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염화카바모일술페닐과 그 유도체의 합성

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The Synthesis of Carbamoylsulfenyl Chloride and its Derivatives

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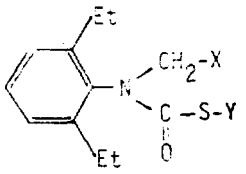
요 약 : N-Methylidene-2,6-diethylaniline (III)은 2,6-diethylaniline (II)과 과량의 paraformaldehyde와의 반응으로 만들었으며, 이 화합물 III에서 $N=CH_2$ 프로톤은 AB스핀계를 나타냈다. 화합물 III과 chlorocarbonylsulfenyl chloride (IV)를 반응시켜서 N-(chloromethyl)-N-(2,6-diethylphenyl)-carbamoylsulfenyl chloride (V)를 합성하였다. 화합물 V와 여러 종류의 알콜을 반응시켜서 Alkyl N-(chloromethyl)-N-(2,6-diethylphenyl)-carbamoylsulfenate (VI~XVI)를 71~95 %의 수득률로 합성하였다. VI~XVI은 서서히 분해되지만 S—O 결합이 S=O 결합으로 변하지는 않았다. 과량의 알콜은 V의 2가 황과 N-chloromethyl기의 α-탄소에 대해 친핵성 공격을 할 수 있었으며, 이렇게 하여 생긴 화합물 (XVII, XVIII)은 상당한 안정성을 가지고 있었다.

ABSTRACT. N-Methylidene-2,6-diethylaniline (III) was prepared by the reaction of 2,6-diethylaniline (II) with an excess paraformaldehyde. The protons of $N=CH_2$ in the compound III exhibited a second order NMR spectrum. The compound III reacted with bifunctional chlorocarbonylsulfenyl chloride (IV) to give N-(chloromethyl)-N-(2,6-diethylphenyl)-carbamoylsulfenyl chloride (V). The reaction of the compound V with various alcohols resulted in the formation of Alkyl N-(chloromethyl)-N-(2,6-diethylphenyl)-carbamoylsulfenate esters (VI~XVI) in 71~95 % yields. The compound VI~XVI decomposed gradually, but the thermal rearrangement of S—O bonding to S=O bonding was not found. The nucleophilic attack of an excess alcohol to the compound V was made on both divalent sulfur and α-carbon of N-chloromethyl group. The corresponding substituted products (XVII, XVIII) had considerable stability.

INTRODUCTION

The first thiocarbamate herbicide, S-ethyldipropylthiocarbamate (EDTC), was introduced in 1954 as an experimental herbicide to control annual grasses and many broad-leaved weeds[1]. Since then, many compounds in this group were synthesized[2]. Alachlor containing 2,6-diethylphenyl group was introduced in 1966 as a promising new herbicide[3] and also Butachlor was reported to control grasses and specific broad-leaved weeds selectively in rice[4]. Thus it is interesting to synthesizing new compounds with the moiety of thiocarbamate, Alachlor, and Butachlor. It was described how to synthesize new compounds (V-XVIII) as follows with the structural skeleton which was similar with thiocarbamate and amide herbicides.



X = Cl, Alkoxy

Y = Cl, Alkoxy

EXPERIMENTAL

Material and Methods-Melting Point. were uncorrected and taken on a Thomas-Hoover capillary apparatus. IR absorption spectra were determined on a Perkin-Elmer model 267 grating infrared spectrometer. The NMR spectra were recorded on a Varian T-60A spectrometer. Mass spectra were determined with a Hewlett-Packard HP 5985A mass spectrometer. Elemental analysis were performed on a Hewelett-Packard HP 185 B CHN analyzer. 2,6-Diethylaniline (Aldrich Chem. Co.) (II) was heated to reflux with sodium hydroxide pellets, then distilled under reduced pressure (61°C/0.3 mmHg). Trichloromethanesulfenyl chloride (Aldrich Chem. Co.) and paraformaldehyde were used without further purification. Alcohols were heated to reflux over calcium oxide and fractionated pyridine and triethylamine were heated to reflux from calcium oxide, distilled, and kept over sodium hydroxide pellets.

