INFRARED SPECTRA OF CHALCONE ANALOGS CONTAINING THE SELENOPHENE NUCLEUS

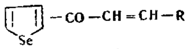
S. V. Tsukerman, V. D. Orlov, Yu. S. Rozum, and V. F. Lavrushin

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 4, pp. 623–629, 1969

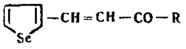
UDC 547.739.3:543.422.4

The IR spectra of 30 chalcone analogs containing a selenophene nucleus have been measured in the 1800–500 cm^{-1} region and an assignment of frequencies has been carried out. It has been confirmed that the selenophene radical in the static state has a greater electron-donating influence than the furyl and thienyl radicals. A linear relationship has been found between the shift of the frequency of the stretching vibrations of the carbonyl ($\Delta\nu_{C=O}$) under the influence of substituents in the 1-(selenien-2-yl)-3-arylpropenones and the σ parameters of Hammett's equation. The absorption curve of analogous compounds of the selenophene and thiophene series have been compared. The PMR spectra of selenophene, the isomeric 1-(selenien-2-yl)-3-phenylpropenones, and their thiophene analogs have been obtained.

Continuing a study of the IR spectra of α,β-unsaturated ketones containing heterocyclic radicals—furyl [1], thienyl [2], pyrryl [3], and quinolyl [4]—we decided to investigate a systematic series of selenophene analogs of the chalcones of types **A** and B (see Table 1):



and



A

B

It was mainly the IR spectra and Raman spectra of only selenophene itself and some of its simplest derivatives that had been studied previously [5–11]. In our preceding papers [12–14] there are likewise only fragmentary data on the characteristic frequencies of the vibrations of some carbonyl compounds of the selenophene series.

We have measured the IR spectra of chalcone analogs containing the selenophene nucleus in the solid state and in some cases in solutions in carbon tetrachloride and chloroform. The characteristic frequencies of the vibrations of the individual groups obtained are given in Tables 1 and 2 and some characteristic absorption curves are shown in Fig. 1.

The frequency of the stretching vibrations of the carbonyl group ($\nu_{C=O}$) for all the compounds investigated is located in the 1633–1668 cm^{-1} region. In carbon tetrachloride solution (see Table 2), $\nu_{C=O}$ is higher by 5–12 cm^{-1} than for absorption in the solid phase. We have found a similar rule for other α,β-unsaturated ketones of the heterocyclic series [1–4] and have explained it by a change in the force constant of the C=O bond under the influence of the crystal field and by the weakening of dipole orientation [15]. In chloroform, $\nu_{C=O}$ is always somewhat lower (by 4–9 cm^{-1}) than in carbon tetrachloride because of the formation of hydrogen bonds, which is also confirmed by a study of the electronic spectra [16]. A similar phenomenon is observed for the stretching vibrations of the vinylene group ($\nu_{C=O}$). In a paper published recently [17] on the influence of the solvent on the $\nu_{C=O}$ and $\nu_{C=C}$ absorption bands in α,β-unsaturated ketones with the s-cis conformation, the same shifts in the frequencies on passing from solutions in carbon tetrachloride to solutions in chloroform were reported.

If we compare $\nu_{C=O}$ for the selenophene chalcones with $\nu_{C=O}$ for the ketones of analogous structure of the furan [1] and thiophene [2] series, it is not difficult to be convinced that, as a rule, in the first group the frequency of the stretching vibrations of the carbonyl group is always somewhat lower. It is known that a strengthening of the donor properties of radicals leads to a lowering of the order of the C=O bond [18]. Thus, the conclusion put forward previously [12] that the selenophene radical in the static state has a greater electron-donating influence than its oxygen and sulfur-containing isologs is confirmed. It is interesting that the rate constants of deuterium exchange [19] (for the α-position) also decrease in the sequence selenophene > > thiophene > furan.

