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Structure and Tautomerism of Cyclopentadiene Derivatives: X.* 1,5-Sigmatropic Shifts of the *p*-Nitrobenzyl Group in Tetramethyl 5-Methylcyclopentadienetetracarboxylate**

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Abstract—The reaction of thallium 5-methyl-1,2,3,4-tetrakis(methoxycarbonyl)cyclopentadienide with *p*-nitrobenzyl bromide gave a mixture of isomeric *p*-nitrobenzylcyclopentadienes. The isomers were separated, and the structure of each isomer was established by ^{1}H and ^{13}C NMR spectroscopy. 1,5-Sigmatropic shifts of the *p*-nitrobenzyl group along the cyclopentadienyl ring were revealed, their Gibbs activation energies $\Delta G^{\neq}_{120°C}$ ranging from 29.5 to 30.6 kcal/mol.

Reversible and irreversible alkyl group migrations in the cyclopentadiene systems were studied in sufficient detail [2–4]. They are characterized by fairly high energy barriers ($\Delta G^{\neq}_{25°C}$ = 36–48 kcal/mol) and follow intramolecular 1,5-sigmatropic shift pattern with retention of configuration in the migrating group [2–4]. Intermolecular shifts of alkyl groups in the corresponding cyclopentadiene derivatives occur very rarely and only as side processes which require more severe conditions [5]. The most convincing proofs for the intramolecular mechanism of 1,5-sigmatropic shift of methyl group in cyclopentadienes were obtained by Borodkin *et al.* [6] who performed complete assignment of signals in the ^{1}H NMR spectra of 5-trideuteromethyl-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene on the basis of ^{13}C–^{13}C coupling constants of the ring carbon nuclei and the data of selective double heteronuclear ^{13}C–{^{1}H} resonance, followed by analysis of the time dependence of the ^{1}H NMR spectra in the temperature range from 225 to 320°C. The following activation parameters were obtained: $\Delta G^{\neq}_{25°C}$ = 43.1 ± 0.5 kcal/mol, $\Delta H^{\neq}$ = 41.7 ± 0.5 kcal × mol^{-1}, and $\Delta S^{\neq}$ = –4.8 ± 1.0 J mol^{-1} K^{-1}.

We made an attempt to reduce the barrier to alkyl group migration in the cyclopentadiene system by introduction of acceptor substituents into both the migrating group and the five-membered carbocycle. For this purpose we synthesized *p*-nitrobenzyl derivatives **II**–**IV** of tetramethyl 5-methylcyclopentadiene-1,2,3,4-tetracarboxylate by reaction of thallium cyclopentadienide **I** with *p*-nitrobenzyl bromide in THF (Scheme 1), and rearrangements of the resulting compounds were studied by ^{13}C and ^{1}H spectroscopy.

According to the ^{1}H NMR data, the fractions of isomers **II**–**IV** in the reaction mixture were 14, 30, and 56%, respectively. We succeeded in isolating each isomer in the pure state by column chromatography on silica gel (Silokhrom). Their ^{1}H NMR spectra in benzene-d_6 are given in Figs. 1–3 and Table 1. There were no difficulties in identifying isomer **II** by ^{1}H NMR spectroscopy. Its methoxycarbonyl groups give two singlets at δ 3.09 and 3.15 ppm (Fig. 1). The methyl group in **II** is attached to the sp^3-carbon atom of the cyclopentadiene ring, and it appears more upfield (δ 1.23 ppm; Fig. 1) relative to the corresponding signals of isomers **III** and **IV** where it is

* For communication IX, see [1].

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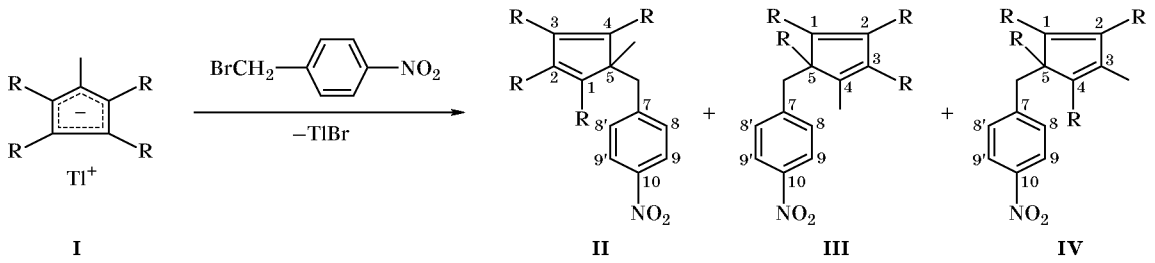
Scheme 1.



