KINETICS OF REACTIONS IN THE THERMAL DECOMPOSITION OF TETRAPHENYLHYDRAZINE IN THE PRESENCE OF A MIXTURE OF STERICALLY HINDERED PHENOL AND HYDROPEROXIDE

V. T. Varlamov and E. T. Denisov

UDC 541.127:542.92:547.556.8

The previously studied [1, 2] reactions of diphenylaminyl radicals (In•) with cumyl hydroperoxide and 2,4,6-tri-tert-butylphenol (ArOH) take place with inhibiton of oxidation of the hydrocarbons by mixtures of phenols and aromatic amines, where the synergism of their action is manifested [3, 4]. To determine the role of the individual stages of the real process, the kinetic features of the reactions which take place in the decomposition of tetraphenylhydrazine (InIn) in the presence of a mixture of ArOH with cuymyl and tert-butyl hydroperoxides (ROOH) were studied in the present article.

EXPERIMENTAL

The purity of the ArOH and ROOH used was no less than 99.5%. InIn was synthesized from diphenylamine (InH) by the method in [5], and it was 99.8% pure. The solvent, CCl_4, (especially pure) was purified by passing through a column with freshly activated Al_2O_3 and distillation in Ar. The experiments were conducted at 348.0 ± 0.15°K in silane-coated glass reactor ampuls in an atmosphere of Ar. The reaction mixtures were analyzed by liquid chromatography, UV, IR, and EPR spectrometry, and the methods are described in [6]. The error of the analyses was 3% (chromatography) or 4% (spectrophotometry). The pulsed photolysis experiments were conducted at 293°K in cyclohexane [7].

DISCUSSION OF THE RESULTS

With equal initial concentrations of ArOH and ROOH (Fig. 1), both compounds are consumed at the same rates regardless of the depth of the reaction: $v_{ArOH} = 0.62 \cdot 10^{-6}$ and $v_{ROOH} = 0.63 \cdot 10^{-6}$ mole/liter•sec, and InIn is decomposed according to the first order with a rate constant of $1.4 \cdot 10^{-4}$ sec^{-1}, which practically coincides with the data in [8] ($k = 1.48 \cdot 10^{-4}$ sec^{-1}). After total consumption of ArOH and ROOH, k_{dec} decreases to $0.62 \cdot 10^{-4}$ sec^{-1}, which coincides with the value found in [8] for decomposition of InIn in the absence of In• radical acceptors. In the presence of ArOH and ROOH, $v_{InH} = 1.22 \cdot 10^{-6}$ mole/liter•sec $\approx v_{ArOH} + v_{ROOH}$ and $v_{InH}/2v_{InIn} \approx 0.90$. After total consumption of ArOH and ROOH, $v_{InH}/2v_{InIn}$ becomes equal to 0.26, as in the decomposition of InIn in inert media in the preence of InH additives [9]. During the entire experiment, it was not possible to find any acetophenone, cumyl alcohol, or diphenyl nitroxide ($Ph_2NO^\bullet$), and the only products of transformations of ArOH and ROOH were quinoline peroxides (QP) whose presence was demonstrated chromatographically and spectroscopically based on the absorption bands at ~1640 and 1660 cm^{-1} in the IR spectra [10, 11].

These mechanisms in the consumption of the starting substances and the formation of products do not change if the experiments (see Fig. 1) are conducted with initial addition of InH ($2.15 \cdot 10^{-3}$ mole/liter) and with substitution of cumyl hydroperoxide by tert-butyl hydroperoxide. In the latter case, it was also not possible to detect acetone, tert-butyl alcohol, and $Ph_2NO^\bullet$.

If $[ROOH]_0 = 2[ArOH]_0$, then the disappearance of both reagents takes place with the same rates in this case (Fig. 2) up to the total consumption of ArOH, and the rates of consumption are the same as in the experiment conducted with $[ROOH]_0 = [ArOH]_0$. The formation of QP only takes place in the preence of ArOH, and the concentration of QP does not change as the ArOH is consumed (see Fig. 2, curve 6). An increase in $[ROOH]_0$ by two times does not alter the rate of accumulation of InH; a slight decrease in v_{InH} is only observed after consumption of ArOH, and accumulation of cumyl alcohol, acetophenone, $Ph_2NO^\bullet$, phosgene, and other products formed in the decomposition of InIn in CCl_4 in the presence of ROOH alone

---

Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2417-2422, November, 1986. Original article submitted April 29, 1985.