The introduction into the aromatic nucleus of the selenophene chalcones of electron-donating substituents (CH_3, CH_3O, OH, NH_2, and $N(CH_3)_2$) or electron-accepting substituents (F, Cl, NO_2) causes, respectively, a lowering or a raising of $\nu_{C=O}$ in comparison with the unsubstituted ketones I and **II**. These changes of frequency, both for the 1-(selenien-2-yl)-3-arylpropen-1-ones and for the propen-3-ones isomeric with them, are fairly satisfactorily correlated with the σ parameters of McDaniel and Brown [20] by the equation (see Fig. 2):

$$\Delta\nu_{C=O}\cdot\frac{hc}{2.3\ KT}=\rho\sigma,$$

where $\Delta\nu_{C=O}$ is the difference in frequencies of the stretching vibrations of the carbonyl group in, respectively, I and II and their substituted derivatives; K is Boltzmann's constant; h is Planck's constant; c is the velocity of light; and T is the absolute temperature. It follows from this that all the compounds studied, regardless of the electronic nature of the substituent introduced, are present in one and the same conformational state. The replacement of a phenyl group in compounds I and II by a furyl, thienyl, or selenienyl group (see **XXII–XXVI**) also leads to a lowering of $\nu_{C=O}$ because of their electron-donating nature, which increases in the sequence 2-furyl < 2-thienyl < 2-selenienyl. Conversely, pyrid-2- and -3-yls (**XXVII** and **XXVIII**) exert an electron-accepting influence and raise $\nu_{C=O}$ of the chalcones. It is also a general characteristic that pyrid-2-yl has a greater influence than pyrid-3-yl. The quinoline nucleus (**XXIX,XXX**) somewhat lowers $\nu_{C=O}$ in comparison with phenyl (I,II), probably because of

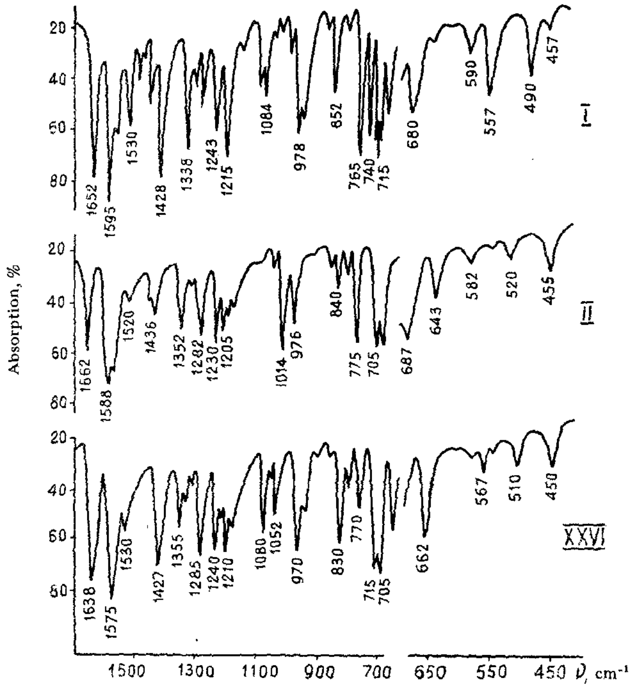


Fig. 1. IR spectrograms of compounds I, II, and XXVII.

