

## SYNTHESES IN THE FIELD OF 5-NITRO-2-FURYLPOLYALKENALS AND 5-NITRO-2-FURYLPOLYALKENONES

VIII\*. Synthesis and Electronic and Vibrational Spectra of Some  $\omega$ ,  $\omega'$ -Bis-(5-nitro-2-furyl)polyalkenones\*\*

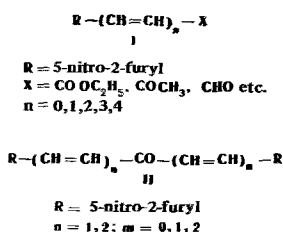
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Khimiya Geterotsiklicheskikh Soedinanii, Vol. 4, No. 3, pp. 405-412, 1968

UDC 547.722.5'727.07:543.422.4.6

A series of  $\omega$ ,  $\omega'$ -bis(5-nitro-2-furyl)polyalkenones has been synthesized by the condensation of 5-nitro-2-furylalkenones with 5-nitro-furan aldehydes in acetic acid (concentrated sulfuric acid catalyst). In the  $\omega$ ,  $\omega'$ -bis(5-nitro-2-furyl)polyalkenone series, the keto group acts as a partial insulator of conjugation, which is shown most clearly in the case of 1,3-bis(5'-nitro-2'-furyl)prop-2-en-1-one and 1,5-bis(5'-nitro-2-furyl)-penta-2,4-dien-1-one, i.e. compounds having the keto group directly linked to a 5-nitrofuran ring. The electronic spectra of the semicarbazones of the  $\omega$ ,  $\omega'$ -bis(5-nitro-2-furyl)polyalkenones exhibit a stronger disturbing effect of the conjugation in the molecule than in the case of the ketones, which may be connected with a disturbance of coplanarity. In a number of cases, the infrared spectra of the  $\omega$ ,  $\omega'$ -bis(5-nitro-2-furyl)polyalkenones exhibit splitting of the symmetrical and antisymmetrical vibrations of the nitro group.

Using functional derivatives of 5-nitro-2-furyl-polyalkenes of type I as examples, we have previously [3, 4] investigated the influence of the length of the chain of conjugation and of terminal substituents on the electronic and vibrational spectra of these compounds.



In development of the preceding work, we have studied a carbonyl-containing polyene system having a 5-nitrofuryl radical at each end of the polyene chain. Of the  $\omega$ ,  $\omega'$ -bis(5-nitro-2-furyl)polyalkenones of type II considered in the present paper, before the beginning of our investigations only 1,5-bis(5'-nitro-2'-furyl)penta-1,4-dien-3-one (II, n = m = 1) had been studied [5-9].

The symmetrical and asymmetrical ketones II are extremely interesting models of conjugated electronic systems for spectroscopic investigations. From the point of view of electron spectroscopy, all the structural elements of the molecules of the compounds studied are chromophores: the nitro group, the furan ring, the carbonyl group, and the conjugated ethylenic

bonds. All these groups are more or less closely conjugated and come into complex interaction. The electron-accepting properties of the individual structural elements of the molecules are also distributed in an extremely peculiar manner. The terminal groups themselves exhibit conjugation of the strongly electron-accepting nitro groups with the electron-donating furan ring and are connected by a "bridge" of ethylenic bonds and a ketonic carbonyl group. In these circumstances the latter is, as was shown previously [10, 11], only an incomplete insulator of intramolecular interactions.

Two limiting cases may be considered as the starting point of the investigation: a) the two terminal 5-nitrofuryl radicals completely isolated from one another, as is the case in bis(5-nitro-2-furyl) sulfide (III). The spectrum of this compound differs from the spectrum of 5-nitrofuran only by the doubled intensity of the bands, with a very slight displacement [12]; b) the two terminal 5-nitrofuryl radicals directly conjugated, as is the case (see Fig. 1) in 5,5'-dinitrobifuryl (IV). Here the general pattern of the structure of the spectra of the 5-nitrofurans is preserved, but there is a marked bathochromic shift of the long-wave band and strong hyperchromism as compared with the spectrum of 5-nitrofuran.