Chlorocarbonylsulfenyl Chloride(IV). It was prepared according to the method introduced by Zumach and Kühle[5]. bp 28~30°/40mmHg (reported[5], 98°C/760mmHg); IR (NaCl plate) 1780 (C=O), 800cm^{-1}(C—S)

N-Methylidene-2, 6-Diethylaniline (III). 2.7g (0.072mole) of paraformaldehyde (80 % grade) in excess was added to 5.4g (0.036 mole) of II in 40 m*l* of anhydrous benzene and 2 m*l* of triethylamine was added to the solution. The mixture was heated to reflux with vigorous stirring for 3 hours, during which time water was collected more than the theoretical amount (0.7 m*l*) in a Dean-Stark trap because paraformaldehyde had a little moisture. The benzene phase was dried over potassium hydroxide pellets for an additional half hour. Hydrated potassium hydroxide and unreacted remaining paraformaldehyde were filtered. After removal of benzene and triethylamine from the filtrate by a rotatory evaporator, the residue was distilled with a micro distillation apparatus under reduced pressure. The distillate was obtained in 91 % yield (5.3 g), a colorless liquid. bp 50°C/0.3mmHg; IR(NaCl plate) 1650 (C=N), NMR(CCl_4) δ7.6(*d*, 1H, N-CH, J=19Hz), 7.3(*d*, 1H, N-CH, J=19 Hz), 6.9(*s*, 3H, Ar), 2.5(*q*, 4H, CH_2, J=7 Hz), 1.2ppm (*t*, 6H, CH_3, J=Hz).

N-(Chloromethyl)-N-(2,6-Diethylphenyl)-Carbamoylsulfenyl Chloride (V). A solution of 4.7g (0.029mole) of III in 20m*l* of benzene was added dropwise with vigrous stirring for one hour at 15~25°C to a solution of 3.8g (0.029 mole) of IV in 50m*l* of benzene, care being taken to ensure a little chlorocarbonylsulfenyl chloride was still present at the end of the reaction. The mixture was stirred for additional one hour in a water-bath (15~25°C). The moment a drop of the imine solution fell, the yellow reaction solution turned to a deep red. A little later the deep red colour changed to yellow. The adduct was concentrated under reduced pressure and dried completely by a mechanical oil pump, then crude yellow solid remained. The solid was recrystallized from anhydrous *n*-hexane. The product, after twice recrystallizations from *n*-hexane, was 7.0 g(yield 83%) a yellow solid. mp 56~57°C; IR(KBr) 1700cm^{-1} (C=O); NMR(CCl_4) δ7.3(*m*, 3H, Ar), 5.5 (*s*, 2H, NCH_2Cl), 2.8(*q*, 4H, CH_2, *J*=7 Hz), 1.4ppm(*t*, 6H, CH_3, *J*=7 Hz); Mass Spect. (70eV) 291(M^+.), 256, 224, 160(base peak), 132, 105, 67, 65, 46, 29, 27.

Anal. Calcd. for C_{12} $Cl_{12}H_{15}NOS$: C, 49.3; H, 5.2; N, 4.8. Found: C, 48.9; H, 5.4; N, 4.7

Preparation of Methyl N-(Chloromethyl)-N-(2.6-Diethylphenyl)-Carbamoylsulfenate—6.8m mole of methyl alcohol and 0.54g(6.8 mmole) of distilled pyridine in 10 m*l* of anhydrous *n*-pentane was added dropwise with vigrous stirring over a period of thirty minutes to a solution of 2.0g(6.8m mole) of V dissolved in 20m*l* of anhydrous *n*-pentane. The reaction mixture was kept at room temperature. Complete esterification was judged by the disappearance of the yellow color of V. After additional stirring for thirty minutes the reaction mixture was filtered by the suction filtration using glass filter. The solvent in the filterate was evaporated by a rotatory evaporator under reduced pressure. The residue, a viscous liquid, was recrystallized from anhydrous *n*-hexane. It weighed 1.5g (75% yield). A white crystalline, mp 46~47°C; IR(KBr) 2820 (methoxy, C—H), 1690cm^{-1} (C=O); NMR(CCl_4) δ7.2 (*m*, 3H, Ar), 5.5 (*s*, 2H, NCH_2Cl), 3.7(*s*, 3H, OCH_3), 2.7(*q*, 4H, CH_2, *J*=7Hz), 1.4ppm(*s*, 6H, CH_3, *J*=7Hz); Mass Spect. (70eV) 287(M^+.), 252, 224, 160 (base peak), 146, 132, 105, 91, 77, 63, 45, 29, 27

Anal. Calcd. for $C_{13}ClH_{18}NO_2S$: C, 54.2; H, 6.3; H, 4.9. Found: C, 53.2; H, 6.2; N, 4.9.

