The reactivity of organothallium compounds. Kinetics and mechanism of iodination of diarylthallium salts by molecular iodine in dioxane

I. F. Gun'kin[a]* *and K. P. Butin*[b]

[a]*Saratov State Technical University, Technological Institute,*
17 pl. Svobody, 413100 Engel's, Russian Federation
[b]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 5546. E-mail: butin@org.chem.msu.su

The kinetics and mechanism of the reactions of diarylthallium trifluoroacetates with molecular iodine in dioxane solutions have been studied. The reaction has the overall second order with the first order with respect to each reagent. The effect of substituents in the aromatic ring on the rate constant of iodination is described by the equation $\log k_2 = \rho\sigma^+ (\rho = -1.60, r = 0.97)$. The reaction is catalyzed by the iodide ion. The activation enthalpies and entropies of iodination of diarylthallium trifluoroacetates in dioxane and di(*p*-anisyl)thallium trifluoroacetate in various solvents have been calculated. The effect of solvents on the rate constant of iodination of di(*p*-anisyl)thallium trifluoroacetate has been studied. The reaction mechanism is considered as an electrophilic S_EC process.

Key words: organothallium compounds, diarylthallium trifluoroacetates, iodination, iodine, reactivity, mechanism, kinetics.

Halodemetallation of organometallic compounds is one of the most known reactions. Iododemercuration,[1] iododestannation,[2,3] and halodeboration[1] are especially well studied.

Iodination of organothallium compounds by molecular iodine has been described long ago.[4–6] The iodination by molecular iodine with carbon—thallium bond cleavage was used in the study of organothallium compounds of the dibenzofuran series.[4,6] The reaction of di(β-chlorovinyl)thallium with iodine in chloroform[5] and the cleavage of the carbon—thallium bond by molecular iodine in bis(pentaphenyl)thallium bromide[7,8] were reported. The iodination of diarylthallium trifluoroacetates by molecular iodine in boiling chloroform was used for the preparation of aryl iodides.[9] The iodination of arylthallium bis(fluoroacetates) by I_2 in acetonitrile in darkness was also reported.[10] However, these works are of synthetic character, and the mechanism of iodination of organothallium compounds has not been studied up to now. At the same time, the mechanisms of iodination of organomercury and organotin compounds are well studied.[1]

Developing the works listed above, we synthesized various diarylthallium salts[9,11,12] and studied the kinetics and mechanism of iodination of these compounds in dioxane ($C_4H_8O_2$) in darkness (reaction (1)).

$$\underset{\textbf{1--12}}{(p\text{-}RC_6H_4)_2TlX} + I_2 \xrightarrow{C_4H_8O_2} p\text{-}RC_6H_4I + p\text{-}RC_6H_4TlXI \quad (1)$$

X = $OCOCF_3$, R = H (**1**), Me (**2**), Bu^t (**3**), MeO (**4**), F (**5**), Cl (**6**), Br (**7**), Pr^i (**8**), EtO (**9**);
R = H, X = OCOMe (**10**), OC_6F_5 (**11**), Br (**12**)

Experimental

Dioxane (chemically pure grade) was stored for 5 days above KOH and distilled in an argon flow above sodium metal. Then benzophenone and sodium were added to dioxane, and the mixture was boiled to the formation of a blue solution and distilled slowly under argon. Iodine (pure grade) was purified by double sublimation. Diarylthallium trifluoroacetates were prepared by the known procedures.[9,11,12]

Spectra of reaction mixtures and iodine were recorded on an SF-26 spectrophotometer. Cells with a thickness of 1 cm were placed in a thermostatted attachment, which was mounted in the spectrophotometer. Iodine in dioxane has an absorption maximum at λ = 530 nm, which obeys the Lambert—Beer law in the 530—580 nm wavelength range. The optical density of I_2 during the reaction was measured at λ = 580 nm. The starting organothallium compounds and reaction products do not absorb in this region and do not impede measurement of the optical density of iodine.

The kinetics of reaction (1) was studied in a thermostatted cylindrical reactor in the dark. The volume of the reaction mixture was 5 mL. Samples (3.5 mL) were taken at certain intervals from the reactor, the optical density was rapidly measured, and the samples were returned into the reactor. "Fast" reactions were carried out directly in a thermostatted 1-cm cell. Using the measured values of the optical density of I_2, we calculated the concentrations of reacting substances, plotted the kinetic curves, and calculated the rate constants of the reactions (Tables 1—4). The values of the calculated rate constants coincide within the experimental error (±5%).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 451—455, March, 1999.