R = CO_2Me.

located at the sp^2-hybridized carbon atom (δ 2.35 and 2.11 ppm, respectively; Figs. 2, 3, Table 1). It was much more difficult to distinguish between structures

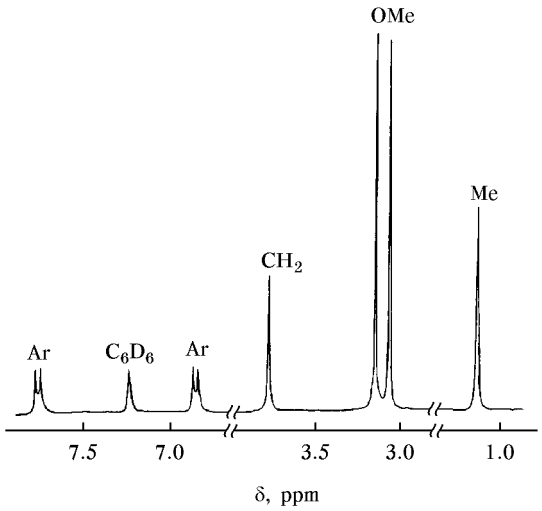


Fig. 1. ^1H NMR spectrum (360 MHz) of tetramethyl 5-methyl-5-(4-nitrobenzyl)cyclopentadiene-1,2,3,4-tetracarboxylate (**II**) in C_6D_6 at 24°C.

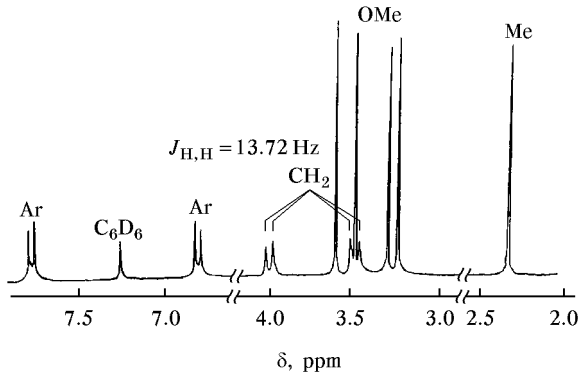


Fig. 2. ^1H NMR spectrum (360 MHz) of tetramethyl 4-methyl-5-(4-nitrobenzyl)cyclopentadiene-1,2,3,5-tetracarboxylate (**III**) in C_6D_6 at 24°C.

III and **IV** on the basis of the ^1H NMR data, for each of these has nonequivalent methoxycarbonyl groups (Figs. 2, 3). An additional information can be deduced from the appearance of benzyl methylene protons. The molecule of isomer **II** has a symmetry plane, and these protons give a singlet at δ 3.79 ppm (Fig. 1). Isomers **III** and **IV** lack symmetry elements, and the methylene group therein is prochiral, so that the corresponding protons appear as an *AB* system. Judging by the isomer structure, the difference in the environment of the CH_2 protons in **III** is stronger than in **IV**. Therefore, the difference between the chemical shifts of H_A and H_B in the spectrum of **III** should be greater than the corresponding difference for isomer **IV**. The experimental values of $\Delta\delta_{AB}$ = are 0.507 (**III**) and 0.018 ppm (**IV**) (Figs. 2, 3). The geminal coupling constants $^2J_{AB}$ are 13.72 and 13.31 Hz for isomers **III** and **IV**, respectively.

