strated by smaller relative standard deviations of 1.9 to 10.1% for ethylene analysis, compared to 7.9 to 33.0% for dimethylethephon determination. The steady increase of ethephon concentration in treated tomatoes confirms earlier observations (Hurter, 1975). It is unusual for pesticides, in general, but represents the systemic transport of this growth regulator from leaves into fruit (Yamaguchi, 1971). The incorporation into fruit tissue explains the fact that residues of this highly water-soluble growth regulator are not washed off by rainfall. The maximum residue of 6.8 ppm appears to be surprisingly high at an applied concentration of 0.2% of ETHREL. Reducing the active ingredient to 0.15 and 0.10% diminished these figures to 5.3 and 3.4 ppm, respectively. However, the biological response declined markedly as the fruits only colored slightly.

The characteristic increase of ethephon residues was found also in apples and cherries within 2 and 8 days after application. Maximum residues were found to be 1.2 ppm in apples and 4.1 ppm in cherries. The corresponding flame photometric determination yielded 2.0 and 4.3 ppm.

It is concluded that the analytical procedure proposed is a satisfactory method for determining ethephon. It allows to avoid time-consuming lyophilization of crop material and methylation of the phosphonic acid. Esterification in the presence of fruit extracts, using diazomethane proposed by Schlenk and Gellerman (1960), converted only 38–65% of the growth regulator into dimethylethephon. As methylation in general, the success of this procedure may depend on the solvent system. Further experiments to investigate this point have not been conducted.

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# Trifluoroacetylation of Pesticides and Metabolites Containing a Sulfoxide Moiety for Quantitation by Gas Chromatography and Chemical Confirmatory Purposes

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The Pummerer reaction was evaluated as a means of derivatizing pesticides and their metabolites, which contain a S→O moiety for analysis by gas chromatography. Dasanit, dasanit oxon, and the sulfoxides of Mesurol, Nemacur, and aldicarb all readily reacted with trifluoroacetic anhydride at RT/15 min to give trifluoroacetoxymethyl sulfide analogues. For compounds possessing an NH moiety, more vigorous reaction conditions were required in order to form the di-trifluoroacetyl derivative as a single product in high yield. Oxydemeton-methyl, oxycarboxin, Counter, and phorate sulfoxides also reacted with trifluoroacetic anhydride, but gave anomalous products. The secondary trifluoracetoxy moiety of oxydemeton-methyl thermally decomposed on-column to give *cis*- and *trans*-dehydrooxydemeton-methyl. Oxycarboxin underwent both an additive and transannular Pummerer reaction, depending on the reaction conditions, while phorate and Counter sulfoxides were transformed to their respective oxons.

Pesticides containing a sulfide group readily undergo oxidation to their sulfoxide and sulfone analogues. These metabolites normally exhibit some pesticidal activity and must therefore be considered in any residue analysis study. Generally, sulfoxides do not gas chromatograph (GC) well due to their polar nature and are analyzed by conversion to their sulfones.

Perfluoroacylation, which is frequently employed to enhance the thermal stability of carbamate insecticides (Khalifa and Mumma, 1972; Seiber, 1972; Wong and Fisher, 1975), has been used to quantitate Mesurol and its metabolites (Greenhalgh et al., 1976). Reaction with trifluoroacetic anhydride (TFAA) has revealed that the Mesurol sulfoxide forms a di-trifluoroacetyl (TFA) de-

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rivative due to reaction with both the carbamate and sulfoxide moieties. The latter reaction involves rearrangement of the acylated sulfoxide to an $\alpha$-acyloxymethyl sulfide and is an example of the Pummerer reaction (Pummerer, 1910; Kise and Oae, 1970). Variations of the basic Pummerer reaction have been demonstrated for the phenol of Mesurol sulfoxide (Greenhalgh et al., 1976) and oxycarboxin (King et al., 1977). Regardless of structural differences of the resultant sulfoxide TFA derivatives, they have all shown good GC characteristics. Hence it appears that the Pummerer reaction may prove useful for both quantitative and qualitative purposes.

