ELECTRONIC ABSORPTION SPECTRA OF THE CATIONS AND ANIONS FORMED FROM PYRROLE ANALOGS OF THE CHALCONES

S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin

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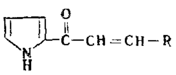
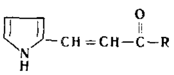
The electronic absorption spectra of 29 pyrrole analogs of the chalcones have been studied in solutions of strong acids and alkalies, in which the corresponding cations and anions are formed. It has been shown by means of the IR spectra that the protonation of the pyrrole chalcones takes place at the carbonyl group. Considerations are given of the structure of the organic cations and anions studied and of the characteristic features in the change in their coloration as a function of their chemical structure. Satisfactory correlations have been found between the shift of the absorption frequency of the long-wave band which takes place at the transition from a neutral solution (molecules) to an acid solution (cations) or to an alkaline solution (anions) and Hammett's σ constants. Three 3-(4-halophenyl)-1-(2-pyrryl)propenones not previously reported in the literature have been synthesized.

In the preceding communication [1] we described the results of a study of the electronic absorption spectra of the molecular forms of α, β-unsaturated ketones of the pyrrole series in solutions of ethanol and cyclohexane. As is well known, pyrrole and its derivatives possess simultaneously relatively weak basic and weak acidic properties. Consequently it might have been expected that in sufficiently acid and alkaline media the pyrrole analogs of the chalcones would form the corresponding cations and anions; we decided to study the spectra of these ions in the present work.

As the subjects for investigation we selected the isomeric pyrrole chalcones of the types:

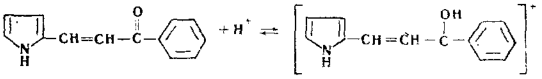


and

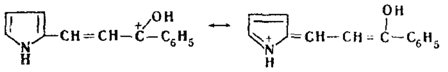


where R represents phenyl (I, II), substituted phenyls with electron-donating and electron-accepting substituents (V–XX), 2-furyl (XXI–XXII), 2-thienyl (XXIII–XXIV), 2-selenienyl (XXV–XXVI), 2-pyrryl (XXVII), and 2-quinolyl (XXVIII–XXIX), and also the N-methyl derivatives of the ketones I and II (III and IV) (see table).

The majority of the compounds studied form colored solutions of a halochromic nature when they are dissolved in 85% trichloroacetic acid, in 98% phosphoric acid, in 5–50% solutions of sulfuric acid in glacial acetic acid, and in aqueous solutions of sulfuric acid (50–100%), these solutions readily being decolorized on dilution with water. When the spectra of ketones II and XXVII, are measured in solutions of various concentrations of phosphoric acid in glacial acetic acid (at a constant concentrations of the ketones), isobestic points are found on the absorption curves. This shows the existence of acid-base equilibria which can be illustrated in the following way:



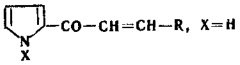
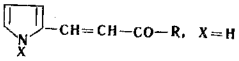
The structure of the conjugate carbenium ion formed can be illustrated by two limiting structures (carbenium and immonium structures):



The fact that protonation in an acid medium takes place at the carbonyl group and not at the pyrrole ring is confirmed by a study of the IR spectra that we obtained of the fairly stable hydrochlorides of the ketones VII and IX. The nature of these salts is apparently analogous to the nature of those that are formed in solutions of sulfuric acid, since the solid hydrochlrides (ratio 1 : 1) isolated give colored solutions in dichloroethane the absorption maxima of which coincide satisfactorily with λ_{max} of the corresponding halochromic solutions. The IR spectra of salts of the ketones VII and IX lack the bands of the stretching vibrations of C=O and N—H groups. Moreover, the number of absorption bands in the salts is far less than in the corresponding ketones. We have not observed the characteristic "immonium" bands that were observed by Yu. E. Sklyar et al. [2] in the spectrum of 3-acetyl-2,4-dimethylpyrrole hydrochloride (1798 and 1957 cm^{-1}) and the other bands for NH_2^+ and NH^+ cited by Bellamy [3]. Attention is attracted by the strong and broad absorption band in the 1560–1610 cm^{-1} region and the considerable absorption at 3100 cm^{-1} which is probably due to the $[C-OH]^+$ group [4]. However, the positive charge is delocalized to a considerable extent and it is impossible to give preference to either the immonium or the carbenium structure. The pyrrole analogs of the chalcones can be considered as vinylogs of amides in which the electron density is displaced from the nitrogen atom to the carbonyl group. The nitrogen bears a strong positive charge and is already partially quatervalent ($\sigma^3 \pi$ state) in consequence of which, as is known from the data of IR [5] and NMR [6–8] spectroscopy, the protonation of amides takes place at the oxygen atom. We come across an analogous transfer of the reaction center from the nitrogen atom to the oxygen atom in the addition of a proton to α, β-unsaturated β-amino carbonyl compounds [9], to α- and γ-pyridones [10, 11], and also to some carbonyl derivatives of pyrrole [2].

