3. E. A. Medyantseva, O. M. Babeshko, and V. I. Minkin, Zh. Org. Khim., 12, 837 (1976).
4. P. Beak, Acc. Chem. Res., 10, 186 (1977).
5. Yu. R. Jencks, in: Modern Problems of Physical Organic Chemistry [Russian translation], Mir, Moscow (1967), p. 342.
6. R. É. Val'ter, Ring-Chain Isomerism in Organic Chemistry [in Russian], Zinatne, Riga (1978), p. 87.

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# SYNTHESIS AND STUDY OF THE LIGHT-STABILIZING ACTIVITY OF SOME DITHIOCARBAMATES THAT INCLUDE A HETEROAROMATIC RING

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A number of new dithiocarbamates of transition metals that contain thiophene, furan, benzo[b]thiophene, and benzo[b]selenophene rings were synthesized. The compounds obtained were investigated as light stabilizers for polymers. It is shown that the effectiveness of the light-stabilizing effect of the dithiocarbamate depends on the structure of the heterocyclic fragment included in its composition.

At the end of the nineteen fifties in the laboratory of heterocyclic compounds of the Institute of Organic Chemistry of the Academy of Sciences of the USSR a number of thiophene derivatives were synthesized in order to search for new vulcanization accelerators and antioxidants for rubbers [1, 2]. During testing of these compounds it was established that some of them have the properties of inhibitors of the oxidation of rubbers, although to a smaller degree than the compounds that do not include a thiophene ring that are used for this purpose. Later one of the authors of the present paper in collaboration with B. P. Fedorov and G. I. Gorushkina [3] synthesized some dithiocarbamates that include a thiophene ring, the properties of which, however, were not investigated. It has been recently established that the dithiocarbamates of some transition metals are effective light and heat stabilizers of polymers [4]. In this case it should be noted that the nature of the transition metal plays a substantial role in the effectiveness of the dithiocarbamates. In connection with all of the information pointed out above we again turned to the synthesis of dithiocarbamates of the type mentioned above by extending the number of transition metals. The resulting dithiocarbamates were studied as light stabilizers. The results of the study are set forth below.

The new dithiocarbamates were synthesized by known methods. The reaction of 2-formylthiophene (I) and substituted 2-formylthiophenes (II), as well as furfural (V) and 2-formylbenzo[b]thiophene (III) or 2-formylbenzo[b]selenophene (IV), with the corresponding amines (VI-VIII) gave azomethines IX-XV, which were reduced to amines XVI-XXII. The latter were converted to alkali metal or ammonium salts of N,N-disubstituted dithiocarbamic acids, from which dithiocarbamates XXIII-XXXV were obtained by exchange reactions with transition metal salts. The properties of the dithiocarbamates obtained are presented in Table 1. Let us note that the synthesis of dithiocarbamate complexes XXX and XXIX was accompanied by the formation of a compound with an unestablished structure, the decomposition of which in an acidic medium led to the formation of XXX.*

Complexes XXXIV and XXXV were obtained from the crystalline ammonium salts of the dithiocarbamic acids with a benzo[b]thiophene or benzo[b]selenophene fragment in the molecules. These salts are convenient to use directly for the preparation of complexes XXXIV and XXXV.

Using ethyl- and methoxythiophene as the ligand for the preparation of nickel complex XXXIII we strove, as in the introduction of a tert-butyl group as the substituent attached to the nitrogen atom in XXIII, to increase the solubility [5] and the effectiveness of the

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*As in Russian original — Publisher.

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TABLE 1. Characteristics of the Synthesized Dithiocarbamates $R^1-CH_2-\underset{CS_2M/_n}{\underset{|}{N}}-R^2$

