FORMYL AND FORMYLVINYL DERIVATIVES OF 2-METHYLENEBENZO-1,3-DITHIOLE

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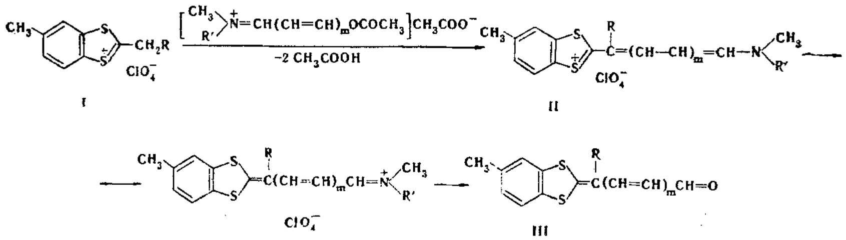
UDC 547.738:543.422.25.6'52

2,5-Dimethyl- and 2-ethyl-5-methyl-1,3-benzodithiolium perchlorates react with dimethylformamide and N-phenyl-N-methylaminoacrolein to give monoiminium salts, the hydrolysis of which yields the corresponding aldehydes. The trans-transoid structure of β-formylvinyl-substituted 2-methylenebenzo-1,3-dithioles was established by a comparison of the experimental and calculated dipole moments, absorption maxima, and intensities of the electron transitions and also by analysis of the PMR spectra.

The possibility of extension of the Vilsmeier reaction to the formylation of compounds with activated methyl or methylene groups in the composition of the heterocyclic cation was previously demonstrated in [1, 2].

In the present paper we describe formyl and formylvinyl derivatives of the heterocyclic series obtained on the basis of 1,3-benzodithiolium salts.

The formylation and vinylformylation reactions were accomplished via the following scheme:



a R=H, R'=CH$_3$, m=0; b R=H, R'=C$_6$H$_5$, m=1; c R=R'=CH$_3$ m=0; d R=CH$_3$, R'=C$_6$H$_5$, m=1

1,3-Benzodithiolium iminium salts II were obtained in quantitative yields by heating 2-methyl- and 2-ethyl-1,3-benzodithiolium perchlorates I with an excess of the formylating agents [dimethylformamide (DMFA) and N-phenyl-N-methylaminoacrolein] in acetic anhydride. Monoiminium salts II are readily hydrolyzed to aldehydes III in alkaline media. The characteristics of the compounds obtained are presented in Table 1.

In [3] it is shown by means of an evaluation of the electronic energies by the Pariser–Parr–Pople (PPP) method [4] and the energies of the nonvalent interactions by the Kitaigorodskii potentials [5] that the trans-transoid conformation is energically advantageous for polyene aromatic aldehydes. This conclusion was confirmed by an analysis of the dipole moments.

It seemed of interest to verify this regularity in the case of the synthesized polyenes of the IIIb,d types and also to obtain information regarding the electron structures of these compounds. In this connection we studied their PMR and UV spectra and dipole moments.

Rostov State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1485-1488, November, 1974. Original article submitted September 11, 1973.

TABLE 1. Products of the Formylation and Vinylformylation of 1,3-Benzodithiolium Salts

Compound	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	S	C	H	S	
IIa	217—218	$C_{12}H_{14}ClNO_4S_2$	43,1	4,0	18,8	43,0	4,2	19,1	70
IIIa*	86—87	$C_{10}H_8OS_2$	57,6	4,0	30,5	57,7	3,8	30,8	75
IIb	210—211	$C_{19}H_{18}ClNO_4S_2$	53,8	4,0	15,5	54,0	4,2	15,1	80
IIIb	132—133	$C_{12}H_{10}OS_2$	61,4	4,4	26,9	61,6	4,3	27,4	45
IIc	216—217	$C_{13}H_{16}ClNO_4S_2$	44,5	4,3	18,6	44,7	4,6	18,3	85
IIIc†	107—108	$C_{11}H_{10}OS_2$	59,3	4,6	28,6	59,5	4,5	28,8	42
IId	209—210	$C_{20}H_{20}ClNO_4S_2$	54,7	4,4	14,9	54,9	4,6	14,6	78
IIId	159—160	$C_{13}H_{12}OS_2$	62,8	4,7	25,5	63,0	4,8	25,8	55

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* PMR spectra (δ): 2.3 (singlet, CH_3–Ar), 6.5 (doublet HC=C), 7.1 (multiplet, H–Ar), and 9.37 ppm (doublet, HC=O).