However, in a strongly acid medium further protonation at the pyrrole ring is not excluded. This conclusion can be deduced from the fact that λ_{max} for the ketones I and III changes only slightly—from 418 to 425 nm—when the concentration of sulfuric acid in water is increased from 50 to 90%, while in 95–100% sulfuric acid it is 45 nm. This additional

Spectral Characteristics of Acid and Alkaline Solutions of the Pyrrole Chalcones

R	 (1-propenones)			 (3-propenones)		
	compound	30% solution of sulfuric acid in glacial acetic acid	20% ethanolic solution of caustic potash	compound	30% solution of sulfuric acid in glacial acetic acid	20% ethanolic solution of caustic potash
		λ_{max}, nm (ε)	λ_{max}, nm (ε)		λ_{max}, nm (ε)	λ_{max}, nm (ε)
Phenyl	I	260(6270); 415(37600)	267(10600); 293(13680); 380(18230)	II	252(3890); 280(4380); 313(3734); 473(43800)	255(7834); 460(25330)
Phenyl	III*	260(5139); 315 i**; 411(30440)	—	IV*	280(2569); 315(1976); 365 i; 480 (51390)	—
4-Methylphenyl	V	265(7462); 320 i; 427(41050)	265(9185); 300(14570); 380(20160)	VI	260(4230); 285(4780); 325(5330); 483(53300)	270(9436); 458(24840)
4-Methoxyphenyl	VII	273(8090); 330(5750); 462(44900)	260(6339); 317(14600); 380(23940)	VIII	265(5165); 350(7440); 500(61980)	295(5473); 455(14930)
2,4-Dimethoxyphenyl	IX	280(6370); 342(5960); 490(49400)	250(9033); 382(23860)	—	—	—
4-Dimethylaminophenyl	X	256(5980); 400(36200)	—	XI	270(5761); 463(36000)	—
4-Fluorophenyl	XII	325 i; 415(38200)	265(11300); 290(14730); 381(17990)	—	—	—
4-Chlorophenyl	XIII	265(6990); 325 i; 417(40200)	271(12900); 295(16260); 385(18000)	XIV	260(3090); 285(4520); 325(4520); 475(50000)	261(10300); 470(29000)
4-Bromophenyl	XV	265(5710); 325 i; 417(39700)	268(14490); 290(18730); 388(18730)	XVI	260(4231); 288(4615); 323(4999); 473(46150)	257(11740); 465(27760)
4-Nitrophenyl	XVII	290(11500); 403(36500)	313(21260); 417(13200)	XVIII	280(13400); 335(4400); 470(35200)	276(13450); 395(8448); 505(14830)
4-Biphenylyl	XIX	278(15090); 340 i; 440(36000)	316(20550); 390(21520)	XX	273(10860); 353(6760); 507(57970)	294(15770); 470(25670)
2-Furyl	XXI	270(5670); 350(4020); 455(45700)	—	XXII	263(4470); 288(4600); 335(5340); 498(49000)	—
2-Thienyl	XXIII	263(4070); 328(4740); 453(38900)	—	XXIV	285(5830); 333(4940); 500(44100)	—
2-Selenienyl	XXV	270(4700); 353(6052); 462(41200)	—	XXVI	255(3250); 293(5490); 502(48700)	—
2-Pyrryl	XXVII	267(4850); 331(5450); 477(40000)	—	—	—	—
2-Quinolyl	XXVIII	228(15000); 260(12900); 308(9870); 408(37600)	—	XXIX	260(12400); 323(4200); 456(42600)	—

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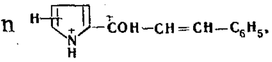
* X=CH_3.

