# Chemical Ionization Mass Spectrometry. XIII. Reactions of Methylthiomethyl Acetate and Methylthiomethyl Propionate in Isobutane

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**Abstract:** The chemical ionization spectra of methylthiomethyl acetate and methylthiomethyl propionate have been determined at several temperatures using isobutane as reactant. The major ions observed (relative intensity greater than 10% of total ionization) are the protonated molecule ions, the ion produced by a displacement of the carboxylic acid by $C_4H_9^+$, protonated dimethylthioether ion, and methylthiomethyl ion. Rate constants, activation energies, and frequency factors are given for the production of the latter ion from the two esters. The methylthiomethyl cation is formed in chemical ionization much more readily than is methoxymethyl cation. It thus appears that the relative stabilizing effects of $CH_3S$ and $CH_3O$ on a charge center are different in gas phase and in solution.

In an earlier paper[1] we described the chemical ionization mass spectra of methoxymethyl formate and methoxymethyl acetate using both methane and isobutane as the reactant gases. When isobutane was used, that is, when the acidic plasma in the ionization chamber was composed almost totally of *tert*-butyl cations,[2] we observed reactions which were initiated by the attack of *tert*-butyl cation on the oxygen in the alkyl portion of the substrate. This results in the formation of the $(M + 57)^+$ ion, **1**, where M is the molecular weight. That work allowed the elucidation

$$\underset{\textbf{1}}{R-\overset{\overset{\textstyle O}{\|}}{C}-O-CH_2-\overset{\overset{\textstyle \textit{tert}\text{-Bu}}{|}}{\underset{+}{O}}-CH_3}$$

of a similar reaction which had been observed, but not understood at the time, for substituted benzyl acetates.[2a,3] In that case the phenyl ring of the benzyl group was acting as the nucleophilic center with which the *tert*-butyl cation became complexed. We now report on the reactions of methylthiomethyl acetate (**2a**) and methylthiomethyl propionate (**2b**) which

$$R-\overset{\overset{\textstyle O}{\|}}{C}-O-CH_2-S-CH_3$$
**2a**, R = Me
**b**, R = Et

provide a third type of compound in which there is a nucleophilic center (sulfur) in the alkyl portion of the ester.
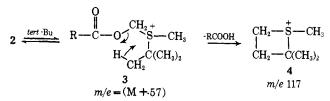
## Results and Discussion

Chemical ionization mass spectra of **2a** and **2b** at several source temperatures using isobutane as the reactant are shown in Tables I and II. There are some striking differences in the behavior of these com-

pounds when they are compared with their oxygen analogs. However, we shall consider first the similarities.

It is evident straightway that the reaction elucidated previously,[1] which is the displacement of carboxylic acid by *tert*-butyl cation and which is initiated by the formation of the $(M + 57)^+$ ion, is occurring for the sulfur compounds as well. One sees for each compound the $(M + 57)^+$ ion, **3**, at *m/e* 177 for **2a** and *m/e* 191 for **2b** and an $(M + 57 - RCOOH)^+$ ion, **4**, of high intensity at *m/e* 117. The pathway, the analog of which was elucidated for the oxygen compounds by the use of a deuterium tracer, is shown in Scheme I.

**Scheme I**

$$\textbf{2} \underset{}{\overset{\textit{tert}\cdot Bu}{\rightleftharpoons}} \quad \underset{\substack{\textbf{3}\\ m/e=(M+\cdot 57)}}{R-\overset{\overset{\textstyle O}{\|}}{C}-O\underset{H}{\overset{CH_2}{\diagup}}\overset{+}{\underset{\underset{CH_2}{|}}{\underset{C(CH_3)_2}{S}}}-CH_3} \quad \xrightarrow{-RCOOH} \quad \underset{\substack{\textbf{4}\\ m/e\ 117}}{\overset{CH_2-\overset{+}{S}-CH_3}{\underset{CH_2-C(CH_3)_2}{|\qquad\quad|}}}$$

There are several other reactions which are common to methoxymethyl acetate or formate and **2a** and **2b**. None of these result in ions of major intensity, and they will be described only briefly. The chemical ionization of **2a** gives an ion at *m/e* 181 and **2b**, at *m/e* 195. These ions result from the formation of a protonated dimer $(2M + 1)^+$ and the subsequent loss of the carboxylic acid. The protonated dimers appear in the spectrum of each compound but in very low abundances and thus are not tabulated. Compounds **2a** and **2b**, like their oxygen analogs, give $(M + 39)^+$ ions which are the result of association with $C_3H_3^+$ (probably cyclopropenium) which is present as about 3% of the total ionization of isobutane under the conditions of the experiments.