Identification of isomers **III** and **IV** is very important for studying substituent migration in the methyltetrakis(methoxycarbonyl)cyclopentadiene system by NMR spectroscopy; otherwise, it would be impossible to choose between 1,5- and 1,3-sigmatropic shifts. Therefore, we performed a detailed analysis of their ^{13}C NMR spectra (Table 2) recorded with and without decoupling from protons. The most informative are signals from the sp^3-hybridized carbon atom of the cyclopentadiene ring (C^5). In the ^{13}C monoresonance spectrum of **III**, the C^5 signal appears as a complex multiplet (δ_C 69.45 ppm) due to spin–spin coupling with protons of the methyl and prochiral methylene groups. The corresponding coupling constants were determined by the selective double-resonance technique: $^2J_{C,H}$ = 5.29 Hz and $^3J_{C,H}$ = 3.38 Hz. The sp^3-carbon signal in the spectrum of **IV** is a triplet, δ_C 66.70 ppm, $^2J_{C,H}$ = 5.70 Hz. It is split due to coupling with only two almost equivalent methylene protons, whereas protons of the methyl group are separated from C^5 by four bonds, and the corresponding coupling constant $^4J_{C,H}$ is too small to be observed in the spectrum [7].

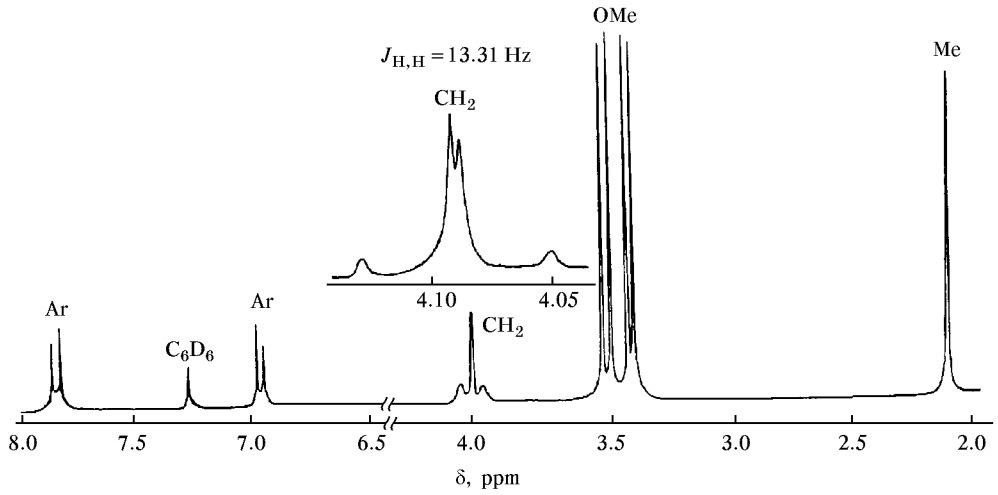


Fig. 3. ^{1}H NMR spectrum (360 MHz) of tetramethyl 3-methyl-5-(4-nitrobenzyl)cyclopentadiene-1,2,4,5-tetracarboxylate (**IV**) in C_6D_6 at 24°C.

On the basis of the ^{13}C monoresonance spectrum of **III** we were able to unambiguously assign the signal from C^3 (δ_C 132.25 ppm), which is separated by three bonds from the methyl group protons (quartet, $^3J_{C,H}$ = 5.12 Hz). The other signals from the cyclopentadiene ring carbon atoms are observed in the same region as those from the benzene ring carbons. Therefore, they were assigned by the double resonance technique with selective decoupling from the methyl and methylene protons (in the case of isomer **III**, selective decoupling from only one methylene proton, δ 3.99 ppm, was performed) and also from protons of the benzene ring.

The signal at δ_C 162.34 ppm is a complex multiplet. Selective decoupling from protons of the methyl group gives a doublet of doublets due to coupling with two diastereotopic methylene protons, J = 2.25 and 6.39 Hz). In turn, selective decoupling from the methylene protons transforms the above multiplet into a doublet of quartets, the quartet coupling constant being 7.53 Hz. These data allowed us to assign the signal at δ_C 162.34 ppm to the C^4 atom of the cyclopentadiene ring, which is directly linked to the methyl group. It should be noted that in this case the coupling constants $^2J_{C,H}$ between exocyclic protons and carbon nuclei of the cyclopentadiene ring are greater in absolute value than the corresponding coupling constants through three bonds.

