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UNUSUAL EFFECTS OF STERIC HINDRANCES IN NMR SPECTRA OF o,o'-DIALKYLSUBSTITUTED BENZYLIDENE DICHLORIDES

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Abstract. It has been found that steric hindrances of the $CHCl_2$ group rotation around C_{Ar}-$CHCl_2$ bond in o,o'-dialkylsubstituted benzylidene dichlorides call forth a non-equivalence of the alkyls in positions 2 and 6. The non-equivalence displays in ^1H and ^{13}C NMR spectra at room temperature and at -20 °C. At the latter temperature, the spectra of 2,4,6-trimethyl-3-chloromethylbenzylidene dichloride and bis(dichloromethyl)mesitylene indicate the presence of two conformations, the assignment of signals having been accomplished for each of them.

Introduction

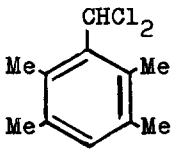
We have found[1] a new route of Rieche reaction: under the action of dichloromethyl methyl ether in the presence of $AlCl_3$ mesitylene gives besides 2,4,6-trimethylbenzaldehyde also respective substituted benzylidene dichloride and products of further formylation and dichloromethylation of the latter. For one of minor products of the reaction, 3-dichloromethyl-2,4,6-trimethylbenzaldehyde a broadening of the signal of 2-methyl group in ^1H NMR spectrum at room temperature was noted. This broadening might be considered as the result of hindered rotation of formyl and (or) dichloromethyl groups. More detailed analysis of ^1H NMR spectra of some other compounds has shown similar broadening for such dichloromethyl-substituted derivatives which do not contain additional functional groups; moreover in the case of dichloromethyldurene (1) o-methyl and o'-methyl groups which seem to be equivalent ones display as two different broad signals.

To our knowledge, these anomalous phenomena in such compounds were not observed previously. In particular, ^1H NMR spectra of more than 40 monosubstituted mesitylenes have been studied in detail[2], none of them however reveals the broadening of ortho-methyl group signals. It should

be noted, nevertheless, that dichloromethylmesitylene was not studied in the report cited[2]. The present paper is devoted to the study of specific steric interactions of dichloromethyl group with neighbouring alkyl groups using ^{1}H and ^{13}C NMR spectra.

Results and Discussion

Six benzene derivatives (1-6) with $CHCl_2$ group shielded by two neighbouring methyl or ethyl groups and differing in their steric overcrowding were chosen for the investigation, ^{1}H and ^{13}C NMR spectra of these compounds beeng studied at room temperature, -20 °C and +50 °C.



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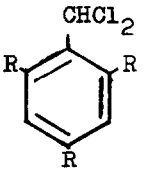
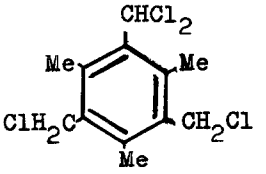


2 R=Me, 3 R = Et



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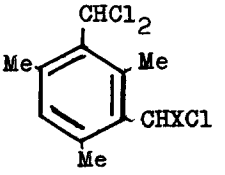
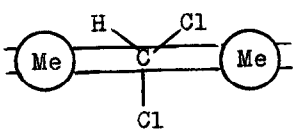
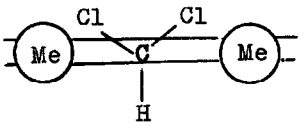


5 X=H, 6 X=Cl

The effects observed in the NMR spectra are undoubtedly conditioned by both the $CHCl_2$ group steric requirement and specific features of its geometry. This follows from the fact that in NMR spectra of similar compounds having more bulky trichloromethyl group, e.g. trichloromethylmesitylene, no broadening of methyl group signals was observed. One may suggest this broadening to be the consequence of hindered inner rotation about C_{Ar}-$CHCl_2$ bond which stipulates the non-equivalence of two neighbouring methyl groups in the conformation a (Scheme 1). In this scheme the "symmetric" conformation b is also pictured in which both chlorine atoms of $CHCl_2$ group located at one of the sides of the benzene ring plane, however, this conformation should be excluded from the consideration because of maximal steric hindrances that make it really incredible.



a



b

Scheme 1

The further limitation of inner rotation at -20 °C leads, in the ^{1}H NMR spectrum of dichloromethylmesitylene 2, to the arising of two relatively narrow signals of ortho-methyl groups remoted by 0.35 ppm and two individual signals of ring protons which are also non-equivalent (Table 1).

