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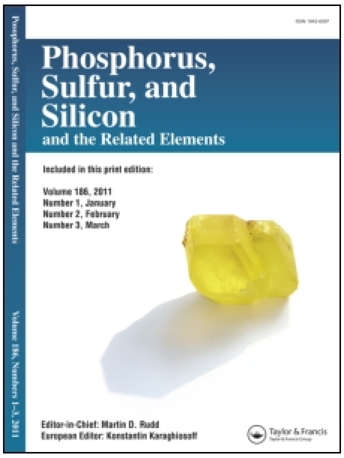

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KINETIC STUDY ON PYROLYTIC ELIMINATION OF ETHYLPHENYLSULFONIUM DICYANOMETHYLIDE

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KINETIC STUDY ON PYROLYTIC ELIMINATION OF ETHYLPHENYLSULFONIUM DICYANOMETHYLIDE

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Ethyl(Substituted phenyl)sulfonium dicyanomethylides (**1**) were prepared and pyrolyzed in sealed tubes in benzene. The rate for pyrolysis of the substrate was correlated in a good first-order kinetic equation ($\gamma = 0.999$).

The rate constant was $11.4 \times 10^{-4}\ s^{-1}$ at 150°C. Pyrolysis of (**1**) was found to proceed about 3 times faster than that of ethylphenylsulfonium bis(methoxycarbonyl)methylide (**2**). Activation parameters calculated from the Arrhenius equation were as follows: $\Delta H^{\ddagger} = 128$ (KJ/mol), $\Delta S^{\ddagger} = 1.7$ J/K/mol (150°C, $\gamma = 0.999$), in which the magnitude of activation enthalpy was almost the same as that of (**2**), while the activation entropy was considerably larger compared with that of ethyl phenyl sulfoxide (−75.1 J/K/mol). Thus, the S—Cα bond of (**1**) was found to be looser in the transition state. The reactivities of sulfonium ylides, sulfoxides and sulfilimines estimate the magnitude of the activation entropies of the substrates. Substituent effect on the phenyl group afforded a positive Hammett ρ-value ($\rho = 0.42$, $\gamma = 0.996$) vs. σ-values.

From these results, it was suggested that pyrolysis of sulfonium ylides proceeds via essentially concerted intramolecular *cis*-elimination in which the transition state is E1-like.

Key words: pyrolysis; elimination; mechanism; kinetics; sulfonium ylide.

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INTRODUCTION

Ylides can be defined as substances in which a carbanion is attached directly to a heteroatom carrying a high degree of positive charge, as represented by the general formula below (see Figure 1).[1]

Among them, some sulfonium ylides, formally zwitterions in which a carbanion achieves stabilization by interaction with an adjacent sulfonium center, have been prepared for over fifty years[2] since the report of Ingold and Jessop on the isolation of dimethylsulfonium fluorenylide.[3,4] A variety of stable and unstable sulfonium ylides have been prepared and studied by a number of investigators. Little was known about the behavior on pyrolysis of such species.[5,6]

In general, organic sulfur compounds have been used widely in synthetic chemistry. Sulfonium ylides have played an especially important role in the synthesis of organic compounds. For the purpose of the investigation of the nature of sulfonium ylides, relatively stale species have been prepared by the following methods[5]: treatment of sulfonium salts having α-hydrogen with base,[7] acylation or alkylation of

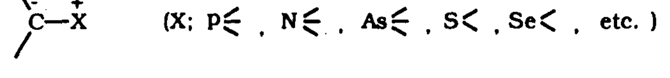

FIGURE 1 General formula of ylides.

sulfonium and oxosulfonium ylides,[8] reaction of active methylene compounds with sulfoxides,[9] and reaction of sulfides with carbene.[10-13]

The well-known reactions concerned with sulfonium ylides are as follows: (a) addition to carbonyl group, i.e., epoxidation or Corey-Chaykovsky reaction,[2,14] (b) addition to carbon-carbon double bond, i.e., cyclopropanation or Michael addition,[15] (c) sigmatropic rearrangements,[16] and (d) pyrolytic elimination, i.e., Ei reaction.[16,17] Reactions (a)-(c) have been studied in detail and summarized.[4,18]