Ethyl N-(Chloromethyl)-N-(2.6-Diethylphenyl-Carbamoylsulfenate (VII). (The residue, a viscous liquid, was recrystallized from anhydrous *n*-hexane. It weighed 1.45g(71 % yield), A white crystalline; mp 48~49°C; IR (KBr) 1960cm^{-1}(C=O); NMR(CCl_4) δ7.2(*m*, 3H, Ar), 5.5(*s*, 2H, NCH_2Cl), 3.9(*q*, 2H, OCH_2, *J*=7Hz), 2.7(*q*, 4H, CH_2, *J*=7Hz), 1.4ppm(*m*, 9H, CH_3); Mass spect. (70 eV) 301(M^+), 266, 224, 160, 146, 132, 117, 105, 91, 77($CH_3CH_2SO^+$), 29, 27.

Anal. Calcd. for $C_{14}ClH_{20}NO_2S$: C, 55.6; H, 6.6; N, 4.6. Found: C, 54.9; H, 6.6; N, 4.7.

***n*-Propyl N-(Chloromethyl)-N-(2, 6-Diethylphenyl)-Carbamoylsulfenate (VIII).** Compound VIII, a colorless visocus liquid, was obtained in 1.97g(92% yield); IR(NaCl plate) 1690cm^{-1} (C=O); NMR(CCl_4) δ7.2(*m*, 3H, Ar), 5.5(*s*, 2H, NCH_2Cl), 3.8(*t*, 2H, OCH_2, *J*=6 Hz), 2.7(*q*, 4H, CH_2), 1.7(*m*, 2H, CH_2), 1.4(*t*, 6H, CH_3), 1.0ppm(*t*, 3H, CH_3, *J*=6 Hz).

***i*-Propyl N-(Chloromethyl)-N-(2.6-Diephenyl)-Carbamoylulfenate (IX).** Compound IX, a colorless viscous liquid, was obtained in 2.04g(95% yield); IR (NaCl plate) 1690cm^{-1} (C=O); NMR(CCl_4) δ7.2(*m*, 3H, Ar), 5.4(*s*, 2H, NCH_2Cl), 3.8(*m*, 1H, OCH), 2.7(*q*, 4H, CH_2), 1.3ppm(*m*, 12, CH_3).

***n*-Butyl N-(Chloromethyl)-N-(2, 6-Diethylphenyl)-Carbamoylsulfate (X).** Compound X, a colorless viscous liquid, was obtained in 2.0g (90% yield); IR(NaCl plate) 1690cm^{-1}(C=O); NMR(CCl_4) δ7.2(*m*, 3H, Ar), 5.4(*s*, 2H, NCH_2 Cl), 3.8(*m*, 2H, OCH), 2.7(*q*, 4H, CH_2), 1.4(*m*, 10H, CH_2, CH_3), 0.9ppm(*t*, 3H, CH_3).

***i*-Butyl N-(Chloromethyl)-N-(2.6-Dimethylphenyl)-Carbamoslyulfenate (XI).** Compound XI, a colorless viscous liquid, was obtained in 1.9g(85% yield); IR(NaCl pate) 1690cm^{-1} (C=O); NMR(CCl_4) δ7.2(*m*, 3H, Ar), 5.4 (*s*, 2H, NCH Cl), 3.6 (*d*, 2H, OCH_2, *J*=6 Hz), 2.7(*q*, 4H, CH_2), 1.9(*m*, 1H, CH), 1.3(*t*, 6H, CH_3), 0.9ppm(*d*, 6H, CH_3, *J*=7 Hz).

***sec*-Butyl N-(Chloromethyl)-N-(2.6-Diethylphenyl)-Carbamoylsulfenate (XII).** Compound XII, a colorless viscous liquid, was obtained in 2.0g (90% yield); IR(NaCl plate) 1690cm^{-1}(C=O); NMR(CCl_4) δ7.2(*m*, 3H,

Ar), 5.4(*s*, 2H, NCH_2Cl), 3.7(*m*, 1H, OCH), CH_2, CH_3), 1.0CH_2, J=7 Hz), 1.3(*m*, 8H, 2.7(*q*, 4H, ppm(*m*, 6H, CH_3).