| Compound | R¹ | R² | Metal (n) | Form and color | Dec. temp., °C | Found, % | | | | | Empirical formula | Calc., % | | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | S | M | | C | H | N | S | M | |
| XXIII | 2-Thienyl | tert-Butyl | Ni(II) | Green powder | >270 | 44,0 | 5,2 | — | 34,8 | 10,9 | $C_{20}H_{28}N_2NiS_6$ | 43,9 | 5,2 | — | 35,1 | 10,7 | 27 |
| XXIV | „ | Cyclohexyl | Cu(II) | Brown crystals | 228—230 | 48,2 | 5,4 | — | 31,3 | 10,4 | $C_{24}H_{32}CuN_2S_6$ | 47,7 | 5,3 | — | 31,8 | 10,5 | 99 |
| XXV | „ | „ | Ni(II) | Green crystals | 212—213 | 48,5 | 5,4 | 4,7 | 31,7 | 9,7 | $C_{24}H_{32}N_2NiS_6$ | 48,1 | 5,4 | 4,7 | 32,1 | 9,8 | 91 |
| XXVI | „ | „ | Zn(II) | White crystals | 226—227 | 48,1 | 5,4 | 4,6 | 31,4 | 10,5 | $C_{24}H_{32}N_2S_6Zn$ | 47,5 | 5,3 | 4,6 | 31,7 | 10,8 | 99 |
| XXVII | „ | „ | Co(III) | Green powder | 141—143 | 50,1 | 5,7 | — | 32,8 | 6,1 | $C_{36}H_{48}CoN_3S_9$ | 49,7 | 5,6 | — | 33,2 | 6,4 | 93 |
| XXVIII | „ | „ | Fe(III) | Black crystals | 135—140 | 49,9 | 5,6 | — | 32,7 | 6,2 | $C_{36}H_{48}FeN_3S_9$ | 49,9 | 5,6 | — | 33,3 | 6,4 | 86 |
| XXIX | „ | p-Hydroxyphenyl | Cu(II) | Brown crystals | 248—250 | 46,0 | 3,2 | — | 30,5 | 10,6 | $C_{24}H_{20}CuN_2O_2S_6$ | 46,2 | 3,2 | — | 30,8 | 10,2 | 5 |
| XXX | „ | „ | Ni(II) | Green crystals | 262—264 | 46,4 | 3,3 | — | 30,8 | 10,0 | $C_{24}H_{20}N_2NiO_2S_6$ | 46,5 | 3,3 | — | 31,0 | 9,5 | 10 |
| XXXI | 2-Furyl | „ | Ni(II) | Green crystals | 241—243 | 49,0 | 3,4 | — | 21,7 | 10,3 | $C_{24}H_{20}N_2NiO_4S_4$ | 49,1 | 3,4 | — | 21,8 | 10,0 | 7 |
| XXXII | „ | „ | Zn(II) | Yellow crystals | 82—83 | 48,8 | 3,6 | — | 21,1 | 10,7 | $C_{24}H_{20}N_2O_4S_4Zn$ | 48,5 | 3,4 | — | 21,6 | 11,0 | 30 |
| XXXIII | 2-Methoxy-5-ethyl-3-thienyl | Cyclohexyl | Ni(II) | „ „ | 175—180 | 50,5 | 6,1 | 4,0 | 26,8 | 8,1 | $C_{30}H_{44}N_2NiO_2S_6$ | 50,3 | 6,2 | 3,9 | 26,9 | 8,2 | 75 |
| XXXIV | 2-Benzo[b]-thienyl | „ | Ni(II) | Green powder | 126—127 | 55,2 | 5,3 | 4,1 | 27,3 | 8,3 | $C_{32}H_{36}N_2NiS_6$ | 54,9 | 5,2 | 4,1 | 27,5 | 8,4 | 94 |
| XXXV* | 2-Benzo[b]-selenienyl | „ | Ni(II) | Green crystals | >240 | 48,4 | 4,6 | — | 15,9 | 7,2 | $C_{32}H_{36}N_2NiS_4Se_2$ | 48,4 | 4,6 | — | 16,2 | 7,4 | 70 |

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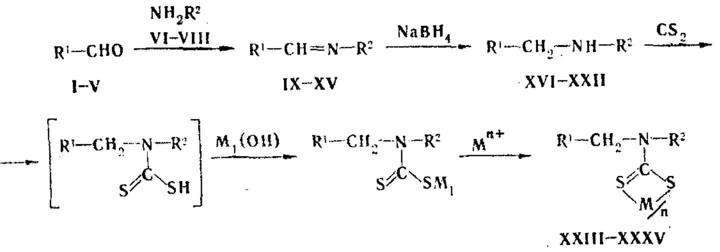
*Found: Se 19.6%. Calculated: Se 19.9%.

