Nuclear Magnetic Resonance, Infrared, and Mass Spectroscopic Studies of Carbamoyl Sulfoxides

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NMR, IR, and mass spectra of carbamoyl sulfoxides are reported. In dilute solution the IR spectra of carbamoyl sulfoxides exhibited two carbonyl stretching bands which are attributed to two possible rotational isomers, cis and gauche forms. Rotational barriers around the C–N bonds of carbamoyl sulfoxides and sulfones were also determined from NMR data.

Carbamoyl sulfoxides have been synthesized independently in our laboratory and elsewhere (Gozzo et al., 1975) by reacting the corresponding thiocarbamates with 1 molar equiv of *m*-chloroperbenzoic acid.

The NMR spectra of carbamoyl sulfoxides are generally complicated due to the presence of an asymmetric sulfur atom and the restricted rotation about the C–N amide bond. The IR spectra of the sulfoxides generally exhibit two carbonyl absorption bands. To study the characteristics spectral parameters of carbamoyl sulfoxides, we have synthesized aryl *N,N*-dimethylcarbamoyl sulfoxides and sulfones. We wish here to report the NMR, IR, and mass spectral data of carbamoyl sulfoxides.

EXPERIMENTAL SECTION

The NMR spectra were obtained on a Varian HA-60-IL or a T-60A spectrometer in deuterated chloroform solution with tetramethylsilane as an internal reference. The mass spectra were measured on a Varian MAT CH-5 mass spectrometer using a direct insertion probe operated at 70 eV ionization energy. The IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Melting points are uncorrected. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer.

Preparation of Carbamoyl Sulfoxides. Carbamoyl sulfoxides and sulfones were prepared according to the methods described by Casida et al. (1974) and Gozzo et al. (1975). Ethyl *N,N*-di-*n*-propylcarbamoyl sulfoxide (1), ethyl hexahydro-1*H*-azepine-1-carbonyl sulfoxide (2), ethyl *N,N*-diisobutylcarbamoyl sulfoxide (3), and *p*-chlorobenzyl *N,N*-diethylcarbamoyl sulfoxide (4) were reported by Casida et al. (1974). Carbamoyl sulfoxides 1, 3, and 4 were also reported by Gozzo et al. (1975).

Phenyl *N,N*-Dimethylcarbamoyl Sulfoxide (5). Mp 94.5–96 °C. The IR, MS, and NMR parameters are listed in Table I. Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.82; H, 5.58. Found: C, 54.6; H, 5.8.

***p*-Chlorophenyl *N,N*-Dimethylcarbamoyl Sulfoxide (6).** Mp 122–123 °C. The IR, MS, and NMR parameters are listed in Table I. Anal. Calcd for $C_9H_{10}ClNO_2S$: C, 46.65; H, 4.32. Found: C, 46.7; H, 4.5.

Phenyl *N,N*-Dimethylcarbamoyl Sulfone (7). Mp 103–104 °C (lit. 102–103 °C, Senning et al., 1968); IR (KBr) 1695 cm^{-1} (C=O), 1302 and 1150 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 3.02 (s, 3 H, methyl), 3.48 (s, 3 H, methyl), 7.53–8.01 (m, 5 H, aromatic).

***p*-Chlorophenyl *N,N*-Dimethylcarbamoyl Sulfone (8).** Mp 107–108 °C (lit. 104–105 °C, Senning et al., 1968); IR (KBr) 1695 cm^{-1} (C=O), 1300 and 1149 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 3.02 (s, 3 H, methyl), 3.47 (s, 3 H, methyl), 7.44–7.94 (m, 4 H, aromatic).

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RESULTS AND DISCUSSION

The characteristic IR, NMR, and MS parameters are listed in Table I. The IR spectra of carbamoyl sulfoxides have characteristic S=O and C=O absorption bands. The S=O absorption bands are in the range of 1052–1070 cm^{-1}. It is interesting to note that two carbonyl bands at 1664–1667 and 1688–1693 cm^{-1} were observed for carbamoyl sulfoxides 1–4 recorded as thin films but only one carbonyl band at 1708 cm^{-1} was observed for carbamoyl sulfoxides 5 and 6 recorded as KBr pellets. We attributed the two carbonyl absorption bands as arising from two possible rotational isomers of carbamoyl sulfoxides; the more polar cis form, I, and the less polar gauche form, II. In the structures presented, we believe the carbonyl groups to be eclipsed to O, R, or nonbonded electrons. It is also possible that the C–N bond can be eclipsed to O, R, or nonbonded electrons as shown in formula III and IV. In their studies by electron diffraction and dipole moment measurement, Kimura et al. (1954) reported that the C–N and C–Cl bonds of chloroacetamide were in cis configuration with dihedral angle of about 15°. They also proposed that an intramolecular hydrogen bond was present between NH and chlorine. However, replacement of two amide hydrogens with two alkyl groups (R′) makes the steric condition quite different from that in chloroacetamide. It is important to note that all three bonds involving nitrogen are coplanar with the carbonyl bond. Due to this coplanarity, Dreiding stereomodels show extensive steric interference in structures III and IV.