Table 1. Rate constants (k_2) and activation parameters of the reactions of diarylthallium trifluoroacetates **1—9** with molecular iodine in darkness

Compound	R	$k_2 \cdot 10^4$/L mol^{-1} s^{-1}					$\Delta H^{\neq}$/kJ mol^{-1}	$-\Delta S^{\neq}$/J K^{-1} mol^{-1}
		20 °C	25 °C	30 °C	34.8 °C	45 °C		
1	H	2.68	3.67	7.70	9.08	21.50	64.561	94.847
2	Me	—	4.94	13.25	16.61	42.08	64.452	88.492
3	Bu^t	—	6.66	17.75	21.96	49.02	61.646	95.812
4	MeO	—	46.20	119.00	161.40	284.60	59.993	84.872
5	F	—	1.63	3.35	4.48	8.22	65.557	96.011
6	Cl	—	2.11	3.47	4.57	8.22	67.641	88.730
7	Br	—	2.20	—	—	—	—	—
8	Pr^i	—	8.77	—	—	—	—	—
9	EtO	—	66.40	—	—	—	—	—

Results and Discussion

The order of reaction (1) was determined for compound **1**, because it is relatively highly soluble in dioxane, which makes it possible to vary its concentration from $1 \cdot 10^{-4}$ to $3 \cdot 10^{-2}$ mol L^{-1}.

It has been established that reaction (1) has the overall second order, with the first order with respect to each of reagents. The variation of the concentrations of compound **1** and I_2 shows that along the kinetic curve, the rate constant retains an unchanged value of $2.68 \cdot 10^{-4}$ L mol^{-1} s^{-1} at 20 °C.

To study the temperature dependences and the effect of substituents, we carried out the reactions at equimolar ratios of the reagents at the concentration of $1.5 \cdot 10^{-3}$ mol L^{-1}. The measured second-order rate constants (k_2) and calculated values of the activation enthalpy and entropy for diarylthallium trifluoroacetates **1—9** in dioxane in darkness are presented in Table 1.

The study of the effect of substituents in the aromatic cycle shows that electron-donating substituents accelerate and electron-withdrawing substituents retard reaction (1) (see Table 1). The effect of substituents on the reaction rate constant at 25 °C does not obey the Hammett equation, but is satisfactorily described by the Brown equation $\log k_2 = \rho\sigma^+$ ($\rho = -1.60$, $r = 0.97$) (Fig. 1). It follows from the data in Table 1 that the formation of the arenonium ion is the rate-limiting stage of reaction (1). The low value $\rho = -1.60$ (see Fig. 1), as compared to those found for the reactions of chlorination and bromination of aromatic hydrocarbons by molecular chlorine and bromine ($\rho = -10$; -12.1, respectively),[13] indicates that the easiness of electrophilic iodination of diarylthallium trifluoroacetates *via* the S_E mechanism is determined not only by the degree of electrophilicity of I_2, but also by the capability of iodine of coordinating at the Tl atom of the organothallium compound. A similar phenomenon was also observed for several organomercury compounds and was named the nucleophilic assistance or nucleophilic catalysis.[1] When organomercury salts are iodinated in DMF by molecular iodine, $\rho = -1.95$, and in the case of symmetrical organomercury compounds of the Ar_2Hg type, $\rho = -2.3$.[1]

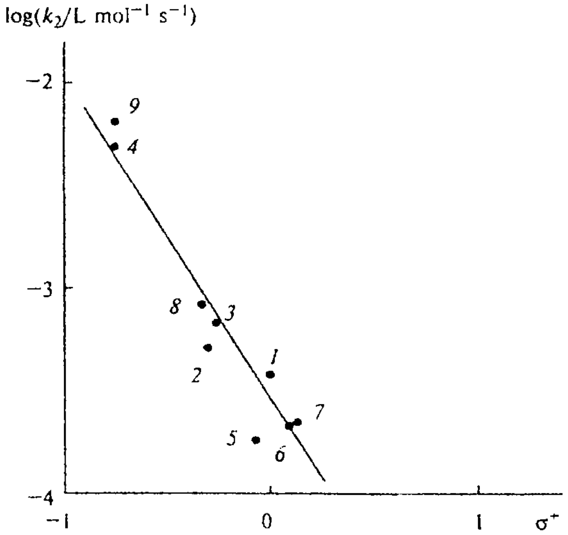
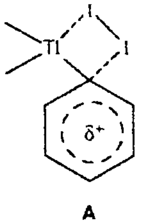


Fig. 1. Dependences of the logarithm of the rate constant of iodination of diarylthallium trifluoroacetates (**1—9**) on the σ^+ values in dioxane at 25 °C. The numeration of points corresponds to the numbers of compounds.