The compounds of type II that we have studied exhibit various intermediate effects. On the one hand, in the asymmetric  $\omega$ ,  $\omega'$ -bis(5-nitro-2-furyl)polyalkenones the keto group located close to a nitrofuran ring acts as a kind of potential barrier, which is shown in the presence of two dissimilar electronic systems of the corresponding parts of the molecule on the two sides of the keto group. For example, for compound II, n = 1, m = 0, and for II, n = 2, m = 0, in the long-wave region of the electronic spectra there are two absorption maxima (at 365 and 315 nm and at 395 and 315 nm, respectively) which are extremely close to the corresponding values for aldehydes and ketones of type I containing only one 5-nitrofuran group, i.e. compounds Ia, n = 1; Ib, n = 1; Ia, n = 0; Ib, n = 0; Ia, n = 2; and Ib, n = 2 (see Table 1).

On the other hand, in the spectra of the ketones II some bathochromic shift is nevertheless observed in comparison with their mono-5-nitrofuryl analog I, which can be explained by the appearance of a "residual" conjugation effect taking place through the keto group.

\*For part VII, see [1].

\*\*Preliminary results of the present investigation were given for the first time at the 2-nd All-Union Scientific Conference on the Chemistry of Furan Compounds, Saratov, 23-26 January, 1962, see [2].

It must be mentioned that in the case of compound II,  $n = 2$ ,  $m = 1$ , we have been unable to detect any splitting of the long-wave band in the electronic spectra into two maxima. This is apparently due to the fact that as the keto group recedes from the furan ring the steric hindrance to the favorable relative position of the  $\pi$ -electron systems of the keto group and the polyene chain, becomes weaker, which facilitates the transfer of the mutual electronic influence.

On the other hand, in the absorption spectra of the symmetrical ketones II,  $n = m = 1$  and II,  $n = m = 2$ , as was to be expected, no splitting of the long-wave band is observed and the electronic spectrum of these compounds gives the pattern characteristic for derivatives of 5-nitrofuran, which we have studied in detail previously [3,12] and the developing intense long-wave and the less intense shortwave band.

On comparing the 5-nitropyran ketones that we have studied with the corresponding furans and aromatic compounds it is easy to find definite laws in the change of the long-wave absorption maximum. Thus, for example, while chalcone [1,3-bis(phenyl)prop-2-en-1-one] has its absorption maximum at 310 nm [10,11], the corresponding figures for 1,3-bis(2'-furyl)prop-2-en-1-one and for 1,3-bis-(5'-nitro-2'-furyl)prop-2-en-1-one (II,  $n = 1$ ,  $m = 0$ ) are 351 and 365 nm, respectively. We, see therefore, that the long-wave absorption band in the series of terminal substituents phenyl-, 2-furyl-, and 5-nitro-2-furyl- shifts successively in the direction of shorter waves. It is worthy of note that the bathochromic contribution of the nitro group is comparatively small, 14 nm. A similar shift in the maxima is observed in the following sequence: 1,5-bis-phenylpenta-1,4-dien-2-one, 1,5-bis(2'-furyl)penta-1,4-dien-3-one, and 1,5-bis(5'-nitro-2'-furyl)penta-1,4-dien-3-one, II,  $n = m = 1$ , where the corresponding values of the long-wave absorption maximum are: 320, 370, and 375 nm.

A similar effect is observed in the furan analogs and vinylogs of chalcone [10,11]. The analysis of this phenomenon has led the authors of these studies to the conclusion that in these molecules there are "separate chromophores" and that each band must be assigned to transitions within distinct electronic systems. The opinions of the authors differ only with respect to the question of the assignment of the bands to the particular functional groups in the molecules.