Table 1

Characteristic Frequencies of Selenophene Analogs of the Chalcones, cm^{-1}

Compound	Name of the ketone	$\nu_{C=O}$	$\nu_{C=C}$	ν_{trans} $H-C=C-H$	$\nu_{selenienyl}$			β_{C-H}	ν_{C-H}	
I	1-(Selenien-2-yl)-3-phenylpropen-1-one	1652	1595	978	1428	1338	1243	1084	852	715
II	1-(Selenien-2-yl)-3-phenylpropen-3-one	1662	1588	976	1436	1352	1230	1079	840	705
III	1-(Selenien-2-yl)-3-(4-tolyl)propen-1-one	1650	1590	969	1425	1331	1240	1088	818	710
IV	1-(Selenien-2-yl)-3-(4-tolyl)propen-3-one	1658	1586	970	1437	1354	1235	—	817	—
V	1-(Selenien-2-yl)-3-(4-anisyl)propen-1-one	1648	1594	970	1428	1340	1232	1083	822	710
VI	1-(Selenien-2-yl)-3-(4-anisyl)-propen-3-one	1655	1593	975	1440	1358	1240	1080	832	705
VII	1-(Selenien-2-yl)-3-(2,4-dimethoxyphenyl)propen-1-one	1635	1608	970	1424	1348	1242	1083	838	705
VIII	1-(Selenien-2-yl)-3-(2,4-dimethoxyphenyl)propen-3-one	1638	1600	960	1438	1350	1230	1070	835	710
IX	1-(Selenien-2-yl)-3-(2,4,6-trimethoxyphenyl)propen-1-one	1642	1595	984	1440	1340	1238	1088	843	705
X	1-(Selenien-2-yl)-3-(2,4,6-trimethoxyphenyl)propen-3-one	1644	1615	970	1425	1345	1238	1088	837	720
XI	1-(Selenien-2-yl)-3-(4-hydroxyphenyl)-propen-1-one	1646	1615	976	1428	1345	—	1080	830	720
XII	1-(Selenien-2-yl)-3-(4-aminophenyl)propen-1-one	1643	1620	970	1423	1335	1230	1084	823	718
XIII	1-(Selenien-2-yl)-3-(4-dimethylaminophenyl)propen-1-one	1633	1605	971	1425	1340	1242	1085	821	715
XIV	1-(Selenien-2-yl)-3-(4-dimethylaminophenyl)propen-3-one	1634	1605	980	1442	1345	1240	1068	823	715
XV	1-(Selenien-2-yl)-3-(4-fluorophenyl)propen-1-one	1662	1598	973	1435	1343	1232	1090	835	717
XVI	1-(Selenien-2-yl)-3-(4-chlorophenyl)propen-1-one	1655	1603	970	1431	1332	1239	1090	818	700
XVII	1-(Selenien-2-yl)-3-(4-chlorophenyl)propen-3-one	1662	1598	975	1440	1333	1235	1096	823	697
XVIII	1-(Selenien-2-yl)-3-(4-nitrophenyl)propen-1-one	1655	1595	968	1428	1350	1243	1089	840	710
XIX	1-(Selenien-2-yl)-3-(4-nitrophenyl)propen-3-one	1657	1578	976	1436	1348	1235	1087	830	705
XX	1-(Selenien-2-yl)-3-(4-xenyl)propen-1-one	1648	1590	965	1428	1332	1235	1085	834	700
XXI	1-(Selenien-2-yl)-3-(4-xenyl)propen-3-one	1662	1585	985	1440	1356	1240	1080	831	705
XXII	1-(Selenien-2-yl)-3-(2-furyl)propen-1-one	1652	1592	972	1428	—	1240	1082	828	712
XXIII	1-(Selenien-2-yl)-3-(2-furyl)propen-3-one	1657	1603	962	1443	1358	1258	1079	835	692
XXIV	1-(Selenien-2-yl)-3-(2-thienyl)propen-1-one	1643	1579	970	1424	1335	1234	1083	832	710
XXV	1-(Selenien-2-yl)-3-(2-thienyl)propen-3-one	1650	1580	970	1440	1360	1245	1086	830	720
XXVI	1,3-Di(selenien-2-yl)propenone	1638	1575	970	1427	1355	1240	1080	830	705
XXVII	1-(Selenien-2-yl)-3-(pyrid-2-yl)propen-3-one	1668	1580	—	1433	1357	1234	1073	845	695
XXVIII	1-(Selenien-2-yl)-3-(pyrid-3-yl)propen-3-one	1663	1600	970	1440	1355	1235	1072	830	710
XXIX	1-(Selenien-2-yl)-3-(quinol-2-yl)propen-1-one	1647	1590	973	1421	1350	1236	1080	825	712
XXX	1-(Selenien-2-yl)-3-(quinol-2-yl)propen-3-one	1658	1580	975	1432	1353	1230	1078	850	718

the considerable increase in the mass of the substituent. However, as has been shown [4], it nevertheless possesses an electron-accepting nature, which finds its reflection in the fact that $\nu_{C=O}$ for XXX is greater than $\nu_{C=O}$ for XXIX.

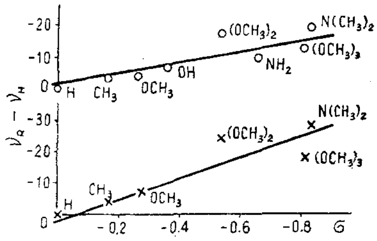


Fig. 2. Correlation between the shift of the frequency of the carbonyl group ($\Delta\nu_{C=O} = \nu_R - \nu_H$) and the σ parameters of the substituents: ○) for the 1-(selenien-2-yl)-3-aryl-propen-1-ones [$\rho = (4.0 \pm 0.3) \cdot 10^{-2}$; r = 0.83*]; ×) for the isomeric propen-3-ones [$\rho = (6.5 \pm 0.4) \cdot 10^{-2}$; r = 0.91].