The remaining four downfield signals belong to the carbonyl carbon atoms. The most downfield of these, δ_C 168.76 ppm, is a complex multiplet, indicating that the corresponding substituent is located in position *5*. This is confirmed by experiments with selective decoupling from the methyl and methylene protons.

Table 1. Proton chemical shifts (δ, ppm) in the ^{1}H NMR spectra of isomeric tetramethyl methyl(4-nitrobenzyl)cyclopentadienetetracarboxylates **II**–**IV** (C_6D_6, 24°C)

Isomer	CH_3 (3H)	CH_2[a] (2H)	OCH_3	8-H, 8′-H[b] (2H)	9-H, 9′-H[b] (2H)
II	1.232	3.793	3.094 (6H), 3.151 (6H)	6.87	7.83
III	2.349	3.483 3.990	3.265 (3H),[c] 3.315 (3H),[d] 3.517 (3H), 3.633 (3H)	6.84	7.81
IV	2.108	4.081 4.098	3.435 (3H),[d] 3.455 (3H), 3.524 (3H), 3.555 (3H)	6.98	7.84

[a] Calculated chemical shifts of diastereotopic methylene protons.

[b] The *AA′BB′* system was not analyzed.

[c] Protons of the methoxycarbonyl group on C^3.

[d] Protons of the methoxycarbonyl group on C^5.

Table 2. Carbon chemical shifts (δ, ppm) in the ^{13}C NMR spectra of isomeric tetramethyl methyl(4-nitrobenzyl)cyclopentadienetetracarboxylates **III** and **IV** (C_6D_6, 24°C)

Isomer	CH_3	CH_2	OCH_3	Cyclopentadiene ring, C^1–C^5	Benzene ring, C^7–C^{10}	C=O
III	13.75	37.77	51.41,[a] 51.76, 52.00, 52.83[b]	133.84 (C^1), 148.37 (C^2), 132.25 (C^3), 162.34 (C^4), 69.45 (C^5)	141.72 (C^7), 129.87 (C^8, $C^{8'}$), 123.13 (C^9, $C^{9'}$), 147.47 (C^{10})	161.91,[a] 162.15, 164.53, 168.76[b]
IV	13.32	37.89	51.41,[c] 52.04, 52.09, 52.70[b]	140.49 (C^1), 149.32 (C^2), 152.86 (C^3), 137.42 (C^4), 66.70 (C^5)	142.70 (C^7), 130.28 (C^8, $C^{8'}$), 122.83 (C^9, $C^{9'}$), 147.37 (C^{10})	162.26, 163.34,[c] 163.87, 168.16[b]

[a] Methoxycarbonyl group on C^3.
[b] Methoxycarbonyl group on C^5.
[c] Methoxycarbonyl group on C^4.

Table 3. Correlation between proton and carbon signals (δ, δ_C, ppm) from the methoxycarbonyl groups in the ^1H and ^{13}C NMR spectra of isomers **III** and **IV**

Nucleus	Isomer **III**	Isomer **IV**
^{13}C, C=O	168.76, 164.53, 162.15, 161.91	168.16, 163.87, 163.34, 162.26
^{13}C, OCH_3	52.83, 52.00, 51.76, 51.41	52.70, 52.04, 51.41, 52.09
^1H, OCH_3	3.31, 3.63, 3.52, 3.27	3.43, 3.46, 3.55, 3.52

The signal at δ_C 161.91 ppm (which originally appears as a broadened unsymmetrical quartet) is transformed into a regular quartet with $^3J_{C,H}$ = 3.67 Hz on selective decoupling from protons of the methyl group. This means that this signal belongs to the carbonyl carbon atom in position *3*. The other two carbonyl signals, δ_C 164.53 and 162.15 ppm (quartets in the monoresonance spectrum) do not change in the above experiments with selective decoupling from protons. Therefore, they were assigned to substituents attached to C^1 and C^2, but we failed to distinguish between the C^1- and C^2-substituents.

