HETEROCYCLIC ANALOGS OF XANTHONE

IV.* PHYSICOCHEMICAL PROPERTIES OF 9-OXOCHROMENO-[3,2-d]PYRAZOLES, 9-OXOTHIOCHROMENO[3,2-d]PYRAZOLES, AND 8-OXODIPYRAZOLOPYRANS

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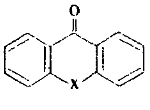
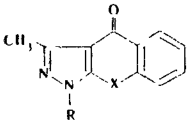
A comparative investigation of the acid-base properties, the polarographic behavior, and the spectral characteristics of oxochromeno- and oxothiochromenopyrazoles, oxodipyrazolopyrans, and their electronic analogs xanthone and thioxanthone, has been performed. The difference in properties is due to the electron-accepting nature of the condensed pyrazole ring.

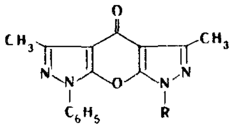
Methods for the synthesis and some properties of the 9-oxochromeno- and 9-oxothiochromeno[3,2-d]-pyrazoles and the 8-dipyrazolopyrans, which we consider to be electronic analogs of xanthone and thioxanthone, formally representing a route for the substitution of condensed benzene rings by aromatic pyrazole rings, have been described previously [1, 2]. To determine the influence of such a change in the structure a comparative determination of the acid-base properties of xanthone (I), thioxanthone (VI), and the pyrazole analogs synthesized (II-V, VII, VIII) has been performed, their polarographic reduction has been carried out, and their spectral characteristics have been used. The results obtained are given in Table 1.



I, VI



II, III VII, VIII



IV, V

I-III X = O, VII, VIII X = S, II, IV VII R = CH_3; III, V, VIII R = C_6H_5

The basicity of the oxochromenopyrazoles was determined spectrophotometrically in sulfuric acid solutions of various concentrations. The presence of isosbestic points on the spectral curves obtained shows the absence of other processes in the reaction of the compounds studied with sulfuric acid. The linear dependence of H_0 on the logarithm of the concentration of the protonated and nonprotonated forms shows the applicability of Hammett's acidity scale to the determination of the basicities of these compounds.

It is known that salt formation in the case of xanthone and thioxanthone takes place through the protonation of the oxygen of the carbonyl group [3, 4]. The oxodipyrazolopyrans (IV and V) do not protonate even in 95% sulfuric acid, and the oxochromenopyrazoles (II and III) and the oxothiochromenopyrazoles (VII and VIII) on protonation form cations the spectra of which are similar to the spectra of the cations of xanthone and thioxanthone. This permits us to consider that the protonation of the compounds studied also takes place at the carbonyl group.

It can be seen from the figures in the table that the pK_a values of the oxochromenopyrazoles and the oxothiochromenopyrazoles are 2.5-3.0 units lower than those of xanthone and thioxanthone. This substan-

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* For communication III, see [8].

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TABLE 1. Physicochemical Properties of Xanthone and Its Heterocyclic Analogs

Oxygen analogs of xanthone	λ_{max}, nm (EtOH)	lg ε	ν_{CO}, cm^{-1}	A·10^3, liter/mole·cm^2	pK_a	$E_{1/2}$, V	Sulfur analogs of xanthone	λ_{max}, nm (EtOH)	lg ε	ν_{CO}, cm^{-1}	A·10^3, liter/mole·cm^2	pK_a	$E_{1/2}$, V
I	238 260 285 332	4,62 4,11 3,85 3,82	1665	4,1	−4,08	1,70 2,25	VI	217 256 377	4,15 4,62 3,80	1625		−4,03	1,62 2,18
II	265 310	4,15 3,66	1670	4,25	−7,02	2,100	VII	246 330	4,34 3,56	1635	4,15	−6,64	1,86 1,93
III	238 315	4,37 3,44	1670	5,6	−7,09	1,99 2,45	VIII	248 338	4,53 3,62	1640	4,25	−6,88	1,87 2,20
IV	235	4,28	1660	6,1	—	2,18							
V	232	4,42	1660	5,9	—	2,09							

tial reduction in basicity is obviously the result of the great electron-accepting effect of the condensed pyrazole ring, decreasing the polarizability of the carbonyl group, as compared with the effect of a benzene ring.