The temperature effect on reaction (1) was studied for compounds **1—6** (see Table 1). Plotting the dependence $\ln(k_2/T)$ on $1/T$ for various compounds, we calculated the standard activation enthalpy and then the activation entropy (see Table 1). It follows from the data in Table 1 that for compounds **1—6**, the values of the activation enthalpy and entropy of reaction (1) vary within $\Delta H^{\neq} = 59.993$ to 67.641 kJ mol^{-1}, $\Delta S^{\neq} = -96.011$ to -84.872 J K^{-1} mol^{-1}, which corresponds well to the bimolecular electrophilic reaction in the solution. The negative value of the activation enthalpy of reaction (1) indicates that the transition state is ordered. Perhaps, it contains the four-membered cycle (**A**).



A

Table 2. Effect of the concentration of additives of various Bu_4NX salts on the rate constant (k_2) of the reaction of di(*p*-anisyl)thallium trifluoroacetate with I_2 at 25 °C in darkness

$[Bu_4NI] \cdot 10^5$ /mol L^{-1}	$k_2 \cdot 10^3$ /L mol^{-1} s^{-1}	$[Bu_4NClO_4] \cdot 10^5$ /mol L^{-1}	$k_2 \cdot 10^3$ /L mol^{-1} s^{-1}	$[Bu_4NBF_4] \cdot 10^5$ /mol L^{-1}	$k_2 \cdot 10^3$ /L mol^{-1} s^{-1}
0	4.62	0	4.74	0	4.74
0.5	6.33	5	6.75	20	10.44
1.5	10.79	20	8.88	200	19.06
5	23.48	200	16.71	500	24.07
9.57	40.76	500	23.91	1000	29.53
15	52.26	1000	25.56	—	—
30	89.30	—	—	—	—
45	147.40	—	—	—	—

To confirm the possibility of nucleophilic assistance from I_2, we studied the effect of various salt additives of the Bu_4NX type (X = ClO_4 (**13**), BF_4 (**14**), I (**15**)) for compound **4**. The second-order rate constants (k_2) for the reaction of di(*p*-anisyl)thallium trifluoroacetate with I_2 in dioxane in darkness at different concentrations of salts **13**—**15** at 25 °C are presented in Table 2. It can be seen from the data in Table 2 that additives **13**—**15** accelerate reaction (1). The effect of the single-type salts **13** and **14** is almost the same and, most likely, due to an increase in the ionic strength of the solution, on the one hand, and the polarization of the iodine molecule under these conditions, on the other hand. When salt **15** is added, the same factors, as in the case of salts **13** and **14**, act; however, the effect of salt **15** on reaction (1) is much more efficient. At equal concentrations of salts **13**—**15**, the ionic strength of the solution is the same, but salt **15** catalyzes reaction (1) much more strongly than salts **13** and **14**. The linear dependences of $\log k_2$ on $\log[Bu_4NX]$ (Fig. 2) are characterized (for salts **13** and **14**) by the same slope angle (the tangent is equal to 0.3), and for salt **15**, the slope angle is greater (0.65). If it is taken into account that when the uniform salts are added, the effects in the reaction mixture are approximately equal, then the difference in these values (0.35) reflects the strength of nucleophilic catalysis by iodide ions. Probably, the iodide ion catalyzes reaction (1) due to the formation of the triiodide ion according to Eq. (2).

$$I_2 + Bu_4NI \rightleftharpoons Bu_4NI_3 \qquad (2)$$

In fact, the study of solutions of I_2 in dioxane shows that the maximum at λ = 430 nm, which can be assigned to the triiodide ion, appears in the absorption spectra of these solutions in the presence of salt **15**. The I_3^- anion exerts a greater nucleophilic assistance than the I_2 molecules due to the negative charge, since it is better coordinated with the Tl atom of compound **4**. In this case, an additional catalysis can also appear due to the formation of a less strained five-membered cycle in the transition state.