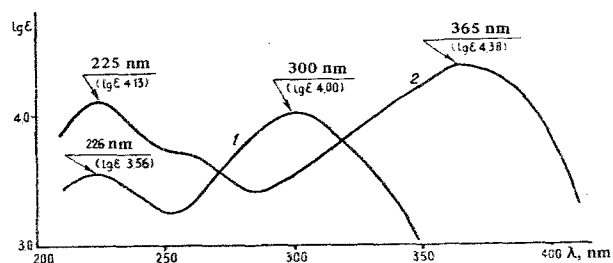


Fig. 1. Electronic absorption spectra of 2-nitrofuran (1) and 5,5'-dinitrobifuryl (2) (in ethanol).

However, careful investigations carried out subsequently, in particular investigations of the dich-

roism of the electron bands, the analysis of the vibrational structure of the bands at low temperatures,

Table 3  
Frequencies of the Symmetrical ( $\nu^S$ ) and Antisymmetrical ( $\nu^{aS}$ ) Vibrations of the Nitro Group

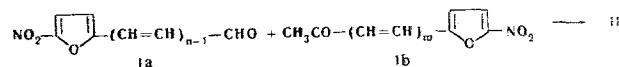
Ketones II		$\nu^S_{\text{NO}_2}, \text{cm}^{-1}$	$\nu^{aS}_{\text{NO}_2}, \text{cm}^{-1}$
$n$	$m$		
1	0	1360	1540; 1550
1	1	1350; 1360	1510; 1520
2	0	1356; 1370	1520; 1537
2	1	1350; 1365	1510
2	2	1358; 1373	1520

and the study of the Raman spectra [13,14] and the infrared absorption spectra [4] and, finally, quantum-mechanical calculations compel a reconsideration of this point of view. More convincing is a treatment of the bands as the result of various electronic transitions within a single  $\pi$ -electronic system extending throughout the molecule. The relative "stability" of the shortwave band is explained by the relatively constant position of the higher free electronic levels, as is confirmed by calculations that will be published in one of our future communications. A curious pattern is observed in the electronic absorption spectra of the semicarbazones of the  $\omega$ ,  $\omega'$ -bis(5-nitro-2-furyl) polyalkenones that we have obtained (see Table 2).

Even the semicarbazone of 1,3-bis(5'-nitro-2'-nitro-2'-furyl)prop-2-en-1-one (V) gives an absorption pattern differing little from the electronic spectrum of the semicarbazone of 5-nitrofurfural (IX) although, at first sight it would appear that the spectrum should exhibit a considerable bathochromic shift. This phenomenon appears successively also in the semicarbazones of VI and VII. Even in the vinylog with the longest polyene chain, absorption is no higher than in the semicarbazones of  $\beta$ -(5-nitro-2-furyl)acrolein (X) and 1-(5'-nitro-2'-furyl)-penta-2,5-dienal (XI). An explanation of this may be given by the assumption of pronounced steric hindrance introduced into the system of conjugation of the molecule of the semicarbazide grouping which, evidently, leads to an enhancement of the disturbance of coplanarity.

The features of the conjugated systems of the ketones II containing two 5-nitrofuran groupings that have been considered also appear in the infrared spectra. In contrast to the IR spectra of the mono-5-nitrofuran compounds of type I that we studied previously [4], a splitting of the bands of the symmetrical and antisymmetrical vibrations of the nitro group is observed, as can be seen from Table 3.

So far as concerns the synthesis of the symmetrical and antisymmetrical ketones of type II that we have studied, they were obtained by the proton-catalyzed condensation of the 5-nitro-2-furylalkenals Ia ( $n = 1, 2$ ) with the 5-nitro-2-furylalkenones Ib ( $m = 0, 1, 2$ ).



As catalyst, we used concentrated sulfuric acid and as solvent acetic acid.