The pyrolysis of sulfonium ylides bearing β-hydrogen has been examined by Ando *et al.*,[17,19-21] and a wide investigation was published by Bielmann *et al.*[22] Little has been studied by kinetics, which is considered to be an effective method to throw light on the pyrolytic mechanism of the sulfonium ylides, in spite of much kinetic research on pyrolysis of sulfoxides and sulfilimines. Tsukurimichi and Yoshimura,[23] prepared some alkylphenylsulfonium bis(methoxycarbonyl)methylide derivatives and subjected them to pyrolysis. From the results obtained a mechanism of the pyrolysis of the ylide was proposed.

In order to obtain the information for the electronic structure in the transition state for Ei reaction of these trivalent organic sulfur compounds, it is necessary to examine kinetically the pyrolysis of the sulfonium ylides in connection with that of the sulfoxides and sulfilimines.

To study the pyrolysis of sulfonium ylides, it is preferable to use compounds having the same structure as the standard substrates used for the Ei reaction of sulfoxides and sulfilimines.

Some ethylphenylsulfonium dicyanomethylides (**1**), which are also known as relatively stable ylides, were prepared and subjected to pyrolysis, and kinetic investigations were carried out.

This paper describes a detailed account of a possible mechanism of the pyrolysis of (**1**).

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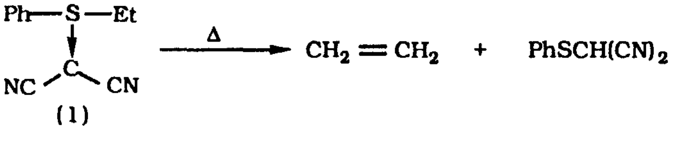
RESULTS AND DISCUSSION

Thermal Decomposition

Pyrolysis was carried out by heating a benzene solution of (**1**) in a sealed tube in a thermostat adjusted to within the range ±0.1°C at the desired temperature. The products formed were not isolated, for the resulting product is very unstable. Gas generating from reaction systems as the pyrolysis proceeded was identified as ethylene by comparing the GC with an authentic sample. A thermal decomposition path of (**1**) follows Scheme I.



SCHEME I Thermal decomposition of ethylphenylsulfonium dicyanomethylide.

Kinetics

The reaction rates for sulfonium ylides were determined by following the intensity of the IR absorption at 2170 cm^{-1} due to $\nu_{C\equiv N}$ for (**1**). The reaction rates were found to closely follow a first-order kinetic equation with respect to the concentration of the substrate (γ = 0.999). The kinetic data and activation parameters obtained from the pyrolysis of (**1**) are summarized in Table I. The pyrolysis rate of (**1**) was found to proceed about 3 times faster than that of ethylphenylsulfonium bis(methoxycarbonyl)methylide (**2**).[23]

The Arrhenius plot for the pyrolysis of (**1**) afforded a good straight line (γ = 0.999). Activation enthalpy is larger than those of the sulfoxides ($\Delta H\ddagger$ = 108 KJ/mol)[24] and sulfilimines ($\Delta H\ddagger$ = 110 KJ/mol).[25] In the activation parameters the difference of activation entropy for Ei reaction is considered to be reflected by looseness of the S—Cα bond in the transition state, because the cyclic transition state will give a negative value of activation entropy, while with the S—Cα bond cleavage the activation entropy will deviate in the positive direction. Thus, the S—Cα bond in sulfonium ylide lengthens to a considerable degree compared with the sulfoxide and sulfilimine until the reaction takes place. The pyrolysis of sulfonium ylides is therefore considered to proceed through a nearly E1-like type of transition state.

