Fraction V was found to be composed of 2-pyridylmethyl phenylacetate and phenylacetic acid in a mole ratio of 3:1 by nmr.

Acidification of the basic aqueous washings of the original product mixture and extraction with methylene chloride gave phenylacetic acid contaminated with unreacted 2-picoline N-oxide. The yield of phenylacetic acid was 80.0 mmoles (100%).

(B). Quantitative Analysis. Subsequent procedures for quantitative analysis of the products of the reaction were similar to that just described except that a small aliquot of the anhydride solution was removed after refluxing in acetonitrile for a few minutes but before the N-oxide was added and analyzed for hydrolysis by nmr. Small amounts of hydrolysis did occur in some cases, and the yields reported are corrected for the hydrolysis as determined in this way. After gas evolution ceased, the solvent was distilled at reduced pressure, and the residue was dissolved in carbon disulfide and extracted with saturated sodium carbonate solution. The remaining carbon disulfide solution was dried and analyzed directly for benzaldehyde and the ester mixture by the glpc and nmr methods. Control experiments showed all of the 2-picoline N-oxide remained in the aqueous phase, and no more benzaldehyde or esters were extracted from the aqueous phase on washing with methylene chloride.

An alternative procedure was mixing the two reactants in a flask with a breakseal side arm. The system was degassed, sealed under vacuum, and heated at 70° for 10 hr. The gaseous product was measured on a calibrated vacuum line and identified by its infrared spectrum. The solution was then treated as above.

Trifluoroacetic anhydride reactions were carried out in methylene chloride solution in a closed system attached through a drying tube to a gas buret. The 2-picoline N-oxide (10.5 g, 0.10 mole) was dissolved in 75 ml of spectral grade methylene chloride, and the system equilibrated at 0° in an ice bath. The trifluoroacetic anhydride (25 g, 0.12 mole) was added slowly over 15 min. No gas evolution occured in 1 hr at 0°. The solution was allowed to warm to room temperature. Nmr analysis indicated an 80% yield of 2-pyridylmethyl trifluoroacetate. An aliquot of the product solution was extracted with cold 5% sodium bicarbonate and dried over calcium chloride. The nmr and infrared spectra of the resulting solution were nearly identical with those obtained from a methylene chloride solution of 2-pyridylcarbinol treated with trifluoroacetic anhydride and worked up in a similar manner.

The solvent was evaporated from the total product mixture, and the residue was warmed with 10% sodium hydroxide solution. The resulting red liquid was continuously extracted with methylene chloride for 12 hr. Crude 2-pyridylcarbinol (6.50 g, 60% yield) was obtained after solvent evaporation and was identified by spectral and glpc retention time comparison with an authentic sample. A picrate was obtained which had a melting point of 154–156° (undepressed when mixed with known material).

Trichloroacetic anhydride reactions were carried out in refluxing spectral quality chloroform as outlined above. The anhydride (15 g, 0.05 mole) was added to the refluxing solution of 2-picoline N-oxide (2.20 g, 0.020 mole) in 25 ml of solvent. Less than 10 cc of gas was evolved during the 1-hr reflux period, and direct nmr analysis indicated 74% 2-pyridylmethyl trichloroacetate formation. The spectra of an aliquot of this solution after washing with cold sodium bicarbonate solution were nearly identical with those of a solution obtained from 2-pyridylcarbinol which had been treated with trichloroacetic anhydride and worked up in a similar manner. The solvent was evaporated from the total product solution, and the residual dark oil was treated with 10% sodium hydroxide on a steam bath for 10 min. The 2-pyridylcarbinol was obtained and identified as outlined above (1.44 g, 65% yield).

Acknowledgment. Grateful acknowledgment is made to Professor D. F. Swinehart for making the mass spectral measurements and to C. Klopfenstein for the use of his computer program for MO calculations and also to Professors L. J. Dolby and W. T. Simpson for critical comments. This work was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society.

Mass Spectrometry in Structural and Stereochemical Problems. CXIV.[1] Electron Impact Induced Rearrangement of Thiocarbonates, Carbamates, and Thiocarbamates[2]

J. B. Thomson,[3a] Peter Brown,[3b] and Carl Djerassi

Contribution from the Department of Chemistry, Stanford University, Stanford, California. *Received April 25, 1966*

Abstract: The mass spectra of all possible methyl phenyl, and diphenyl mono-, di-, and trithiocarbonates and of a number of methyl- and phenyl-substituted carbamates and mono- and dithiocarbamates have been examined in order to compare the possible elimination of CS, COS, or CS_2 with the well-documented one of CO and CO_2. Rearrangement, with elimination of the central portion of the molecule, is insignificant in the case of the carbamates and thiocarbamates. In the case of the thiocarbonates, loss of CS or of CS_2 is negligible. Significant loss of COS requires the presence of the group $CSOCH_3$ while expulsion of CO_2 is important in the presence of the group $COOCH_3$. In C_6H_5XCOYR (X = O or S; Y = O or S; R = CH_3 or C_6H_5) CO_2 is lost when X = Y = O or when Y = O and R = CH_3; otherwise CO is eliminated. A preliminary rearrangement of the molecular ion of compounds with the group C_6H_5OCS, to C_6H_5SCO, is observed.