Similar effects are observed in the ^{13}C NMR spectrum using total proton decoupling (Table 2). Thus, at room temperature, the spectrum of compound 2 contains a narrow signal of methyl group in the position 4, a broadened one from two ortho-methyl groups, a narrow signal of $CHCl_2$ group, two narrow signals of C-1 and C-4 atoms along with four broad signals from remaining four benzene ring carbon atoms. The spectrum of 2 at -20 °C contains individual narrow signals, each of these corresponds to its own carbon atom.

The ^1H NMR spectrum of dichloride 1 at room temperature displays two very broad signals of ortho-methyl groups which, at -20 °C, change for two narrow signals whereas the increase of the temperature untill +50 °C results in the coalescence of these two into one broad signal (Table 1). The ^{13}C NMR spectrum at +24 °C contains two broadened signals of ortho-Me groups partially separated, a broadened signal of two methyl groups in positions 3 and 5, narrow signals from $CHCl_2$ group, C-1 and C-4 benzene ring atoms, as well as three very broad signals of remaining aromatic cycle carbon atoms. In the spectrum of compound 1 recorded at -20 °C narrow signals correspond to each of 11 carbon atoms.

The shape of NMR spectra described here for dichlorides 1 and 2 also retains in progressing to their more sterically hindered analogs, i.e. 2,4,6-triethylbenzylidene dichloride (3) and 2,4,6-trimethyl-3,5-bis(dichloromethyl)benzylidene dichloride (4). The ^1H NMR spectrum of compound 4 at +20 °C contains a very broadened signal from two ortho-methyl groups which becomes more narrow with increasing the temperature to +50 °C. In the spectrum of 4 at -20 °C, each of three methyl groups and two $CHCl_2$ ones display as the separate signals. The dichloride 3, closely related to compound 2 and differing from that in more bulky substituents in the ortho-positions with respect to the $CHCl_2$ group, reveals two broadened signals of CH_2 groups in the ^1H NMR spectrum at +20 °C, with the signals not narrowing markedly if the temperature is raised to +50 °C. It is of interest that this compound, unlike dichloride 2, shows the non-equivalence of aromatic ring protons at +20 and 50 °C (Table 1). In the ^{13}C NMR spectrum (Table 2), each carbon atom is answered by a separate signal (the broadening of signals is observed at room temperature).

The ^1H NMR spectrum of 2,4,6-trimethyl-3-(chloromethyl)benzylidene dichloride (5) at room temperature contains narrow signals of methyl group in position 4 and of CH_2Cl group, broadened signals of $CHCl_2$ and of the proton in the position 5 of the cycle as well as two very broad signals of methyl groups in the ortho-position to $CHCl_2$ group. At +50 °C, all the signals become more narrow, whereas at -20 °C each of ortho-methyl, CH_2Cl, $CHCl_2$ signals and that of H-5 proton are splitted into nar-

row signals with an intensities ratio 3:1 (Table 1). The ^{13}C NMR spectrum contains signals of all the three methyl groups as well as of chloromethyl and dichloromethyl groups. Only two of the ring carbon atom signals reveal distinctly whereas remaining four atoms are broadened considerably. The spectrum at +20 °C contains a double set of signals from CH_3, CH_2Cl and $CHCl_2$ groups as well as those of almost all C-atoms of the cycle (Table 2).