***t*-Butyl (N-Chloromethyl)-N-(2.6-Diethylphenyl)-Carbamoylsulfenate (XIII).** Compound XIII, a colorless viscous liquid, was obtained in 1.9g (85%); IR (NaCl plate) 1690 cm^{-1}(C=O); NMR(CCl_4) δ7.3(*m*, 3H, Ar), 5.4(*s*, 2H, NCHCl), 2.7(*q*, 4H, CH_2, J=7 Hz), 1.3 ppm(*m*, 15H, CH_3).

***n*-Amyl N-(Chloromethy)-N-(2.6-Diethylhenyl)-Carbamoylsulfenate (XIV).** Compound XIV, a colorless viscous liquid, was obtained in 2.1g (90% yield); IR(NaCl plate) 1690cm^{-1} (C=O); NMR(CCl_4) δ7.2(*m*, 3H, Ar), 5.4 (*s*, 2H, NCH_2Cl), 3.8(*t*, 2H, OCH_2, J=6 Hz), 2.7(*q*, 4H, J=7 Hz), 1.7~1.0ppm (*m*, 15H, CH_2, CH_3).

***t*-Amyl N-(Chloromethyl)-N-(2.6-Diethylphenyl)-Carbamoylsulfenate (XV).** Compound XV, a colorless viscous liquid, was obtained in 2.0g (85% yield); IR (NaCl plate) 1690cm^{-1} (C=O); NMR(CCl_4) δ.3(*m*, 3H, Ar), 5.4(*s*, 2H, NCH_2Cl), 2.7(*q*, 4H, CH_2 J=7 Hz), 1.6 ~1.2(*m*, 14H, CH_2, CH_3), 1.0ppm(*t*, 3H, CH_3, J=7 Hz).

Benzyl N-(Chloromethyl)-N-(2.6-Diethylphenyl)-Carbamoylulfenate (XVI). Compound XVI, a colorless viscous liquid, was obtained in 2.3g (95% yield); IR(NaCl plate) 1690cm^{-1} (C=O); NMR(CCl_4) δ7.3(*m*, 8H, Ar), 5.5(*s*, 2H, NCH_2Cl), 4.8(*s*, 2H, OCH_2), 2.7(*q*, 4H, CH_2, J=7 Hz), 1.3ppm(*t*, 6H, CH_3, J=7 Hz).

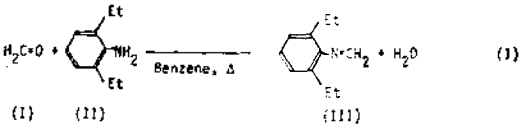
Preparation of Methyl N-(methoxymethyl)-N-(2.6-Diethylphenyl)-Carbamoylsulfenate (XVII). 2.0g(0.0068 mole) of N-(chloromethyl)-N-(2,6-diethylphenyl)-carbamoylsulfenyl chloride was dissolved in 20m*l* of methylalcohol in the flask, then 1.1g (0.0136mole) of pyridine was added dropwise with stirring for 10 minutes. The reaction mixture was stirred, kept at room temperature. After complete evaporation of methyl alcohol 20m*l* of *n*-pentane was added, then the precipitate (pyridine hydrochloride salt) was filtered. The solvents was removed from the filtrate by distillation. The residue was a colorless viscous liquid.

Compound XVII, a colorless viscous liquid, was obtained in 1.7g (89% yield); IR (NaCl plate) 2820(methoxy C—H), 1690cm^{-1}(C=O); NMR(CCl_4) δ7.3(*m*, 3H, Ar), 5.0(*s*, 2H, NCH_2O), 3.8(*s*, 3H, SO-CH_3), 3.6(*s*, 3H, O-CH_3), 2.7(*q*, 4H, CH_2, J=7 Hz), 1.4ppm (*t*, 6H, CH_3, J=7 Hz).

Ethyl N-(Ethoxymethyl)-N-(2.6-Diethylphenyl)-Carbamoylsulfenate (XVIII). Compound XIII, a colorless viscous liquid, was obtained in 1.9g (90% yield); IR(NaCl plate) 1680cm^{-1}(C=O); NMR(CCl_4) 7.2(*m*, 3H, Ar), 4.9(*s*, 2H, NCH_2O), 385(*q*, 2H, SO-CH_2, J=5.5Hz), 3.75(*q*, 2H, O-CH_2, J= 5.5Hz), 1.3(*m*, 12H, CH_3).