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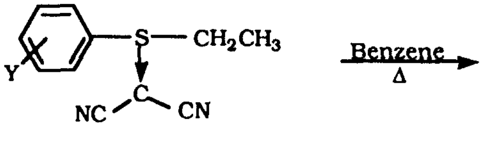
TABLE I

The Kinetic data for pyrolysis of Ethyl(Substituted phenyl)sulfonium dicyanomethylide



(1)

Y	Temp. (±0.1°C)	k × 10^4 (sec^{-1})	γ	
H	130	1.72 ± 0.01[a]	0.999	
p-OCH$_3$	140	3.28 ± 0.05	0.999	$\Delta H^\ddagger$=128.5±1.5(KJ/mol)[b]
p-CH$_3$	140	3.67 ± 0.03	0.999	(at 150°C)
H	140	4.49 ± 0.04	0.999	$\Delta S^\ddagger$=1.7±2.1(J/K/mol)[b]
p-Cl	140	5.31 ± 0.03	0.999	(at 150°C)
m-Cl	140	6.13 ± 0.03	0.999	ρ=0.42 (γ=0.996)
H	150	11.4 ± 0.01	0.999	
H	160	26.4 ± 0.3	0.999	

[a] The rate constants were calculated by least-squares method and errors are standard deviations.

[b] Activation parameters were calculated from Arrhenius equation and errors are standard deviations.

The pyrolytic reaction rate should vary with change of solvent. The solvent effect for the pyrolysis of (**2**) as a related substrate was previously investigated using four solvents (benzene, 1,4-dioxane, acetonitril and methanol).[23] In general, there was a tendency that the higher the polarity of solvent, the lower the reaction rate. The reaction rate was little affected by change from a non-polar solvent such as benzene to a polar one such as methanol. The highest pyrolytic rate (in benzene) was only about 2–3 times larger than the lowest rate (in methanol). Similar results have also been obtained in the pyrolysis of other related substrates such as sulfoxides and sulfilimines. From the results obtained, it was concluded that the solvents used did not bring about any change in the pyrolytic mechanism of these substrates.

Substituent Effects

The substituent effect on the S-phenyl groups for the pyrolysis of (**1**) was examined in benzene and the results obtained are shown in Table I. The logarithms of the rate constants correlated nicely with Hammett σ-values showing a positive trend, as is apparent from Figure 2. Electron-withdrawing groups such as m-Cl were found to accelerate the reaction for pyrolysis of (**1**).

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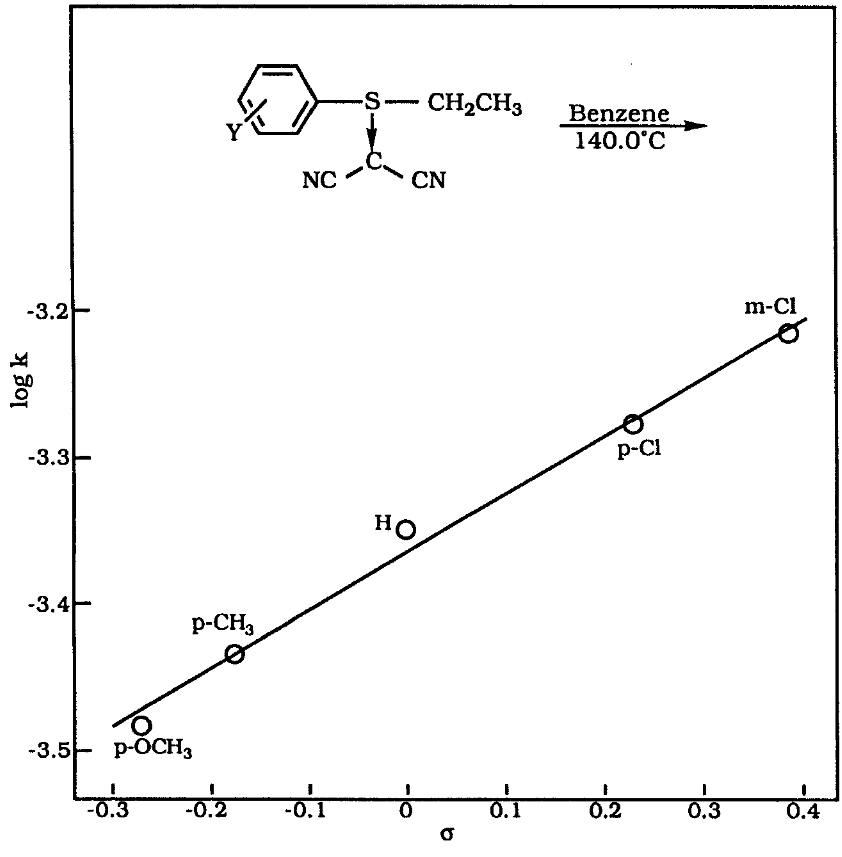


FIGURE 2 Hammett plot for pyrolysis of ethy(substituted phenyl)dicyanomethylide vs σ-value.