0568-5230/86/3511-2211$12.50

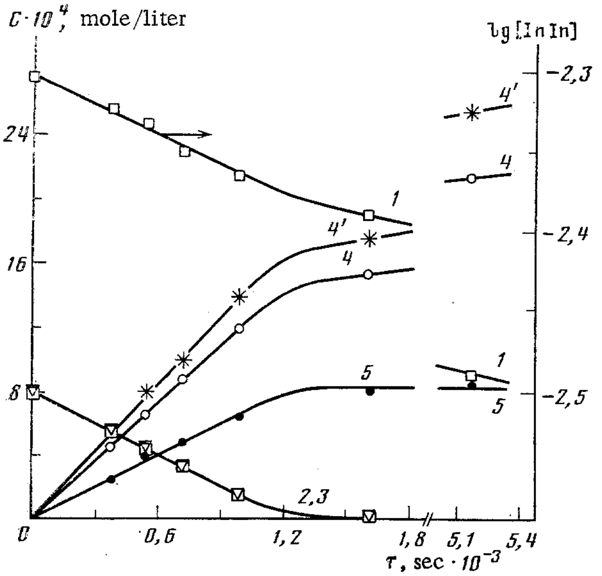

Fig. 1. Kinetic curves of consumption of the starting substances and accumulation of the products of the reaction in decomposition of InIn ($5.0 \cdot 10^{-3}$ mole/liter) in the presence of ArOH ($0.79 \cdot 10^{-3}$ mole/liter) and cumyl hydroperoxide (ROOH) ($0.81 \cdot 10^{-3}$ mole/liter): 1) InIn (in semilogarithmic coordinates); 2) ArOH; 3) ROOH; 4) InH (chromatographic analysis); 4') InH (OR analysis); 5) quinoline peroxides. 348°K, CCl_4, argon.

begins at this time [6]. Until total consumption of ArOH, the aroxyl radical $ArO^{\bullet}$ is subsequently replaced by $Ph_2NO^{\bullet}$ (see Fig. 2, curves 7 and 7'). Rapid accumulation of $ArO^{\bullet}$ only takes place at the very beginning of the experiment (~1 min after heating of the cell in the resonator of the EPR spectrometer begins), then $[ArO^{\bullet}]$ decreases.

As we see, regardless of the experimental conditions, the reaction takes place according to the simple stoichiometric equation

$$\text{InIn} + \text{ROOH} + \text{ArOH} \rightarrow 2\text{InH} + \text{QP}$$

This result cannot be explained by the equality of the reaction rates: $In^{\bullet}$ + ArOH (1) and $In^{\bullet}$ + ROOH (2), with subsequent recombination of $ArO^{\bullet}$ with $RO_2^{\bullet}$, since k_1 is approximately 100 times higher than k_2 [1, 2]. The last hypothesis was tested in the present study in a series of experiments on pulsed photolysis of InIn in the presence of a mixture of ArOH and ROOH. The experiments were conducted in the absence of quadratic recombination of $In^{\bullet}$, i.e., in conditions where addition of ArOH alone was sufficient for total acceptance of the $In^{\bullet}$ formed after the flash. It was found that in the presence of a mixture of ArOH and ROOH, consumption of $In^{\bullet}$ takes place along two channels, and the efficiency of attack of $In^{\bullet}$ on ArOH is $1.2 \cdot 10^2$ (±15%) times higher than for ROOH (293°K, cyclohexane).

In the decomposition of InIn in the presence of a mixture of ArOH and ROOH, the simple stoichiometry of the reaction is thus the result of a complex mechanism with such fine tuning of the concentrations of radicals that their quenching primarily takes place with respect to the reaction of $ArO^{\bullet}$ with $RO_2^{\bullet}$.

The complete scheme of the reactions which take place in the system is reported in Table 1. Since the values of k_1, k_{-1}, and k_2 in [1, 2] were obtained at 293°K, a preexponential factor for each of them, equal to 10^8 liter/mole·sec, was hypothesized for their estimation at 348°K. The values of k_4, k_5, and k_7 were set equal to those found at ~295°K, since the activation energies of radical recomination are usually low.