The higher carbonyl band should be assigned to the cis form, I, and the lower to the gauche form, II. Rotational isomerism has been observed in substituted ketones, esters, and amides (Bellamy and Williams, 1957; Hallam and Ray, 1964; Tseng et al., 1971). In a diluted solution, all carbamoyl sulfoxides gave two carbonyl stretching frequencies. The intensities of these absorption bands are solvent dependent and are listed in Table II. It is well known that the population of the more polar form of the rotameters increases in solvents of high dielectric constants (Mizushima, 1954). Therefore, the intensity of the higher frequency carbonyl absorption should increase as the dielectric constant of the solvent increases. This is confirmed by the data in the last column of Table II. Due to solvent interferences, we have not looked into the solvent effect on the S–O bonds in carbamoyl sulfoxides.

The solvent effect on the carbonyl bond in carbamoyl sulfones was also studied. In every case only one band was observed. Because of solubility problems, we were unable to test solvents less polar than carbon tetrachloride.

The NMR spectra of thiocarbamates and their corresponding sulfoxides show significant differences. For an example, *S*-*p*-chlorobenzyl *N,N*-diethylthiocarbamate has chemical shifts at 1.13 (t, 2 CH_3), 3.35 (q, 2 CH_2N), 4.09 (s, CH_2S), and 7.25 (s, C_6H_4Cl). The two ethyl groups are

Table I. Spectral Data of Carbamoyl Sulfoxides ($RSOCONR'_2$)

Compd no.	R	R'	IR,[a] cm^{-1}	NMR,[b] ppm	MS[c]
1	C_2H_5	n-C_3H_7	1667, 1690 (C=O), 1070 (S=O)	0.94 (t, 2 CH_3), 1.37 (t, CH_3), 1.70 (m, 2 CH_2), 2.99 (q, CH_2S), 3.24-3.77 (m, 2 CH_2N)	27 (10), 29 (8), 41 (20), 43 (100), 61 (2), 78 (3), 86 (15), 189 (0.1)
2	C_2H_5	$-(CH_2)_6-$	1664, 1688 (C=O), 1070 (S=O)	1.35 (t, CH_3), 1.65 (s, 4 CH_2), 2.98 (q, CH_2S), 3.62 (m, 2 CH_2N)	27 (9), 29 (17), 41 (8), 43 (7), 44 (10), 55 (100), 83 (12), 98 (5), 126 (28), 187 (0.3)
3	C_2H_5	i-C_4H_9	1666, 1693 (C=O), 1073 (S=O)	0.91 (d, CH_3), 0.94 (d, CH_3), 1.34 (t, CH_3), 2.02 (m, 2CH), 2.98 (q, CH_2S), 3.30 (m, 2 CH_2N)	29 (30), 41 (30), 57 (100), 61 (20), 78 (1), 100 (5), 156 (15), 174 (0.6), 217 (0.3)
4	p-$ClC_6H_4CH_2$	C_2H_5	1664, 1688 (C=O), 1062 (S=O)	0.94 (t, CH_3), 1.12 (t, CH_3), Ca. 3.22 (m, CH_2N), Ca. 3.37 (m, CH_2N), 4.19 (s, CH_2S), 7.29 (s, C_6H_4)	29 (35), 44 (25), 72 (65), 85 (7), 125 (25), 139 (8), 257 (0.3)
5	C_6H_5	CH_3	1708 (C=O), 1052 (S=O)	3.02 (s, CH_3), 3.14 (s, CH_3), 7.40-7.85 (m, C_6H_5)	15 (9), 42 (6), 44 (4.5), 51 (9), 56 (5), 72 (100), 77 (9), 97 (3), 125 (4), 181 (~0.1)
6	p-Cl-C_6H_4	CH_3	1708 (C=O), 1052 (S=O)	2.99 (s, CH_3), 3.14 (s, CH_3), 7.39-7.80 (m, C_6H_4)	15 (7), 42 (5), 44 (5), 56 (3), 72 (100), 75 (4), 108 (2), 111 (2), 159 (3), 215 (~0.2)

[a] IR spectra of 1, 2, 3, and 4 were obtained from thin films; IR spectra of 5 and 6 were obtained from KBr pellets. [b] NMR spectra were obtained in $CDCl_3$, the notations s, d, t, q, and m stand for singlet, doublet, triplet, quartet, and multiplet, respectively. [c] m/e values are given followed by relative intensities in parentheses.