The substituent effects on *S*-phenyl groups of sulfonium ylides (**1**) gave the positive Hammett ρ-value (Table I), which was the same as that of (**2**), ($\rho = 0.40$, $\gamma = 0.997$),[23] and was also similar to that of the sulfoxide ($\rho = 0.51$)[24] but smaller than the sulfilimine ($\rho = 0.90$).[26] The above results show that the rate of pyrolysis increases with the increase of electron density on the sulfur center in the transition state. Further, in the pyrolysis of the substrate the reaction proceeds with the more advanced S—Cα bond cleavage rather than proton abstraction, that is E1-like type. Ethyl phenyl sulfoxides and ethyl phenyl *N*-tosylsulfilimines act in a similar manner. The elimination reaction of the sulfonium ylides is not greatly affected by the substituents on *S*-phenyl group.

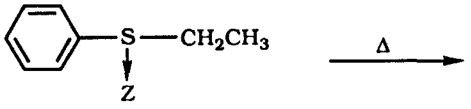
From the above results, the following conclusion may be obtained. Activation entropy for pyrolysis of (**1**) has a positive value, though nearly zero. This value is large in this case when compared with those of similar substrates such as sulfoxide and sulfilimine. The large activation entropy, thus suggests that the transition state is not very rigid. In the transition state of the pyrolysis of sulfonium ylide, therefore, the transition of S—Cα bond cleavage may be relatively large.

Secondarily the substituent effect for the pyrolysis gave positive Hammett ρ-values, and the activation entropy was a small positive value. Thus, the development of S—Cα bond cleavage proceeds in the transition state.

However, the difference in the atoms attached to the sulfur center by semipolar bond should affect the reactivity for pyrolysis of trivalent sulfur compounds. Comparing the reaction rate for (**1**) ($7.19 \times 10^{-6}\ s^{-1}$) with those for (**2**) ($2.34 \times 10^{-6}\ s^{-1}$),[23] ethylphenylsulfoxide ($1.65 \times 10^{-6}\ s^{-1}$)[28] and ethylphenyl *N*-tosylsulfilimine ($9.85 \times 10^{-5}\ s^{-1}$)[27] at 100°C, the relative rate is 1:0.3:0.2:13.7. Reactivity of the substrate would be dependent on basicity of the anionic atom, i.e., sulfoxide-oxygen, sulfilimine-nitrogen, and sulfoniumylide-carbon. In other words, the stronger basicity would show the higher reactivity of the substrate, because of the great

TABLE II

Activation entropies for pyrolysis of Ethyl phenyl sulfoxide, Ethyl phenyl *N*-Tosyl, sulfilimine, Ethyl phenylsulfonium bis(methoxycarbonyl)-methylide, and Ethyl phenylsulfonium dicyanomethylide



Z	Temperature (±0.1 °C)	Solvent	$\Delta S^{\ddagger}$ (J/K/mol)
→O	90.0	1,4-Dioxane	-75.1 ± 15.8[24,a,b]
→N Ts	100.0	Benzene	-24.1[25]
-C-$(CH_3COO)_2$	100.0	Benzene	-2.4 ± 9.1[23,a,b]
-C-$(CN)_2$	100.0	Benzene	1.6 ± 2.4[a,b]

[a] Errors are standard deviations.

[b] Calculated value from Arrhenius equation.

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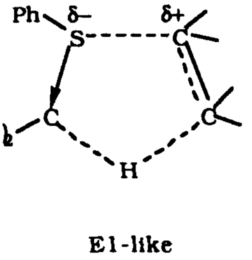

SCHEME II Transition state of pyrolysis of ethyl phenylsulfonium dicyanomethylide.

ability of β-proton abstraction. But, since basicity of the atom is varied by the electronic effect of other substituents attached to the atom, it is difficult to discuss the reactivity with only the value of pk_a or electronegativity of the atom. Otherwise, activation entropy in the reaction could be taken as a measure to estimate the reactivity in place of basicity of the atom attached on the sulfur center in the substrate, as is shown in Table II. Thus, the behavior of the reaction for sulfonium ylides described above is considered to be due to structural factors: the two of cyano groups which are relatively strong electron-attracting groups attach to the carbanionic carbon atom.