This work explores the general applicability of the derivatizing pesticides containing a sulfoxide moiety with TFAA. The reaction was applied to dasanit, dasanit oxon, oxydemeton-methyl, and the sulfoxides of aldicarb, carboxin, Counter, Nemacur, and phorate. The products of the various reactions were characterized spectroscopically and their analysis by GC demonstrated.

## EXPERIMENTAL SECTION

**Chemicals.** TFAA was purchased from Aldrich Chemicals Co., Milwaukee, Wis. and used without further purification. Dasanit, dasanit oxon, oxydemeton-methyl, Mesurol, and Nemacur sulfoxides were provided by Chemagro Corp., Kansas City, Mo.; Counter, phorate, and phorate oxon were supplied by American Cyanamid, Princeton, New Jersey; carboxin was obtained from Uniroyal Chemicals, Naugatuck, Conn.

The sulfoxides of carboxin, Counter, and aldicarb were prepared by oxidation of the parent compound with $H_2O_2$–acetone at 4 °C overnight. The products were purified using high-pressure liquid chromatography (HPLC) and the purity checked by thin-layer chromatograph (TLC) and nuclear magnetic resonance (NMR).

**Gas Chromatography.** A Pye gas chromatograph Model 104 was fitted with a Pye alkali flame ionization detector (Rb C1) for phosphorus and a Perkin-Elmer NPD detector for nitrogen compounds. A general purpose, 1 m × 4 mm i.d. glass column packed with 100–120 mesh Chromosorb W coated with 3% OV-17 was employed for analysis. The column flow (nitrogen) was 50 mL/min; air and hydrogen flows to the detectors were selected for optimum response.

**Derivatization.** Ethyl acetate solution (2 mL) of the insecticide (10 $\mu$g/mL) was placed in a 15-mL Teflon-lined screw-cap centrifuge tube together with 0.2 mL of TFAA. The tube was sealed, kept at 30 °C/15 min, then cooled, opened, and excess reagent blown off with a stream of dry nitrogen at room temperature. The solution volume was adjusted to 10 mL with ethyl acetate and analyzed by GC. Derivatization was also carried out at elevated temperatures (100 °C) for various periods of time and prepared for analysis using the above procedure.

**Instrumentation.** IR spectra were determined as films or Nujol mulls using a Beckman IR-20A spectrophotometer. NMR spectra were obtained in $CDCl_3$ solution with $(CH_3)_4Si$ as the internal standard on a Varian T-60 spectrometer. Pertinent chemical shifts of the starting compounds and their derivatives are presented in Table I. The mass spectra (MS) were determined with a Finnigan 3000 GC/MS coupled to a D 6000 data aquisition system.

## RESULTS AND DISCUSSIONS

The sulfoxides most commonly encountered as pesticides or metabolites are alkyl/alkyl or alkyl/aryl substituted. The type of substitution is significant in that it determines the nature of the products from the Pummerer reaction (Horner and Kaiser, 1959). The *S*-acyloxy group

Table I. $^1$H Chemical Shift of Methyl, Methylene, and Methine Protons Adjacent to S=O Moiety of Insecticides and Metabolites and in the TFA Derivations

| Compound | No. | τ value | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $CH_3S(O)$- | $-OCH_2S$- | $-CH_2S(O)$- | -OCHS- | $-CH_2S$- | $CH_3C$- | $-OCH_2C$- |
| Dasanit | Ia | 7.24 | | | | | | |
| Dasanit TFA | IIa | | 4.41 | | | | | |
| Dasanit HFBA | | | 4.49 | | | | | |
| Dasanit Oxon | Ib | 7.22 | | | | | | |
| Dasanit Oxon TFA | IIb | | 4.38 | | | | | |
| Mesurol SO | Ic | 7.04 | | | | | | |
| Mesurol SO mono-TFA | IIc | | 4.50 | | | | | |
| Mesurol SO di-TFA | IId | | 4.52 | | | | | |
| Nemacur SO | Ie | 7.36 | | | | | | |
| Nemacur SO mono-TFA | IIe | | 4.43 | | | | | |
| Nemacur SO di-TFA | IIf | | 4.46 | | | | | |
| Aldicarb SO | Ig | 7.20 | | | | | | |
| Aldicarb SO mono-TFA | IIg | | 4.60 | | | | | |
| Aldicarb SO di-TFA | IIh | | 4.58 | | | | | |
| Oxydemeton-methyl | III | | | 6.74 | | | | |
| Oxydemeton-methyl TFA | V | | | | 3.72 | | | |
| Oxycarboxin | IX | | | 6.92, 7.08 | | | 7.95 | |
| Oxycarboxin di-TFA | X | | | | | 6.93, 7.02 | 8.10 | |
| Oxycarboxin di-TFA | XI | | | | | 6.74, 7.42 | | 4.62 |
| Phorate SO | | | | 5.92 | | | | |
| Counter SO | | | | 5.84 | | | | |

