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Proton Magnetic Resonance Spectra of Methyliodothiophenes

Kensuke TAKAHASHI,*[1] Ichi ITO and Yasuo MATSUKI

The Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira-cho, Sendai

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PMR data on seventeen compounds, including all of the iodosubstituted derivatives of 2-, 3-methyl and 2, 3-dimethylthiophenes, were given. The signals of β-hydrogens appear at a rather higher applied magnetic field than those of α-hydrogens, while the β-methyl signals appear at a higher field than do the α-methyl signals. The coupling constants between two ring hydrogens, between ring and methyl hydrogens, and between two methyl hydrogens were described.

In a previous work,1) we have found a Jacobsen-type rearrangement from 2, 3-dimethyl-5-iodothiophene to 4-iodoisomer. This finding led us to make further studies of the Jacobsen-type rearrangement of 2-methyl- and 3-methyliodothiophenes.2) In the course of these studies we have obtained the PMR spectra of a series of methyliodothiophenes. The results of the PMR spectral studies were then used to identify the products obtained by the Jacobsen-type rearrangement.

Experimental

The experimental procedure and apparatus were similar to those described previously.3) Spectra were

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[*1] Present address: Department of Industrial Chemistry, Nagoya Institute of Technology, Gokiso-cho Showa-ku, Nagoya.

1) Y. Matsuki, I. Ito and Y. Miyake, Paper presented at the Tohoku District Meeting of the Chemical Society of Japan, Yonezawa, October, 1961.

2) Y. Matsuki and I. Ito, Papers presented at the 15th and 16th Annual Meetings of the Chemical Society of Japan, Kyoto, April, 1962, and Tokyo, April, 1963.

3) K. Takahashi, Y. Matsuki, T. Mashiko and G. Hazato, This Bulletin, **32**, 156 (1959).

TABLE 1. PMR DATA ON SOME METHYLIODOTHIOPHENE DERIVATIVES IN CARBON TETRACHLORIDE, REFERRED TO CYCLOHEXANE AT 60 Mcps

The values in parentheses show the chemical shifts of methyl hydrogens.

Substituent	Bp (°C/mmHg) or mp	Chemical shift, ppm				Coupling constant, cps	
		2-H	3-H	4-H	5-H	$J_{H,H}$	J_{H,CH_3}
2-Me*, 3-I	83—86/11	(0.99_5)	—	5.46_5	5.55_5	5.1	
2-Me, 4-I	86.5—87.5/11	(1.06)	5.25_5	—	5.63	1.2_5	1.0_5
2-Me, 5-I	93—95/16	(1.03_5)	4.95_5	5.50_5	—	3.7_5	1.0_5
2-Me, 3, 4-I_2	mp 44—45	(1.13)	—	—	5.89_5	—	
2-Me, 3, 5-I_2	mp 46.5—48	(1.00)	—	5.63	—	—	
2-Me, 4, 5-I_2	mp 37.5—38.5	(1.04_5)	5.15	—	—	—	1.1_5
2-Me, 3, 4, 5-I_3	mp 100—101.5	(1.13_5)	—	—	—	—	—
3-Me, 2-I	87—88/16	—	(0.79)	5.21	5.82	5.4	0.5_5
3-Me, 4-I	85—87/12	5.41	(0.82)	—	5.88	3.4	1.1_5
3-Me, 5-I	84—84.5/12	5.40	(0.81)	5.51	—	1.5	1.1_5
3-Me, 2, 4-I_2	mp 59—59.5	—	(0.90)	—	6.09	—	
3-Me, 2, 5-I_2	120.8—121/2.5 (mp 10.5—12)	—	(0.77)	5.41_5	—	—	
3-Me, 4, 5-I_2	98.5/0.5 (mp 15.7—17.2)	5.69	(0.93)	—	—	—	1.0_5
3-Me, 2, 4, 5-I_3	mp 73—75	—	(1.01)	—	—	—	—
2, 3-Me_2, 4-I	mp 38	(0.99_5)	(0.70_5)	—	5.66_5	—	
2, 3-Me_2, 5-I	97—98/11 (mp 23)	(0.87_5)	(0.65_5)	5.36_5	—	—	
2, 3-Me_2, 4, 5-I_2	mp 58	(0.98)	(0.80_5)	—	—	—	—

* Me=CH_3

obtained at 24±1°C and at 60 Mcps. The sweep rate of the magnetic field for chemical-shift measurements was calibrated by measuring the displacement between the two peaks for a benzene-cyclohexane mixture (1 : 1 by volume). The value for this displacement in the present work is taken to be 5.746 ppm. All the compounds studied in this work were prepared by the reaction of the corresponding methyllithium derivatives and iodine, or by the elimination reaction of the higher iodinated compounds. 3-Methyl-5-iodothiophene was not obtained in a pure state but in a mixture with a small amount of another isomer, although several methods were tried in an attempt to prepare and isolate it in the pure state. Details of the Jacobsen-type reactions of these compounds will be published later. All the spectra were taken for samples of about 10 wt% or more dilute solutions in carbon tetrachloride, containing 0.5 wt% cyclohexane as an internal reference.

Results and Discussion

Table 1 shows the findings for the chemical shifts and the coupling constants observed. This illustrates that the signals of β-hydrogens appear at a rather higher magnetic field than those of α-hydrogens, and that the β-methyl signals appear at a higher field than do the α-methyl signals. This tendency may be due to the magnetic anisotropy effect of the sulfur atom in the ring.