Consequently, pyrolysis of alkylphenylsulfonium ylides (**1**) is considered to be an Ei reaction which proceeds through a concerted five-membered cyclic transition state trending to the nearly E1-like type (Scheme II). The reactivity of sulfonium ylides is similar to that of sulfoxides and considerably lower than that of sulfilimines.[23]

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EXPERIMENTAL

General. The IR spectra were taken on a JASCO-810 spectrometer and measured in a JASCO-NaCl III liquid fixed cell when the reaction rate was followed. The ^{1}H-NMR spectra were recorded with a HITACHI R24-B spectrometer (60 MHz) in $CDCl_3$ or CD_3CN using TMS as an internal standard. The GC analyses were carried out with a HITACHI 163 and a HITACHI K53 gas-chromatograph with F.I.D. using stainless DEGS column (N_2 as carrier gas). For the former apparatus, the peak areas were measured by a YANACO SYSTEM-1100 integrator. The MS spectra were taken with a JOEL-KMS-D 300 mass spectrometer.

All the reactions were monitored by TLC (Wako Pure Chemical Industries Ltd., Wakogel B-5, or MERCK, Kieselgel 60 GF), and the products were separated by column chromatography using MERCK Kieselgel 60 silica-gel or MERCK Aluminiumoxide 60 aktiv badisch. All the substrates obtained were identified by IR, ^{1}H-NMR, MS, and elemental analysis. Elemental analyses were carried out by Chemical Analysis Center in Toyama Medical and Pharmaceutical University. All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents and solvents used were further purified by general methods. The computations were performed on a NEC PC-9801F and PC-9801VX personal computers.

Kinetics. A pre-cooled solution of the sulfonium ylides (**1**) (7.5×10^{-2} or 10^{-3} mol/l, respectively) in anhydrous solvents were prepared and divided into ten of 1 ml of sealed ampoules, which were immersed in a constant temperature silicon oil bath (±0.1°C). At appropriate time intervals, the tubes were taken out and frozen in an ice bath to stop the reaction. The reaction rate was then measured by following the decreasing absorbance at IR 2170 cm^{-1} due to the cyano group of (**1**), using the liquid fixed cells with 0.1 mm and 1.0 mm thick windows. The rate constants were calculated by a least-squares method using the 6–8 points accumulated during the first 60% of reaction. When the data were plotted as $\ln [(A_0\text{-}A_\infty)/(A_t\text{-}A_\infty)]$ vs. time, where A_0 is the initial absorbance of sulfonium ylide, A_t is the absorbance of sulfonium ylide at a particular time, and A_∞ is the absorbance of sulfonium

TABLE III

Kinetics of Ethyl phenylsulfonium dicyanomethylide in Benzene at 130.0°C

Time (min.)	$\ln[(A_0-A_\infty)/(A_t-A_\infty)]$	$k \times 10^4$ ($\sec^{-1}$)
0	—	—
15	0.146	1.62
30	0.297	1.65
45	0.457	1.69
60	0.607	1.69
75	0.757	1.68
90	0.921	1.70
105	1.082	1.72

$k = (4.26 \pm 0.04) \times 10^{-4}$ ($\sec^{-1}$)[a]

($\gamma = 0.999$)

[a] The reaction rate constant was calculated by least-squares method and the error is standard deviation.

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ylide as infinite time (more than 6 times half-lives), a good linear correlation was observed, suggesting that the kinetics is first-order. A typical example of the kinetics is shown in Table III.

Activation parameters ($\Delta H\ddagger$ and $\Delta S\ddagger$) were calculated by least-squares method using ln k vs. 1/T. The Hammett ρ-value was also computed by least-squares method using σ-values and logarithms of the rate constants.

