (1964).