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STEREOCHEMISTRY AND REACTIVITY OF UNSATURATED COMPOUNDS. POLAROGRAPHIC REDUCTION OF CYCLOALIPHATIC ALDEHYDES AND THEIR DERIVATIVES.

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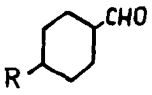
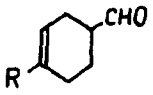
It has been shown previously that the intramolecular interaction is responsible not only for the reactivity of Δ^3-cyclohexenic compounds, but also for a number of their physical properties.(1-6)

In some cases the polarographic method enables the influence of the formally nonconjugated double bond on the electronic density distribution in organic molecules with polar substituents to be found.(7) So in this work a study was made of the reduction of the aldehydes with (I,II) and without (III, IV) double bond and their semicarbazones (Ia-IVa respectively):



I, R=H
II, R=Me



III, R=H
IY, R=Me

The NMR-spectra** of compounds IIIa and IVa display a signal at δ 2.46 and 2.37, respectively (unresolved multiplet of $W_{1/2} \sim$ 25 and 32 Hz) due to the ring methine proton (H_1), and a signal at δ 7.15 and 7.12 (doublet with J=5.1 Hz) due to the azomethine proton. Even if the contribution of the spin-spin coupling of proton H_1 with the azomethine proton (J=5.1 Hz) is subtracted from the δ 2.46 and 2.37 multiplets the halfwidth of the remainder ($W_{1/2} \sim$ 20 and 28 Hz) leaves no doubt that the ring methine proton is in the axial position; for it has been experimentally shown(8) that in such a case:

$$\text{eq. } W_{1/2} = \frac{2\,Jae + 2\,Jee}{2} = J_{ae} + J_{ee} \approx 6 + 3 = 9 \text{ Hz}$$

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** NMR-spectra were recorded with JNM-4H-100 spectrometers in $CDCl_3$ with TMS as internal reference.

$$\text{ax. } W_{1/2} = \frac{2\ J_{ae} + 2\ J_{aa}}{2} = J_{ae} + J_{aa} \approx 6 + 11 = 17 \text{ Hz}$$

In the NMR-spectra of compounds Ia and IIa there are similar signals δ 2.17 and 2.10 (unresolved multiplet with $W_{1/2} \sim$ 31 and 25 Hz) and δ 7.03 and 7.05 (doublet, J=5.1 Hz in both cases) which bears evidence of on axial orientation of the ring methine proton also in these compounds.

The reduction of semicarbazones in pairs Ia,IIIa and IIa,IVa respectively is supposed to take place at the same potential due to the equatorial orientation of the bulky azomethine group and this orientation of the group prevents the intramolecular interaction (in IIIa and IVa). But the reduction of the aldehydes III and IV due to their conformational differences(9,10) (as compared with I and II) should proceed at different potentials.

The results obtained in this work support our concept. We compared the parameters of polarographic reduction waves the cyclohexenic compounds III, IV and their semicarbazones IIIa,IVa with those for the corresponding saturated compounds of the cyclohexane series I,II,Ia and IIa.

The polarogrammes were obtained by usual methods (with potentiometric control of the potentials along the wave(11), the error being ± 5 mV) in the thermostated cell(12) at 25°C. The parameters of the dropping mercury electrode are: m = 1.31 mg/sec, t = 0.36 sec. The 0.1 N lithium borate solution in 20 % ethanol was used as the background for the aldehydes, and the 0.4 N AcOH + 0.1 N AcOK solution in 30 % ethanol - for semicarbazones.

The i_{lim} and $E_{1/2}$ values presented in Table for the 1 mM and 2 mM solutions strongly suggest that the presence of the double bond in a molecule makes the reduction of aldehyde group much easier, but does not influence the reduction of the azomethine group in the semicarbazones.

The conjugation of the carbonyl group with the double bond is known to increase considerably the electron transfer rate from the electrode to the carbonyl group.(13,14)

Thus, the reduction of the compounds III and IV proceeds much easier than that of I and II. This is due to the interaction between the carbonyl group and the double bond (in the case of III and IV), or - to the differences in the electrochemical reaction rate of the axial and equatorial oriented substituents. As for semicarbazones (in which azomethine group is equatorial-situated) there are no differences in the reaction rate of the electroreduction between Ia (IIa) and IIIa (IVa).