An ion of *m/e* 61 of major intensity is observed in the spectra of both the acetate and propionate esters **2a** and **2b**. In the acetate ester the *m/e* 61 ion could logically be expected to be either $CH_3SCH_2^+$ or $CH_3COOH_2^+$, but for the propionate ester the possibility that the ion is $CH_3COOH_2^+$ is remote. We thus assert

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**Table I.** Chemical Ionization Mass Spectra of Methylthiomethyl Acetate and Isobutane Reactant[a]

| m/e | Ion | Rel intensity at t = 67° | 94° | 138° |
|---|---|---|---|---|
| 61 | $^+CH_2SCH_3$ | 0.112 | 0.216 | 0.420 |
| 62 | $^{13}C$ isotope | | 0.006 | 0.011 |
| 63 | $CH_3S^+HCH_3$ | 0.176 | 0.214 | 0.214 |
| 65 | $^{34}S$ isotope | 0.007 | 0.009 | 0.009 |
| 117 | $CH_2-S^+CH_3$ $\quad\vert\qquad\vert$ $CH_2-C(CH_3)_2$ | 0.192 | 0.171 | 0.128 |
| 118 | $^{13}C$ isotope | 0.015 | 0.013 | 0.010 |
| 119 | ? | 0.076 | 0.059 | 0.032 |
| 120 | $^+CH_3COOCH_2SCH_3$ | 0.044 | 0.042 | 0.034 |
| 121 | $^+HCH_3COOCH_2SCH_3$ | 0.192 | 0.148 | 0.081 |
| 122 | $^{13}C$ isotope | 0.013 | 0.009 | 0.006 |
| 123 | $^{34}S$ isotope | 0.028 | 0.018 | 0.011 |
| 159 | $(C_3H_3)^+CH_3COOCH_2SCH_3$ | 0.015 | 0.012 | 0.009 |
| 177 | $CH_3COOCH_2S^+(C_4H_9)CH_3$ | 0.061 | 0.037 | 0.015 |
| 181 | $CH_3COOCH_2S^+(CH_2SCH_3)CH_3$ | 0.031 | 0.027 | 0.016 |
| | Others of rel intensity less than 0.010 | 0.038 | 0.019 | 0.004 |

[a] $P_{i\text{-}C_4H_{10}} = 0.70$ Torr; $P_{AcOCH_2SCH_3} \approx 5 \times 10^{-5}$ Torr; M = 120.

**Table II.** Chemical Ionization Mass Spectra of Methylthiomethyl Propionate and Isobutane Reactant[a]

| m/e | Ion | Rel intensity at t = 68° | 99° | 134° |
|---|---|---|---|---|
| 61 | $^+CH_2SCH_3$ | 0.181 | 0.344 | 0.462 |
| 62 | $^{13}C$ isotope | | 0.012 | 0.015 |
| 63 | $CH_3S^+HCH_3$ | 0.149 | 0.186 | 0.171 |
| 65 | $^{34}S$ isotope | 0.007 | 0.008 | |
| 75 | $EtCOOH_2^+$ | | 0.010 | 0.014 |
| 109 | ? | 0.008 | 0.014 | 0.020 |
| 117 | $CH_2-S^+CH_3$ $\quad\vert\qquad\vert$ $CH_2-C(CH_3)_2$ | 0.152 | 0.115 | 0.092 |
| 118 | $^{13}C$ isotope | 0.012 | 0.011 | 0.009 |
| 119 | ? | 0.061 | 0.041 | 0.020 |
| 134 | $EtCOOCH_2SCH_3^+$ | 0.050 | 0.035 | 0.027 |
| 135 | $^+HEtCOOCH_2SCH_3$ | 0.221 | 0.113 | 0.060 |
| 136 | $^{13}C$ isotope | 0.021 | 0.011 | 0.006 |
| 137 | $^{34}S$ isotope | 0.016 | 0.008 | |
| 173 | $(C_3H_3)^+EtCOOCH_2SCH_3$ | 0.019 | 0.013 | 0.009 |
| 191 | $EtCOOCH_2S^+(C_4H_9)CH_3$ | 0.055 | 0.032 | 0.016 |
| 195 | $EtCOOCH_2S^+(CH_2SCH_3)CH_3$ | 0.020 | 0.013 | 0.010 |
| 273 | ? | | 0.026 | 0.059 |
| | Others of rel intensity less than 0.010 | 0.018 | 0.008 | 0.010 |

[a] $P_{i\text{-}C_4H_{10}} = 0.70$ Torr; $P_{EtCOOCH_2SCH_3} \approx 5 \times 10^{-5}$ Torr; M = 134.