The absorption due to the stretching vibrations of the aliphatic vinylene group ($\nu_{C=C}$) is well-defined in all compounds in the 1575–1620 cm^{-1} region, its intensity being considerably higher than the intensity of $\nu_{C=O}$ (see Fig. 1).

In aliphatic compounds, $\nu_{C=C}$ is generally in the range from 1680 to 1620 cm^{-1}, a lowering of the figure being caused by conjugation of the vinylene group with a carbonyl group or an aromatic or heterocyclic nucleus [21]. In all the spectrograms we also find peaks of medium and high intensity at 985–960 cm^{-1} which are specific for the nonplanar deformation vibrations of the hydrogens of an ethylenic bond in the trans configuration. So far as concerns the mutual arrangement of the vinylene and carbonyl groups, on the basis of the ratio of the intensities of $\nu_{C=O}$ and $\nu_{C=C}$ [22] it must be concluded that we are dealing with s-cis conformations. This conclusion is also confirmed by the influence of the solvent on the change in the $\nu_{C=O}$ and $\nu_{C=C}$ frequencies as was mentioned above.

Table 2

Stretching Vibrations of the Carbonyl and Vinylene Groups Measured in Solutions

Ketones	In CCl$_4$		In CHCl$_3$	
	$\nu_{C=O}$	$\nu_{C=C}$	$\nu_{C=O}$	$\nu_{C=C}$
I	1661	1607	1652	1600
II	1668	1600	1663	1593
V	1654	1600	1649	1594
VI	1663	1608	1659	1605
XVI	1660	1609	1654	1602
XVII	1668	1601	1663	1597
XXVI	1650	1594	1645	1588

The skeletal vibrations of the selenophene ring in the compounds studied as in the case of the thiophene derivatives [2, 23] are found at 1560–1520, 1443–1421 (1433 ± 2), 1360–1332 (1346 ± 3) and 1245–1230 (1237 ± ± 2) cm^{-1}. The first band at 1560–1520 cm^{-1} has a high frequency and a low intensity and, since other aromatic systems also absorb in this region, in a number of cases it is difficult to identify. The most intensive absorption is at 1443–1421 cm^{-1}, this frequency being somewhat lower for the propen-1-ones (1427 ± ± 2 cm^{-1}), than for the propen-3-ones (1438 ± 2 cm^{-1}). The same tendency appears for the vibration of the selenophene ring at 1360–1332 cm^{-1}. This law of the change in the frequencies under the influence of a substituent present in position 2 of the heterocycle apparently has a general nature. Thus, in particular, it can be observed in an analysis of the IR spectra of the thiophene [2] and pyrrole [3] chalcones. Skeletal vibrations of the 2-monosubstituted furans also undergo similar changes in dependence on the electronic nature of the substituent [24].

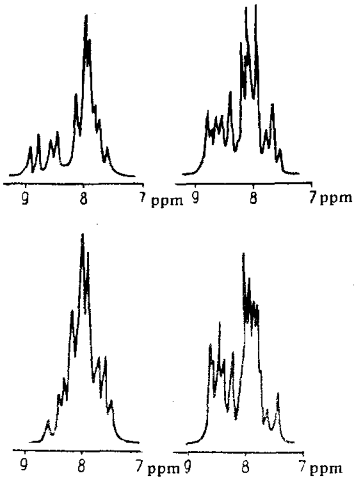


Fig. 3. PMR spectra of the ketones I and II (top) and their thiophene analogs (bottom).

It must be borne in mind that in chalcone itself there is absorption of greater than average intensity at at 1340 cm^{-1}, and therefore the peak in the 1360–1332 cm^{-1} region is not of great interest for distinguishing the selenophene ketones from ordinary chalcones. From this point of view, the absorption at 1237 ± 2 cm^{-1}, which is always well-defined and located in a narrow region, is more convenient. The intensity of the first three types of skeletal vibrations of the selenophene ring in those cases where the carbonyl group is bound directly to the heterocycle (the propen-1-ones) is always higher than for the propen-3-ones (see Fig. 1). This difference in intensities is due to the strong interaction of the electron-donating selenienyl groups with the electron-accepting carbonyl group, in consequence of which a change in the dipole moment arises during the vibrations [24].