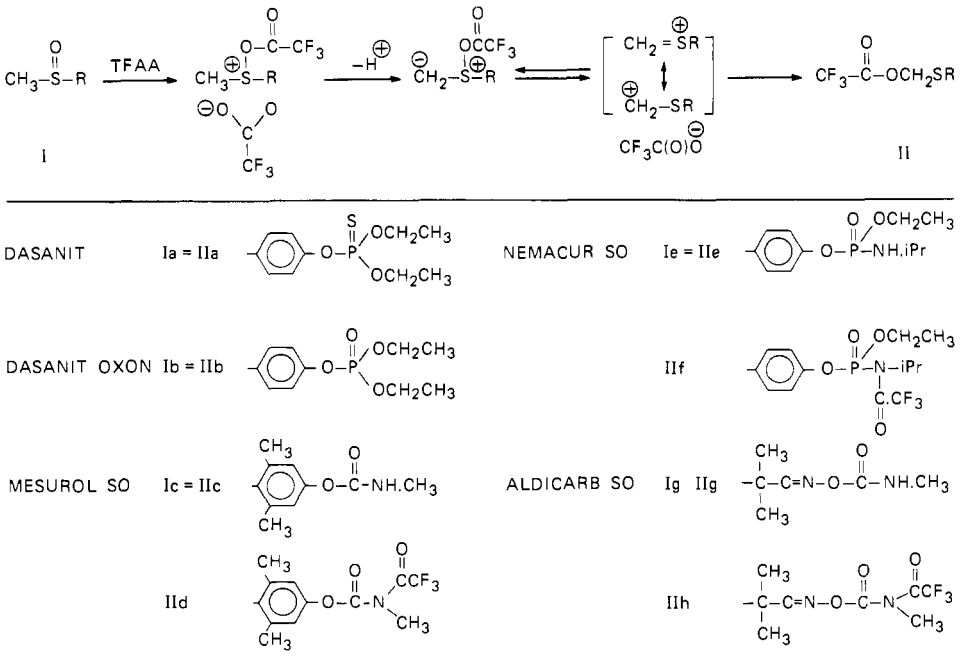


**Figure 1.** Mechanism for the trifluoroacetylation of the methyl/aryl sulfoxide moiety in some insecticides and their metabolites.

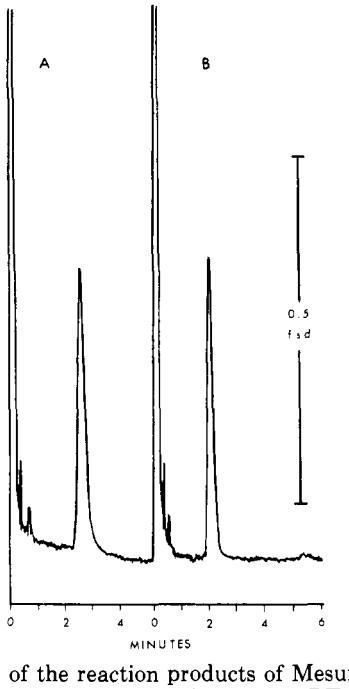


**Figure 2.** GC of the reaction products of Mesurol sulfoxide/TFAA with different reaction conditions: (A) RT/15 min, 10 ng of MSO; (B) 100 °C/30 min, 10 ng of MSO.