Electron impact induced rearrangements of species other than hydrogen may involve a 1,2-alkyl shift or elimination of a neutral molecule from a nonterminal site. Two examples of a 1,2-methyl migration have been reported[4] recently. Elimination of a neutral molecule, by fragmentation of the type $[A–B–C]^{\cdot+} \rightarrow [A–C]^{\cdot+} + B$ has been observed with a variety of structures: for example, elimination of carbon mon-

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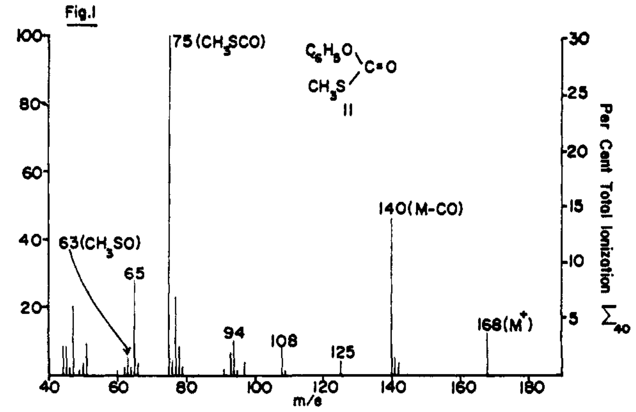
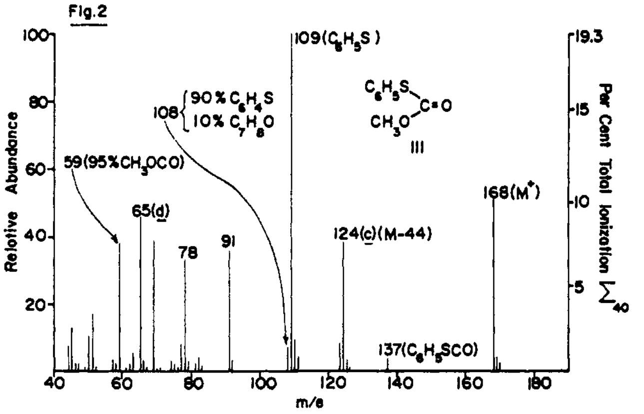
(1) Paper CXIII: D. Goldsmith and C. Djerassi, *J. Org. Chem.* (in press).

(2) Financial support from the National Institutes of Health (Grant No. AM-04257) is gratefully acknowledged.

(3) (a) Recipient of a NIH International Postdoctoral Fellowship while on leave from University College, Dublin; (b) Postdoctoral Fellow, 1964–1966.

(4) F. Komitsky, J. E. Gurst, and C. Djerassi, *J. Am. Chem. Soc.*, 87, 1398 (1965); C. Djerassi, A. M. Duffield, F. Komitsky, and L. Tökès, *ibid.*, **88**, 860 (1966).





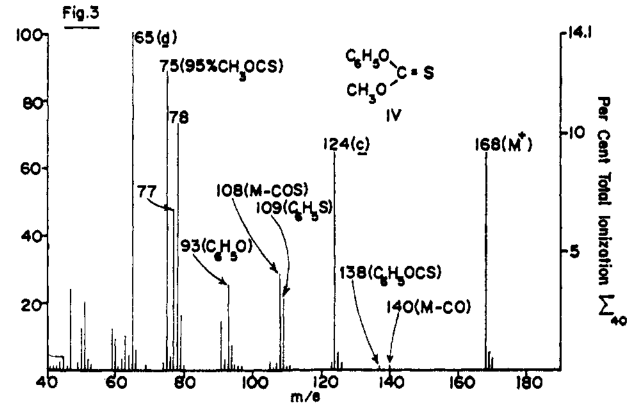


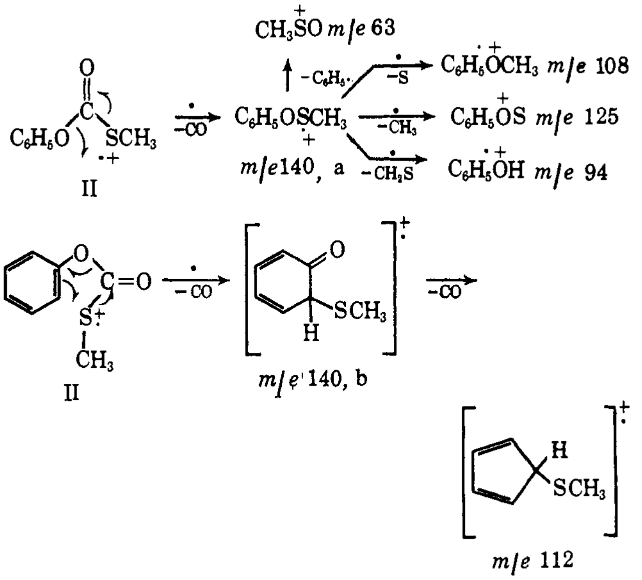
Figure 1. Mass spectrum of S-methyl phenyl thiocarbonate.
Figure 2. Mass spectrum of methyl S-phenyl thiocarbonate.
Figure 3. Mass spectrum of methyl phenyl thioncarbonate.

oxide from anthraquinone,[5] diphenyl ether,[5,6] ethyl acetoacetate,[7] and acetylacetone;[7] elimination of carbon dioxide from trimethylsilyl esters,[8] dimethyl acetylenedicarboxylate,[7] and some malonic esters;[7] elimination of phenyl isocyanate from N,N-diphenylphenylacetamide,[9] nitriles from arylsulfonylhydrazones,[10] and diimide from 1-benzenesulfonyl-2-benzoylhydrazone.[10] Recently, aryl migration has been shown to occur during fragmentation of 3-(β-hydroxy-β-phenylethyl)-2-iminothiazolidine and 6-phenyl-2,3,5,6-tetrahydroimidazo[2,1-*b*]thiazole.[11]

In our recent study[12] of the fragmentation processes following electron bombardment of organic carbonates, it was shown that loss of carbon dioxide is general in this series. In continuation of this work we have now examined the mass spectra of all possible methyl phenyl and diphenyl thiocarbonates and of a number of carbamates and thiocarbamates in order to determine whether other neutral molecules containing heteroatoms can also be eliminated. Such information is indispensible for eventual prediction of the occurrence of skeletal rearrangement peaks in mass spectrometry.