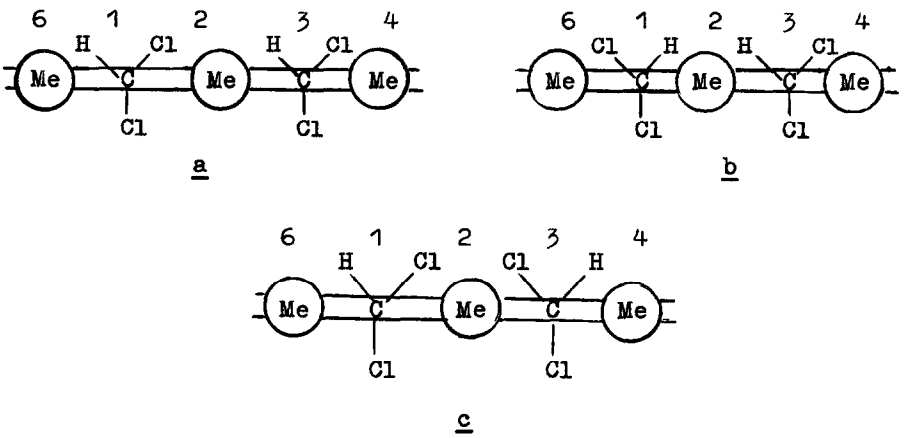
The most interesting are probably the spectra of bis(dichloromethyl)-mesitylene (6). Its ^1H NMR spectrum at room temperature contains two broad signals of methyl groups partially separated and also broadened signals from $CHCl_2$ and aromatic cycle protons. The heating of 6 to +50 °C is followed by nearly full separation of signals of methyl groups and by the narrowing of two other signals. At -20 °C each of methyl groups signals in the spectrum of 6 divides into two narrow singlets; the aromatic proton is presented by two broadened singlets with an intensities ratio 4:1 and, finally, one of $CHCl_2$ groups is answered by two partially separated singlets while the other by a broadened one (Table 1). In the ^{13}C NMR spectrum of 6 at +50 °C, the methyl group disposed between dichloromethyl groups causes the appearance of one signal and two other methyl groups - the other; at +25 °C, both signals are broadened, with two $CHCl_2$ groups being presented by one signal in both cases. At -20 °C, each of signals under consideration separates into two ones; the spectrum also contains 8 signals in the aromatic region, which corroborates the existence of compound 6 as two rotamers.

The assignment of signals from CH_3 groups in the ^{13}C NMR spectra is based on known data[3] on steric γ-effects of substituents at the double bond in benzene and ethylene series. Thus, the comparison of chemical shifts of CH_3 in durene (18.9 ppm) and mesitylene (21.2 ppm)[3] with those of compounds 1 and 2 (Table 2) shows that the introduction of $CHCl_2$ group results in the upfield shift of the CH_3 signals in positions 2 and 6 whereas signals of methyl groups in positions 3 and 5 as well as that of carbon atom in the position 4 of the cycle (in compound 1) show the downfield shift probably due to -I-effect of the substituent. The chemical shift of methyl group in the position 4 of compound 2 does not change essentially.

The confrontation of ^1H NMR spectra of compounds 1 and 2 (Table 1) to the spectra of durene (δ_{Me} 2.19 ppm) and mesitylene (δ_{Me} 2.27 ppm)[3] demonstrates that protons of CH_3 groups which are sterically hindered undergo, as should be expected, the deshielding. Besides, ^1H and ^{13}C NMR spectra display that signals of methyl groups neighbouring to the $CHCl_2$ one are broadened to a greater extent on account of the hindered rotation of the latter as compared with methyl groups more remoted from it. The relative

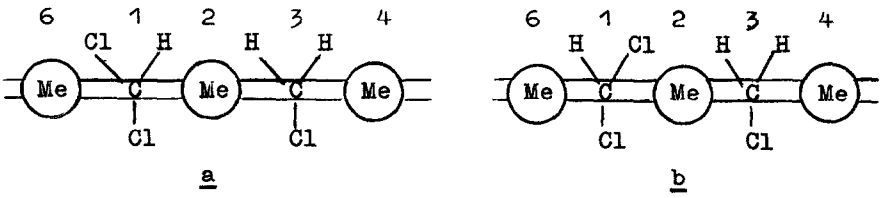
integral intensities and spectral characteristics of (chloromethyl)mesitylene (7) were also taken into account in the assignment of the signals to that or another rotamer of compounds 5 and 6.

The most probable conformations of bis(dichloromethyl)mesitylene 6 are a, b and c (Scheme 2); in this case, just as previously, those conformations are excluded from the consideration which are most strained sterically and have both chlorine atoms of $CHCl_2$ groups located at one of the benzene ring plane sides. Unlike the conformation a, 4-Me and 6-Me should be equivalent in the b and c conformations where the plane of symmetry is common for C-2 and C-5 atoms. Therefore the signals of greater intensities in the ^{13}C NMR spectrum (17.13, 20.72 and 20.98 ppm) should be assigned to three non-equivalent groups: 2-Me, 4-Me and 6-Me in the a conformation; in the ^{1}H NMR spectrum, these groups are presented by signals at 2.78, 2.76 and 2.41 ppm. The remaining signals of lower intensities from 2-Me group (17.89 ppm in ^{13}C and 3.16 ppm in ^{1}H NMR spectra) should be referred, in our opinion, to the more preferable of two other conformations, i.e. to the conformation b. Signals of equivalent, in this case, 4-Me and 6-Me groups apparently coinside with signals of main conformer a.