† PMR spectra (δ): 2.3 (singlet, CH_3–Ar), 2.0 (singlet CH_3–C), 7.1 (multiplet, H–Ar), and 9.3 ppm (singlet, HC=O).

TABLE 2. Dipole Moments of Aldehydes IIIc,d (in Dioxane)

Compound	α	β	R	P_∞	μ_{exp}	μ_π	μ_{calc}
IIIc	10,35	1,45	62,706	595,667	5,10	3,32	4,80
IIId	17,54	2,24	66,496	701,880	5,57	4,00	5,46

TABLE 3. Calculation of the Electronic Absorption Spectra of Aldehydes IIIc,d (the energies of the electron transitions are indicated in electron volts, and the oscillator forces are indicated in parentheses)

Compound	Energy of the excited state	Exptl. E(f)	Calc. E(f)
IIIc	S_1	3,41 (0,15)	3,74 (0,16)
	S_2	—	4,08 (0,02)
IIId	S_1	3,12 (0,29)	3,43 (0,31)
	S_2	3,81 (0,02)	3,99 (0,03)

The position and multiplicity of the signals of the protons attached to the β-carbon atoms, which are overlapped by the signals of the multiplet of the aromatic protons, in the PMR spectra of IIIb,d were determined by the INDOR method. Typical INDOR spectra are presented in Figs. 1 and 2. The spin–spin constants of the protons attached to the α,β-carbon atoms (J 14.7 Hz) in IIIb,d are in agreement with their trans configuration. Variation of the temperature from 30-185° (in hexachlorobutadiene) does not have a substantial effect on the form of the spectrum.

The experimental dipole moments, absorption maxima, and intensities of the electron transitions (Fig. 3) are in satisfactory agreement with the calculated dipole moments and the spectral characteristics for the trans-transoid structure (Tables 2 and 3).

It can be seen that the long-wave electron transmission is a band involving charge transfer from the sulfur atoms to the adjacent carbon atom and carbonyl oxygen atom through the polyene chain. The next electron transition is localized in the aromatic ring.

EXPERIMENTAL

The PMR spectra of hexachlorobutadiene solutions of the compounds were recorded with a Tesla 487C spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The electronic spectra of 10^{-4}-10^{-5} mole/liter solutions of the compounds in propyl alcohol were recorded with a Specord UV-vis spectrometer. The dipole moments were determined in dioxane at 25°. The capacitances of the solutions were measured with an E12-1A apparatus. The polarization at infinite dilution (P_∞) was calculated from the Hedestrand formula [6]. The molecular refractions were calculated as the sums of the refractions of the bonds, and the atomic refractive polarization was disregarded.

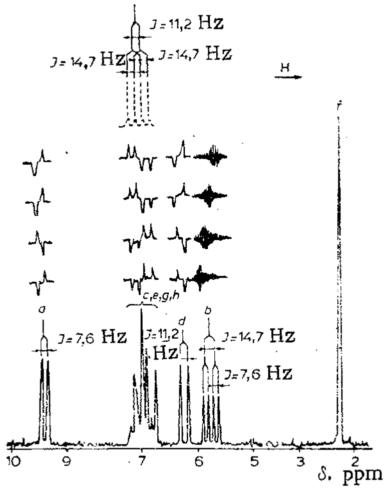


Fig. 1. PMR spectra of IIIb.

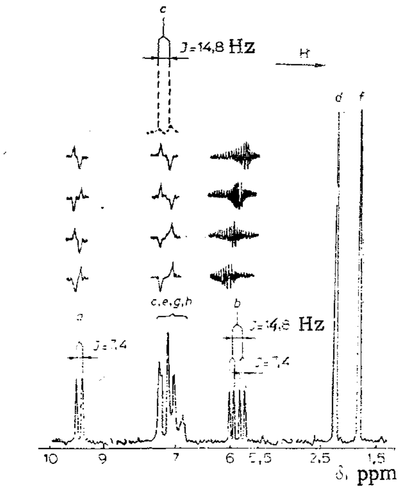


Fig. 2. PMR spectra of IIId.