Results and Discussion

Methyl Phenyl Thiocarbonates. In contrast with methyl phenyl carbonate (I),[12] S-methyl phenyl thiocarbonate (II) suffers no loss of carbon dioxide (Table I). Instead, the rearrangement peak, at *m/e* 140 (Figure 1), corresponds to elimination of carbon monoxide. The formation of the M − CO fragment may be represented[13] as a three- or five-center process leading to the species a or b, respectively. The presence of the appropriate metastable ions shows that M − CO decomposes further with loss of sulfur (*m/e* 108), thioformaldehyde (*m/e* 94), and a methyl radical (*m/e* 125). These fragments can be envisaged as arising from either a or b, but the presence of the species CH_3S^+O (*m/e* 63), together with the absence of any significant peak at *m/e* 112 (for loss[14] of carbon monoxide from b), suggests that the three-center mechanism is mainly operative. From the observation[12] that ^{18}O-methyl phenyl carbonate loses only $C^{18}OO$, it might be expected that the S-methyl compound (II) would eliminate COS. However, no metastable ion could be



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(8) R. M. Teeter, "Tenth Annual Conference on Mass Spectrometry," ASTM Committee E-14, New Orleans, La., 1962, p 51.

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(10) A. Bhati, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc., Sect. C*, 358 (1966).

(11) B. R. Webster, *Chem. Commun.*, 124 (1966).

(12) P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, 88, 2469 (1966).

(13) The presence of a metastable ion for a process in a reaction scheme is indicated by the symbol * over the arrow. The compositions of all fragments discussed were substantiated by high-resolution measurements.

(14) *Cf.* H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1964, p 167.

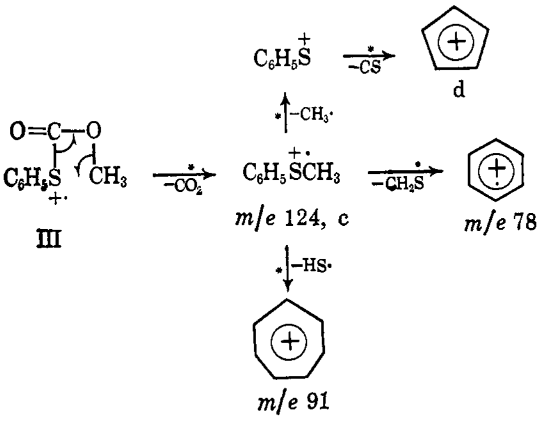
Table I. Important Peaks in the Spectra of Thiocarbonates

	Compound	% Σ_{40}^{M} M	M − CO	M − CS	M − CO_2	M − COS	M − CS_2	Base peak
I	PhOCOOMe	12.7	Absent[a]		11.8			21.1 (C_5H_5)
II	PhOCOSMe	3.6	13.8		Absent[a]	2.4[b]		30.1 (MeSCO)
III	PhSCOOMe	10.0	Absent[a]		7.4	0.15		19.3 (PhS)
IV	PhOCSOMe	9.0	0.14	Absent[a]	9.0	3.9[c]		14.1 (C_5H_5)
V	α-NphOCSOMe	15.8	Absent[a]	Absent[a]	2.7	4.2[c]		18.9 (C_9H_7)
VI	β-NphOCSOMe	16.8	Absent[a]	Absent[a]	2.9	4.6[c]		20.7 (C_9H_7)
VII	PhSCOSMe	6.0	14.0			1.1[b]		15.8 (PhS)
VIII	PhOCSSMe	0.5	4.8	Absent[a]		0.25	0.15	25.1 (MeSCS)
IX	PhSCSOMe	8.2	Absent[a]	Absent[a]		14.3[c]	Absent[a]	16.7 (MeOCS)
X	PhSCSSMe	9.0		0–0.7[d]			0.7	33.4 (MeSCS)
XI	PhOCOOPh	8.8	Absent[a]		8.3			20.8 (Ph)
XII	PhOCOSPh	2.1	10.0		<0.3	Absent[a]		31.5 (PhS)
XIII	PhOCSOPh	0.5	7.8	Absent[a]	<0.25	0.25		26.2 (Ph)
XIV	PhOCSSPh	0.2	6.7	Absent[a]		0.4	Absent[a]	27.5 (Ph)
XV	PhSCOSPh	1.7	12.0			0.8		28.1 (PhS)
XVI	PhSCSSPh	4.7		0.75			1.5	24.5 (Ph) (PhSCS)

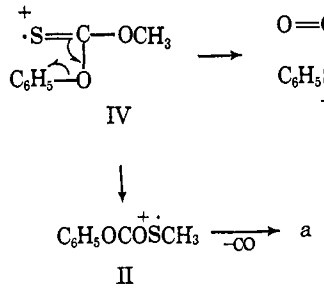
[a] ≪0.1% Σ_{40}^{M}. [b] Metastable ion for (M − CO) → (M − COS). [c] Metastable ion for M → (M − COS). [d] MS-9 direct, absent; CEC heated, 0.7.

detected for the formation of the M − 60 species (*m/e* 108) directly from the molecular ion (Table I). The base peak in the spectrum, at *m/e* 75, is due to the α-cleavage ion CH_3SCO^+.