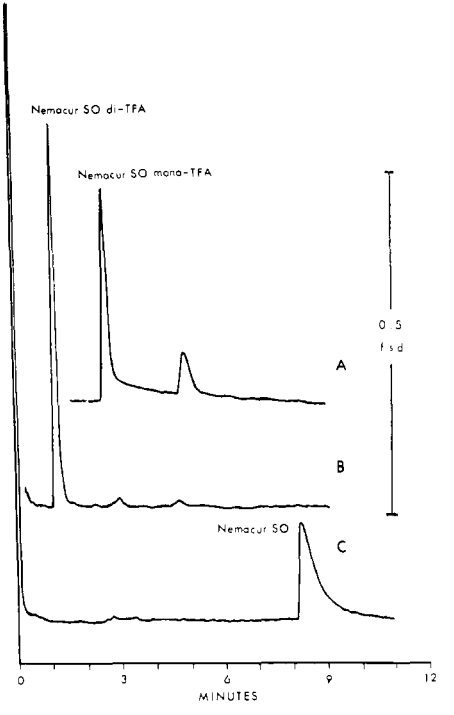


**Figure 3.** GC of the reaction products of Nemacur sulfoxide/TFAA with different reaction conditions: (A) RT/15 min; (B) 100 °C/60 min; (C) standard.

normally migrates to the least-substituted carbon atom (Johnson and Phillips, 1969).

Dasanit (Ia) possesses a methyl/phenyl sulfoxide moiety and reacted with TFAA at RT/15 min to give the trifluoroacetoxy methyl sulfide derivative (IIa) as the only product (yield 91%). The reaction followed the general scheme shown in Figure 1. The derivative was characterized mainly by its proton NMR spectrum, which was similar to that of Ia except the 3 H singlet of the $CH_3S$ protons had been replaced by a 2 H singlet of the $OCH_2S$ protons (Table I). Its MS indicated a parent ion $m/e$ 404 corresponding to a mono-TFA derivative and the presence of a $CF_3C(O)O$ group was confirmed by the carbonyl absorption at 1785 $cm^{-1}$ in the IR. Dasanit also reacted with heptafluorobutyric anhydride; the derivative showed the characteristic NMR signal for the methylenic protons at $\tau$ 4.47. Although the latter reaction went to completion at RT, it was noticeably slower than with TFAA. The reaction of dasanit oxon (Ib) with TFAA was faster than for dasanit, presumably due to the increased acidity of the thiomethyl protons caused by the greater electron negativity of the P=O bond. The product (IIb) was also characterized by NMR (Table I), and its structure confirmed by IR (1792 $cm^{-1}$) and MS (parent ion $m/e$ 388).

Both Mesurol sulfoxide (Ic) and Nemacur sulfoxide (Ie) possess methyl/phenyl substituted moieties, but their reaction with TFAA is complicated by the presence of a NH group in the molecules. At RT/15 min Mesurol sulfoxide gave predominantly a mono-TFA derivative (IIe), but at 100/30 min the di-TFA derivative (IId) was pre-

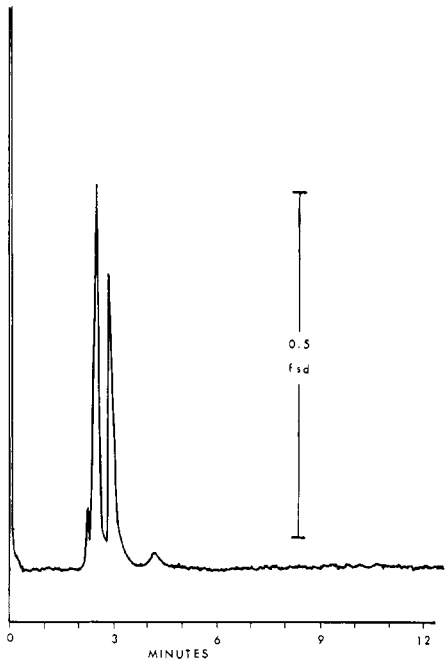


**Figure 4.** GC of the reaction products of oxydemeton-methyl/TFAA.

dominantly formed. In addition to the expected changes of the *S*-methyl protons in the NMR spectrum, the $N(CH_3)$ doublet, $\tau$ 7.12 in Mesurol sulfoxide was shifted down field to $\tau$ 7.02 in IIe. Both the mono-TFA and di-TFA derivatives are formed in high yields under the respective reaction conditions (Figure 2).