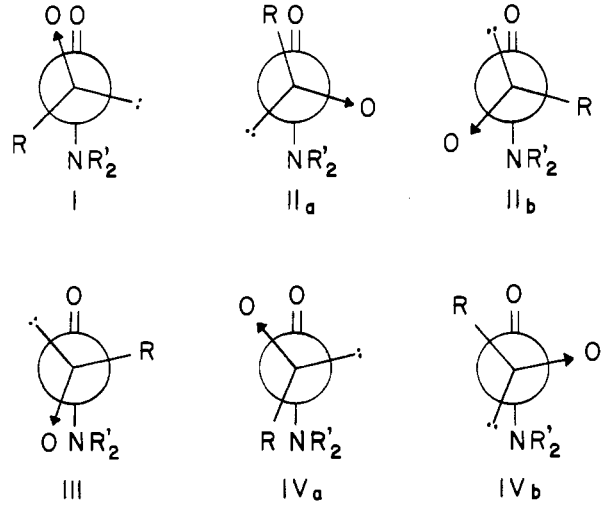

Figure 1. Rotational isomers I, IIa, IIb, III, IVa, and IVb.

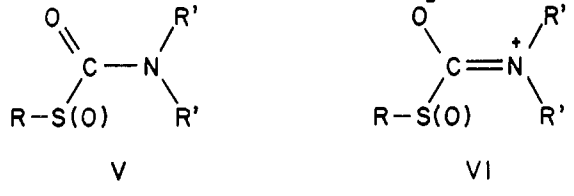

Figure 2. Structures V and VI.

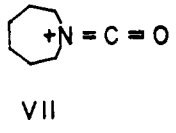

Figure 3. Structure VII.

Table II. Effect of Solvent on Carbonyl Absorption Band

Compd	Solvent	Dielectric constant	$\nu_{C=O}$, cm^{-1} Cis form (I)	$\nu_{C=O}$, cm^{-1} Gauche form (II)	A_I/A_{II}
1	CCl_4	2.24		1667	0
	Neat film		1690	1667	1.00
	CH_3CN	37.45	1692	1667	1.30
5	CCl_4	2.24	1711	1680	0.24
	$CHCl=CCl_2$	3.4	1720	1685	0.89
	$CHCl_3$	4.80	1709	1673	1.55
	CH_3CN	37.45	1710	1677	3.14
6	CCl_4	2.24	1710	1682	0.32
	$CHCl=CCl_2$	3.4	1712	1680	0.76
	$CHCl_3$	4.80	1710	1675	1.43
	$ClCH_2CH_2Cl$	10.65	1710	1679	1.84
	CH_3CN	37.45	1711	1680	2.18

equivalent in *S*-*p*-chlorobenzyl *N*,*N*-diethylthiocarbamate but not in its sulfoxide (4) due to the restricted rotation around the amide C–N bond, one ethyl groups being cis and the other trans to the carbonyl group as shown in V and VI.

The methylene protons connected to the amide nitrogen in sulfoxide 4 exhibit two sets of multiplets instead of quartets. This is due to the asymmetric sulfur atom which causes the methylene protons in each CH_2 group to be magnetically nonequivalent. Once the asymmetric sulfur atom of sulfoxide 4 is oxidized to the corresponding sulfone, the methylene protons become two sets of quartets.

When the NMR spectra of carbamoyl sulfoxides are taken at increasingly higher temperature, the rate of rotation around the C–N amide bond increases, and eventually the two alkyl groups become magnetically equiv-

Table III. NMR Parameters

Compd no.	Solvent	$\Delta\nu$, H_z	T_c, °C	$\Delta G^{\ddagger}$, kcal/mol[b]
5	ODCB[a]	14.0	52	16.8
6	ODCB	13.7	61	17.3
7	ODCB	32.1	93	18.4
8	ODCB	30.7	102	18.9

[a] *o*-Dichlorobenzene. [b] $\Delta G^{\ddagger}$ was calculated according to the following equation (Rauk et al., 1970): $k_c = (\pi/\sqrt{2})\Delta\nu = (kT_c/h)e^{-\Delta G^{\ddagger}/RT_c}$.

alent. The coalescence temperature (T_c), the chemical shift separation ($\Delta\nu$), and the free energy of activation ($\Delta G^{\ddagger}$) of carbamoyl sulfoxides and sulfones are listed in Table III. The coalescence temperatures for carbamoyl sulfoxides are in the range of 52–61 °C and those of carbamoyl sulfones, 93–102 °C. The coalescence temperatures of thiocarbamates are generally in the range of −1 to 7 °C, except for *S*-ethyl hexahydro-1*H*-azepine-1-carbothioate (Ordram), which is 35 °C (Rummens and Louman, 1970). The increase in the barrier of rotation about the amide C–N bond on oxidation of the thiocarbamate to its corresponding sulfoxide and sulfone is believed to be due to the increase in the contribution of the zwitterion structure VI.