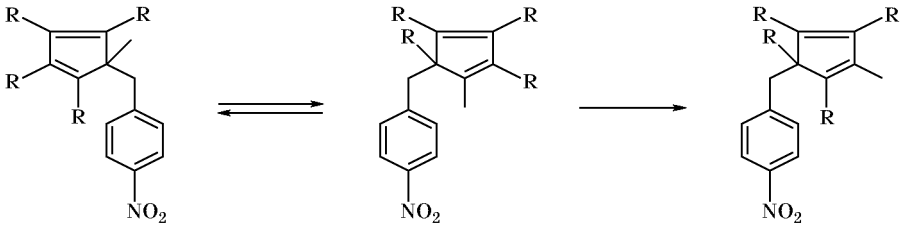
The signal at δ_C 133.84 ppm in the monoresonance spectrum is a broadened doublet with $J_{C,H}$ = 5.93 Hz. It is transformed into a singlet on selective decoupling from the methylene protons. This indicates that it belongs to C^1 of the cyclopentadiene ring. The remaining broadened signal at δ_C 148.37 ppm is not split; therefore, it should be assigned to C^2. In addition, selective decoupling from the methylene protons transforms that signal into a broadened quartet with $^4J_{C,H}$ = 1.47 Hz.

Two signals, δ_C 147.47 and 141.72 ppm, belong to aromatic carbon atoms. Selective decoupling from protons in positions *8,8′* and *9,9′*, as well as from protons of the methylene group, allowed to assign the signal at δ_C 147.47 ppm to C^{10}, and the signal at δ_C 141.72 ppm, to C^7. We failed to assign the ^{13}C signals from methoxy groups to particular positions in the cyclopentadiene ring on the basis of the results of selective double resonance experiments.

Using the two-dimensional heteronuclear correlation technique, we succeeded in establishing correspondence between the ^1H and ^{13}C NMR signals for each methoxycarbonyl group (Table 3) but failed to assign them to specific positions in the cyclopentadiene ring. Taking into account the assignment of carbonyl carbon signals to positions *3* and *5*, which was made by selective double resonance experiments, the corresponding ^{13}C and ^1H signals of methoxy groups can be distinguished. However, it was impossible to assign the ^{13}C and ^1H signals of methoxy groups to C^1- and C^2-substituents in isomer **III**.

Only two signals in the ^{13}C monoresonance spectrum of isomer **IV** could be assigned unambiguously, namely those belonging to C^2 and C^3, δ_C 149.32 and 152.86 ppm, respectively. They are split into quartets due to coupling with the methyl protons, $^3J_{C,H}$ =

Scheme 2.



II **III** **IV**

R = CO_2Me.

4.42 Hz and $^2J_{C,H}$ = 7.43 Hz. This assignment is supported by analogy with $^3J_{C,H}$ and $^2J_{C,H}$ in isomer **III**, as well as by selective decoupling from protons of the methyl group (the quartets are transformed into singlets. By selective decoupling from the aromatic and methylene protons, we succeeded in identifying the C^7 and C^{10} signals, δ_C 142.70 and 147.37 ppm, respectively. It should be noted that the chemical shifts of C^7 and C^{10} change only slightly in going from isomer **III** to **IV** (Table 2).

In the monoresonance spectrum, the signal at δ_C 137.42 ppm is a complex multiplet. Selective decoupling from the methylene protons gives a quartet with $J_{C,H}$ = 5.13 Hz, while decoupling from the methyl protons gives a doublet of doublets. Hence this signal belongs to C^4. The signal at δ_C 140.49 ppm was assigned to C^1.

Two of the four downfield carbonyl signals appear as complex multiplets. The most downfield signal (δ_C 168.16 ppm) belongs to the C^5-substituent, for its multiplicity decreases on selective decoupling from the methylene protons. The multiplicity of the signal at δ_C 163.34 ppm changes on selective decoupling from both methylene and methyl protons; in the latter case, it turns to a quartet with $J_{C,H}$ = 3.38 Hz. Therefore, this signal was assigned to the C^4-substituent. The remaining signals, δ_C 163.87 and 162.26 ppm (quartets in the monoresonance spectra, $^3J_{C,H}$ = 3.98 and 4.01 Hz), do not change their multiplicity in the double resonance spectra. They should be assigned to the C^1- and C^2-substituents, but it is not possible to distinguish between them.