Nemacur sulfoxide (Ie) gave predominantly a mono-TFA derivative (IIe) at RT, the yield decreasing for reaction times greater than 30 min. In order to obtain a single product it was necessary to carry out the trifluoroacetylation at 100 °C/60 min and form the di-TFA derivative (IIf). The latter compound absorbed in the IR at 1790 and 1725 $cm^{-1}$, due to the $CF_3C(O)O$ and $NC(O)CF_3$ groups, respectively. The 6 H doublet of the $NCH(CH_3)_2$ protons was little affected by trifluoroacetylation of the NH, resulting in absorption at $\tau$ 8.84 and 8.80, respectively, for Ie and IIf. The necessity of derivatizing both the sulfoxide and carbamate moieties in order to obtain a single product is shown in Figure 3.

Aldicarb sulfoxide (Ig) reacted like a normal dialkyl substituted sulfoxide at room temperature to give a mono-derivative (IIg). With more vigorous conditions, 100 °C/15 min, the di-TFA derivative (IIh) was the only product. In the NMR spectrum of Ig, the $CCH_3$ protons are nonequivalent and appear as a doublet $\tau$ 8.84 ($J$ = 8 Hz), due to the proximity of the asymmetrical S→O. In both IIg and IIh, these protons are singlets, $\tau$ 8.42 and 8.34, respectively. The $NCH_3$ protons are also doublets at $\tau$ 7.10 and 7.06 ($J$ = 6 Hz) in aldicarb sulfoxide (Ig) and its mono-TFA derivative (IIg) but a singlet $\tau$ 6.6 in the di-TFA (IIh).

Oxydemeton-methyl, phorate, and Counter sulfoxides all possess dialkyl substituted sulfoxide moieties. They reacted readily with TFAA to give derivatives which underwent further rearrangement.

A time study of the trifluoroacetylation of oxydemeton-methyl (III) in ethyl acetate at RT was followed by GC, it showed that the yield of products increased from 41 to 85% during the period 15 and 60 min. The same product was also formed at 100 °C/15 min, and the results were more reproducible. The NMR spectrum of this product (V) showed the methylenic protons as an ABX system and the ratio of the integral for the $CH_3CH_2S$ triplet and the $CH_3OP$ doublet as 1:2.1. This indicates that the migration of the trifluoroacetoxy moiety is specific to the carbon $\beta$ to phosphorus. This can be rationalized by considering the electron-withdrawing effect of the P=O, which will make the methylenic protons of the $\alpha$ and $\beta$ carbon atoms more acidic than those of the *S*-ethyl group. Further evidence that only one trifluoroacetoxy derivative was formed came from the reaction of the TFA derivative with methanol. This product (VI) showed only one extra peak in the NMR $\tau$ 6.52 (singlet, 3 H) as a result of replacement of the secondary TFA group with a methoxyl moiety.

A GC of the TFA derivative of oxydemeton-methyl, however, showed two main peaks, with retention times ($t_R$) of 2.25 and 2.5 min (Figure 4). The ratio of these two peaks remained constant regardless of the reaction conditions, suggesting that they resulted from on-column thermal rearrangement. A GC–MS of these two peaks showed the same parent ion $m/e$ 228 and base ion $m/e$ 45 with strong ions at $m/e$ 118, 79, 103, 109, 58, 47, and 142, but with different intensities. Both spectra had an ion $m/e$ 199 ($M^+$ − 29), attributed to the loss of the $SCH_2CH_3$ moiety. These compounds are undoubtedly the cis and trans isomers of dehydrooxydemeton-methyl. The GC–MS of the small peak, $t_R$ 2.16 min (Figure 4), had a base ion $m/e$ 60 and a parent ion $m/e$ 168. This is consistent with the structure $(CH_3O)_2P(O)SCH{=}CH_2$ resulting from thermal elimination of $S(O)CH_2CH_3$ from the starting material (10). The mechanism shown in Figure 5 is suggested for the reaction of this insecticide with TFAA.