RESULTS AND DISCUSSION

Reaction of Paraformaldehyde with 2.6-Diethylaniline. In the synthesis of the N-methylidene compound (III) was used paraformaldehyde which decomposed to monomer *in vitro*. It reacted with 2, 6-diethylaniline (II) to give N-methylidene-2.6-diethylaniline (III) in 91% yield according to equation (1).



(I) (II) (III) (1)

The water was effectively removed by azeotropic distillation using Dean-Stark trap, as usually in the synthesis of imines. The yield improved when triethylamine (Et_3N) or pyridine was added as catalyst. The synthesized imine

had a strong absorption band in the IR spectrum at 1650cm^{-1} due to the C=N stretching, the protons of N=CH_AH_B in a NMR spectrum exhibited four peaks, the inner peaks of which were more intense. Two protons in N=CH_AH_B were of AB spin system. The coupling constant, J_{HH}(gem)=19 Hz, could be obtained directly from the doublet spacing. Because the intensity of proton A was unequal, the weighted average position of it had to be computed from the coupling constant and the chemical shift difference, $\Delta\nu_{AB}$, might be obtained from equation (2)[6].

$$\Delta\nu_{AB}=(4C^2-J^2)^{1/2} \quad (2)$$

Upon substituting values for the constants, J= 19 Hz, C=13 Hz, which was observed in the spectrum, $\Delta\nu_{AB}$ in equation (3) was 17.8Hz. The actual peaks (δ 7.6, δ 7.3) of proton A and B were determined by adding and substracting 1/2 $\Delta\nu_{AB}$(8.9Hz, 0.15ppm) to the midpoint(δ 7.45) of the entire spectrum. The geminal coupling constant, J_{HH}(gem), in the N=CH_2 with an sp^2 carbon was compared to the coupling in olefins (ethylene, 2.3Hz). The coupling constant was large due to π donation of nonbonding pair of electrons on nitrogen and electronegativity of nitrogen. J_{HH}(gem) in CH_2=N-system had been reported to be larger as the carbon atom of the CH_2 was more positive[7]. Schiff bases from formaldehyde and aromatic amines[19] polymerized spontaneously in most cases to give cylic trimers[9], but a stable imine was yielded without polymerization, due to the steric hindrance of two substituted ethyl groups in the case of 2,6-diethylaniline. The phsical property and reaction condition were listed in *Table* 1.

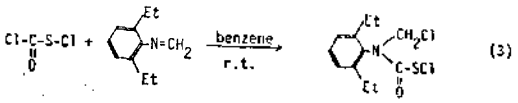
Addition of Acid Chloride to Imine. Chlorocarbonylsulfenyl chloride (IV) was prepared according to the method introduced by

Table 1. Preparation of acid halide, imine, and carbamoylsulfenyl chloride.

Compounds[a]	Yield (%)	bp, 0°C (mmHg) or mp, °C	Reaction condition Temp (°C)	Time (h)
III AR—N=CH_2	91[b]	50(0.3)	80~90	3
IV AR—N(—CH_2Cl)—C(=O)—S—Cl	83	56~57	15~25	2

[a] AR=2,6-Diethylphenyl; [b] Yields listed are for the distillated products; [c] Yield is for the recrystallization products from *n*-hexane.

Zumach and Kühle[5]. This compound was not stable under prolonged boiling temperature, and thus was distilled under prolonged boiling temperature, and thus was distilled under reduced pressure. The compound exhibits a strong absorption band of the carbonyl stretching vibration at 1780cm^{-1} in the IR spectrum in place of strong absorption band (730~770cm^{-1}) of trichloromethanesulfenyl chloride. Compound IV has bifunctional grouping; acid chloride and sulfenyl chloride. The addition of acid halide to imine was reported in the literature[10]. The addition of suflenyl chloride to olefins was also reported[11], but to imines was not reported. Because the sulfenyl chloride moiety of compound IV is possible to react with compound III, however, compound III to be added to the acid chloride, care being taken ensure that a little compound IV is still present at the end of the reaction (equation (3)).



(IV) (III) (V) (3)

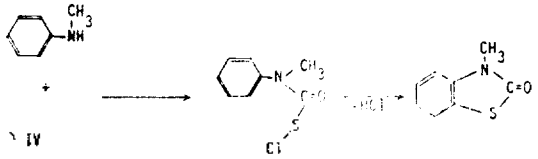
The adduct (V) of bifunctional compound IV was characterized by its IR spectrum. The carbonyl band for the adduct was near 1700cm^{-1}, whereas the absorption of carbonyl grouping in acid halide (IV) were shown in the 1780cm^{-1}.