Most of the carbamoyl sulfoxides do not give measurable molecular ions in their mass spectra. In each structure studied in the molecular ion, if observed at all, was much less than 0.1% of the base peak. In each case $P^{+}\cdot$–O was observed at abundances of about 0.1 to 0.6%. The fragmentation patterns are quite similar to those of the precursor thiocarbamates, i.e., the base peak is R'_2NCO^{+} (or occasionally R'^{+}), with major peaks at $R'NHCO^{+}$, R^{+}, R'^{+}, and, at lower abundance, RS^{+} and RSH^{+}.

One feature, unique to the sulfoxides, is the existence of peaks with masses corresponding to RSO^{+} or $RSOH^{+}\cdot$ in fair abundance (ca. 1 to 8%). Compound 2 is an exception to these rules; most of the fragments above the 1% level arise from the precursor ion, VII, presumably because of the additional stabilization arising from the ring system.

LITERATURE CITED

Bellamy, L. J., Williams, R. C., *J. Chem. Soc.*, 4294 (1957).
Casida, J. E., Gray, R. A., Tilles, H., *Science* **184** (4136), 373 (1974).
Gozzo, F., Massero, M., Santi, R., Galluzzi, G., Barton, D. H. R., *Chem. Ind. (London)*, 221 (1975).
Hallam, H. E., Ray, T. C., *J. Chem. Soc.*, 318 (1964).
Kimura, M., Aoki, M., Kurita, Y., *Bull. Chem. Soc. Jpn.* **27**, 163 (1954).
Mizushima, S., "Structure of Molecules and Internal Rotations", Academic Press, New York, N.Y., 1954.
Rauk, A., Allen, L. C., Mislow, K., *Angew. Chem., Int. Ed. Engl.* **9**, 400 (1970).
Rummens, F. H. A., Louman, F. J. A., *J. Agric. Food Chem.* **18**, 1161 (1970).
Senning, A., Sorensen, O. N., Jacobsen, C., *Angew. Chem., Int. Ed.* **7**, 734 (1968).
Tseng, C. K., Chan, J. H., Baker, D. R., Walker, F. H., *Tetrahedron Lett.*, 3053 (1971).

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Pyrethroid Photochemistry: Decamethrin

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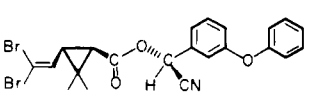
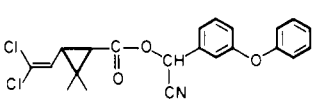
Photolysis of (*S*)-α-cyano-3-phenoxybenzyl *cis*-(1*R*,3*R*)-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate (decamethrin) in various solvents using ultraviolet radiation (λ >290 nm) results initially in cis–trans isomerization, ester cleavage reactions, and loss of bromine. Cis–trans isomerization is the major reaction of sunlight irradiation in the solid phase on glass or silica gel. An additional process for dilute solutions in methanol exposed to sunlight involves racemization at the α position in the alcohol moiety by both photochemical and ground-state reactions. Twenty-five photoproducts are identified from irradiation of decamethrin or its initial photolytic derivatives. The effects of quenchers, sensitizers, and solvent viscosity on the reaction rate and product distribution implicate processes in decamethrin photodecomposition that include both singlet and triplet excited states and sometimes "cage" type intermediates. Decamethrin undergoes photolysis more readily than two related pyrethroids, NRDC 149 and permethrin. The mixtures of decamethrin photoproducts from solution and solid-phase reactions are less toxic than decamethrin to mice treated intraperitoneally.

Decamethrin (1) (also known as Decis and NRDC 161) is the most potent insecticide currently known (Elliott et al., 1974a,b, 1975). The cis-1*R*,3*R* configuration about the cyclopropane ring and the *S* configuration for the cyano group at the benzylic carbon are essential features for this remarkable insecticidal activity (Elliott et al., 1974a,b, 1975; Owen, 1975). Related but less insecticidal compounds of interest are NRDC 149 (Elliott et al., 1975) and permethrin (Elliott et al., 1973).

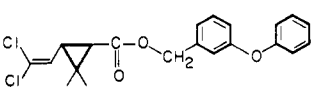
The available knowledge on pyrethroid photochemistry (Elliott and Janes, 1973; Holmstead et al., 1977) and



decamethrin (1)



NRDC 149



permethrin

toxicology is not sufficient to predict the photolytic fate of decamethrin and the persistence and biological activity of its photoproducts. The variety of functional groups in 1 poses challenging aspects in its photochemistry as re-

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