The reactions of phorate and Counter sulfoxides with TFAA were equally intriguing. In ethyl acetate, phorate sulfoxide reacted with TFAA instantaneously, affording a single product by GC analysis (yield 91%). The NMR

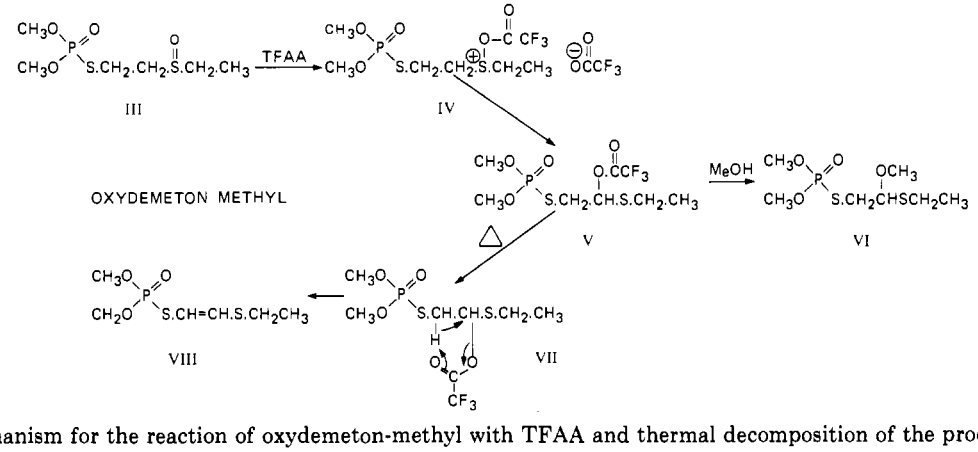


**Figure 5.** Mechanism for the reaction of oxydemeton-methyl with TFAA and thermal decomposition of the product.

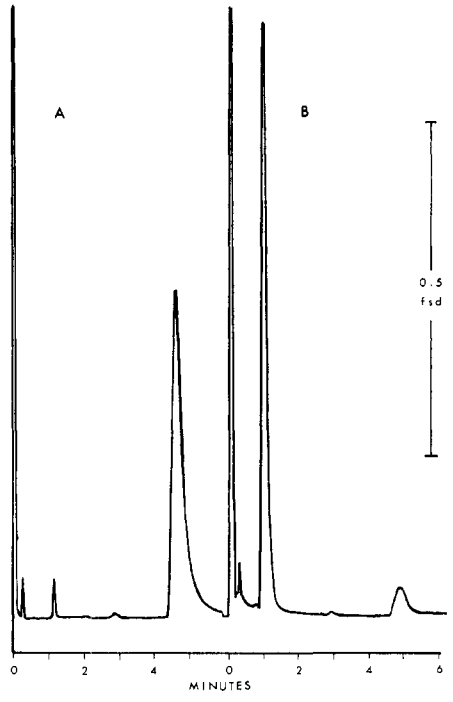


**Figure 6.** GC of phorate sulfoxide before (A) and after (B) treatment with TFAA, RT/15 min.

spectrum of this product showed no peaks in the region $\tau$ 3.5–5.5, which implied that the normal Pummerer reaction had not taken place. The nonequivalence of the $SCH_2CH_3$ protons due to an asymmetrical S→O moiety in the reactant sulfoxide (IX) was absent in the NMR spectrum, also the coupling constant $J_{PSCH_2}$ had decreased from 18 to 12 Hz. These facts are consistent with cleavage of the S→O bond and oxidation of the P=S to P=O, which together with a parent ion $m/e$ 244 for the product, suggest it to be the phorate oxon. This assignment was confirmed by comparison of the NMR and MS of an authentic sample of phorate oxon. A possible mechanism for this reaction could involve initial trifluoroacetylation of the negatively charged sulfur of the P=S with simultaneous bond formation between the negatively charged oxygen of the sulfoxide moiety and the positively charged phosphorus to create a cyclic five-membered $sp^3d^2$ intermediate. This reaction would be facilitated by the stereochemistry of phorate sulfoxide. Cleavage of the S→O bond is initiated by attack of the $CF_3C(O)O^-$ ion, resulting in the formation of TFAA and free sulfur. Numata and Oae (1976) previously postulated a five-member ring intermediate involving attack of the sulfoxide oxygen on positive carbon of a carbonyl group. A GC of phorate sulfoxide before and after treatment with TFAA is shown in Figure 6.