Table 1

Electronic Spectra of Some  $\omega, \omega'$ -Bis(5-nitro-2-furyl)polyalkenones (II),  
5-Nitro-2-furylopolyalkenals (Ia), and 5-Nitro-2-furylopolyalkenones (Ib)

Compound*	$\lambda_{\max}$ , nm (log $\epsilon$ )**
R-CH=CH-CO-R (II, $n=1$ ; $m=0$ )	365 (4.43), 315 (4.23), 235 (4.10)
R-CH=CH-CHO (Ia, $n=1$ )	345 (4.28), 279 (3.79), 240 (4.03)
R-CH=CH-CO-CH <sub>3</sub> (Ib, $n=1$ )	340 (4.30), 285 (3.88), 239 (4.14)
R-CHO (Ia, $n=0$ )	310 (4.05), 226 (3.58)
R-COCH <sub>3</sub> (Ib, $n=0$ )	299 (4.00), 221 (3.88)
R-(CH=CH) <sub>2</sub> -CO-R (II, $n=2$ ; $m=0$ )	395 (4.57), 315 (4.18), 230 (4.10)
R-(CH=CH) <sub>2</sub> -CHO (Ia, $n=2$ )	377 (4.50), 270 (4.20), 225 (3.75)
R-(CH=CH) <sub>2</sub> -CO-CH <sub>3</sub> (Ib, $n=2$ )	377 (4.41), 274 (4.17)
R-(CH=CH) <sub>2</sub> -CO-CH=CH-R (II, $n=2$ ; $m=1$ )	395 (4.65), 230 (4.12)
R-CH=CH-CO-CH=CH-R (II, $n=m=1$ )	375 (4.58), 240 (4.23)
R-(CH=CH) <sub>2</sub> -CO-(CH= =CH) <sub>2</sub> -R (II, $n=m=2$ )	410 (4.73), 270 (4.23)

\*R = 5-nitro-2-furyl.

\*\*In ethanol.

Table 2

Electronic Spectra of the Semicarbazones of  $\omega, \omega'$ -Bis(5-nitro-2-furyl)-  
polyalkenones and 5-Nitro-2-furylopolyalkenals

Compound*	$\lambda_{\max}$ , nm (log $\epsilon$ )
R-CH=CH-C(=NNHCONH <sub>2</sub> )-R (V)**	369 (4.40), 255 (4.05)
R-CH=CH-C(=NNHCONH <sub>2</sub> )-CH=CH-R (VI)**	379 (4.66), 293 (4.21), 260 (4.15)
R-(CH=CH) <sub>2</sub> -C(=NNHCONH <sub>2</sub> )-R (VII)**	385 (4.57), 269 (4.28)
R-(CH=CH) <sub>2</sub> -C(=NNHCONH <sub>2</sub> )-CH=CH-R (VIII)**	390 (4.64), 280 (4.42)
R-CH=NNHCONH <sub>2</sub> (IX)***	367 (4.28), 264 (4.10)
R-CH=CH-CH=NNHCONH <sub>2</sub> (X)***	389 (4.36), 292 (4.29), 245 (3.93)
R-(CH=CH) <sub>2</sub> -CH=NNHCONH <sub>2</sub> (XI)***	413 (4.47), 313 (4.45), 240 (3.89)

\*R = 5-nitro-2-furyl.

\*\*In a mixture of dimethylformamide (5 ml) and ethanol (95 ml). The semicarbazones were first dissolved in the dimethylformamide and the solution was then diluted with the ethanol.

\*\*\*In ethanol.