The substitution effect has been discussed in benzene derivatives by many authors; this discussion is summarized in Smith's paper.[4] Diehl expressed the effect of the X substituent as $S_{o,x}$ or $S_{m,x}$ and stated that the substitution effects in *p*- and *m*-disubstituted benzenes are additive.[5] This was applied in the case of bromothiophene in one of our previous papers,[6] using the expression $S(X)_{ab}$, where X is a substituent and a and b are the positions of the substituent and of the hydrogen in question respectively. By comparing the chemical shifts of the monosubstituted thiophenes with those of the unsubstituted one, the substitution effects for iodine and methyl groups have been estimated to be as shown in Table 2; that table also gives the values for bromine. From these *S*-values, we can estimate the chemical shifts

TABLE 2. PMR SUBSTITUENT CONSTANTS, $S(X)_{ab}$, IN THIOPHENES IN ppm

The negative value indicates the displacement towards higher applied magnetic field.

Substituent, X	Br	I	CH_3
S_{23}	−0.08	0.13	−0.37
S_{24}	−0.28	−0.32	−0.21
S_{25}	-0.13_5	0.00_5	-0.27_5
S_{32}	-0.12_5	0.01_5	-0.46_5
S_{34}	−0.09	0.02	−0.23
S_{35}	−0.11	-0.17_5	-0.15_5

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4) G. W. Smith, *J. Mol. Spectr.*, **12**, 146 (1964).

5) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).

6) K. Takahashi, T. Sone, Y. Matsuki and G. Hazato, This Bulletin, **38**, 1041 (1965).

Table 3. A comparison between the calculated and observed values of the chemical shifts for disubstituted methyliodothiophenes

Substituent	Position	Chemical shift, ppm	
		δ(calcd)	δ(obs)
2-Me*, 4-I	3-H	5.26	5.25
	5-H	5.61_5	5.63
2-Me, 5-I	3-H	4.92	4.95_5
	4-H	5.53	5.50_5
3-Me, 5-I	2-H	5.41_5	5.40
	4-H	5.51	5.51

* Me = CH_3

of 2, 4- and 2, 5-disubstituted thiophenes (Table 3). The *S*-values in Table 2 were obtained in cyclohexane solutions; then, in Table 3, the *S*-values converted to those for carbon tetrachloride solutions were used, assuming that the chemical-shift changes of α- and β-hydrogens due to the solvent effect were 0.14 and 0.07 ppm for all compounds respectively. In spite of this rough assumption of the solvent dependency of *S*-values, the calculated values agree well with the experimental values.

The observed coupling constants between two ring hydrogens listed in Table 1 have a reasonable magnitude.3,7) The magnitudes of the side-chain coupling constants between the ring- and methyl hydrogens in methyliodothiophenes are similar to those observed in methylthiophenesulfonylchlorides;8) the values of $J_{2\text{-CH}_3,3\text{-H}}$ and $J_{3\text{-CH}_3,2\text{-H}}$ are 1.1 ± 0.1 cps, and those of $J_{2\text{-CH}_3,4\text{-H}}$ $J_{3\text{-CH},4\text{-H}}$ and $J_{3\text{-CH}_3,5\text{-H}}$ are in the order of 0.5 cps. An example of the spectra is shown in Fig. 1, which was taken under high-resolution conditions of our spectrometer. The sample is a mixture of 5- and 2-iodo-3-methylthiophenes in cyclohexane. The signals of a and b in Fig. 1 arise from the 4-hydrogen of the 2-iodo-isomer; these signals show a spin-spin interaction with the 3-methyl hydrogens of about 0.5_5 cps. The same kind of interaction is apparent from the signals of e and f which are due to the 5-hydrogen of the 2-iodo-isomer. The c signal arises from the 2-hydrogen of the 5-iodo-isomer and shows two sorts of splittings, of 1.5 and 1.1_5 cps, which are ascribed to the spin-spin interactions with the 4-hydrogen and with the 3-methyl hydrogens respectively. The d signal is due to the 4-hydrogen of the 5-iodo-isomer and shows a weak interaction of 0.5 cps with the 3-methyl hydrogens. Another point of interest is found in the spectrum of 2, 3-dimethyl-4, 5-diiodothiophene. Two methyl signals of this compound have quartet structures, attributed to the coupling between two methyl hydrogens and with a splitting of 0.6_5 cps, similar to those observed in other thiophenes.9)

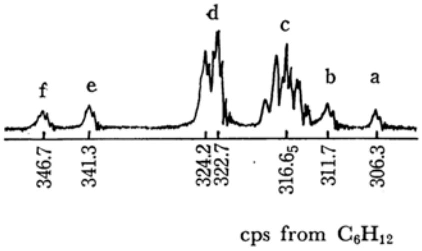

Fig. 1. The proton magnetic resonance spectrum of a mixture of 5- and 2-iodo-3-methylthiophenes in cyclohexane at 60 Mcps. Applied field increases from left to right.

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7) S. Gronowitz and R. A. Hoffman, *Arkiv. Kemi,* **13**, 279 (1958).

8) K. Takahashi, Y. Matsuki, Y. Miyake and G. Hazato, This Bulletin, **34**, 1599 (1962).

9) S. Gronowitz, B. Gestblom and R. A. Hoffman, *Acta Chem. Scand.,* **15**, 1201 (1961).