TABLE 2. Light-Stabilizing Properties of Transition Metal Dithiocarbamates

| Compound | Dithiocarbamate | Solubility in the polymer | Induction period, h |
|---|---|---|---|
| XXIII | Bis{N-tert-butyl-N-(2-thenyl)dithiocarbamato}-Ni(II) | Slightly soluble | 8 |
| XXIV | Bis{N-cyclohexyl-N-(2-thenyl)dithiocarbamato}-Cu(II) | Soluble | 23 |
| XXV | Bis{N-cyclohexyl-N-(2-thenyl)dithiocarbamato}-Ni(II) | „ | 47 |
| XXVI | Bis{N-cyclohexyl-N-(2-thenyl)dithiocarbamato}-Zn(II) | „ | 20 |
| XXVII | Tris{N-cyclohexyl-N-(2-thenyl)dithiocarbamato}-Co(III) | „ | 18 |
| XXVIII | Tris{N-cyclohexyl-N-(2-thenyl)dithiocarbamato}-Fe(III) | „ | 5 |
| XXIX | Bis{N-(p-hydroxyphenyl)-N-(2-thenyl)dithiocarbamato}Cu(II) | Slightly soluble | 10 |
| XXX | Bis{N-(p-hydroxyphenyl)-N-(2-thenyl)dithiocarbamato}Ni(II) | „ „ | 20 |
| XXXI | Bis{N-(p-hydroxyphenyl)-N-(2-furfuryl)dithiocarbamato}Ni(II) | „ „ | 20 |
| XXXII | Bis{N-(p-hydroxyphenyl)-N-(2-furfuryl)dithiocarbamato}Zn(II) | „ „ | 34 |
| XXXIII | Bis{N-cyclohexyl-N-(2-methoxy-5-ethyl-2-thenyl)dithiocarbamato}Ni(II) | Soluble | 70 |
| XXXIV | Bis{N-cyclohexyl-N-(2-benzo[b]thenyl)dithiocarbamato}Ni(II) | „ | 32 |
| XXXV | Bis{N-cyclohexyl-N-(benzo[b]selenophen-2-ylmethyl)dithiocarbamate}Ni(II) | „ | 24 |
| XXXVI | Tris(N,N-diethyldithiocarbamato)Co(III) | „ | — |
| XXXVII | Bis(N,N-dibutyldithiocarbamato)Ni(II) | „ | 90 |
|  | Induction period of the polymer film without s stabilizer |  | 4 |



$M_1$=K, Na, $NH_4$; M=Cu, Ni, Zn, Co, Fe; $R^1$=2-thienyl, 2-furyl, 2-methoxy-5-ethyl-3-thienyl; 2-benzo[b]thienyl; 2-benzo[b]selenienyl; $R^2$ = tert-butyl, cyclohexyl, p-hydroxyphenyl

compounds thus obtained as light stabilizers. However, we achieved the expected result only in the case of XXXIII.

All of the isolated, purified, and thoroughly analyzed metal dithiocarbamates were tested for their light-stabilizing capacity in the IST-30 isoprene–styrene block copolymer with M ∿ 100,000. The induction periods of IST-30 samples containing $1\cdot10^{-2}$ mole/kg of the metal complexes are presented in Table 2. It is apparent that most of the investigated complexes are effective light-stabilizers of polymers. It follows from the data presented in Table 2 that not only the nature of the metal but also the nature of the substituents of the amino group of the dithiocarbamate have a pronounced effect on the photostability of the polymer. It is convenient to trace the effect of the metal in the case of XXIV-XXVIII, which have ligands with the same structure. Of these compounds, the complex that contains Fe (XXVIII) has the lowest light-stabilizing capacity, whereas the metal complexes that contain Cu (XXIV), Zn (XXVI), and Co (XXVII) have similar light-stabilizing capacities in the polymer. The nickel complex (XXV) proved to be the most effective light stabilizer of the XXIV-XXVIII complexes. It is interesting to note that the XXVII complex, which contains trivalent Co, stabilizes the polymer appreciably, while Co(III) diethyldithiocarbamate (XXXVI), which was used in [4], has virtually no effect on its photostability. As one can see, the behavior of the XXVII and XXXVI complexes, which contain Co(III), is associated with replacement of the alkyl group in diethyldithiocarbamate XXXVI by a heterocyclic fragment. In addition to this, the character of the heterocyclic fragment has an appreciable effect on the stabilizing action. Thus replacement of the benzo[b]selenophene grouping by a benzo[b]thiophene grouping entails a 35% increase in the photostability of the polymer (compare XXXIV and XXXV), whereas replacement