As with isomer **III**, the correspondence between the ^1H and ^{13}C signals for each substituent in **IV** was established by the heteronuclear correlation technique. The results are given in Table 3. On the basis of these data and the above assignments of carbonyl carbon signals in positions *4* and *5*, the ^1H and ^{13}C signals of the corresponding methoxy groups can be identified. We did not succeed in distinguishing between the C^1- and C^2-substituents.

Heating of both isomer **II** (for 1 h) and isomer **III** (for 1.5 h) in *o*-dichlorobenzene at 120°C resulted in formation of an equilibrium mixture of isomers **II**, **III**, and **IV** at a ratio of 14 : 30 : 56. According to the ^1H NMR data, isomer **II** is first converted into **III**, and isomer **IV** is then formed (Fig. 4). However, heating of isomer **IV** in *o*-dichlorobenzene for 5 h at 120°C gave no isomer **II** or **III** (^1H NMR data), presumably because of a high energy barrier to the transformation **IV** → **III**. Hoffmann and Backes [8] showed that structures like **IV** have lower energies than those like **II** and **III**; therefore, the formation of isomer **II** or **III** from **IV** should be accompanied by a considerable energy consumption.

The absence of concentration dependence in the variation of the ^1H NMR spectra of compounds **II** and **III** on heating in *o*-dichlorobenzene (c = 0.3–0.01 M), as well as the absence of radical species under these conditions (even in the presence of di-*tert*-butylnitroxide as radical trap; ESR data), indicates that the rearrangement **II** ⇄ **III** → **IV** follows the mechanism of intramolecular 1,5-sigmatropic shift of the *p*-nitrobenzyl group in the methyltetrakis(methoxycarbonyl)-cyclopentadiene system (Scheme 2).

The Gibbs energies of activation $\Delta G^{\neq}_{120°C}$ for the processes **II** ⇄ **III** and **III** → **IV** were determined from the time dependence of the ^1H NMR spectra of compounds **II** and **III** in *o*-dichlorobenzene at 120°C. The following values were obtained: **II** → **III**, 29.5; **III** → **II**, 30.1; **III** → **IV** 30.6 kcal/mol.

EXPERIMENTAL

The ^1H NMR spectra were recorded on Tesla BS-567A (100 MHz) and Bruker AM-360 (360 MHz) spectrometers in benzene-d_6 and *o*-dichlorobenzene (c = 0.01–0.3 M). The ^{13}C NMR spectra were ob-