that for the propionate ester m/e 61 is $CH_3SCH_2^+$. In addition the propionate ester produces $C_2H_5$-$COOH_2^+$, m/e 75, but only in a small amount. We think that the acetate ester will produce $CH_3COOH_2^+$ also only in a small amount, and thus we further assert that in the acetate ester m/e 61 is predominantly $CH_3$-$SCH_2^+$. The ion is probably formed by cleavage of the protonated esters **5a** (acetate ester) and **5b** (propionate

$$2 \xrightarrow{\textit{tert}\text{-Bu}} H^+RCOOCH_2\text{—}S\text{—}CH_3 \xrightarrow{-RCOOH} {}^+CH_2\text{—}S\text{—}CH_3$$
$$\qquad\qquad\qquad\quad \mathbf{5} \qquad\qquad\qquad\qquad\qquad \mathbf{6}$$
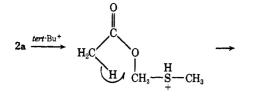
ester). Protonated methoxymethyl esters do not suffer cleavage to methoxymethyl cation in isobutane reactant. However, methoxymethyl cations are generated when the methoxymethyl esters are investigated using the more energetic reactant gas methane.[1] We shall return to the discussion of this process shortly.

Chemical ionization of methylthiomethyl acetate and methylthiomethyl propionate results in several ions which do not appear in the chemical ionization mass spectra of their oxygen analogs. Thus, **2a** and **2b** each yield 3–5% of an $M^+$ ion, which we presume to

be formed by an electron transfer reaction to one (or more) of the components of the $i$-$C_4H_{10}$ plasma. These reactions may be expected to occur more extensively with sulfur compounds than with their oxygen analogs because the ionization potentials of the sulfur compounds are significantly lower.

An ion of major intensity in the chemical ionization mass spectra of these sulfur-containing compounds which does not appear for their oxygen analogs is an ion at m/e 63. The ion is present in much higher abundance than can be accounted for by the $^{34}S$ isotope of methylthiomethyl cation. The ion at m/e 63 contains one sulfur atom since the $^{34}S$ isotope of the appropriate abundance appears at m/e 65. This ion is certainly protonated dimethyl sulfide, which could arise by initial protonation on sulfur followed by fragmentation with loss of the elements of an $\alpha$-lactone.

We illustrate using **2a**. There may be some precedent for this route in the chemical ionization of $p$-nitrobenzyl acetate.[3] Isobutane reactant causes most substituted benzyl acetates to yield the corresponding benzyl cations. However, $p$-nitrobenzyl acetate gives

no p-nitrobenzyl cation but does give an ion with $m/e$ consistent with protonated p-nitrotoluene. A reasonable route for the production of this ion involves the separation of the elements of an α-lactone from the protonated substrate.

The differences in abundance of various ions in the spectra of 2a and 2b are small and depend on a combination of subtle factors. Since the general outlines of chemical ionization of organic molecules are only beginning to emerge we think it not useful to discuss these differences.

Returning now to the reaction which produces methylthiomethyl cation, there is a formal similarity between this reaction and the $A_{AL}1$ mechanism by which these compounds might suffer hydrolysis in aqueous acid. This similarity was noted previously for methoxymethyl esters,[1] for indeed, hydrolysis of the methoxymethyl esters does proceed by this mechanism.[4] Thus, it was not surprising to observe the ion, 6, since we have observed its oxygen counterpart in the chemical ionization of methoxymethyl esters. However, different conditions are needed for the production of the two ions, and the nature of the difference is important and requires discussion.

As may be seen from Tables I and II the intensities of the $^+CH_2SCH_3$ ions increase with increasing temperature at the expense of other ions in the spectra. Using calculational techniques described previously[1,2a] rate constants for the production of 6 were obtained. Arrhenius plots of the rate constants are given in Figure 1, and the kinetic constants obtained from these plots are given in Table III. The activation energies

**Table III.** Kinetic Parameters for Formation of $^+CH_3SCH_2$

| Compound | $E_a$, kcal mol$^{-1}$ | $A$, sec$^{-1}$ | $k_{300}$,$^a$ sec$^{-1}$ |
|---|---|---|---|
| CH$_3$COOCH$_2$SCH$_3$ | 7.6 | 2.5 × 10$^9$ | 8.1 × 10$^3$ |
| EtCOOCH$_2$SCH$_3$ | 7.5 | 3.7 × 10$^9$ | 12.3 × 10$^3$ |

$^a$ Rate constant at 300°K.

for the two reactions are equal to within experimental error, and we are inclined to look upon the $A$ factors and $k_{300}$ values for the two compounds as also being essentially equal. This behavior is quite as one would expect.