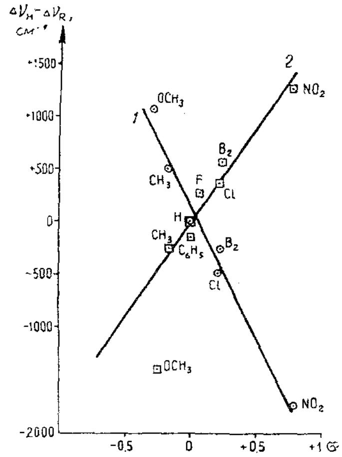
** i—inflection.

marked deepening of the color of the solution can, in our opinion, be explained only by the formation of the doubly-charged ion  since it has been shown previously that the introduction of an electron-accepting substituent (the protonated pyrrole nucleus must possess an electrophilic influence) into the molecule of a chalcone adjacent to the carbenium atom $[C{-}OH]^+$ leads to a deepening of the halochromic coloration [12–14]. However, in this case, the addition of a second proton not to the nitrogen atom of the pyrrole ring but to its α- or β-carbon atoms is likely, as follows from the literature [15–17] and from a study of the NMR spectra of acid solutions of pyrrole and its homologs [18–20].

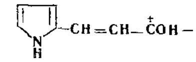
In order to elucidate the characteristic features in the change of the color of the conjugated cations formed in dependence on their structure, we have investigated the electronic absorption spectra of the pyrole analogs of the chalcones in 30% solutions of sulfuric acid (100%) in glacial acetic acid in more detail. These solutions are spectrometrically stable for a very long time (5–10 hr) and, as a rule, contain only the ionic forms of the ketones. The corresponding spectral characteristics are given in the table. In acid solutions a new intense absorption band appears in the region of visible spectrum which is characteristic for the conjugated ions formed. The long-wave absorption maximum of solutions of I–XX (with the exception of X and XI) in 30% sulfuric acid in glacial acetic acid are displaced bathochromically in comparison with λ_{max} or the molecular forms by 50–122 nm. It is interesting that in a series of analogous ketones of the furan series, the transition from the molecular form to the ionic form is accompanied by a considerably larger bathochromic effect of 85–138 nm [21]. The shift of the absorption maxima on passing from the base to the conjugate acid (in our case, to the protonated form of the ketone) depends on pK_a: the greater the basicity of the ketone, the larger must the bathochromic displacement be [22]. The electron-donating influence of pyrryl is greater than that of furyl [1], the basicity of the pyrrole chalcones is higher than that of the furan chalcones [23], and the same law was to be expected. The observed lower shift of λ_{max} in the pyrrole ketones than in the furan ketones can probably be explained, on one hand, by solvation influences weakening the donor influence of the pyrrole nucleus and on the other hand by the fact that, as a result of the conjugation of the pyrrole ring with the protonated carbonyl group the weight of the carbenium structure responsible for the halochromic coloration decreases. In addition to this, in the 3-aryl-1-(2-pyrryl)-1-propenone and, particularly, the 1-aryl-3-(2-pyrryl)propenone series, i.e., monotypical compounds, with a rise in the basicity the shift of the absorption maximum in the passage from the molecule to the cation increases and a fairly satisfactory correlation is found (figure, curve 1) between the differences in the frequencies of absorption of the ketone and its conjugate acid and Hammett's σ-constants*, according to the equation

$$(\Delta\nu_H - \Delta\nu_R)\frac{Nhc}{2.303RT} = \rho\sigma,$$

where $\Delta\nu_H$ is the displacement of the frequency of the absorption on passing from the molecular form to the ionic form for 1-phenyl-3-(2-pyrryl)-1-propenone and $\Delta\nu_R$ is the analogous shift for ketones having a substituent in the benzene nucleus.



Correlation between the σ constants and Δν for 1-aryl-3-(2-pyrryl)-1-propenones and their conjugate acids (the straight line 1, r = 0.988; ρ = 5.54; s = 0.89) and between the σ constants** and Δν for the 3-aryl-1-(2-pyrryl)-1-propenones and the conjugate bases (straight line 2, r = 0.978; ρ = 3.69; s = 0.50).