Table 4

 $\omega, \omega'$ -Bis(5-nitro-2-furyl)polyalkenones II and Their Semicarbazones

Compound		Mp, °C (decomp)	Empirical formula	Found, %			Calculated, %			Yield, %
<i>n</i>	<i>m</i>			C	H	N	C	H	N	
Ketones										
1	0	205—207	C <sub>11</sub> H <sub>6</sub> N <sub>2</sub> O <sub>7</sub>	47.16	2.30	9.99	47.49	2.17	10.07	77
1	1	199*	—	—	—	—	—	—	—	56
2	0	208—210	C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O <sub>7</sub>	51.57	2.63	9.14	51.33	2.65	9.21	46
2	1	196—197	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>7</sub>	54.64	3.22	8.74	54.58	3.03	8.48	55
2	2	240	C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>8</sub>	58.42	3.40	7.55	58.41	3.39	7.86	30
Semicarbazones of the ketones										
1	0	247	C <sub>12</sub> H <sub>9</sub> N <sub>5</sub> O <sub>7</sub>	—	—	21.18	—	—	20.89	—
1	1	237—238**	—	—	—	—	—	—	—	—
2	0	251	C <sub>14</sub> H <sub>11</sub> N <sub>5</sub> O <sub>7</sub>	—	—	18.92	—	—	19.39	—
2	1	238	C <sub>16</sub> H <sub>13</sub> N <sub>5</sub> O <sub>7</sub>	—	—	17.72	—	—	18.08	—

\*According to the literature [7], mp 197° C, 198–200° C.

\*\*According to the literature [9], mp 237° C (decomp).

In the initial ketones Ib, because of the electron-accepting influence of the nitro group transferred through the chain of conjugated bonds a considerable activation of the terminal methyl group takes place and therefore these compounds are extremely reactive.

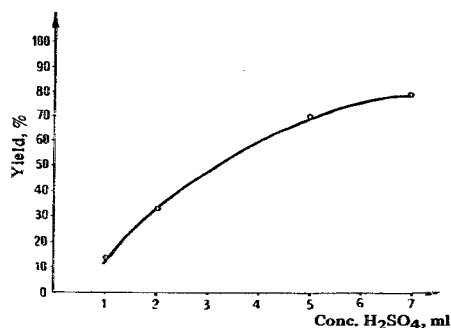


Fig. 2. Yield of II ( $n = 1$ ,  $m = 0$ ) as a function of the amount of sulfuric acid added to the reaction medium. Experimental conditions: 0.005 mole of 5-nitrofurfural and 0.005 mole of 2-acetyl-5-nitrofuran were condensed in 98% acetic acid (15 ml) at 15–20° C for 48 hr.

Our experiments have shown that the selection of the optimum amount of catalysts has a fundamental influence on the yield of the ketone II. For example, when 5-nitrofurfural was condensed with 2-acetyl-5-nitrofuran it was necessary to use an extremely large amount of concentrated sulfuric acid (see Fig. 2) to obtain the maximum yield of 1,3-bis(5'-nitro-2'-furyl)prop-2-en-1-one (II,  $n = 1$ ,  $m = 0$ ), while in other cases (II,  $n = 2$ ,  $m = 1$ ) this amount could be reduced.

Thus, for example, on the condensation of  $\beta$ -(5-nitro-2-furyl)acrolein and 1-(5'-nitro-2'-furyl)but-1-en-3-one (see Fig. 3), the greatest yield of 1,7-bis(5'-nitro-2'-propyl)hepta-1,4,6-trien-3-one (II,  $n = 2$ ,  $m = 1$ ) was found with an amount of sulfuric acid considerably smaller than in the preceding case. In this case, we have the activating influence of the  $\pi$ -electrons of the conjugated vinylidene groups on the reactivity of both the aldehyde groups and of the terminal methyl group of the initial ketone, and less catalyst is therefore necessary. It must also be noted that with lengthening of the chain of conjugation there is an ever-increasing tendency of the  $\omega, \omega'$ -bis(5-nitro-2-furyl)polyalkenones to undergo resinification in acid media. This creates definite preparative difficulties, particularly where acid catalysts are used. Nevertheless, we succeeded in developing a method purification of the compounds obtained which ensured the possibility of the production of material sufficiently pure for the performance of spectroscopic measurements.