The mass spectrum (Figure 2) of methyl S-phenyl thiocarbonate (III) is exactly analogous to that of the oxygen analog (I) except that the base peak now corresponds to $C_6H_5S^+$ rather than the $C_5H_5^+$ species (d) (reflecting the reluctance of $C_6H_5S^+$ to lose CS as compared with elimination of CO from $C_6H_5O^+$). Assuming that a four-center rearrangement mechanism is operative,[12] the M − 44 fragment (*m/e* 124) may be represented as the thioanisole molecular ion (c) and, indeed, the spectrum below this rearrangement peak is very similar to that[15] of thioanisole, with the exception of the α-cleavage species CH_3OCO^+ (*m/e* 59). The peak at *m/e* 108 (7% relative intensity) is shown by high resolution to consist of 90% C_6H_4S and 10% C_7H_8O (M − COS), but no metastable ion could be detected for the direct elimination of carbonyl sulfide from the molecular ion.



The major rearrangement peak in the spectrum (Figure 3) of methyl phenyl thioncarbonate (IV) is found at *m/e* 124 (M − 44) and is shown by high resolution to consist entirely of C_7H_8S (c). The presence of a metastable ion at *m/e* 91.5 ($124^2/168 = 91.5$) shows that carbon dioxide is eliminated in a one-step process and thus requires an initial rearrangement of the molecular ion of IV to that of III. All of the peaks of the spectrum of the thiolcarbonate (III) are present together with those from the unrearranged thioncarbonate (IV) molecular ion. A species of low abundance (1% relative intensity) at *m/e* 140 (a) shows that some rearrangement to the S-methyl thiolcarbonate (II) molecular ion has also taken place.



Chemical precedent for the formation of thiolcarbonates from thioncarbonates exists in the Schönberg rearrangement.[16] When heated[17a] for 0.5 to 3 hr at 250–300°, or when the vapor is passed through a Pyrex tube[17b] at *ca.* 400°, diaryl thioncarbonates rearrange to the corresponding thiolcarbonates in an intramolecular, four-center process.[17] Methyl phenyl thioncarbonate (IV) itself yields[18] the S-methyl compound (II) when heated for 8 hr at 180°. That the rearrangement taking place in the mass spectrometer is probably a true electron impact induced process was shown by heating the thioncarbonate (IV) for 35 min at 100° and then 1 min at 250° (conditions more vigorous, thermally, than in the spectrometer[19]) when the infrared

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(15) "Catalog of Mass Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., Spectrum No. 969.

(16) A. Schönberg and L. Vargha, *Chem. Ber.*, **63**, 178 (1930); A. Schönberg, L. Vargha, and W. Paul, *Ann.*, **483**, 107 (1930).

(17) (a) H. K. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Am. Chem. Soc.*, **77**, 2479 (1955); D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 70 (1956); (b) H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 410 (1966).

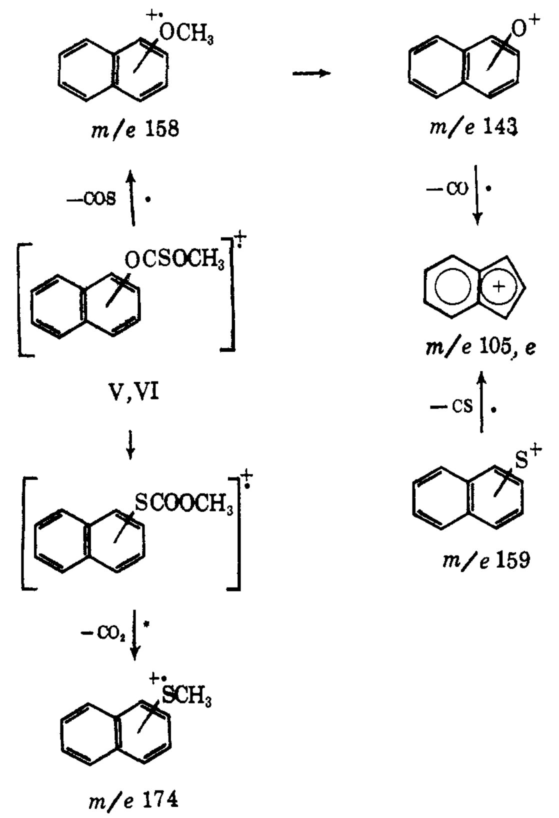
(18) G. Hilgetag and R. Philippson, *Monatsber. Deut. Akad. Wiss. Berlin*, **6**, 585 (1964); *Chem. Abstr.*, **62**, 5165*h* (1965).

(19) The mass spectra of the methyl phenyl compounds were determined using an Atlas CH-4 instrument. The reservoir temperature was 70°, the inlet temperature 150–60°, and the ion-source temperature 190°.

spectrum of the product was identical with that of the starting material (no C=O absorption). S-Methyl phenyl thiocarbonate (II) shows C=O absorption at 1736 cm^{-1} and methyl S-phenyl thiocarbonte (III) at 1742 cm^{-1}. The mass spectrum of methyl ^{18}O-phenyl carbonate[20] shows that all of the ^{18}O is retained in the M − 44 fragment (loss of CO_2), while the spectrum of S-methyl ^{18}O-phenyl thiocarbonate[20] shows complete retention of ^{18}O in the M − 28 (loss of CO) and M − 60 (loss of COS) fragments, demonstrating the absence of this type of molecular ion rearrangement in the absence of the C=S group.

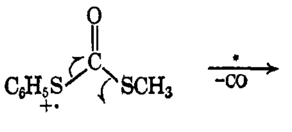
The spectrum of the thioncarbonate (IV) also shows a moderately intense peak at *m/e* 108 (M − 60) with an associated metastable ion for direct elimination of carbonyl sulfide from the molecular ion. The base peak occurs at *m/e* 65 (d) with metastable ions for its formation from both $C_6H_5O^+$ and $C_6H_5S^+$.

The same fragmentation pattern is observed in the spectra (Table I) of methyl α- (V) and β- (VI) naphthyl thioncarbonates, *viz.*, rearrangement of the molecular ion and expulsion of carbon dioxide as well as direct elimination of carbonyl sulfide. The base peak in both spectra, which are almost identical, is species e.