The planar deformation vibrations of the C–H bonds of the selenophene radical (β_{C-H}) in the 1090–1068 cm^{-1} (1082 ± 2) region are fairly well expressed in the

---

*The low correlation coefficients (r), particularly for propen-1-ones, are due to the relatively low changes in $\nu_{C=O}$.

compounds studied. On the other hand, the analogous vibrations at 1030–1060 cm^{-1} have a low intensity and are difficult to distinguish from the absorption of aromatic chalcones in this region. Table 1 gives other frequencies of the nonplanar deformation vibrations of the C—H bonds (γ_{C-H}) at 852–817 cm^{-1} (823 ± 3) and 720–695 cm^{-1} (705 ± 3), which probably relate mainly to the selenophene ring; these are also difficult to distinguish from the corresponding absorption of substituted benzene nuclei and of other heterocycles.

It was of interest also to find characteristic frequencies for the selenophene radical which would permit the selenophene chalcones to be distinguished from the analogous compounds of the thiophene series. On a careful comparison of the spectrograms of compounds I–XX and XXVI with the spectrograms of the completely analogous thiophene derivatives [2], we found no fundamental differences in the numbers and positions of the absorption bands. The characteristic absorption bands for the C—Se bond at 710–760 cm^{-1} reported previously [5–7] we found only in certain compounds. It may also be mentioned that a number of absorption maxima for the selenophene ketones are displaced somewhat into the low-frequency region. Thus, apart from the effect of this type that has already been mentioned for $\nu_{C=O}$ and $\nu_{C=C}$, the same feature is noted for the absorption of the selenophene ring at 1346 ± 3, 1237 ± 2, and 832 ± 3 cm^{-1} (analogous absorptions for thiophene derivatives are: 1365 ± 5, 1241 ± 2, and 841 ± 5 cm^{-1}). Conversely, the stretching vibrations of the selenophenes are located at 1433 ± 2 cm^{-1}, while the corresponding vibrations of the thiophenes are located at 1419 ± 3 cm^{-1}. In many cases, especially for the propen-1-ones, the compounds of the thiophene series have additional weak or medium-intensity absorption at 1354–1375 cm^{-1} and sometimes at about 860 cm^{-1}.

In addition to this, we have found that the selenophene chalcones I and II differ from the corresponding thiophene chalcones to a far greater extent in their PMR spectra (Fig. 3). This difference is caused mainly by the fact that the PMR spectrum of selenophene itself, according to our measurements (Fig. 4) is unlike that of thiophene. In the first case, the signals of the α- and β-protons are clearly separated and their chemical shifts are 7.56 and 7.04 ppm, respectively (standard: tetramethylsilane), while in thiophene the signals from the α-hydrogen atoms are displaced by only 0.125 ppm in the weak-field direction as compared with the signals from the protons in the β position [25]. It must also be mentioned that the ketone I and its thiophene analog in which the carbonyl groups are adjacent to the heterocyclic radicals are distinguished particularly well by their PMR spectra. The chemical shifts of the α- and β-protons of the vinylene groups in ketone I are located at 7.41 and 7.75 ppm and in ketone II at 7.28 and 7.50 ppm, and the spin-spin coupling constants (15.5 and 15.5 Hz) confirm their trans position. A complete interpretation of the PMR spectra of the α,β-unsaturated ketones of the thiophene and selenophene series will be given later.

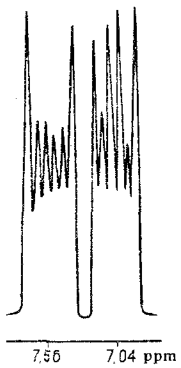


Fig. 4. PMR spectrum of selenophene.

EXPERIMENTAL

The IR spectra of the chalcone analogs containing a selenophene nucleus were measured in the solid phase in potassium bromide tablets (2 mg of substance to 100 mg of KBr) and also in carbon tetrachloride and chloroform solutions (at concentrations of the substances of $2.5–3.5 \cdot 10^{-2}$ M) on a UR-10 instrument in the 1800–500 cm^{-1} region.