We obtained a series of  $\omega, \omega'$ -bis(5-nitro-2-furyl)polyalkenic ketones of type II and also the previously known 1,5-bis(5'-nitro-2'-furyl)penta-1,4-dien-3-one (II,  $n = m = 1$ ) with good yields. The yields and characteristics of the ketones mentioned and of their semicarbazones are given in Table 4.

In conclusion, we must mention that 1,9-bis(5'-nitro-2'-furyl)nona-1,3,6,8-tetraen-5-one (II,  $n = m = 2$ ) can also be obtained by condensing 2 moles of  $\beta$ -(5'-nitro-2'-furyl)acrolein with 1 mole of acetone [15]; however, as our experiments showed, in this case the yield of pure ketone is low (about 15% of theoretical).

#### EXPERIMENTAL

$\omega, \omega'$ -Bis(5-nitro-2-furyl)polyalkenones II. [A. Karklinya took part in the experimental work]. With stirring (temperature not above 15° C), the catalyst, concentrated sulfuric acid ( $d$  1.84) was added in drops to a solution of 0.01 mole of a 5-nitrofuran aldehyde Ia ( $n = 0, 1$ ) and 0.01 mole of a ketone Ib ( $m = 0, 1, 2$ ) in acetic acid (98–100%). The amounts of acetic acid (A) and of sulfuric acid (X) were as follows:

Starting materials *		Acid	
Aldehydes Ia	Ketones Ib	A, ml	X, ml
R-CHO	R-COCH <sub>3</sub>	30	15
R-CHO	R-CH=CH-COCH <sub>3</sub>	30	4
R-CH=CH-CHO	R-COCH <sub>3</sub>	50	2
R-CH=CH-CHO	R-CH=CH-COCH <sub>3</sub>	50	3
R-CH=CH-CHO	R-(CH=CH) <sub>2</sub> -COCH <sub>3</sub>	100	3

\*R = 5-Nitro-2-furyl.

The reaction mixture was kept at low temperature for 48 hr (a longer time of standing leads to a decrease in the yield of the ketone II and an increase in the amount of resinous impurities) and poured into ice water (~4-fold amount with respect to the acetic acid) and, after being kept in the refrigerator (at a temperature of 0 to 5° C for 24 hr), the mixture was filtered and the residue was washed with distilled water to neutrality and was dried first in the air and then in vacuum over phosphorus pentoxide. The crude product obtained in this way was dissolved with heating in anhydrous ethyl acetate. The solution of the ketone II saturated at room temperature was purified by passage through a column filled with active alumina (amount of the latter ~20 times the weight of the crude ketone) and then the solvent was distilled off in the vacuum of a water-jet pump to small bulk and the product that crystallized out was filtered off and recrystallized from dichloroethane. Data on the ketones II obtained in this way are given in Table 4.

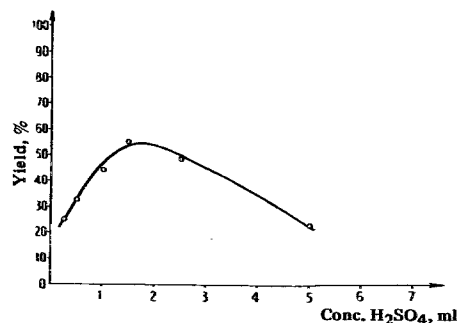


Fig. 3. Yield of II ( $n = 2$ ,  $m = 1$ ) as a function of the amount of sulfuric acid added to the reaction medium. Experimental conditions: 0.005 mole of  $\beta$ -(5-nitro-2-furyl)acrolein and 0.005 mole of 5-nitrofurfurylideneacetone were condensed in 98% acetic acid (25 ml) at 15–20° C for 24 hr.