The preliminary kinetic analysis of the scheme (see Table 1) showed that in the experimental conditions, reactions (i), (1), (–1), (2), and (4) are key, and stages (1) and (–1) take place most rapidly. The ratio between the concentrations of $In^{\bullet}$ and $ArO^{\bullet}$ is determined by reactions (1) and (–1), so that $[In^{\bullet}]/[ArO^{\bullet}] \simeq [InH]/K_1[ArOH]$, where $K_1 = k_1/k_{-1} = 2.9 \cdot 10^3$ [2]. Within the framework of the selected scheme, $v_2 = v_4$ in quasistationary conditions, and as a result, $[RO_2^{\bullet}] \simeq k_2\,[ROOH]\,[InH]/K_1k_4[ArOH]$. Then from the quasistationary condition, $v_i = 2k_4[RO_2^{\bullet}][ArO^{\bullet}]$, we find: $[ArO^{\bullet}] = K_1v_i[ArOH]/2k_2[ROOH][InH]$. The numerical values of

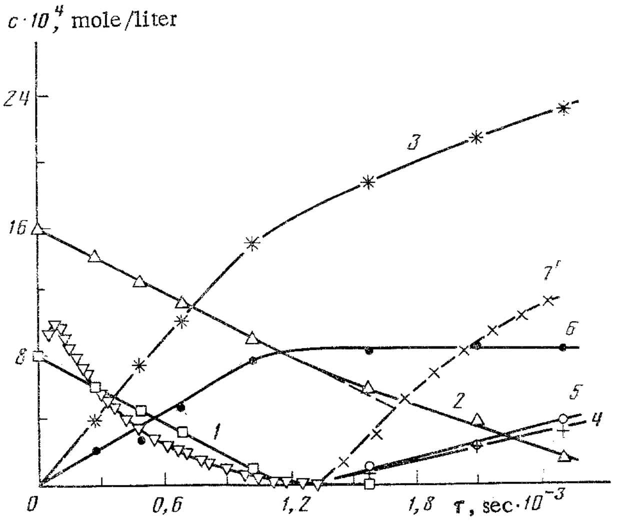

Fig. 2. Decomposition of InIn ($5.0\cdot10^{-3}$ mole/liter) in the presence of ArOH ($0.80\cdot10^{-3}$ mole/liter) and ROOH ($1.60\cdot10^{-3}$ mole/liter): 1) ArOH; 2) ROOH; 3) InH, IR analysis; 4) cumyl alcohol; 5) acetophenone; 6) quinoline peroxides; 7 and 7') $ArO^\bullet$ and $Ph_2NO^\bullet$ (intensity of EPR signal in relative units).

the concentrations of radicals, for example, in the experiment on decomposition of InIn in the preence of a mixture of ArOH and ROOH ($8\cdot10^{-4}$ mole/liter) and InH ($2.15\cdot10^{-3}$ mole/liter), are obtained as follows: $[ArO^\bullet] = 3.1\cdot10^{-6}$, $[In^\bullet] = 2.9\cdot10^{-9}$, and $[RO_2^\bullet] = 1.1\cdot10^{-9}$ mole/liter. The results of calculating the rates of all stages for this experiment are reported in Table 1.

Note that the rates of reactions (−2), (3), (−3), and (5)-(7) are actually small in comparison to v_i ($1.4\cdot10^{-6}$ mole/liter·sec). Stages (1) and (−1) take place ~30 times more rapidly than quenching of the radicals according to reaction (4), so that the $[In^\bullet]/[ArO^\bullet]$ ratio during the entire experiment is determined by the almost equilibrium stage of radical reaction of the inhibitors [4] [reactions (1) and (−1)]. The equality of $v_{ArOH} = v_{ROOH} = 0.5\, v_i$ is due to the fact that during the experiment, $v_4 \gg v_5 + v_6 + v_7$, i.e., quenching of free radicals basically takes place according to reaction (4). Intermediate stages (−2), (3), and (−3) do not perturb this inequality, and their rates are significantly lower than the rates of reactions (1) and (−1): $v_{-2}/v_1 = 0.3\cdot10^{-2}$, $v_3/v_1 = 0.5\cdot10^{-3}$ and $v_{-3}/v_1 = 0.3\cdot10^{-4}$, so that stages (i), (1), (−1), (2), and (4) are actually the key reactions.