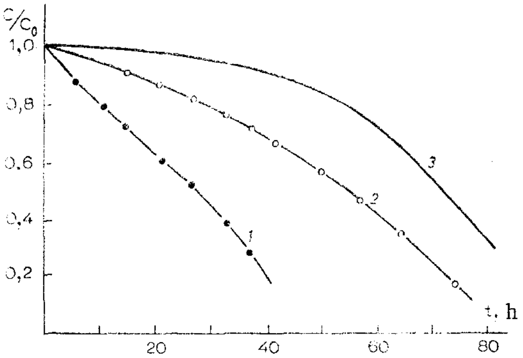


Fig. 1. Kinetic curves of the consumption of the XXV (1) and XXXIII (2) complexes during irradiation of 85 $\mu$m thick IST-30 films with light with $\lambda > 300$ nm at initial concentrations of 0.01 mole/kg; 3) analogous curve for nickel dibutyldithiocarbamate (XXXVII) from the data in [4].

of the benzo[b]selenophene grouping by a thiophene grouping almost doubles the photostability (compare XXXIV and XXV). The light-stabilizing capacity of the dithiocarbamates should naturally depend on their solubility in the polymer. However, XXIII and XXIX-XXXII introduced into the polymer in a concentration of $1 \cdot 10^{-2}$ mole/kg did not dissolve in it completely; nevertheless, the light-stabilizing capacities of some of them surpassed the capacities of related compounds (for example, compare XXVI and XXXII).

It is well known that in the analysis of the mechanism of the effect of complexes one must take into account their shielding capacity, photostability, and their ability to react with free radicals and to decompose hydroperoxides without the formation of free radicals [4]. An analysis of the absorption spectra of the most effective light stabilizers, viz., the soluble XXV, XXXIII, XXXV, and XXXVII nickel complexes, provides evidence that these complexes absorb virtually identically in the visible and near-UV regions. Thus the differences in the effectiveness of the light-protecting effect of the investigated compounds are not associated primarily with the difference in their shielding effects.

In order to study the reason that lead to the development of differences in the effectiveness of the light-stabilizing effect we carried out experiments to study the kinetics of the consumption of XXV and XXXIII under the conditions of testing the photostability. It is apparent from Fig. 1 that, as in the case of other complexes [4], one observes a correlation between the rate of conversion of the polymer and the effectiveness of the action of the complex; the higher the rate of consumption of the complex, the lower its effectiveness. This constitutes evidence that for most of the investigated compounds the reason for the low effectiveness of the light-stabilizing action is low photostability. One important feature must be noted. The most effective light stabilizer among the investigated compounds, viz., the XXXIII complex, virtually from the very start is consumed at a rather high rate that considerably exceeds the rate of consumption of nickel dibutyldithiocarbamate (XXXVII) and, at the same time, is almost equal to it with respect to the effectiveness of its light-protecting action. In our opinion, this constitutes evidence that the XXXIII complex, although it does have lower photostability than simple dialkyldithiocarbamates, acts more effectively as an antioxidant that decomposes hydroperoxides without the formation of free radicals. A comparison of the effectivenesses and photostabilities of the XXV and XXXIII complexes makes it possible to assume that the introduction of electron-donor substituents in the thiophene ring may serve as a means of increasing both the photostability of the complex and its effectiveness as a compound that increases the photostability of the complex. Effective light stabilizers of polymers should therefore be sought in series of precisely such compounds.

In conclusion, one must note the relatively high effectiveness of zinc complex XXXII, which proved to be considerably better than the corresponding zinc diethyldithiocarbamate [4]. Compounds of this type are extremely promising, since they are colorless, do not color the polymer, and protect it sufficiently from the action of light.

Thus we have obtained a number of new dithiocarbamates of transition metals that include thiophene, benzothiophene, benzoselenophene, or furan rings. It was shown that the structure of the heterocyclic fragment of the molecule affects the effectiveness of the light-stabilizing action of the dithiocarbamate.