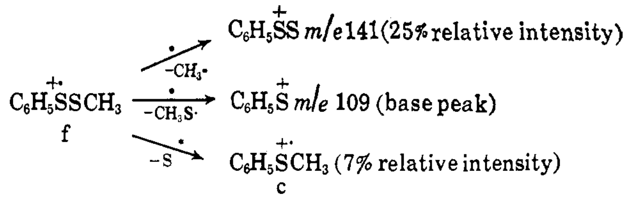


S-Methyl S-phenyl dithiocarbonate (VII) loses carbon monoxide to give an abundant (88% relative intensity) fragment (f, *m/e* 156) which suffers further loss (metastable ions observed) of $CH_3\cdot$, $CH_3S\cdot$, and sulfur. There is no observable metastable ion for direct elimination of carbonyl sulfide to give species c. The α-cleavage fragment, CH_3CO^+, is abundant (98% relative intensity).

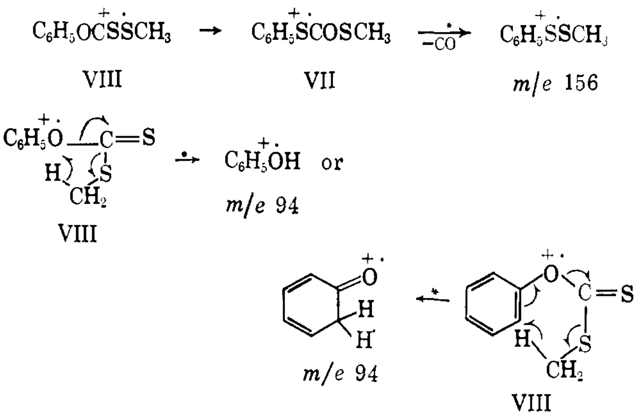
The only significant rearrangement peak (19% relative intensity) in the spectrum of S-methyl O-phenyl



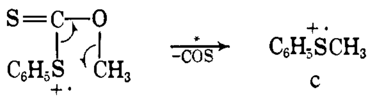
VII



dithiocarbonate (VIII) occurs at *m/e* 156 (M − CO), again indicating rearrangement of the thioncarbonate in the spectrometer. Species of mass 124 (M − COS) and 108 (M − CS_2) are of low abundance, and no metastable ions are observed for their formation from the molecular ion. The base peak at *m/e* 91 is due to the α-cleavage fragment CH_3SCS^+. A prominent peak (53% relative intensity) at *m/e* 94 is shown by high resolution to contain 90% $C_6H_6O^+$. The formation of this fragment may be envisaged as involving a five- or seven-center rearrangement of the molecular ion (a metastable ion is observed).



An abundant M − 60 fragment (loss of COS) is observed for the first time in this series (Table I) in the spectrum of O-methyl S-phenyl dithiocarbonate (IX). A four-center elimination pathway, leading to species c, is suggested by the appearance of the spectrum, below



IX

the rearrangement peak, which is very similar to that of thioanisole[15] except for the α-cleavage ion CH_3OCS^+ (*m/e* 75, base peak). There is no indication of elimination of carbon disulfide or of carbon monoxide (following migration of the methyl group to sulfur).

More than one-third of the total ion current in the spectrum of methyl phenyl trithiocarbonate (X) is carried by the species of mass 91 (95% CH_3SCS^+ and 5% $C_7H_7^+$). The rearrangement peak at *m/e* 124 (M − 76) is weak (2% relative intensity) but has associated with it a metastable ion at *m/e* 76.9 ($124^2/200 = 76.9$) for direct loss of carbon disulfide from the molecular ion. No certain electron impact induced

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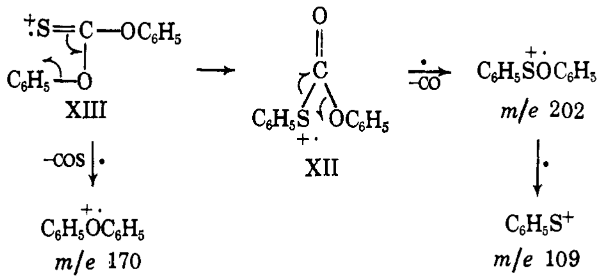
[20] Prepared from 10% enriched ^{18}O-phenol supplied by Yeda Research and Development Co. Ltd., Rehovoth, Israel.

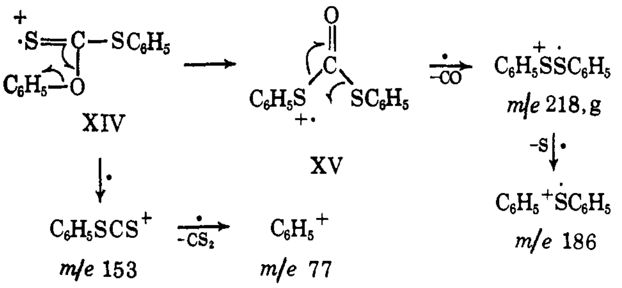
elimination of CS is observed; with a direct inlet system M − 44 is absent, but with a heated inlet system M − 44 carries 0.7% of the total ion current. Of the remaining fragments only $C_6H_5^+$ exceeds 15% relative intensity.

Diphenyl Thiocarbonates. Unlike diphenyl carbonate (XI),[12] phenyl S-phenyl thiocarbonate (XII) loses carbon dioxide to an insignificant extent (Table I) upon electron bombardment. The major rearrangement process, as in the case of the S-methyl analog (II), involves elimination of carbon monoxide. The only other significant peaks ae due to $C_6H_5S^+$ (base peak) and the α-cleavage fragment $C_6H_5SCO^+$ (29% relative intensity).