The replacement in the chalcone (λ_{max} of the halochromic solution 401 nm [26]) of the aromatic nucleus remote from the carbonyl group by a pyrrole nucleus leads to a bathochromic effect of 72 nm. At the same time, the analogous replacement carried out adjacent to the carbonyl group deepens the coloration by only 14 nm (cf. I and II). The latter circumstance led N. Maxim in 1938 [27] to the incorrect statement that the pyrrole ring has no influence on the absorption spectrum of halochromic solutions. The main chromophores responsible for the halochromic coloration in the 1-(2-pyrryl)-propenones is the atom grouping $R{-}CH{=}CH{-}\overset{+}{C}OH{-}$, while in the 3-(2-pyrryl)-1-propenones it is  Hence it is natural that

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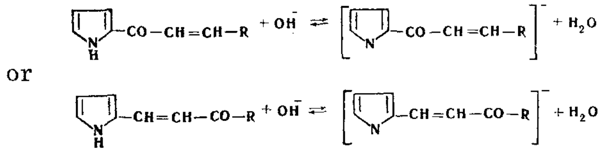
*The legitimacy of this correlation has recently been substantiated by Hancock et al. [24, 25]; at the present time there is still only a limited number of examples of its observation.

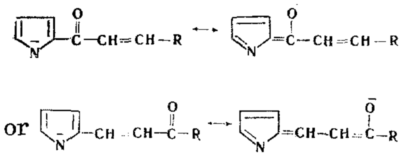
**The point for the methoxy group deviates by a large amount apparently because of the inadequate acidity of the corresponding ketone, and it was not taken into account in the calculation.

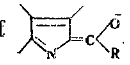
the nature of the radical R in the 1-(2-pyrryl)-1-propenones has a far greater effect on the coloration of the sulfuric acid solutions than in the 3-(2-pyrryl)-1-propenones (see table). It follows from the data given that donor substituents (CH_3, CH_3O, etc.) in the 1-(2-pyrryl)-1-propenones cause a considerably greater bathochromic effect than in the 3-(2-pyrryl)-1-propenones (compare I, II with V–IX). The dimethylamino group is protonated in an acid medium, acquiring acceptor properties, which leads to a hypsochromic displacement. The halogens (F, Cl, Br) in compounds XII–XVI exert no appreciable influence on the halochromic coloration. A nitro group present in the nucleus remote from the carbonyl group in compound XVII causes a relatively small hypsochromic effect, while if these groups are present side by side, as in compound XVIII, it has almost no influence on the position of λ_{max} of the long-wave band. The electron-accepting nature of the nitro group can apparently be considerably weakened because of its interaction with the molecules and protons of the sulfuric acid and the formation of compounds through solvates, hydrogen bonds, etc. [28]. The 2-quinolyl group behaves similarly to the 4-nitrophenyl group (cf. XXVIII, XXIX) and under these conditions it is probably protonated and exhibits electron-accepting properties. The influence of furyl, thienyl, and selenienyl groups on the coloration (compare XXI–XXVI) is approximately the same as that of 4-anisyl. It is interesting that in this case 2-selenienyl possesses a somewhat greater bathochromic influence than 2-furyl and 2-thienyl. The introduction of a second pyrrole ring in place of phenyl leads to a considerable long-wave displacement only where this substitution has taken place remote from the carbonyl group (compare I, II and XXVII), the bathochromic effect for 2-pyrryl being far greater than for furyl, thienyl, and selenienyl (compare XXI–XXVII). This confirms the high electron-donating influence of 2-pyrryl, which exceeds that for five-membered heterocyclic radicals containing heteroatoms of the sixth group of D. I. Mendeleev's periodic system [23].