The peak, δ 5.5ppm, in the NMR spectrum was assigned to be that of NCH_2Cl prnotos. The recrystallization of the crude product from *n*-hexane afforded 83 % yield a yellow crystalline solid. Analytical and physical data of the adduct were listed in *Table* 1 and 2.

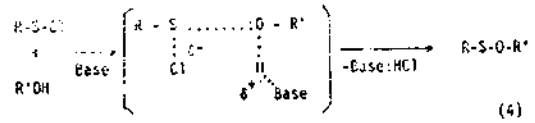
Reaction of N-(Chloromethyl)-N-(2,6-Diethylphenyl)-Carbamoylsulfenyl Chloride (V) with Alcohols. The carbamoylsulfenyl chlorde is not well known, it was reported to readily decompose with elimination of sulfur to form the carbamoyl chlorides[5].

$$2R_2NH + \text{IV} \xrightarrow[-R_2NH_2Cl]{0^\circ C} R_2N-\underset{\underset{O}{\|}}{C}-S-Cl \longrightarrow \underset{-S}{} R_2N-\underset{\underset{O}{\|}}{C}-Cl$$

Also N-phenyl-N-methyl carbamoylsulfenyl chlorides as intermediate was found to give N-methyl benzothiazolone[5].

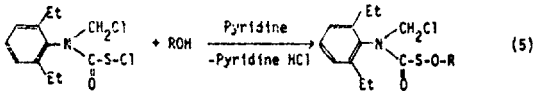


The carbamoylsulfenyl chloride in this work was moderately stable without elimination of sulfur, and did not give thiazolone because of substituted ethyl groupings in 2,6-position of phenyl ring. The reaction of dicoordinated sulfur compound with nucleophiles(*e.g.*, alcohols[12], amines[13], phosphite[14], and disulfide[15]) was reported in the literatures. Parker and Kharasch[16] suggested the availability of divalent sulfur d-orbitals for nucleophilic displace [illegible] accommodated [illegible]. If alcohols [illegible], the possible transition [illegible] was represented by equation (4).



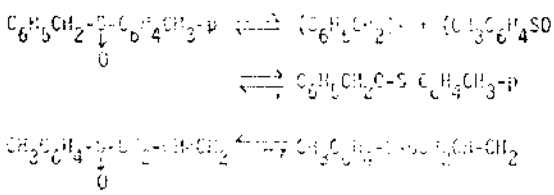
(4)

The sulfenate esters (R-S-O-R′) are sulfur analogues of organic peroxide (R-O-O-R′). However, the carbamoylsulfenate esters in this work according to equation (5) is sulfur analogues of organic peroxy and acid ester.



(V) (VI)~(XVI) (5)

In this work, the carbamoylsulfenate esters were a adequate stabilities to permit their use as derivatives for the alcohols. As might be expected from their structures, however, they could undergo thermal decomposition. About 40 % of compound VI decomposed under heating at 150°C for 30 minutes, about 70 % decomposed for ten days (10~15°C). The decomposition ratio was carried out by NMR integration of NCH_2O protons (δ 5.5). A thermal rearrangement of sulfenate to sulfoxide does not seem to have occurred because of no strong absorption band at 1050 cm^{-1}. The thermal rearrangement occurred in some papers[17].



In the IR spectra, the carbonyl stretching vibration in carbamoylsulfenate esters was near 1650 cm^{-1}, whereas that of carbamoylsulfenyl chlorides was 1700cm^{-1}. Analytical and physical data of the carbamoylsulfenate esters

Table 2. Spectral and analytical data of the sulfenyl chloride and sulfenates

Compounds*	IR, cm^{-1}	*Anal.*, Found (Calcd.)		
	C=O	C	H	N
IV Cl—C(=O)—S—Cl	1780			
V AR—N(—CH_2Cl)—C(=O)—S—Cl	1700	48.9 (49.3)	5.4 (5.2)	4.7 (4.8)
VI AR—N(—CH_2Cl)—C(=O)—S—OCH_3	1690	53.2 (54.2)	6.2 (6.3)	4.9 (4.9)
VII AR—N(—CH_2Cl)—C(=O)—S—OCH_2CH_3	1690	54.9 (55.6)	6.6 (6.6)	4.7 (4.6)