Preparation of Ethylphenylsulfonium dicyanomethylylides (**1**).[29] The substrate (**1**) was prepared by treating ethyl phenyl sulfide (3.0 g) with equivalent tetracyanoethylene oxide (TCNEO) in ether-THF at room temperature for 1 day, and the solvent was removed. The residue was separated by basic alumina column chromatography using 1,2-dichloroethane and acetonitrile as eluents followed by silica-gel column chromatography with chloroform. The oily substance was recrystallized from ether-methanol to yield the desired product.

Tetracyanoethylene Oxide (TCNEO).[30] A solution of tetracyanoethylene (25.6 g, 0.2 mol) in 150 ml of acetonitrile was cooled to 3–4°C, and 25 ml of 35%-hydrogen peroxide was added at a rate such that the temperature remained between 25 and 30°C. When the addition was complete, the reaction mixture was stirred for 5 minutes and diluted with 750 ml of ice-cold water. The precipitated solid was collected by filtration, washed with water, and air-dried for 3 hours. The crude product was recrystallized from 1,2-dichloroethane (10 ml/g) to give 13.0 g (45%) of long, light purple needles; m.p. 176.0–177.0°C (sealed tube); IR (KBr, cm^{-1}) 2210 (C≡N), 1600 (—O— of epoxide).

Ethyl(substituted phenyl)sulfonium dicyanomethylides, substituent *p-OCH*$_3$: ^{1}H-NMR ($CDCl_3$, TMS, ppm) 8.00–7.00 (m, 4H, —C_6H_4—), 3.80 (s, 3H, —OCH_3), 3.80–3.00 (m, 2H, —CH_2—), 1.50 (t, 3H, —CH_3); IR (KBr, cm^{-1}) 2200, 2190 (C≡N); Anal. Found: N 11.92, C 61.87, H 5.29%, Calcd. for $C_{12}H_{12}N_2OS$: N 12.06, C 62.04, H 5.21%; m.p. 78.7–79.0°C; MS (m/z) 232.0.

p-CH$_3$: ^{1}H-NMR ($CDCl_3$, TMS, ppm) 8.00–7.00 (m, 4H, —C_6H_4—), 3.70–3.00 (m, 2H, —CH_2]), 2.45 (m, 3H, —CH_3); IR (KBr, cm^{-1}) 2200, 2180 (C≡N); Anal. Found: N 12.75, C 66.47, H 5.67%, Calcd. for $C_{12}H_{22}N_2S$ N 12.95, C 66.63, H 5.59%; m.p. 119.0–119.5°C; MS (m/z) 216.0.

H: ^{1}H-NMR ($CDCl_3$, TMS, ppm) 7.72 (s, 5H, —C_6H_5), 3.95–3.15 (m, 2H, —CH_2—), 1.56 (t, 3H, —CH_3); IR (KBr, cm^{-1}) 2190, 2170 (C≡N); Anal. Found: N 13.68, C 65.46, H 5.01%, Calcd. For $C_{11}H_{10}N_2S$: N 13.85, C 65.32, H 4.98%; m.p. 68.0–70.0°C; MS (m/z) 202.0.

Mp-Cl: ^{1}H-NMR (CDCl$_3$, TMS, ppm) 7.60 (s, 4H, —C_6H_4—), 3.80–3.20 (m, 2H, —CH_2—), 1.60 (t, 3H, —CH_3); IR (KBr, cm^{-1}) 2190, 2180 ($C\equiv H$); Anal. Found: N 11.85, C 55.81, H 3.87%, Calcd. for $C_{11}H_9N_2SCl$: N 11.98, C 55.81, H 3.83%; m.p. 125.0–126.5°C; MS (m/z) 236.0.

m-Cl: ^{1}H-NMR (CDCl$_3$, TMS, ppm) 7.50 (s, 4H, —C_6H_4—), 3.70–3.10 (m, 2H, —CH_2—), 1.60 (t, 3H, —CH_3); IR (KBr, cm^{-1}) 2200, 2190 ($C\equiv N$); Anal. Found: N 11.86, C 55.67, H 3.90%, Calcd. for $C_{11}H_9N_2SCl$: N 11.98, C 55.81, H 3.83%; m.p. 91.5–92.5°C; MS (m/z) 236.0.

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