When the pyrrole analogs of the chalcones are dissolved in 20% ethanolic caustic potash or in 2 M sodium ethoxide solution, in the majority of cases there is a deepening of the color as compared with the neutral solutions (table). Thus, for example, in alkaline solutions the ketones I and II have a deeper coloration than in ethanol by 40–70 nm. In a study of the absorption spectra of the ketone II in ethanolic solutions of caustic potash of various concentrations, an isobestic point was observed. Consequently, the pyrrole chalcones exhibit acidic properties and react with strong bases:



The negative charge is apparently not localized on the nitrogen atom and the structure of the anion formed can be represented as:



In the literature there is information obtained on the basis of a study of the IR spectra [29] that the alkali-metal salts of carbonyl compounds of pyrrole are not N-metal derivatives but salts at the carbonyl group of the type of  . We have succeeded in isolating the sodium salts of ketones XII, XIII, and XV by their reaction with metallic sodium in absolute toluene solution. However, because of their high hygroscopicity, on measuring their IR spectra in paraffin oil we did not observe the complete disappearance of the bands of the stretching vibrations of the C═O and N—H groups, although their intensity had fallen. The appearance of a pronounced peak at 1530–1550 cm^{-1} can also be noted; by analogy with the absorption of the carboxylate ion [3] we ascribe this band to the stretching vibrations of C—O$^-$.

The introduction of electron-accepting substituents in the molecules of ketones I and II leads to a deepening of of the color of the corresponding anion (compare XII–XVIII). Thus, for example, a nitro group causes a considerable bathochromic effect amounting to 37–45 nm. Electron-donating groups (CH_3, CH_3O), on the other hand, lead to a slight hypsochromic displacement when they are located in the aromatic nucleus adjacent to the carbonyl group (compare VI and VIII) while in the 1-(2-pyrryl)-1-propenones (compare V and VII) they have no influence whatever on the coloration of the anion. Since electron-accepting substituents must stabilize the structure with the negative charge on the oxygen atom, this is apparently responsible for the color of the anion and is to be preferred. Thus, the characteristics of the electronic absorption spectra to some extent confirm the fact that the alkali-metal salts of the carbonyl compounds of pyrrole are salts at the carbonyl group to a greater extent than at the nitrogen atom [29].

In a comparison of the absorption frequencies of the long-wave band of the ketones in a neutral solvent (ethanol) and in an alkaline medium (20% ethanolic solution of caustic potash), it is easy to see that here, also, there is a correlation similar to that which we have observed for the acid solutions. However, while for acid solutions this correlation is observed better for the 1-aryl-3-(2-pyrryl)-1-propenones, in this case it is followed more satisfactorily for the corresponding 1-(2-pyrryl)-1-propenones (Figure, curve 2).

The properties of the pyrrole analogs of the chalcones that have been given permit the assumption that the latter can be used not only for determining Hammett's H_0 function of acid solutions but also for determining the H_- acidity function of strongly basic solutions.

EXPERIMENTAL

The synthesis and properties of the pyrrole analogs of the chalcones, with the exception of XII, XV, and XVI, has been described previously [1, 30, 31]. Compounds XII, XV, and XVI were also obtained by the crotonic condensation of the corresponding aldehydes and methyl ketones in an alkaline medium.

3-(4-Fluorophenyl)-1-(2-pyrryl)-1-propenone (XII)—from 2-acetylpyrrole and 4-fluorobenzaldehyde. Colorless plates. Yield almost quantitative. Mp 138° C (from methanol). Found, %: N 6.69, 6.60. Calculated for $C_{13}H_{10}FNO$, %: N 6.53.

3-(4-Bromophenyl)-1-(2-pyrryl)-1-propenone (XV)—from 2-acetylpyrrole and 4-bromobenzaldehyde. Colorless plates. Yield quantitative. Mp 181° C (from methanol). Found, %: N 5.00, 5.03. Calculated for $C_{13}H_{10}BrNO$, %: N 5.07.

1-(4-Bromophenyl)-3-(2-pyrryl)-1-propenone (XVI)—from pyrrole-2-aldehyde and 4-bromoacetophenone. Yellow-green plates. Yield quantitative. Mp 192° C (from methanol). Found, %: N 5.11, 5.23. Calculated for $C_{13}H_{10}BrNO$, %: N 5.07.

Hydrochloride of the ketone VII. An ether solution of hydrogen chloride saturated in the cold was added to an ether solution of the ketone (0.001 mole). The bright red crystalline precipitate that deposited was filtered off, washed repeatedly with absolute ether, and dried in vacuum for 2 hr. Mp 119–120° C. Found, %: Cl 13.38, 13.21. Calculated for $C_{14}H_{14}NO_2Cl$, %: Cl 13.42.

The **hydrochloride of ketone** X was obtained similarly to the preceding compound. Dark red needles, mp 130–132° C. Found, %: Cl 11.89, 11.80. Calculated for $C_{15}H_{16}NO_3Cl$, %: Cl 12.08.