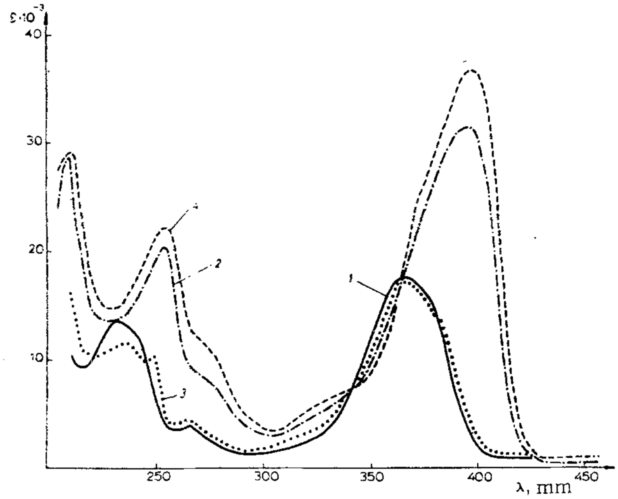
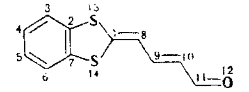


Fig. 3. Electronic spectra of aldehydes: 1) IIIa; 2) IIIb; 3) IIIc; 4) IIId.

The electron distributions, dipole moments, and spectral characteristics of III were calculated by the self-consistent field (SCF) MO method within the PPP approximation. The principal details of the calcula-

TABLE 4. Distribution of the Charges in the Ground (N), First Singlet (S_1), and Second Singlet (S_2) Excited States of Aldehydes

IIIa,b



Atom No.	IIIa			IIIb		
	N	S_1	S_2	N	S_1	S_2
1	0,067	−0,303	0,063	0,034	−0,282	−0,127
2	−0,010	0,034	−0,020	−0,090	0,015	−0,029
3	−0,040	−0,060	−0,036	0,042	0,218	0,269
4	0,001	0,022	−0,001	−0,009	0,015	−0,029
5	0	0,018	−0,002	−0,005	−0,005	−0,016
6	−0,004	−0,002	−0,036	—	0,012	0,017
7	−0,012	0,033	−0,020	−0,001	0,009	−0,007
8	−0,041	−0,077	−0,034	−0,006	−0,003	−0,001
9	—	—	—	0,062	−0,142	−0,027
10	—	—	—	−0,025	−0,077	−0,012
11	0,294	0,070	0,291	−0,010	0,014	0,006
12	−0,378	−0,516	−0,378	−0,379	−0,464	−0,412
13	0,044	0,284	0,084	0,042	0,218	0,269
14	0,044	0,442	0,089	0,042	0,319	0,284

tion were previously set forth in detail in [7]. The geometrical characteristics of the dithiole fragment were taken from the results of x-ray diffraction analysis [8]. The σ moments were calculated from the moments of the bonds with the parameters in [9].

Iminium salts II (Table 1) were obtained by heating a mixture of 0.01 mole of the appropriate dithiole salts [10] with a five- to tenfold excess of the formylating agent (DMFA or N-phenyl-N-methylaminoacrolein) in acetic anhydride at 100° for 3-5 min. The mixture was cooled and diluted with ether, and the precipitate was removed by filtration and crystallized from glacial acetic acid.

The iminium salts were hydrolyzed in acetonitrile solution with excess 2 N KOH solution. The mixture was stirred at room temperature for 4 h, after which it was diluted with water and extracted with ether or benzene. The extract was washed with water and dried with anhydrous sodium sulfate. The solvent was vacuum evaporated, and the residue was diluted with chloroform and chromatographed with a column filled with aluminum oxide in chloroform. The chloroform was removed by distillation until the product began to crystallize intensively. Aldehydes III (Table 1) were crystallized from carbon tetrachloride.

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