Scheme 2

Based on a similar consideration, one may believe that the more intence signals in the spectra of compound 5 at -20 °C (first lines in Tables 1 and 2) refer to the conformation a (Scheme 3) with Me-group less sterically hindered, whereas less intensive signals (second lines, Tables 1 and 2) belong to the conformation b in which this group is more sterically overcrowded.



Scheme 3

Table 1. ^{1}H NMR Spectra of Substituted Dichlorides 1-6 and Chloride 7

Compound	Temperature, °C	Chemical shifts, ppm							
		2-Me ($2\text{-}CH_2$)	3-Me / 5-Me (4-Alk)	6-Me ($6\text{-}CH_2$)	$CHCl_2$	CH_2Cl	3-H	4-H	5-H
1	20	2.70*	2.36s / 2.36s	2.40*	7.45s	-	-	7.12s	-
	50	2.55*	2.35s / 2.35s	2.55*	7.45s	-	-	7.11s	-
	-20	2.66s	2.31s / 2.31s	2.38s	7.41s	-	-	7.09s	-
2	20	2.60 br.	2.30s	2.60 br.	7.22s	-	6.90s	-	6.90s
	-20	2.81s	2.36s	2.46s	7.28s	-	7.04s	-	6.90s
3	20	1.35m* (3.20*)	1.30q** (2.65t**)	1.35m* (2.75*)	7.23s	-	7.09br.	-	6.84br.
	50	1.32* (3.20*)	1.28t** (2.65q**)	1.32* (2.75*	7.24s	-	7.06*	-	6.88*
4	20	2.66*	2.54s	2.66*	7.33s	4.70s	-	-	-
	50	2.69*	2.53s	2.69*	7.34s	4.70s	-	-	-
	-20	2.82s	2.53s	2.50s	7.32s	4.71s 4.67s	-	-	-
5	25	2.75*	2.44s	2.48*	7.26s	4.70s	-	-	6.94s
	50	2.71 br.	2.43s	2.54 br.	7.27s	4.68s	-	-	6.94s
	-20	a 2.84s	2.44s	2.42s	7.22s	4.70s	-	-	6.92s
		b 2.77s	2.44s	2.49s	7.33s	4.67s	-	-	7.04s
6	25	2.80 br.	2.55*	2.55*	7.25 br.	-	-	-	6.94 br.
	50	2.83 br.	2.57 br.	2.57 br.	7.27s	-	-	-	6.94s
	-20	a 2.78s	2.76s	2.41s	7.35s 7.19s	-	-	-	6.97s
		b 3.16s	2.41s	2.41s	7.35s	-	-	-	6.87s
7	-20	2.56s	2.44s	2.56s	-	4.80s	7.05s	-	7.05s

* A broad signal.
** J = 7 Hz.