The sodium salts of the pyrrole chalcones were synthesized by the method of Treibs and Dietl [29].

The UV absorption spectra were measured on an SF-4 spectrophotometer at concentrations of the solutions from 2×10^{-5} to 4×10^{-5} M. The IR spectra were recorded in tablets with KBr (concentration of the substance 2 mg/200 mg of KBr) and in paraffin oil on a UR-10 spectrometer.

REFERENCES

1. S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, KhGS, collection: Nitrogen-containing Heterocycles [in Russian], 1, 9, 1967.
2. Yu. E. Sklyar, R. P. Evstigneeva, O. D. Saralidze, and N. A. Preobrazhenskii, DAN, 157, 367, 1964.
3. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL, Moscow, p. 372, 1963.
4. B. E. Zaitsev, Yu. D. Koreshkov, M. E. Vol'pin, and Yu. I. Sheinker, DAN, 139, 1107, 1961.
5. B. I. Sukhorukov, A. I. Finkel'shtein, E. P. Zil'berman, A. E. Kulikova, and V. I. Ganina, ZhFKh, 35, 1600, 1961.
6. G. Fraenkel and C. Franconi, J. Am. Chem. Soc., 82, 4479, 1960.
7. T. Birchall and R. J. Gilespie, Can. J. Chem., 41, 2642, 1963.
8. D. Cook, Can. J. Chem. 42, 2721, 1964.
9. H. E. Kramer and R. Gompper, Tetrah. Let., 969, 1963; Z. Phys. Chem. 48, 349, 1964.
10. D. Cook. Can. J. Chem., 43, 749, 1965.
11. P. J. Hoak and Th. J. Boer, Rec. trav. chim., 83, 186, 1964.
12. S. V. Tsukerman, V. M. Nikitchenko, and V. F. Lavrushin, ZhOKh, 33, 1255, 2563, 1963.
13. S. V. Tsukerman, A. I. Artemenko, and V. F. Lavrushin, ZhOKh, 33, 2528; 1963, 34, 488, 1964.
14. S. V. Tsukerman, I. K. Gintse, and V. F. Lavrushin, ZhOKh, 34, 2317, 1964.
15. A. Treibs, E. Herrman, E. Meissner, and A. Kuhn, Ann., 602, 153, 1957.
16. A. Treibs and H. G. Kolm, Ann. 606, 166, 1957.
17. A. Treibs and G. Fritz, Ann., 611, 162, 1958.
18. R. J. Abraham, E. Bullock and S. S. Mitra, Can. J. Chem., 37, 1859, 1959.
19. E. B. Whipple, J. Chiang and R. L. Hinnan, J. Am. Chem. Soc., 85, 26, 1963.
20. J. Chiang and E. B. Whipple, J. Am. Chem. Soc., 85, 2763, 1963.
21. A. I. Artemenko, Thesis [in Russian], Khar'kov, 1964.
22. M. Rapoport, C. K. Hancock, and E. A. Meyers, J. Am. Chem. Soc., 83, 3489, 1961.
23. S. V. Tsukerman, Yu. N. Surov, V. F. Lavrushin, and Yu. K. Yur'ev, KhGS [Chemistry of Heterocyclic Compounds], 2, 868, 1966.
24. L. A. Jones and C. K. Hancock, J. Org. Chem., 25, 226, 1960.
25. L. E. Scoggins and C. K. Hancock, J. Org. Chem., 26, 3490, 1961.
26. V. F. Lavrushin, S. V. Tsukerman, and A. I. Artemenko, ZhOKh, 32, 2551, 1962.
27. N. Maxim and J. Copuzeanu, Bull. Soc. chim. France [5], 5, 57, 1938.
28. P. Pfeiffer, Organische Molekulverbindungen, Stuttgart, 1922.
29. A. Treibs and A. Dietl, Ann., 619, 80, 1958.
30. S. V. Tsukerman, V. P. Izvekov and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], 1, 527, 1965.
31. S. V. Tsukerman, V. D. Orlov, V. P. Izvekov, V. F. Lavrushin, and Yu. K. Yur'ev, KhGS [Chemistry of Heterocyclic Compounds], 2, 34, 1966.

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