It should be emphasized, that the limiting currents of the aldehydes under consideration are too low (see the table). As a result of the experiments specialy undertaken it was found that these limiting currents show the kinetic character due to the retarded dehydration of the carbonyl group.

Table 1. Potentials of halfwaves and limiting currents

Compound No.	1 mM solutions		2 mM solutions	
	$E_{1/2}$ (V vs.SCE)	i_{lim} μA	$E_{1/2}$ (V vs.SCE)	i_{lim} μA
I	-1.790	1.20	-1.808	2.29
II	-1.803	0.63	-1.835	1.03
III	-1.763	1.20	-1.765	2.19
IV	-1.783	1.26	-1.790	2.70
Ia	-1.189	4.2	-1.209	8.6
IIa	-1.173	4.3	-1.197	8.6
IIIa	-1.185	4.3	-1.205	8.8
IVa	-1.170	4.0	-1.197	8.5

In fact the changes of pH (in the range of 0.5 of pH) and of the buffer capacity of the solution practically did not affect the wave heights, which suggests that this case the protonation of aldehyde group cannot be the determining step. On the other hand, the increase of the content of organic solvent (dimethylformamide) in the solution results in a considerable increase of the limiting kinetic current.* In the case of the semicarbazones the wave heights are limited by diffusion.

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* The increase in the dimethylformamide content shifts the equilibrium in the carbonyl group hydration towards free (nonhydrated) aldehydes molecules.(15)

REFERENCES

(1) G.P.Kugatova-Shemyakina and Yu.A.Ovchinnikov, Tetrahedron, 18,1697 (1962).

(2) G.P.Kugatova-Shemyakina, G.M.Nikolaev and V.M.Andreev, Tetrahedron, 23, 2721 (1967).

(3) V.M.Andreev, G.P.Kugatova-Shemyakina and L.Sh.Anarkulova, Zhurn. Org. Khim., Biolog. Aktivn. Soedin., 1968, 79

(4) G.P.Kugatova-Shemyakina, V.M.Andreev and S.A.Kazaryan, Zhurn. Org.Khim., 2, 2065 (1966).

(5) G.P.Kugatova-Shemyakina and G.M.Nikolaev, Tetrahedron, 23, 2987 (1967).

(6) L.Sh.Anarkulova, G.P.Kugatova-Shemyakina, G.M.Nikolaev and V.M.Andreev, Zhurn. Org. Khim., 3, 1801 (1967).

(7) S.G.Mairanovskii, N.Ya.Grigorjeva, N.V.Barashkova and V.F.Kucherov, Izv. Akad. Nauk SSSR, Otdel.Khim.Nauk, 1963, 240.

(8) V.I.Sheichenko, G.M.Nikolaev et al., Izv.Akad.Nauk SSSR,Otdel.Khim.Nauk, (in press).

(9) N.S.Zefirov, V.N.Chekulaeva and A.I.Belozerov, Zhurn. Org.Khim., 5, 630 (1969); N.S.Zefirov et al., Tetrahedron, 25, 1997 (1969).

(10) N.S.Zefirov, N.M.Sergeev, V.N.Chekulaeva and L.G.Gurvich, Dokl. Akad. Nauk SSSR, 190, 345 (1970).

(11) S.G.Mairanovskii, A.A.Fainzilberg, S.S.Novikov and V.A.Klimova, Dokl. Akad. Nauk SSSR, 125, 351 (1959).

(12) S.G.Mairanovskii and F.S.Titov, Zhurn. Anal. Khim., 15, 121 (1960).

(13) M.Fields and E.R.Blout, J.Am.Chem.Soc., 70, 930 (1948).

(14) S.G.Mairanovskii, L.Yanovskaya, N.V.Kondratova and G.V.Kryshtal, Elektrokhim., 4, 1127 (1968).

(15) S.G.Mairanovskii, D.I.Dzhaparidze and O.I.Sorokin, Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1964, 795.