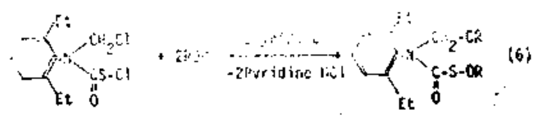
*AR=2, 6-diethylphenyl

Table 3. Products by Reaction of N-(Chloromethyl)-N-(2, 6-Diethylphenyl) Carbamoylsulfenyl Chloride (V) with Alcohols

Compound No.	AR—N(—CH_2—X^a)—C(=O)—S—OR X	R	Yield^b (%)	mp(°C)^c
VI	H	Methyl	75	46~47
VII	H	Ethyl	71	48~49
	H	*n*-Propyl	92	Oil
IX	H	*i*-Propyl	95	Oil
X	H	*n*-Butyl	90	Oil
XI	H	*i*-Butyl	85	Oil
XII	H	*s*-Butyl	90	Oil
XIII	H	*t*-Butyl	85	Oil
XIV	H	*n*-Amyl	90	Oil
XV	H	*t*-Amyl	85	Oil
XVI	H	Benzyl	95	Oil
XVII	Methyl	Methyl	89	Oil
XVIII	Ethyl	Ethyl	90	Oil

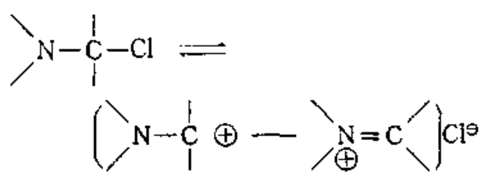
^{a} AR=2, 6-diethylphenyl; ^{b} Yields in runs, 1 and 2, are for the recrystallization products from *n*-hexane, yields in other run are for the crude, dry products, based on amount of sulfenyl chloride used; ^{c} The products of compounds VI-XVIII are viscous liquids with difficulty of recrystallization from many solvents (*n*-hexane, petroleum ether, polar solvents, *etc*).

(VI-XVI) were summerized in *Table* 2 and 3. The nucleophilic displacement of N-α-halo-compounds was shown in the literature[18]. In this work, pyridine was added as base, the nucleophilic substitution reaction was represented by equation (6).



(V) (XVII, XVIII)

The protons of NCH_2OR grouping exhibited the NMR peaks in δ 5.0~4.9ppm. Analytical and physical data of the compound (XVII, XVIII) are summerized in *Table* 3. Other alcohols in equation (6) failed to give structural compounds as like XVII and XVIII. When XVII and XVIII were prepared, reagent(alcohol) was used as solvent. The bond (C-Cl) of >N—C< —Cl had a little ionic character[18].



Dielectric constant and polarity of methyl alcohol and ethyl alcohol are large, thus XVII, XVIII was prepared without vigrous reaction conditions (*e.q.*, heating, use of strong base). Vigrous conditions in the reaction of compound V with less polar alcohols than methanol and ethanol could not be introduced because compound V decomposed on the condition. All synthetic routes in this work was given in ***Fig.*** 1.

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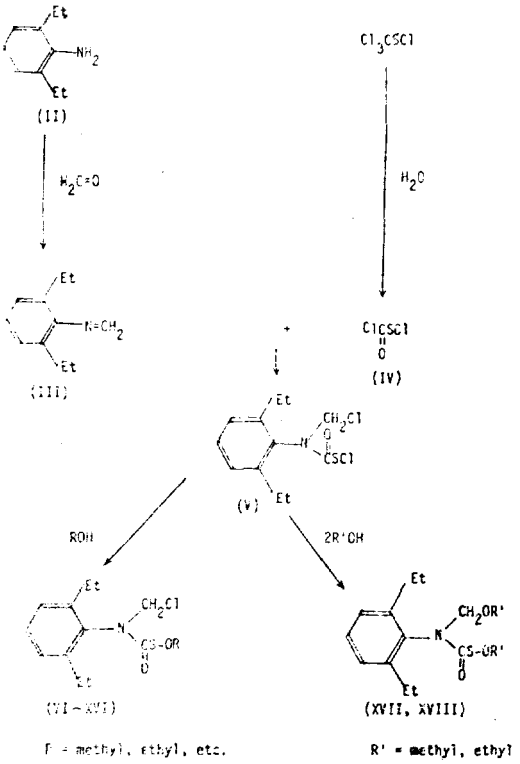

Fig. 1. All Synthetic routes

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