Counter sulfoxide also gave an oxon with TFAA. Identification of the product was made by its IR spectrum, which showed absorption at 1220 $cm^{-1}$ attributed to the P=O bond, a parent ion $m/e$ 272 in the MS and a coupling constant $J_{PSCH_2}$ = 8 Hz as compared with 16 Hz for counter sulfoxide in the NMR. The best reaction conditions for trifluoroacetylation of Counter were RT/15 min. More vigorous conditions resulted in the formation of a number of products as shown in Figure 7.

Trifluoroacetylation of oxycarboxin (IX) at RT proceeded via an additive Pummerer intermediate (X) involving substitution across the double bond. This compound slowly rearranged to a second di-TFA derivative (XI). The latter derivative is also formed when the reaction is carried out at 100 °C/45 min; unfortunately,

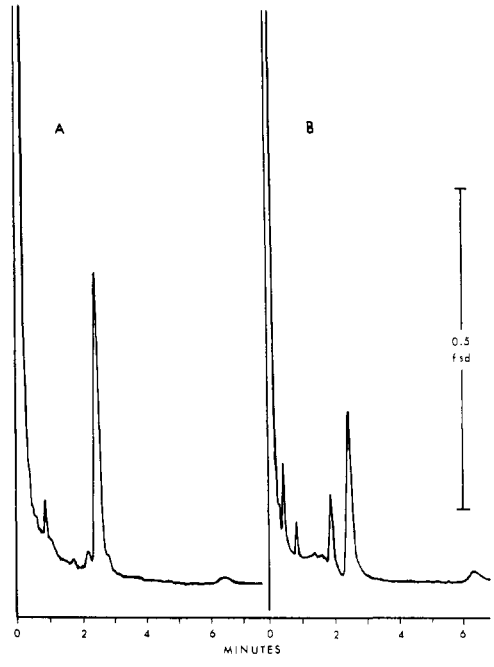


**Figure 7.** GC of the reaction products from Counter sulfoxide at different reaction conditions: (A) RT/15 min; (B) 100 °C/15 min.

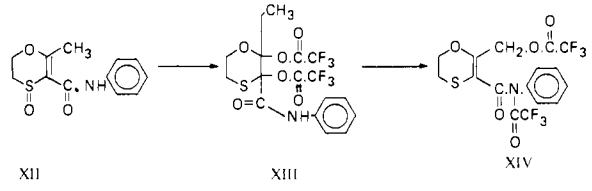


**Figure 8.** Mechanism for the trifluoroacetylation of oxycarboxin.

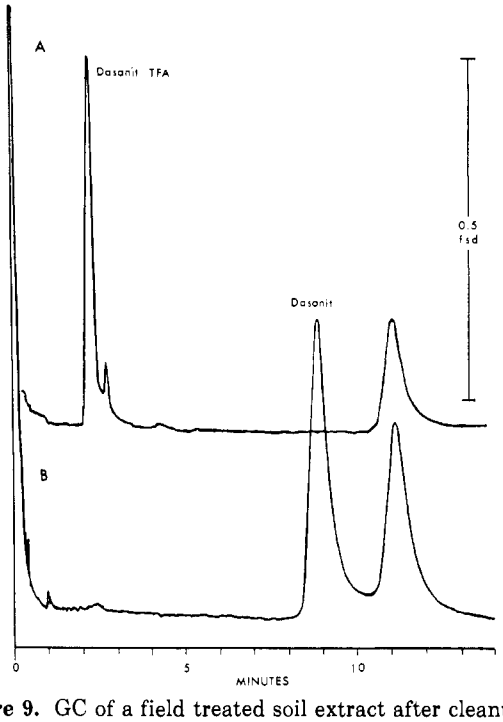


**Figure 9.** GC of a field treated soil extract after cleanup and after derivatization of the extract: (A) soil extract (1.1 ppm Dasanit); (B) above extract derivatized with TFAA; RT/15 min in ethyl acetate.

various side reactions occurred. The structures are shown in Figure 8.