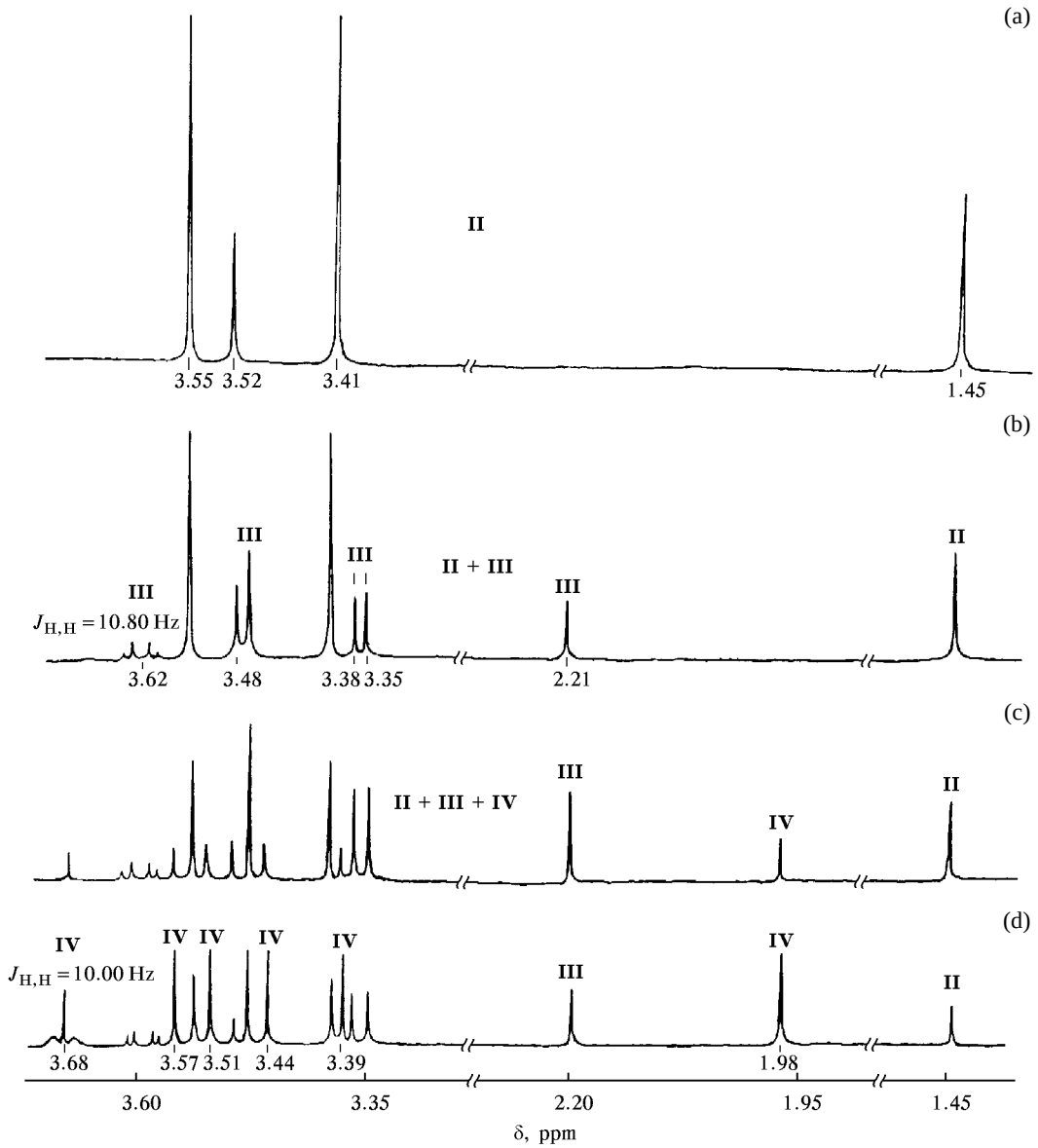


Fig. 4. ^{1}H NMR spectra (360 MHz) of tetramethyl 5-methyl-5-(4-nitrobenzyl)cyclopentadiene-1,2,3,4-tetracarboxylate (**II**) in *o*-dichlorobenzene recorded after heating at 120°C for (a) 0 min, (b) 18 min, (c) 28 min, and (d) 68 min.

tained on a Bruker AM-360 instrument at 90.56 MHz in benzene-d_6 (c = 0.1–0.3 M). The IR spectra were measured on a Specord IR-75 spectrometer from samples dispersed in mineral oil. The Gibbs energies of activation for nondegenerate shifts of the *p*-nitrobenzyl group were calculated by the procedure described previously [9].

Thallium 5-methyl-1,2,3,4-tetrakis(methoxycarbonyl)cyclopentadienide (**I**) was synthesized by reaction of tetramethyl 5-methylcyclopentadiene-1,2,3,4-tetracarboxylate [10] with Tl_2CO_3 according to the procedure reported in [11]. The product was recrystallized from acetone. Yield 80%. Colorless crystals, mp 147–148°C. IR spectrum, ν, cm^{-1}: 1740, 1700, 1680, 1660 (C=O); 1510, 1480 (C=C). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 3.21 s (6H), 3.19 s (6H), 1.58 s (3H). Found, %: C 32.57; H 3.01; Tl 39.01. $C_{14}H_{15}O_8Tl$. Calculated, %: C 32.61; H 2.93; Tl 39.64.