We will analyze the question of the conditions in which the ratio of the rates of radical recombination required for this is satisfied to estimate the concentration ratios of the reagents when the mechanism of transformations which include the five reactions indicated as determining is preserved. The ratio of $v_4 > v_7$ is satisfied with $[ROOH] > (k_7v_i)^{1/2}k_2 \simeq 0.01\, v_i^{1/2} \simeq 1\cdot10^{-5}$ mole/liter. Inequality $v_4 > v_6$ is satisfied in the condition of $[ArOH]/[ROOH][InH] > 2k_2(k_6/v_i)^{1/2}/K_1k_4 \simeq 8.7\cdot10^{-5}v_i^{-1/2} \simeq 0.07$ liter/mole. Another ratio is derived from the condition $v_4 > v_5$: $[ArOH]/[InH] > k_5/K_1k_4 \simeq 1\cdot10^{-3}$. All three inequalities are combined and satisfied when $[ROOH] > 1\cdot10^{-5}$ mole/liter. The range of variation of the concentrations of the starting reagents is thus very broad.

Within the framework of the scheme in Table 1, the process develops as follows. In the very first moments of the reaction, $In^\bullet$ almost exclusively attack ArOH in correspondence with the values of k_1 and k_2 and the concentrations of ArOH and ROOH. As reaction (1) takes place, the concentrations of $ArO^\bullet$ and InH increase, and the rate of back reaction (−1) increases. The orientational calculations show that after 10-20 sec, $v_1 \simeq v_{-1}$. As a consequence of the continuous generation of $In^\bullet$ due to decomposition of InIn, the concentrations of $In^\bullet$, like $ArO^\bullet$ and InH, continue to increase so that the rates of stages (1) and (−1) become significantly greater than v_i in time (see Table 1). An increase in $[In^\bullet]$ at this time results in an increase in the rate of reaction (2), where $RO_2^\bullet$ radicals are formed, and the latter are primarily quenched in the experimental conditions according to the reaction with the $ArO^\bullet$ radicals which accumulated in the system. The rate of reaction (2), which takes place against the background of equilibrium of reactions (1) and (−1), can only increase to the value of $v_2 =$

TABLE 1. Reactions, Rate Constants, and Reaction Rates in Decomposition of InIn ($5.0 \cdot 10^{-3}$ mole/liter) in the Presence of an Equimolar Mixture of ArOH and ROOH ($8.0 \cdot 10^{-4}$ mole/liter each) and Addition of InH ($2.15 \cdot 10^{-3}$ mole/liter), CCl_4, 348°K

No.	Reaction	k, liter/mole · sec	v, mole/liter · sec	Literature
i	$InIn \rightarrow 2In^{\cdot}$	$k_{Decomp} = 1.4 \cdot 10^{-4}$ sec^{-1}	$v_i = 1.4 \cdot 10^{-6}$	
1	$In^{\cdot} + ArOH \rightarrow InH + ArO^{\cdot}$	$2 \cdot 10^7$	$4.7 \cdot 10^{-5}$	[2]
−1	$ArO^{\cdot} + InH \rightarrow ArOH + In^{\cdot}$	$7 \cdot 10^3$	$4.7 \cdot 10^{-5}$	[2]
2	$In^{\cdot} + ROOH \rightarrow InH + RO_2^{\cdot}$	$3 \cdot 10^5$	$7 \cdot 10^{-7}$	[1]
−2	$RO_2^{\cdot} + InH \rightarrow ROOH + In^{\cdot}$	$6 \cdot 10^4$	$1.4 \cdot 10^{-7}$	[12]
3	$RO_2^{\cdot} + ArOH \rightarrow ROOH + ArO^{\cdot}$	$2.8 \cdot 10^4$	$2.5 \cdot 10^{-8}$	[13]
−3	$ArO^{\cdot} + ROOH \rightarrow ArOH + RO_2^{\cdot}$	0.65	$1.6 \cdot 10^{-9}$	[14]
4	$ArO^{\cdot} + RO_2^{\cdot} \rightarrow QP$	$2 \cdot 10^8$	$7 \cdot 10^{-7}$	[14]
5	$In^{\cdot} + RO_2^{\cdot} \rightarrow$ Products	$6 \cdot 10^8$	$1.9 \cdot 10^{-9}$	[7]
6	$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow$ Products	$2k = 1.5 \cdot 10^4$	$1.8 \cdot 10^{-14}$	[12]
7	$In^{\cdot} + In^{\cdot} \rightarrow$ Products	$2k = 3.6 \cdot 10^7$	$3.0 \cdot 10^{-10}$	[7]