**Semicarbazones.** To a solution of 0.001 mole of a ketone II in hot ethanol was added 1.12 g (0.01 mole) of semicarbazide hydrochloride in 7 ml of water and the mixture was boiled in the water

bath under reflux for 5 hr. Then it was left to the following day at a temperature of 15–20° C, and the crystals that had deposited were filtered off, washed with water and hot acetone, and dried at 105° C. Vacuum evaporation of the mother liquor gave an additional amount of the semicarbazone, which was washed with water and hot acetone. Data on the semicarbazones of the ketones II obtained in this way are given in Table 4.

Synthesis of 1,9-bis(5'-nitro-2'-furyl)nona-1,3,6,8-tetraen-5-one (II,  $n = m = 2$ ) by the condensation of  $\beta$ -(5-nitro-2-furyl)acrolein with acetone. At 15° C, 8 ml of concentrated H<sub>2</sub>SO<sub>4</sub> and then, slowly, in drops over 4 hr, a solution of 120 g (0.02 mole) of acetone in 20 ml of acetic acid were added to a solution of 6.68 g (0.04 mole) of  $\beta$ -(5-nitro-2-furyl)acrolein in 200 ml of 98% acetic acid. The mixture was left at 15°–20° C for 48 hr and was then diluted with 1200 ml of ice water, and after 1 hr the precipitate that had deposited was filtered off and was washed with water and dried in the air and then in vacuum over phosphorous pentoxide. The crude product obtained was dissolved with heating in methyl acetate (about 3 l) and was purified by the passage of the solution through a column of active alumina. The solvent was distilled off in the vacuum of a water-jet pump. The yield of the ketone II ( $n = m = 2$ ) was 1.27 g (14.8%), mp > 240° C (decomp.). The material obtained was identical with that obtained by the condensation of  $\beta$ -(5-nitro-2-furyl)acrolein with 1-(5'-nitro-2'-furyl)hexa-1,3-dien-5-one by the method that we have described above.

The UV spectra were taken on an SF-4 A spectrophotometer.

The IR spectra in the ranges from 700 to 1700 and 3000 to 3200 cm<sup>-1</sup> were taken on UR-10 (Zeiss) and IAS-14 spectrometers. The carefully purified ketones were prepared in the form of mulls in paraffin oil or, for the frequency ranges 1300–1500 and 3000–3200 cm<sup>-1</sup>, in hexachlorobutadiene.

The numerical values of the absorption frequencies\* (cm<sup>-1</sup>) of the ketones II in the IR spectra were as follows:

II,  $n = 1$ ;  $m = 0$ : 693 (m), 723 (vw), 736 (m), 817 (s), 839 (vw), 898 (vw), 961 (s) 978 (s), 1026 (vs), 1057 (s), 1175 (s) 1236 (sh), 1246 (vs), 1285 (vw), 1330 (s), 1360 (vs), 1390 (s), 1405 (sh), 1486 (m), 1540, 1550 (s;d), 1580 (w), 1600 (vs), 1660 (s), 3065 (vw), 3142 (sh), 3167 (m).

II,  $n = m = 1$ : 707 (w), 735 (m), 746 (vw), 810 (s), 821 (s), 851 (w), 888 (vw), 904 (w), 956 (s), 966 (s), 977 (s), 992 (s), 1024 (s), 1096 (vs), 1160 (m), 1239 (vs), 1265 (sh), 1318 (sh), 1350, 1360 (vs;d), 1400 (m), 1410 (sh), 1480 (s), 1510–1520 (d), 1570 (s), 1590 (s), 1623 (vs), 1672 (s), 3050 (w), 3070 (vw), 3120–3130 (w;d), 3140 (w), 3160 (m).