Tetramethyl methyl-5-(*p*-nitrobenzyl)cyclopentadienetetracarboxylates II–IV (mixture of isomers). A solution of 0.003 mol of *p*-nitrobenzyl bromide in 10 ml of dry tetrahydrofuran was added dropwise over a period of 30 min on stirring at room tempera-

ture to 0.003 mol of thallium salt **I** in 30 ml of dry THF. The mixture was stirred for 24 h at room temperature, the precipitate of TlBr was filtered off and washed with 15 ml of THF, and the filtrate was combined with the washings and evaporated to dryness under reduced pressure. According to the ^{1}H NMR data, the residue (a white powder) was an equilibrium mixture of isomers **II**–**IV**. Yield 78%. Isomers **II**–**IV** were separated by column chromatography on Silokhrom silica gel using chloroform as eluent. R_f 0.97 (**II**), 0.75 (**IV**), 0.68 (**III**).

Tetramethyl 5-methyl-5-(4-nitrobenzyl)cyclopentadiene-1,2,3,4-tetracarboxylate (II). Yield 3%. Colorless crystals, mp 121–122°C. IR spectrum, ν, cm^{-1}: 1765, 1740 (C=O); 1640, 1630 (C=C); 1540, 1350 (NO_2). Found, %: C 56.09; H 4.79; N 3.27. $C_{21}H_{21}NO_{10}$. Calculated, %: C 56.37; H 4.73; N 3.13.

Tetramethyl 4-methyl-5-(4-nitrobenzyl)cyclopentadiene-1,2,3,5-tetracarboxylate (III). Yield 15%. Colorless crystals, mp 97–98°C. IR spectrum, ν, cm^{-1}: 1750, 1730, 1720, 1660 (C=O); 1610, 1570 (C=C); 1530, 1350 (NO_2). Found, %: C 56.41; H 4.71; N 3.29. $C_{21}H_{21}NO_{10}$. Calculated, %: C 56.37; H 4.73; N 3.13.

Tetramethyl 3-methyl-5-(4-nitrobenzyl)cyclopentadiene-1,2,4,5-tetracarboxylate (IV). Yield 30%. Colorless crystals, mp 107–108°C. IR spectrum, ν, cm^{-1}: 1760, 1730, 1710 (C=O); 1620, 1610 (C=C); 1530, 1350 (NO_2). Found, %: C 56.39; H 4.69; N 3.08. $C_{21}H_{21}NO_{10}$. Calculated, %: C 56.37; H 4.73; N 3.13.

REFERENCES

1. Dushenko, G.A., Mikhailov, I.E., Reck, G., Schulz, B., Zschunke, A., Kharabaev, N.N., and Minkin, V.I., *Russ. J. Org. Chem.*, 2002, vol. 38, no. 3, pp. 982–994.
2. Mironov, V.A., Fedorovich, A.D., and Akhrem, A.A., *Usp. Khim.*, 1981, vol. 50, no. 7, pp. 1272–1303.
3. Spangler, Ch.W., *Chem. Rev.*, 1976, vol. 76, no. 2, pp. 187–217.
4. Childs, R.F., *Tetrahedron*, 1982, vol. 38, no. 5, pp. 567–608.
5. Wilcott, M.R. and Rathburn, I.M., *J. Am. Chem. Soc.*, 1974, vol. 96, no. 3, pp. 938–939.
6. Borodkin, G.I., Susharin, E.R., and Shubin, V.G., *Zh. Org. Khim.*, 1983, vol. 19, no. 5, pp. 1004–1010.
7. Hansen, P.E., *Progress in Nuclear Magnetic Resonance Spectroscopy*, Emsley, J.W., Feeney, J., and Sutcliffe, L.H., Eds., Oxford: Pergamon, 1981, vol. 14, pp. 175–296.
8. Hoffmann, R.W. and Backes, J., *Chem. Ber.*, 1976, vol. 109, no. 5, pp. 1928–1941.
9. Mikhailov, I.E., Kompan, O.E., Struchkov, Yu.T., Minkin, V.I., Dushenko, G.A., Klenkin, A.A., and Olekhnovich, L.P., *Zh. Org. Khim.*, 1987, vol. 23, no. 5, pp. 1029–1038.
10. Bruce, M.I. and White, A.H., *Aust. J. Chem.*, 1990, vol. 43, no. 6, pp. 949–995.
11. Bruce, M.I., Walton, J.K., Williams, M.L., Hall, S.R., Skelton, B.W., and White, A.H., *J. Chem. Soc., Dalton Trans.*, 1982, no. 11, pp. 2209–2220.