Diphenyl thioncarbonate (XIII), a compound that readily undergoes the Schönberg rearrangement,[16,17] loses carbon monoxide [*cf.* methyl phenyl thioncarbonate (IV), above] and, to a minor extent, carbon dioxide. The initial rearrangement, of XIII to XII, is probably an electron impact induced phenomenon as there is no appearance of carbonyl absorption in the infrared spectrum after heating the thioncarbonate (XIII) at 200° for several minutes.[21] Although elimination of carbon monoxide is represented here as a three-center process, there is no evidence to exclude the alternative five-center pathway [*cf.* S-methyl phenyl thiocarbonate (II)]. Electron bombardment of the S-phenyl compound XII does not result in a similar migration of the O-phenyl group to the carbonyl oxygen as the spectrum of ^{18}O-phenyl S-phenyl thiocarbonate[20] shows no loss of $C^{18}O$. The spectra of the thion- (XIII) and thiol- (XII) carbonates are very similar except that the thioncarbonate shows some loss of carbonyl sulfide (*m*/*e* 170, 1% relative intensity) and the base peak is now at *m*/*e* 77 ($C_6H_5^+$) as it is for diphenyl carbonate (XI).[12]



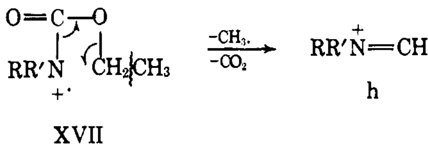
Phenyl S-phenyl dithiocarbonate (XIV) also shows a loss of carbon monoxide from the molecular ion. Formulation of the M − 28 species as the diphenyl disulfide molecular ion (g) then accounts for all the remaining peaks in the spectrum, with the exception of the α-cleavage fragments $C_6H_5SCS^+$ (*m*/*e* 153, 71% relative intensity) and $C_6H_5OCS^+$ (*m*/*e* 137, 9% relative intensity), although $C_6H_5^+$ now accounts for the base peak. A fragment of low abundance (2% relative intensity) at *m*/*e* 186 (M − 60) could be formed by loss of carbonyl sulfide from the molecular ion or by elimination of sulfur from M − CO (M − 32 is present in the spectrum of diphenyl disulfide[22]); metastable ions were not observed for either process.

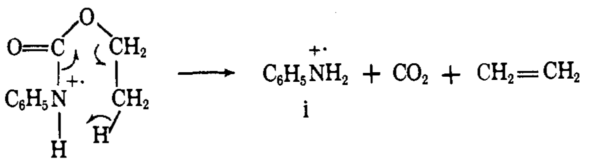


The spectrum of S,S-diphenyl dithiocarbonate (XV) itself shows the expected M − 28 species. Apart from the molecular ion and the α-cleavage fragment $C_6H_5SCO^+$, the spectra of diphenyl disulfide and the dithiocarbonate XV are identical. Again there are no observable metastable ions for elimination of sulfur from g or of carbonyl sulfide from XV.

The α-cleavage species $C_6H_5SCS^+$ and the ion $C_6H_5^+$, of equal abundance, together carry 49% of the total ion current in the mass spectrum of diphenyl trithiocarbonate (XVI). Rearrangement peaks are observed at *m*/*e* 218 (g, 2% relative intensity) and *m*/*e* 186 (M − CS_2, 6% relative intensity). Whether the latter is formed directly from the molecular ion or by elimination of sulfur from the M − CS species (g) is not known, as no metastable ions were observed.

Carbamates and Thiocarbamates. Electron bombardment of ethyl carbamates (XVII, R and R′ = H, alkyl, or aryl) has been shown[23] to result in loss of a methyl radical followed by elimination of carbon dioxide to yield the even-electron species (h). In the mass spectrum of ethyl phenylcarbamate[23] (XVII, R = C_6H_5; R′ = H) the molecular ion is abundant (70–80% relative intensity) and the base peak is due to the McLafferty rearrangement species (i). In contrast, methyl phenylcarbamate (XVIII) gives a minute molecuar ion and no rearrangement peaks (Table II). The spectrum is very similar to that of phenyl isocyanate and, as no metastable ions are observed for the formation of fragments directly from the molecular ion, it is probable that a considerable amount of thermal dissociation takes place. Similarly, the spectra of phenyl phenylcarbamate (XIX) and phenyl methylcarbamate (XX) are essentially those of mixtures of phenol and the appropriate isocyanate with no rearrangement peaks.





The α-cleavage fragments j (base peak) and k (88% relative intensity) dominate the spectrum (Table II) of phenyl N-methyl-N-phenylcarbamate (XXI). The only other abundant species is the molecular ion (57% relative intensity), and no rearrangement peaks are observed. Phenyl N,N-diphenylcarbamate (XXII) frag-

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[21] The mass spectrum was obtained using an AEI MS-9 instrument, ion-source temperature 200°, with a direct insertion probe.

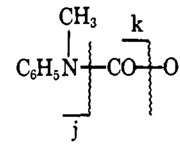
[22] (a) J. O. Madsen, C. Nolde, S.-O. Lawesson, G. Schroll, J. H. Bowie, and D. H. Williams, *Tetrahedron Letters*, 4377 (1965). (b) The mass spectra of diphenyl disulfide and the dithiocarbonates XIV and XV were recorded under the same conditions.

[23] C. P. Lewis, *Anal. Chem.*, **36**, 176, 1582 (1964).