II,  $n = 2$ ;  $m = 0$ : 738 (m), 768 (w), 809, 818 (s;d), 841 (m), 939 (m), 967 (m), 999 (vs), 1019 (s), 1073 (m), 1175 (m), 1237 (sh), 1255, 1263 (s;d), 1282 (sh), 1288 (m), 1335 (vs), 1356, 1370 (vs,d), 1400 (s), 1470 (s), 1490 (m), 1520 (s), 1537 (s), 1560 (vw), 1580 (sh), 1597 (vs), 1620 (w), 1663 (vs), 3015 (vw), 3065 (w), 3132 (m), 3145 (sh), 3162 (m).

II,  $n = 2$ ;  $m = 1$ : 680 (m), 698 (vw), 714 (vw), 735 (s), 768 (w), 790 (m), 809 (s), 833 (m), 870 (w), 903 (w), 957 (m), 974 (m), 999 (s), 1022 (s), 1089 (s), 1159 (w), 1205 (sh), 1240 (vs), 1268 (w), 1332 (s), 1350, 1365 (vs,d), 1400 (m), 1485 (vs), 1512 (s), 1570 (sh), 1587 (s), 1620 (s), 1672 (s), 3015 (vw), 3046 (w), 3060 (w), 3137 (m), 3155 (m), 3170 (w).

II,  $n = m = 2$ : 718 (vw), 734 (s), 768 (vw), 793 (m), 806 (m), 822 (vw), 845 (m), 888 (vs), 957 (s), 968 (w), 992 (vs), 1020 (m), 1060 (w), 1130 (m), 1166 (m), 1192 (m), 1234 (sh), 1252 (vs), 1318 (vs), 1358 (vs), 1373 (vs), 1476 (vs), 1520 (vs), 1565 (w), 1595 (s), 1610 (sh), 1625 (w), 1658 (s), 3030 (vw), 3060 (vw), 3130 (w), 3150 (m).

## REFERENCES

1. S. A. Hiller, S. P. Saeva, K. K. Venter, L. N. Alekseeva, L. V. Kruzmetra, and S. K. Germane, KhGS [Chemistry of Heterocyclic Compounds], 1, 187, 1965.
2. Second All-Union Scientific Conference on the Chemistry of Furan Compounds, Abstracts of papers [in Russian], Saratov, 35, 1962.
3. Ya. A. Eidus, K. K. Venter, and S. A. Hiller, DAN, 141, 655, 1961.
4. Ya. A. Eidus, K. K. Venter, and I. V. Zuika, KhGS [Chemistry of Heterocyclic Compounds], 3, 402, 1967.
5. H. Uota and A. Kuriyama, Japanese Patent 2974, 1952, C.A., 48, 2115, 1954.
6. T. Sasaki, Bull. Chem. Soc. Japan, 27, 398, 1954.
7. Z. N. Nazarova, ZhOKh, 27, 2931, 1957.
8. Z. N. Nazarova and T. V. Ustimenko, ZhOKh, 30, 2017, 1960.
9. K. Miura, M. Ikeda, T. Kondo, and K. Setogawa, Kanazawa Daigaku Yakugakubu Kenkyu Nempo, 11, 9, 1961, C.A., 56, 4766, 1962.
10. V. F. Lavrushin, S. V. Tsukerman, and A. I. Artemenko, ZhOKh, 32, 2551, 1962.
11. V. F. Lavrushin, S. V. Tsukerman, and V. M. Nikitchenko, ZhOKh, 32, 2677, 1962.
12. S. A. Hiller and Ya. A. Eidus, Izv. AN Latv. SSR, 1223, 1951.
13. Ya. S. Bobovich and Ya. A. Eidus, Opt. i spektr., 16, 424, 1964.
14. Ya. A. Eidus and I. V. Zuika, Izv. AN Latv. SSR, ser. fiz-tekhn., 2, 75, 1965.
15. A. Takai and I. Saikawa, Yakugaku Zasshi, 84, 1, 1964.

29 June 1966

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\*The relative intensities are given in brackets: vs—very strong, s—strong, m—medium, w—weak, vw—very weak, d—double, sh—shoulder.