For a derivatization reaction to be useful, it should be easy to carry out, rapid, and give a single product in high

yield with improved GC characteristics. By this criteria, the reaction of TFAA with compounds containing a sulfoxide group appears to offer some real advantages for both GC quantitation and confirmatory tests, together with increased sensitivity to electron-capture detection.

As this study shows, most pesticides with a sulfoxide moiety react readily with TFAA under mild conditions (RT/15 min) to give a product, the nature of which is dependent on the type of substitution. Regardless of the ease of the Pummerer reaction, the presence of an NH group in the same molecule necessitated forcing conditions (100 °C) to form the di-TFA derivative in order to obtain a single product. Although phorate and Counter sulfoxide do not undergo the normal Pummerer reaction with TFAA, the reaction is both rapid and complete, thus providing a good confirmatory test. This also holds for the reaction of oxydemeton-methyl, which forms two dehydro products due to thermal decomposition.

The last figure (Figure 9) illustrates an application of the Pummerer reaction for the chemical confirmation of dasanit residues in soil. Analysis of a sandy loam soil extract after clean-up showed the presence of the insecticide ($t_R$ 9 min) at a level of 1.1 ppm. Treatment of the extract with TFAA (RT/15 min) gave the TFA derivative with a $t_R$ of 2.31 min (Dasanit TFA standard $t_R$, 2.34 min). The impurity present in the extract was not affected by TFAA and its retention time remained the same at 11.1 min.

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# Gas Chromatographic Determination of Organophosphorus Pesticides by In-Block Methylation

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Microgram quantities of selected organophosphate, phosphorothioate, and phosphorodithioate pesticides were mixed with methanolic solutions of trimethylanilinium hydroxide (TMAH) and injected into a gas chromatograph equipped with a phosphorus-sensitive flame photometric detector. The efficiency of the reaction of TMAH with the various pesticides was determined by measurement of the quantity of trialkyl phosphates formed. The efficiency of the in-block reaction in 0.01 M TMAH varied from 61% for phoxim to 100% for azinphosmethyl. The rate of reaction of the pesticides with TMAH at ambient temperatures was also determined. Under these conditions the rate varied from 0% per day for malathion to 75% per day for chlorphoxim. The derivitization technique is useful for the identification and quantitation of many organophosphorus pesticides.

Brochmann-Hanssen and Oke (1969) developed a method for determination of barbituates, phenolic alkaloids, and xanthene bases based on the methylation of these materials with trimethylanilinium hydroxide (TMAH) in the block of a gas chromatograph. Prior to this, tetramethylammonium hydroxide (TAH) was used in a similar manner for determination of carboxylic acids by Robb and Westbrook (1963), for barbituates by Stevenson (1966), and for purine and pyrimidine bases by McGee (1966). It was concluded that TMAH was superior to TAH as a methylating agent when used in this manner. The first use of TMAH for analysis of a pesticide was reported by Dale et al. (1976), who used the technique for analysis of residues of chlorphoxim. They found that TMAH in methanol solution reacted slowly with chlorphoxim at room temperature to form diethyl methyl thiophosphate (DEMTP) but reacted instantaneously when injected into the block of a gas chromatograph at 280 °C. The efficiency of the in-block reaction varied from 40% in 0.0005 M TMAH to 74% in 0.1 M TMAH. The purpose of the present work was to explore the use of TMAH as a derivitizing reagent for other pesticides.

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EXPERIMENTAL SECTION

**Apparatus.** Gas chromatograph, Micro-Tek MT-220, equipped with a Melpar flame photometric detector with interference filter for spectral isolation of phosphorus emission at 526 nm. Chromatographic columns: 6 ft × 0.25 in. o.d. aluminum packed with 5% OV-225 on 100–120 mesh Chromosorb W (HP) and 6 ft × 0.25 in. o.d. aluminum packed with 3% OV-275 on 100–120 mesh Chromosorb W (HP). Inlet and outlet blocks were maintained at 280 °C, detector 280 °C; nitrogen carrier gas 145 mL/min at 70 psi; hydrogen 50 mL/min at 20 psi; and