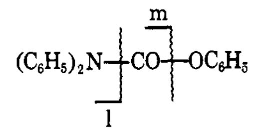
Table II. Important Peaks in the Spectra of Carbamates and Thiocarbamates

		% $\Sigma_{M_{40}}$							
	Compound	M	M − CO	M − CS	M − CO_2	M − COS	M − CS_2	M − HNCO or M − HNCS	Base peak
XVIII	PhNHCOOMe	<0.1	Absent		Absent			Absent	34.0 (PhNCO)
XIX	PhNHCOOPh	1.7	Absent		Absent			Absent	34.2 (C_6H_6O)
XX	PhOCONHMe	<0.1	Absent		Absent			Absent	30.9 (C_6H_6O)
XXI	PhNMeCOOPh	13.8	Absent		Absent			Absent	24.0 (PhNMe)
XXII	$Ph_2NCOOPh$	5.8	Absent		Absent			Absent	17.6 (Ph_2N)
XXIII	PhNHCOSMe	6.4	0.3			Absent		0.3	27.1 (PhNCO)
XXIV	PhSCONHMe	4.5	Absent			Absent		0.5	47.0 (C_6H_6S)
XXV	$PhSCONMe_2$	6.0	Absent			Absent		M − MeNCO <0.1	68.5 (Me_2NCO)
XXVI	$Ph_2NCOSPh$	7.0	0.2			Absent		Absent	16.3 (Ph_2NCO)
XXVII	PhNHCSOMe	1.0		Absent		0.25		Absent	28.6 (PhNCS)
XXVIII	PhNHCSSMe	0.8		Absent			Absent	Absent	26.8 (PhNCS)
XXIX	PhSCSNHMe	0.4		Absent			Absent	0.2	23.0 (C_6H_6S)

ments in an analogous manner, with species l providing the base peak and being accompanied by a strong (81% relative intensity) l − H peak. The second α-cleavage fragment m (90% relative intensity) and the molecular ion (33% relative intensity) are again prominent.

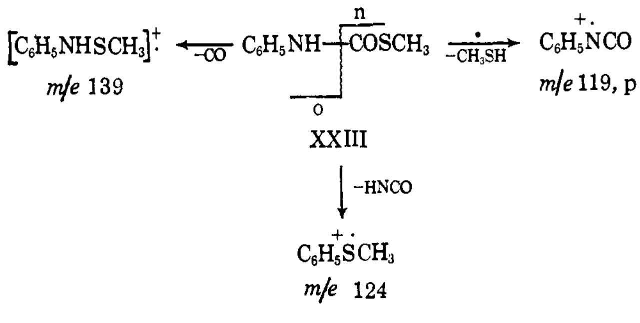


XXI

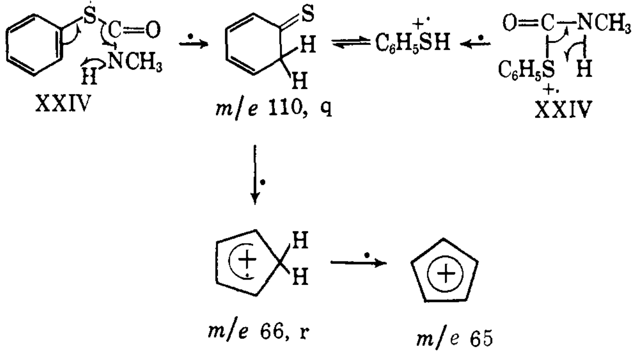


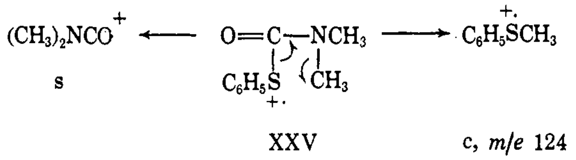
XXII

The mass spectrum of S-methyl phenylthiocarbamate (XXIII) is essentially that of phenyl isocyanate but there is a strong metastable ion for the formation of species p from the molecular ion. Two weak rearrangement peaks are observed at *m/e* 139 (M − CO, 1% relative intensity) and *m/e* 124 (M − HNCO, 1% relative intensity). α-Cleavage, to give species n (9% relative intensity) and o (15% relative intensity), is relatively unimportant.

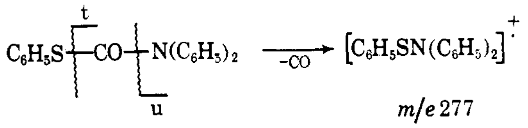


S-Phenyl methylthiocarbamate (XXIV) gives a weak (1% relative intensity) rearrangement peak at *m/e* 124 (M − HNCO). The spectrum is dominated by the species $C_6H_6S\cdot^+$ (q, *m/e* 110) which carries 47% of the total ion current. The formation of this species from the molecular ion (a metastable ion is observed at *m/e* 72.5; $110^2/167 = 72.5$) may be envisaged as involving either a four- or six-center pathway. Only two other peaks in the spectrum exceed 10% relative intensity, *viz.*, *m/e* 109 ($C_6H_5S^+$) and *m/e* 66 (r). In view of the abundance of the hydrogen-transfer fragment (q) it was of interest to examine the spectrum of S-phenyl N,N-dimethylcarbamate (XXV). In accord with expectation, the rearrangement peak at *m/e* 124 (M − CH_3NCO) in XXV is extremely weak (*ca.* 0.1% relative intensity). The base peak (*m/e* 72) corresponds to the α-cleavage fragment s which carries almost 70% of the total ion current. Of the remaining peaks in the spectrum only that at *m/e* 109 ($C_6H_5S^+$) and the molecular ion exceed 5% relative intensity.