## EXPERIMENTAL

2-Formylthiophene (I) [8], 2-metnoxy-3-formyl-5-ethylthiophene (III) [9], 2-formylbenzo[b]thiophene (III) [10], and 2-formylbenzo[b]selenophene (IV), which was obtained in the same way

TABLE 3. Characteristics of the Synthesized Azomethines and Amines

| Compound | Name of the compound | mp, °C | Yield, % | Compound | Name of the compound | mp or bp (gPa), °C | Yield, % |
|---|---|---|---|---|---|---|---|
| IX | 2-Thenylidene-2-aminoisobutane | — | 97 | XVI | 2-Thenyl-tert-butylamine | 96—97 (18,6) | 82 |
| X | 2-Thenylideneaminocyclohexane | — | 100 | XVII | 2-Thenylcyclohexylamine | 116—118 (2,7) | 61 |
| XI | 2-Thenylidene-p-aminophenol | 204—205 | 90 | XVIII | 2-Thenyl-p-hydroxyphenylamine | 105—106 | 80 |
| XII | 2-Furfurylidene-p-aminophenol | 194—195 | 92 | XIX | 2-Furfuryl-p-hydroxyphenyleneamine | 112—113 | 86 |
| XIII | 2-Methoxy-5-ethyl-3-thenyldeneaminocyclohexane | — | 97 | XX | | — | 91 |
| XIV | 2-Benzo[b]thenylideneaminocyclohexane | 77—78 | 98 | XXI[б] | 2-Methoxy-5-ethyl-3-thenylcyclohexylamine | 55—56 | 95 |
| XV | 2-Benzo[b]selenalaminocyclohexane | 172—173 | 98 | XXII[в] | N-Cyclohexyl-2-benzo[b]selenophenemethaneamine | 96—97 | 99 |

[a] Compounds X-XII and XVI-XIX were described in [1, 6, 7, 12-14].
[b] Found: C 73.7; H 7.9; N 5.7; S 12.9%. $C_{15}H_{19}NS$. Calculated: C 73.4; H 7.8; N 5.7; S 13.1%. [c] Found: C 61.7; N 6.4; Se 27.1%. $C_{15}H_{19}NSe$. Calculated: C 61.7; H 6.6; Se 27.0%.

as aldehyde III from benzo[b]selenophene [11], and industrial-grade furfural (V), tert-butylamine (VI), cyclohexylamine (VII), and p-aminophenol (VIII) were used as the starting compounds.

Azomethines IX-XV were obtained by reaction of equimolar amounts of aldehydes I-V and amines VI-VIII without a solvent by heating to 100°C with subsequent removal of the resulting water and unchanged substances by distillation with benzene. Compounds XI and XII were recrystallized from ethanol, XIV was recrystallized from methanol with water, and XV was recrystallized from methanol. Azomethines IX-XV were reduced at 20-30°C with $NaBH_4$ (1.5-2.0 moles per mole of azomethine) in ethanol or methanol. The alcohol solutions were diluted with water, and the liberated amines were extracted thoroughly with ether or n-hexane. Amines XVI-XXII were distilled or recrystallized. Data on azomethines IX-XV and amines XVI-XXII are presented in Table 3.

Dithiocarbamates XXIII-XXVIII and XXXIII-XXXV. An equimolar amount of $CS_2$ was added to amine XVI, XVII, or XX-XXII, and the resulting viscous liquid was dissolved in excess 25% ammonium hydroxide or in an equivalent amount of an aqueous solution of NaOH or KOH. Crystalline ammonium salts were obtained in the case of amines XXI and XXII. The calculated amount of a solution of the metal chloride or acetate (see Table 1) in the same solvent was added to the resulting aqueous ammonia solution of the N,N-disubstituted dithiocarbamic acid, to an aqueous solution of its Na or K salt, or to an aqueous (alcohol) solution of the isolated crystalline ammonium salt. The resulting precipitates of XXIII-XXVII (from 22% ammonium hydroxide), XXXIV (from water), XXXIII (from a mixture of ammonia and alcohol), or XXXV (from alcohol) were washed with the same solvent and water and air dried. The resulting compounds were recrystallized: XXIII from aqueous dimethylformamide (DMF), XXIV from DMF, XXV and XXVI from benzene, XXVII, XXXIII and XXXIV from n-hexane—benzene, XXVIII from DMF—alcohol, and XXXV from chloroform. The recrystallized compounds were air dried at 20-30°C below their melting points.