$0.5 v_i$, when half of the $In^{\cdot}$ radicals have been replaced by $ArO^{\cdot}$. However, even in these conditions, the rate of consumption of $ArO^{\cdot}$ according to reaction (4) is essentially small in comparison to the rates of formation and consumption of $ArO^{\cdot}$ in reactions (1) and (−1) (see Table 1). This also permitted us to consider $[ArO^{\cdot}]$ as quasiequilibrium above.

The usual kinetics of consumption of ArOH and ROOH in the decomposition of InIn are thus in complete agreement with the proposed scheme of the reactions (see Table 1). The experimentally observed equality of the rates $v_{ArOH} = v_{ROOH}$ is first caused by the very fast establishment of equilibrium

$$In^{\cdot} + ArOH \rightleftarrows InH + ArO^{\cdot}$$

which is shifted toward $ArO^{\cdot}$. The second cause is the very high activity of $In^{\cdot}$ in reactions of cleavage of H from ArOH and ROOH.* Finally, due to the absence of self-recombination of $ArO^{\cdot}$ and the reaction of $ArO^{\cdot}$ with $In^{\cdot}$, as well as the significantly lower activity of $ArO^{\cdot}$ in comparison to $In^{\cdot}$ in reactions of cleavage of H, the inequality $[ArO^{\cdot}] \gg [In^{\cdot}]$ is satisfied, which also results in quenching of the radicals only according to the reaction of $ArO^{\cdot}$ with $RO_2^{\cdot}$ with $k_4 \sim k_5$. This scheme of the reactions is realized when the concentrations of reagents are varied within wide limits.

CONCLUSIONS

1. In the decomposition of tetraphenylhydrazine in the presence of 2,4,6-tri-tert-butylphenol and cumyl hydroperoxide (or tert-butyl hydroperoxide), both compounds are consumed with equal rates close to the rate of decomposition of tetraphenylhydrazine. Diphenylamine is formed with a rate equal to the sum of the rates of consumption of the phenol and hydroperoxide, and quinoline peroxides are formed with a rate equal to the rate of consumption of the phenol (or hydroperoxide). These mechanisms are preserved when the initial concentrations of the phenol and hydroperoxide are varied and when diphenylamine is added.

2. The results obtained are explained and quantitatively described with a kinetic scheme which includes 11 reactions involving aminyl, aroxyl, and peroxide radicals. The reversible character of the reaction of the aminyl radical with the phenol is an important moment in the scheme.

LITERATURE CITED

1. V. T. Varlamov, R. L. Safiullin, and E. T. Denisov, Khim. Fiz., 4, 789 (1985).
2. V. T. Varlamov, R. L. Safiullin, and E. T. Denisov, Khim. Fiz., 4, 901 (1985).
3. G. V. Karpukhina, Z. K. Maizus, and N. M. Emanuel, Dokl. Akad. Nauk SSSR, 160, 158 (1965).
4. G. V. Karpukhina, Z. K. Maizus, and N. M. Emanuel, Dokl. Akad. Nauk SSSR, 182, 870 (1968).
5. L. Hatterman and G. Veland, Practical Studies in Organic Chemistry [Russian translation], NKhTI Vsekhimprom SSSR, Leningrad (1930), p. 263.
6. V. T. Varlamov and E. T. Denisov, Kinet. Katal., 24, 547 (1983).

---

*The value of the rate constant for reaction (2) for the reaction of In· with tert-butyl peroxide, obtained by pulsed photolysis, is equal to $4.5 \cdot 10^4$ liter/mole·sec (±20%) at 293°K in cyclohexane. The calculations were performed by the method described in [1].