It is noteworthy that at high degrees of conversion (70—80%), we observed a slight acceleration of reaction (1). The analysis of the spectra showed that a maximum at λ = 430 nm, which corresponds to I_3^-, appears in this case as well, but the concentration of the anion is low. The formation of I_3^- occurs, perhaps, due to the complex formation of molecular iodine with the reaction products by Eq. (3).

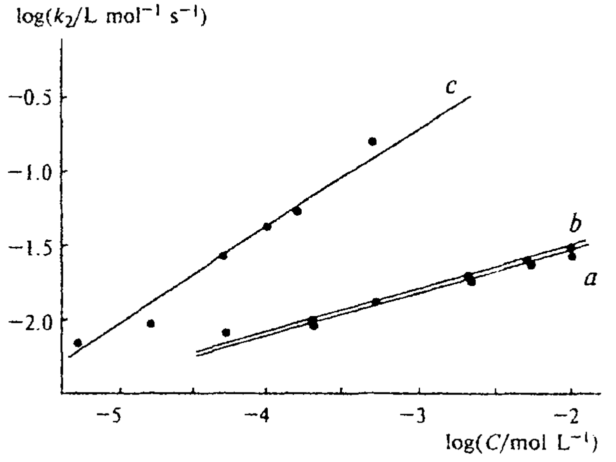


Fig. 2. Dependence of the logarithm of the rate constant of iodination of di(*p*-anisyl)thallium in dioxane at 25 °C on the logarithm of the concentration of the salt added: **13** (*a*), **14** (*b*), and **15** (*c*).

$$ArTlXI + I_2 \rightleftharpoons ArTlXI_3 \qquad (3)$$

Similar phenomena were observed for iodination of other organometallic compounds.[1] For compound **4**, the effect of solvents was studied at 25 °C, and the temperature dependences of reaction (1) in various solvents were obtained (see Table 3).

The study of the temperature dependences $\ln(k_2/T)$ on $1/T$ for six different solvents and calculation of the values of the activation enthalpy and entropy, as described previously, showed the compensation effect for the iodination of di(*p*-anisyl)thallium trifluoroacetate. When the nature of the solvent changes, the activation enthalpy and entropy of the reaction change in parallel (Fig. 3). The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values change smoothly and

Table 3. Rate constants (k_2) and activation parameters of the reaction of di(*p*-anisyl)thallium trifluoroacetate with molecular iodine in various solvents

Sol-vent	$k_2 \cdot 10^3$/L mol^{-1} s^{-1}					$\Delta H^{\neq}$ /kJ mol^{-1}	$-\Delta S^{\neq}$ /J K^{-1} mol^{-1}
	21 °C	25 °C	30 °C	34.8 °C	40 °C		
Dioxane	—	4.62	11.90	16.14	28.4^e	59.993	84.872
THF	—	30.00	38.30	—	79.10	56.806	83.679
DMF	16.99^a	26.92	39.5	—	90.6	62.890	64.413
DMSO	0.83	1.45	1.90	—	5.1	73.008	55.382
AcOEt	149	180	281	—	500	50.113	90.416
MeCN	—	1595	1938,^{b} 2171^c	2671^d	3801	42.282	99.060
MeOH	—	24.1	—	—	—	—	—
EtOH	—	35.6	—	—	—	—	—
PrOH	—	37.4	—	—	—	—	—
BuOH	—	48.4	—	—	—	—	—
Py	—	29.0	—	—	—	—	—

^{a} At 20.5 °C. ^{b} At 28 °C. ^{c} At 31 °C. ^{d} At 33.6 °C. ^{e} At 45 °C.

linearly in dioxane, THF, DMF, DMSO, AcOEt, and MeCN. Different viewpoints concerning similar correlations are advanced. In this case, these dependences are due, to some extent, to the methods of calculation of the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values.

It follows from the data in Table 3 that the reaction rate, depending on the nature of the solvent, decreases in the order MeCN > AcOEt > BuOH > PrOH > EtOH > THF > Py > DMF > MeOH > dioxane > DMSO and changes by 1100 times on going from MeCN to DMSO. No broad correlation was observed when the effect of solvents on the reaction rate constant of iodination of compound **4** was studied. However, two tendencies can be mentioned. On the one hand, when the dielectric constant of the solvent (ε) increases, the reaction is accelerated in the order dioxane, THF, Py, MeCN. In this series, the dielectric constant of the solvents correlates with the reaction rate constant expressed in the logarithmic form (Fig. 4, *a*). On the other hand, in the series AcOEt, BuOH, PrOH, EtOH, MeOH, DMF, the rate constant decreases, by contrast, as ε increases (Fig. 4, *b*). These dependences, which exclude each other, can be most likely explained by an increase in the electrophilicity of I_2 in the order dioxane, THF, Py, MeCN due to the increasing polarizing effect of the solvent on the iodine molecule. Organothallium compound **4** is ionized in this solvent and exists, most likely,