Polarographic reduction was performed in dimethylformamide. Two one-electron waves were observed, of which the first was the most characteristic (Table 1). As can be seen, the half-wave potentials for all the compounds synthesized are in a more negative region than for xanthone and thioxanthone. Apparently, the introduction of a pyrazole ring makes the reduction of these compounds more difficult, just as it makes the formation of a cation in their protonation more difficult, which confirms the conclusion on the nature of the influence of the pyrazole ring drawn in the study of basicity. 3-Methyl-9-oxo-1-phenylchromeno[3,2-d]prazole (III), which has a longer chain of conjugated bonds, undergoes reduction more readily than 1,3-dimethyl-9-oxochromeno[3,2-d]pyrazole (II). The values for the 1-methyl- and 1-phenyl-substituted oxodipyrazolopyrans (IV and V) differ by the same magnitude (0.1 V), probably for the same reason.

The sulfur-containing compounds have a more positive value of $E_{1/2}$ than the oxygen analogs, and in the oxothiochromenopyrazoles (VII and VIII) no influence of methyl and phenyl groups on the value of $E_{1/2}$ is found.

On passing from chromone to xanthone, the C=O band in the IR spectrum scarcely changes its position [5]. In the oxochromenopyrazoles, a slight change in ν_{CO} is observed in comparison with xanthone (± 5 cm^{-1}), but the intensity of the carbonyl absorption, measured by Ramsay's method, changes over a fairly wide range (150-2000 liter · mole^{-1} · cm^{-2}). In the sulfur-containing compounds the values of the integral intensities of the carbonyl groups are lower than in the oxygen analogs and depend little on a substituent on a nitrogen atom in the pyrazole ring.

The fusion of a chromone ring with a pyrazole ring leads to a decrease in the number of absorption bands in the electronic spectra and to a shift of the maximum in the short-wave direction by 17-22 nm, and in the case of the thiochromone derivatives by 39-47 nm. In a consideration of the electronic spectra of 1,3-dimethyl-9-oxochromeno[3,2-d]pyrazole (II) and its sulfur analog (VII) it can be seen that the replacement of the oxygen atom by sulfur leads to a bathochromic shift in this case as well.

Thus, the results obtained show a considerable electron-accepting action of a condensed pyrazole ring. This conclusion is in good harmony with the results of previous work [6, 7].

EXPERIMENTAL

The determination of the pK_a values was performed on a VSU 2-P spectrophotometer.

A sample of 0.039 g of xanthone was dissolved in 100 ml of absolute ethanol, and 1 ml of this solution was diluted with sulfuric acid solution of known concentration to 100 ml. The concentration of the working solution was $2 \cdot 10^{-5}$ M. At λ_{max} 332 nm, the optical density of the absorption of the solution of xanthone was plotted against H_0, and the percentage of the ionized form C_{BH^+} or log (C_{BH^+}/C_B) against the concentration of sulfuric acid. The determinations were performed similarly for 3-methyl-9-oxo-1-phenylchromeno[3,2-d]pyrazole at λ_{max} 315 nm.

The polarographic reduction was performed on an LP-60 electronic polarograph at a temperature of 20 ± 0.1°C. The polarograms were recorded in dimethylformamide on a support of a 0.02 M solution of tetraethylammonium perchlorate. The cathode was a dropping mercury electrode with m = 4.41 mg/sec and t = 2 sec at a height of the mercury column of 60 cm. The anode was a saturated calomel electrode. The concentration of the substance was $4.0 \cdot 10^{-4}$ M. Before the measurements, argon was passed through the solution for 20 min to eliminate dissolved oxygen.

The IR spectra were taken on an IKS-14 spectrophotometer in chloroform.

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