7. V. T. Varlamov, R. L. Safiullin, and E. T. Denisov, Khim. Fiz., 2, 408 (1983).
8. V. T. Varlamov, Izv. Akad. Nauk SSSR, Ser. Khim., 1629 (1982).
9. V. T. Varlamov, Izv. Akad. Nauk SSSR, Ser. Khim., 1481 (1982).
10. I. A. Shlyapnikova, V. Z. Dubinskii, V. A. Roginskii, and V. G. Miller, Izv. Akad. Nauk SSSR, Ser. Khim., 57 (1977).
11. V. A. Roginskii, L. G. Plekhanova, V. Z. Dubinskii, G. A. Nikiforov, V. B. Miller, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1327 (1975).
12. E. T. Denisov, Rate Constants of Homolytic Liquid-Phase Reactions [in Russian], Nauka, Moscow (1971), pp. 245, 399.
13. V. F. Tsepalov, Dissertation, Chernogolovka (1975), p. 31.
14. A. P. Griva and E. T. Denisov, Int. J. Chem. Kinet., 5, 869 (1973).

EXCHANGE IN TWO-PHASE CATALYTIC SYSTEMS.

COMMUNICATION 1. NUCLEOPHILIC REPLACEMENT OF BROMINE IN HEXYL BROMIDE BY CHLORINE AND THE ROLE OF THE SOLID SALT M^+Cl^-

O. I. Danilova, I. A. Esikova,
and S. S. Yufit

UDC 541.128:541.12.012

The nucleophilic replacement reaction has been well studied in homogeneous solutions [1] and in the two-phase catalyst system of aqueous salt solution—organic phase (OP) [2-4]. In this work we investigate the replacement of Br by Cl in hexyl bromide in the presence of a solid phase (SP), the chlorides of the alkaline metals M^+Cl^- and the onium salts Q^+X^- in benzene and toluene

$$\underset{OP}{n\text{-}C_6H_{13}Br} + \underset{SP}{M^+Cl^-} \xrightleftharpoons{Q^+X^-} \underset{SP}{M^+Br^-} + \underset{OP}{n\text{-}C_6H_{13}Cl}$$

EXPERIMENTAL

In the reaction were used hexyl bromide RBr, bp 155.5°C, concentration of the major product > 90%; the solvents were thoroughly dried benzene or toluene; the solid salts M^+Cl^- were chemically pure or analytical grade; the catalysts were: $(C_4H_9)_4HBr$ (mp 119°C), $(C_8H_{17})NBr$ (mp 95°C), or $(CH_3)_3H_{33}NBr$ (mp 231-236°C). The chemically pure grade KCl consisted of particles 0.2 mm in diameter (89%); 0.125-0.2 mm (11%); 0.1-0.125 (32%); and 0.071-0.1 mm (traces). The mean diameter of the particles $\bar{\ell} = 0.195$ mm.

The reaction was run at 80-84°C in a thermostatted flat-bottomed reactor (30 mm i.d.), fitted with a reflux condenser with a potassium chloride tube and an effective Teflon stirrer (rate of revolution 1900-2300 rpm). Ordinarily 13 g of the solid salt MCl were taken for the reaction, the molar ratio MCl/RBr = 8.9; 7.0; 4.3 for NaCl, KCl, and RbCl, respectively; concentrations of RBr were between 0.97 and 1, of QX between 0.02–0.06 mole/liter. As the reaction progressed, samples were taken from the organic layer and the concentration of RBr and hexyl chloride, RCl, were determined by GLC.

The sole product of the reaction was RCl, the consumption of RBr corresponding to the formation of RCl. The degree of conversion after 13 h in the presence of 0.02 mole/liter $(C_8H_{17})_4NBr$ did not exceed 7% for NaCl, 23% for KCl, and 43% for RbCl. Figure 1 shows the kinetic curves obtained in the presence of the different salts and catalysts.

The study of the granulated state of the solid phase (KCl) was performed for the run for which there was no preliminary activation of the salt (cf. below). For the microscopic analysis, a sample of KCl from the reactor was placed on a microscope slide and photographed. The photograph of the particles (enlarged 125 diameters) was analyzed statistically. The data obtained are summarized in Tables 1 and 2. At the same time the concentrations of RBr and RCl were determined (Table 3).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2422-2427, November, 1986. Original article submitted May 17, 1985.

0568-5230/86/3511-2215$12.50