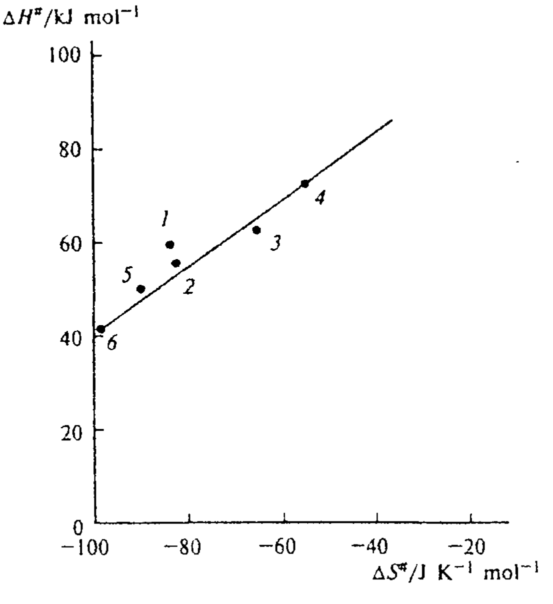


Fig. 3. Compensation effect in the iodination of di(*p*-anisyl)thallium trifluoroacetate in various solvents: *1*, dioxane; *2*, THF; *3*, DMF; *4*, DMSO; *5*, AcOEt; and *6*, MeCN.

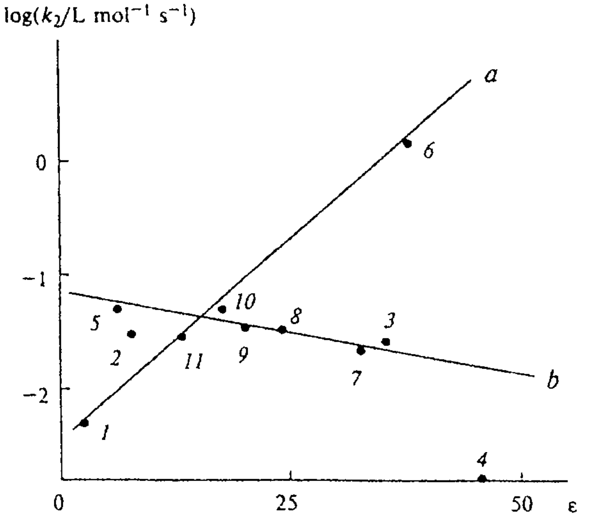


Fig. 4. Dependences of the logarithm of the rate constant of iodination of di(*p*-anisyl)thallium trifluoroacetate on the dielectric constants of solvents (ε): *1*, dioxane; *2*, THF; *3*, DMF; *4*, DMSO; *5*, AcOEt; *6*, MeCN; *7*, MeOH; *8*, EtOH; *9*, Pr^{n}OH; *10*, Bu^{n}OH; and *11*, Py.

Scheme 1

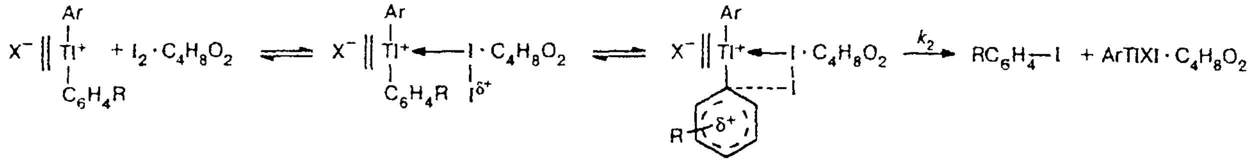


Table 4. Effect of the nature of the counterion in the iodination of diphenylthallium salts by molecular iodine in dioxane at 25 °C in darkness