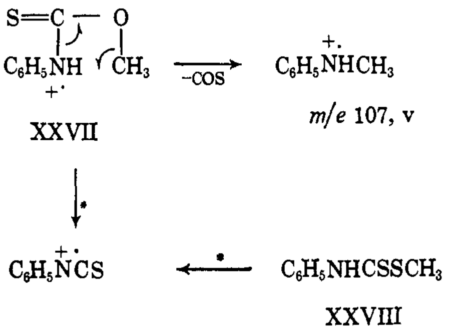


S-Phenyl N,N-diphenylthiocarbamate (XXVI) fragments in the same way as its oxygen analog (XXII) with the α-cleavage ions t (base peak) and u (54% relative intensity) and the molecular ion (42% relative intensity) providing the prominent peaks in the mass spectrum. A weak (1% relative intensity) rearrangement peak occurs at *m/e* 277 (M − CO).



XXVI

The spectrum of methyl phenylthioncarbamate (XXVII) is essentially that of phenyl isothiocyanate, with the addition of a weak (3% relative intensity) molecular ion and a weak (1% relative intensity) rearrangement peak at *m/e* 107 (v). Methyl phenyldithiocarbamate (XXVIII) fragments in the same way but no rearrangement peak is apparent. Phenyl methyldithiocarbamate (XXIX) shows the same behavior as its oxygen analog (XX) with $C_6H_6S\cdot^+$ (*m/e* 110) and CH_3N^+CS (*m/e* 73) abundant. A weak (1% relative intensity) rearrangement peak is observed at *m/e* 124 (M − HNCS).



In summary, the important conclusion can be drawn from the present study that substitution of one heteroatom by another, in otherwise identical substances, can profoundly modify the fragmentation pattern. This conclusion constitutes an important limitation to the *a priori* prediction of fragmentation modes as well as to the application of the "element mapping" technique[24] in such compounds.

Experimental Section

Low-resolution spectra were obtained, for liquid samples, by Dr. A. M. Duffield using an Atlas CH-4 mass spectrometer (ionizing voltage 70 ev, trap current 10 μa, reservoir temperature 70°, inlet temperature 150–160°, ion-source temperature 190°) and, for solid samples, by Mr. R. G. Ross using an AEI MS-9 instrument with direct insertion probe (ionizing voltage 70 ev, ion-source temperature 200°). High-resolution measurements were made with the MS-9 instrument (apparent resolution 1 part in 15,000).

Thiocarbonates. The thiocarbonates were prepared by reaction of the appropriate acid chloride with methanol or phenol in pyridine[12,25] or with a suspension of the sodium salt of methyl mercaptan, thiophenol, or naphthol in benzene.[26] The following compounds have not been described previously: methyl S-phenyl thiocarbonate (III), bp 86–88° (1.5 mm); methyl α-naphthyl thioncarbonate (V), mp 52–53° (hexane); methyl β-naphthyl thioncarbonate (VI), mp 50–51° (hexane); S-methyl phenyl dithiocarbonate (VIII), bp 108–109° (1.5 mm).

Carbamates and Thiocarbamates. Compounds XVIII and XXIX were prepared by the classical method[27] of shaking the anhydrous methanol, or thiophenol, with phenyl isocyanate, or methyl isothiocyanate, at room temperature. Compounds XXVII and XXVIII were prepared by shaking phenyl isothiocyanate with methanol or methyl mercaptan in 30% aqueous sodium hydroxide, followed by acidification of the solution.[28] Compound XXIII was obtained by rearrangement of the thioncarbamate XXVII in the presence of methyl iodide.[29] The remaining compounds were obtained by treatment of the appropriate amine with phenyl chloroformate or S-phenyl thiochloroformate.

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Diazotetracyanocyclopentadiene[1]

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Wilmington, Delaware 19898. Received May 31, 1966

Abstract: In aqueous acid, hexacyanobutenediide cyclizes to 1-amino-2,3,4,5,5-pentacyanocyclopentadiene. Nucleophiles cause this labile compound to lose a cyano group giving aminotetracyanocyclopentadienide. This ion is readily converted to diazotetracyanocyclopentadiene by nitrous acid. The chemistry of diazotetracyanocyclopentadiene parallels that of aromatic diazonium compounds. Pentacyanocyclopentadienide, tetracyanocyclopentadienide, and chloro-, bromo-, iodo-, mercapto-, nitro-, phenyl-, *p*-hydroxyphenyl-, carboxy-, azido-, and azotetracyanocyclopentadienide resulted from substitution reactions. Coupling reactions gave 4-(dimethylamino)-phenyl- and 1-(2-hydroxynaphthyl)azotetracyanocyclopentadienide, while addition reactions produced triphenylphosphonium, sulfonato-, and cyanoazotetracyanocyclopentadienide.

As part of a broad study of polycyano compounds,[2] undertaken to determine the effect of a multitude of cyano groups on the chemical and physical properties of organic structures, we have synthesized diazotetracyanocyclopentadiene[3] (DTCC, **4**), a stable, light yellow solid which decomposes at about 200°. Its structure is supported by elemental analysis, infrared and ultraviolet spectral data, and its chemical properties. The stabilizing power of the four cyano groups coupled with that of the 6 π electron, cyclopentadienide system are likely the major factors in determining which resonance form (**4**), the diazonium or the diazo, will contribute

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(1) Part of this work has been published as a Communication to the Editor: O. W. Webster, *J. Am. Chem. Soc.*, **87**, 1820 (1965).

(2) For a review of cyanocarbon chemistry, see T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961); B. C. McKusick and T. L. Cairns, "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1965, p 625.

(3) Other reported diazocyclopentadienes are the parent compound: W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953); tetrabromo-, 2-nitro-, 3-nitro- 2,5-diiodomercuri-, 2,5-diiodo-, and 2-tricyanovinyldiazocyclopentadiene: D. J. Cram and R. D. Partos, *ibid.*, **85**, 1273 (1963); 2,3,4-triphenyl- and 2,3,5-triphenyldiazocyclopentadiene: P. L. Paulson and B. J. Williams, *J. Chem. Soc.*, 4153 (1961).