Table 2. ^{13}C NMR Spectra of Substituted Dichlorides 1-6 and Chloride 7

Compound	Temperature, °C	Chemical shifts, ppm					
		2-Me ($2\text{-}CH_2$)	3-Me / 5-Me / 4-Alk	6-Me ($6\text{-}CH_2$)	$CHCl_2$	CH_2Cl	Carbon atoms of benzene ring
1	20	15.52 br.	20.50 / 20.50	16.84*	68.83	-	135.85 (1-C); 135.5*; 133.33 (4-C); 129.5*
	-20	15.40	20.42 / 21.04	17.14	68.67	-	135.52 (1-C); 136.50; 133.47; 133.30 (4-C); 134.83; 129.58
2	21	20.17 br.	20.95	20.17 br.	68.30	-	132.94 (1-C); 133.5*, 139.0* (2-C, 6-C); 139.64 (4-C); 131.76*, 129.07* (3-C, 5-C)
	-20	20.17	21.03	20.42	68.14	-	128.75, 131.87 (3-C, 5-C); 132.55 (1-C); 133.43, 138.72 (2-C, 6-C); 146.09 (4-C)
3	-20	15.39 (25.10)	16.31 (28.51)	15.98 (27.78)	67.49	-	126.22, 129.17 (3-C, 5-C); 132.15 (1-C); 139.63, 145.28 (2-C, 6-C); 146.09 (4-C)
4	24	16.43 br.	15.62	16.43 br.	68.00	41.40	135.27; 139.32; 134.9*
	-20	15.97	15.74	17.13	67.85	41.27 41.82	132.39; 134.21; 134.91; 135.12; 139.28; 139.39
5	25	16.10 br.	19.52	20.38 br.	68.10	41.04	139.29; 134.42; 131*; 135*; 139*
	50	15.82 br.	19.42	20.31	68.18	41.00	139.31; 134.59; 131*; 135*; 139*
	-20 a	16.63	19.87	20.69	68.12	41.28	130.84; 133.43; 134.39; 134.48; 134.91; 138.89; 139.63; 132*; 134*; 139.5*
	b	15.57	20.09	21.01	68.44	41.80	
6	25	16.81 br.	20.47	20.47	67.69	-	130*; 133*; 135.5*; 140.5*
	50	16.79 br.	20.43	20.43	67.81	-	130*; 133*; 135.5*; 140.5*
	-20 a	17.13	20.72	20.98	67.85	-	130.57; 133.24 (5-C); 133.76; 134.98; 135.46; 135.86; 140.86
	b	17.89	20.72	20.72	67.73		
7	27	19.13	21.02	19.13	-	41.15	129.22 (3-C, 5-C); 131.12 (1-C); 137.39 (2-C, 6-C); 138.40 (4-C)
	-20	19.23	21.08	19.23	-	41.22	129.12 (3-C, 5-C); 130.93 (1-C); 137.30 (2-C, 6-C); 138.44 (4-C)

*A broad signal.

Experimental

^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker AM-300 spectrometer (300 MHz for protons). Chemical shifts were measured with respect to the solvent (7.27 and 77.1 ppm, respectively).

The preparation of 2,4,6-trimethylbenzylidene dichloride (2), 3-(chloromethyl)-2,4,6-trimethylbenzylidene dichloride (5) and 1,3-bis(dichloromethyl)mesitylene (6) was described previously[1]. 2,4,6-Trimethylbenzyl chloride (7) was prepared using known procedure[5].

2,3,5,6-Tetramethylbenzylidene dichloride (1) and 2,4,6-triethylbenzylidene dichloride (3) were prepared in 95-96% yields similarly to the compound 2 using the action of PCl_5 on respective aldehydes[6]. Dichloride 1, m.p. 105-106 °C (from hexane). Found: C 60.92, H 6.66, Cl 32.27%. $C_{11}H_{14}Cl_2$ calcd.: C 60.84, H 6.50, Cl 32.66%. Dichloride 3, b.p. 140-143 °C (5 mm Hg), n_D^{20} 1.5380. Found: C 63.34, H 7.60, Cl 28.87%. $C_{13}H_{18}Cl_2$ calcd.: C 63.68, H 7.40, Cl 28.92%.

3,5-Bis(chloromethyl)-2,4,6-trimethylbenzylidene dichloride (4). A solution of 10.59 g (0.092 mol) of dichloromethyl methyl ether and 10.0 g (0.046 mol) of bis(chloromethyl)mesitylene[7] in 100 ml of CH_2Cl_2 was added to a stirred solution of 20 ml (0.184 mol) of $TiCl_4$ in 100 ml of CH_2Cl_2 at room temperature, the stirring mixture was boiled for 1.5 h, then poured onto ice and washed with 2N HCl (3x150 ml). After the solvent had been removed, the residue was recrystallized from 80 ml of hexane-benzene mixture (3:1) to give 7.23 g (66%) of 3,5-bis(chloromethyl)-2,4,6-trimethylbenzaldehyde (9), m.p. 96-97 °C. Found: C 58.73, H 5.88, Cl 28.86%. $C_{12}H_{14}Cl_2O$ calcd.: C 58.79, H 5.75, Cl 28.92%. Reaction of 1 g (4 mmol) of aldehyde 9 with 1.2 g (6.0 mmol) of PCl_5 in 50 ml of CH_2Cl_2 (20 °C, 1.5 h) affords 1.2 g (98%) of compound 4, m.p. 162-164.5 °C. A pure sample of dichloride 4 was obtained by recrystallization from hexane - benzene mixture (1:1), m.p. 163-164-5 °C. Found: C 48.40, H 4.82, Cl 46.97%. $C_{12}H_{14}Cl_4$ calcd.: C 48.03, H 4.69, Cl 47.26%.

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