The PMR spectra were measured by A. I. Yatsenko on a high-resolution instrument ($1 \cdot 10^{-8}$) at a frequency of 40 MHz; the range of variation of the magnetic field was 9400–10 000 G. The chemical shifts of the signals given in the text and in Figs. 3 and 4 were measured relative to hexamethyldisiloxane as internal standard and were recalculated to tetramethylsilane. The measurement of selenophene was carried out on a liquid sample and those of I, II, and their thiophene analogs in carbon tetrachloride solution at several concentrations of the substances (of the order of 0.5, 0.3, and 0.15 M) with subsequent extrapolation to infinite dilution.

REFERENCES

1. S. V. Tsukerman, A. I. Artemenko, V. F. Lavrushin, and Yu. S. Rozum, ZhOKh, **34**, 2309, 1964.
2. S. V. Tsukerman, V. M. Nikitchenko, Yu. S. Rozum, and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], **3**, 452, 1967.
3. S. V. Tsukerman, V. P. Izvekov, Yu. S. Rozum, and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], **4**, 1101, 1968.
4. S. V. Tsukerman, Chan Chuok Shon, Yu. S. Rozum, and V. F. Lavrushin, Zh. prikl. spektrosk. [Journal of Applied Spectroscopy], **5**, 489, 1966.
5. H. Gerding, G. Milazzo, and H. Rossmark, Rec. trav. chim., **72**, 957, 1953.
6. F. Ya. Perveev and D. N. Glebovskii, Vestnik LGU, **22**, 135, 1956.
7. N. A. Chumaevskii, V. M. Tatevskii, and Yu. K. Yur'ev, Opt. i spektr., **6**, 45, 1959.
8. Yu. K. Yur'ev, N. N. Mezentsova, and E. G. Treshchova, Vestn. MGU, no. 1, 60, 1962.
9. Ya. Eidus, T. Polka, and Yu. K. Yur'ev, Izv. AN LatvSSR, no. 2, 63, 1963.
10. E. G. Treshchova, D. Ekkkhardt, and Yu. K. Yur'ev, ZhFKh, **38**, 295, 1964.

11. Ya. M. Kimel'fel'd, V. T. Aleksanyan, N. N. Magdesieva, and Yu. K. Yur'ev, ZhSKh, **7**, 42, 1966.

12. S. V. Tsukerman, V. D. Orlov, V. M. Nikitchenko, Yu. S. Rozum, V. F. Lavrushin, and Yu. K. Yur'ev, Teor. i eksp. khim., **2**, 399, 1966.

13. S. V. Tsukerman, V. D. Orlov, V. F. Lavrushin, and Yu. K. Yur'ev, KhGS [Chemistry of Heterocyclic Compounds], **2**, 918, 1966.

14. S. V. Tsukerman, V. D. Orlov, Yu. N. Surov, and V. F. Lavrushin, ZhSKh, **9**, 67, 1968.

15. R. Jones and C. Sandorfy, "The application of infrared and Raman spectroscopy to the elucidation of molecular structure," Chemical Applications of Spectroscopy, ed. by W. West [Russian translation], IL, Moscow, p. 370, 1959.

16. S. V. Tsukerman, V. D. Orlov, V. F. Lavrushin, and Yu. K. Yur'ev, KhGS [Chemistry of Heterocyclic Compounds], **2**, 913, 1966.

17. K. Noack, Spectrochim. Acta, **18**, 1625, 1962.

18. M. V. Vol'kenshtein, The Structure and Physical Properties of Molecules [in Russian], Izd-vo AN SSSR, Moscow-Leningrad, p. 431, 1955.

19. A. I. Shatenshtein, A. G. Kamrad, I. O. Shapiro, Yu. N. Panneva, and E. N. Zvyagintseva, DAN, **168**, 364, 1966.

20. D. H. McDaniel and H. C. Brown, J. Org. Chem., **23**, 420, 1958.

21. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL, Moscow, p. 54, 1963.

22. O. Wintersteiner and M. Moore, J. Am. Chem. Soc., **78**, 6193, 1956.

23. A. R. Katritzky and A. J. Boulton, J. Chem. Soc., 3500, 1959.

24. A. R. Katritzky and A. P. Ambler, Physical Methods in the Chemistry of Heterocyclic Compounds [Russian translation], Khimiya, Moscow-Leningrad, p. 507, 1966.

25. R. J. Abraham and N. J. Bernstein, Can. J. Chem., **37**, 2095, 1959.

23 January 1967

Gor'kii Khar'kov State University

Institute of Organic Chemistry AS UkrSSR, Kiev