Dithiocarbamates XXXI and XXXII. Carbon disulfide and NaOH dissolved in a small amount of water (the ratio and amounts of the components were 0.05:0.10:0.25 mole, respectively) were added to amine XIX, and the yellow crystalline mass that formed when the mixture was stirred was dissolved in the minimum amount of water and treated with DMF. Acetone was added to the DMF extract, the mixture was filtered, and ether was added to the filtrate. The precipitate Na salt of the corresponding N,N-disubstituted dithiocarbamic acid was removed by filtration and dried in vacuo over KOH. Dithiocarbamates XXXI and XXXII were obtained by reaction of the isolated Na dithiocarbamate and nickel or zinc chloride in aqueous methanol solutions. Compounds XXXI was recrystallized from chloroform, while XXXII was washed with n-hexane.

Dithiocarbamates XXIX and XXX. A solution of an equivalent amount of nickel chloride or copper acetate in 22% ammonium hydroxide was added to a solution of the ammonium salt of the corresponding dithiocarbamic acid obtained by the method in [3], and the precipitate was removed by filtration and treated with DMF or acetone. The mixture was then treated with an equimolar amount of acetic acid, and the resulting solution was diluted with water and extracted thoroughly with chloroform. Compounds XXIX-XXX were isolated by incomplete evaporation of the chloroform. The constants of the compounds obtained are presented in Table 1.

Testing of the light-stabilizing capacities of the XXIII-XXXV complexes was conducted with IST-30 isoprene—styrene block copolymer with M ∿ 100,000. Films of the polymers containing the metal complexes were obtained by the method described in [4]. Samples of the polymer with a thickness of ∿85 μm were irradiated with the light of a DRSh-120 high-pressure mercury lamp with a wavelength higher than 300 nm. The induction period was used as a measure of the photostability of the polymer. The consumption of the metal complexes XXIII-XXXVI during irradiation was followed spectrophotometrically from the change in the absorption band of the complexes at 400 nm.

## LITERATURE CITED

1. L. G. Angert, Ya. L. Gol'dfarb, G. I. Gorushkina, A. I. Zenchenko, A. S. Kuz'minskii, and B. P. Fedorov, Zh. Prikl. Khim., 32, 408 (1959).
2. A. S. Kuz'minskii, Ya. L. Gol'dfarb, B. P. Fedorov, A. I. Zenchenko, A. P. Kogerman, G. I. Gorushkina, and L. G. Angert, Zh. Prikl. Khim., 33, 1182 (1960).
3. B. P. Fedorov, G. I. Gorushkina, and Ya. L. Gol'dfarb, Zh. Org. Khim., 1, 777 (1965).
4. V. B. Ivanov, Lu Teng Hsu, E. L. Lozovskaya, and V. Ya. Shlyapintokh, Vysokomol. Soedin., A23, No. 8, 1711 (1981).
5. B. Ranby and J. Rabek, Photodegradation, Photooxidation, and Photostabilization of Polymers, Wiley (1975).
6. C. H. Godt and R. E. Wann, J. Org. Chem., 27, 1459 (1962).
7. M. A. Ryashentseva, Kh. M. Minachev, O. A. Kalinovskii, and Ya. L. Gol'dfarb, Zh. Org. Khim., 1, 1104 (1965).
8. A. Reiche, H. Gross, and E. Hoft, Chem. Ber., 93, 88 (1960).
9. Ya. L. Gol'dfarb and M. A. Kalik, Khim. Geterotsikl. Soedin., No. 2, 171 (1971).
10. R. P. Dickinson and B. Iddon, J. Chem. Soc., C, No. 22, 2733 (1968).
11. N. N. Magdesieva and V. A. Vdovin, Khim. Geterotsikl. Soedin., No. 11, 1475 (1970).
12. W. Kampe, E. Fauland, M. Thiel, H. Stork, and W. Schaumann, West German Patent No. 2.426682; Chem. Abstr., 84, 150915 (1976).
13. R. C. Coumes, A. Gaset, J. P. Gorrichon, and G. Michel, Eur. J. Med. Chem.-Chim. Ther., 13, 527 (1978); Chem. Abstr., 90, 162573 (1979).
14. H. Adkins and C. F. Winans, US Patent No. 2175585; Beilstein, 18, IV, 7077.