Compound	X	$k_2 \cdot 10^2$/L mol^{-1} s^{-1}	pK_a
1	$OCOCF_3$	0.0367	0.25
10	OCOMe	0.123	4.75
11	OC_6F_5	1.23	5.5
12	Br	4.52	−9.0

as ion pairs. Therefore, when the electrophilicity of I_2 increases (which occurs as ε increases in the series indicated), the reaction rate constant increases. In the series AcOEt, BuOH, PrOH, EtOH, MeOH, DMF, the electrophilicity of I_2 is most likely approximately the same, since the same polarizing center (the oxygen atom of the hydroxyl or carbonyl group) acts upon the I_2 molecule. Probably, the state of compound **4** in the solution changes substantially in this series. Compound **4** becomes more ionized on going from AcOEt to DMF and, hence, the reaction rate constant decreases (see Fig. 4, *b*). Thus, both the ionization processes of organothallium compounds and the electrophilicity of I_2 in the given solvent should be taken into account in the study of the effect of solvents on reaction (1). It follows from Fig. 4 that the electrophilicity of I_2 plays an important role, since the straight line *a* has a greater slope.

To confirm the effect of ionizing processes on reaction (1), we studied the dependence of the iodination rate constant in dioxane on the nature of the anion in compounds **1**, **10—12** at 25 °C in darkness (see Table 4).

It follows from the data in Table 4 that the rate constant of the iodination of diphenylthallium salts **1**, **10—12** changes in the series **1** < **10** < **11** < **12**. For compounds **1**, **10**, and **11**, the degree of ionization of diphenylthallium salts decreases in the same sequence, since the strength of the corresponding acids forming these salts decreases in this series. The strength of the acids can be estimated by the pK_a value (see Table 4). In the series indicated, the rate constant of iodination increases by 33.5 times, and the acidity of the corresponding OH-acids and ionization of diarylthallium salts **1**, **10**, and **11** decrease as well. For compound **12**, the iodination rate is higher, although HBr is a strong acid. In this case, I_2 is activated by the bromide ion and, probably, for salt **15**, by the iodide ion.

Thus, the iodination of diarylthallium salts by molecular iodine in dioxane occurs *via* the electrophilic mechanism to form the transition state (Scheme 1).

The I_2 molecule is coordinated at the Tl atom of the organothallium compound existing in dioxane as ion pairs. This coordination enhances the positive charge on the second iodine atom, which attacks electrophilically the C atom of the aromatic cycle. The electrophilic attack of the iodine atom is the limiting stage of the process.

References

1. O. A. Reutov, I. P. Beletskaya, and V. I. Sokolov, *Mekhanizmy reaktsii metalloorganicheskikh soedinenii* [*Mechanisms of Reactions of Organometallic Compounds*], Khimiya, Moscow, 1972, 368 pp. (in Russian).
2. I. P Beletskaya, A. N. Kashin, A. Ts. Malkhasyan, and O. A. Reutov, *Zh. Org. Khim.*, 1973, **9**, 2215 [*J. Org. Chem. USSR*, 1973, **9** (Engl. Transl.)].
3. A. Ts. Malkhasyan, Ph.D. (Chem.) Thesis, Moscow State University, Moscow, 1973, 150 pp. (in Russian).
4. H. Gilman and R. K. Abbott, *J. Am. Chem. Soc.*, 1943, **65**, 122.
5. R. Kh. Freidlina, A. K. Kochetkov, and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*], 1948, 445 (in Russian).
6. V. P. Glushkova and K. A. Kocheshkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*], 1957, 1391 (in Russian).
7. G. B. Deacon and J. C. Parrott, *J. Organomet. Chem.*, 1969, **17**, P17.
8. G. B. Deacon and J. C. Parrott, *J. Organomet. Chem.*, 1970, **22**, 287.
9. E. C. Taylor, H. W. Altland, and A. McKillop, *J. Org. Chem.*, 1975, **40**, 2351.
10. I. F. Gun'kin, *Zh. Obshch. Khim.*, 1995, **65**, 518 [*Russ. J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
11. I. F. Gun'kin, A. I. Idelevich, and M. N. Rakhlevskaya, *Zh. Obshch. Khim.*, 1987, **57**, 1789 [*J. Gen. Chem. USSR*, 1987, **57** (Engl. Transl.)].
12. I. F. Gun'kin, A. I. Idelevich, and K. P. Butin, *Metalloorg. Khim.*, 1990, **3**, 602 [*Organomet. Chem. USSR*, 1990, **3** (Engl. Transl.)].
13. A. S. Dneprovskii and T. I. Temnikova, *Teoreticheskie osnovy organicheskoi khimii* [*Theoretical Foundations of Organic Chemistry*], Khimiya, Leningrad, 1979, 374 pp. (in Russian).

Received May 12, 1998;
in revised form July 27, 1998