However, when we compare the production of CH$_3$-SCH$_2^+$ ions from 2 with the production of CH$_3$OCH$_2^+$ ions from methoxymethyl acetate and methoxymethyl formate[1] the behavior is not readily understood. The spectra given in Tables I and II and the kinetic parameters in Table III were obtained using $i$-C$_4$H$_{10}$ as

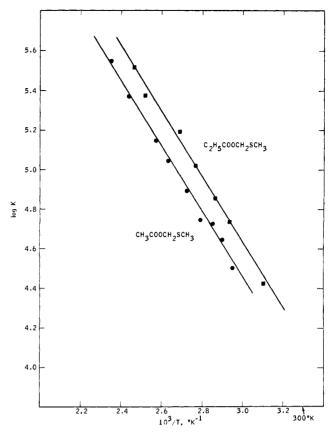(4) P. Salomaa, *Acta Chem. Scand.*, 11, 132 (1957); 14, 586 (1960).

Figure 1. Arrhenius plots for CH$_3$COOCH$_2$SCH$_3$H$^+$ → CH$_3$S-CH$_2^+$ + CH$_3$COOH and C$_2$H$_5$COOCH$_2$SCH$_3$H$^+$ → CH$_3$SCH$_2^+$ + C$_2$H$_5$COOH.

reactant gas, but by contrast we were not able to produce CH$_3$OCH$_2^+$ from the methoxy esters using $i$-C$_4$H$_{10}$ even by heating to 250°. It was necessary to use CH$_4$ as reactant, which constitutes a much stronger acidic reagent than $i$-C$_4$H$_{10}$. We also obtained the spectrum of methylthiomethyl acetate with CH$_4$ as reactant at the lowest temperature available with the mass spectrometer (33°). Very extensive decomposition to produce CH$_3$SCH$_2^+$ ion occurred, and, indeed, the intensity of the H$^+$CH$_3$COOCH$_2$SCH$_3$ ion was too small to calculate a reliable rate constant for the decomposition reaction. From the experiments with CH$_4$ we conclude that both CH$_3$OCH$_2^+$ and CH$_3$-SCH$_2^+$ can be formed if a strong enough gaseous acid is used, and from the experiments with $i$-C$_4$H$_{10}$ we conclude that CH$_3$SCH$_2^+$ is formed much more readily than CH$_3$OCH$_2^+$, although we cannot make a quantitative comparison. We can point out that a decomposition with a rate constant of about 10$^3$ sec$^{-1}$ can be detected, and with $i$-C$_4$H$_{10}$ reactant the rate constant for the formation of CH$_3$SCH$_2^+$ is 8.1 × 10$^3$ sec$^{-1}$ at 27°, but for the formation of CH$_3$OCH$_2^+$ the rate constant must be less than 10$^3$ sec$^{-1}$ at 250°. Thus it appears that the difference in the tendencies to form the two kinds of ions is appreciable.

We undertake to compare these relative rates with the relative rates of solvolysis reactions involving ions stabilized by CH$_3$O and CH$_3$S, and we also compare the relative energies of these ions in the gas phase. Rate data are not available for the hydrolysis of methylthiomethyl acetate and propionate, but it can be predicted that they should suffer hydrolysis at a much

slower rate than the methoxymethyl esters. For example, in aqueous dioxane, ethyl chloromethyl ether solvolyzes some 1600 times faster than ethyl chloromethyl sulfide.[5] It is certain that the solvolysis of $\alpha$-chloroethers proceeds via the methoxymethyl cation.[6] In the acid-catalyzed aqueous hydrolysis of 2-aryl,1,3-oxathiolanes the substrate, after protonation, could undergo ring opening to give a cation stabilized by adjacent oxygen or adjacent sulfur. Evidence[7] points to C–S bond cleavage leading to an oxygen-stabilized cationic intermediate.

The values of $\sigma_P^+$ given by Stock and Brown[8] for $CH_3O$ and $CH_3S$ are $-0.778$ and $-0.604$, respectively, which also shows that in condensed phase the methoxy group is more effective in stabilizing a positive charge than the methylthio group.

The evidence concerning the gas-phase behavior is somewhat conflicting. Taft, Martin, and Lampe[9] have investigated the stabilizing effects of different X groups on the relative energies of gaseous $CH_2X^+$ ions by measuring the appearance potentials for the reactions

$$CH_3X + e \longrightarrow CH_2X^+ + H + 2e$$

for a series of X groups. They find that $A(CH_3OCH_2^+)$ = 11.4 eV and $A(CH_3SCH_2^+)$ = 11.2 eV, which corresponds to a 5 kcal/mol greater stabilizing effect of $CH_3S$ as compared with $CH_3O$. On the other hand, Hobrock and Kiser[10] report a value of 11.8 eV for $A(CH_3SCH_2^+)$ from $CH_3SCH_3$, which is higher than $A(CH_3OCH_2^+)$. The most recent results are those of Harrison and coworkers,[11,12] which allow the following comparisons

$$A(CH_3OCH_2^+) - A(CH_3SCH_2^+) = 11.55^{12} - 11.50^{11} = 0.05 \text{ eV}$$

from $CH_3XCH_3$ (X = O or S), and

$$A(CH_3OCH_2^+) - A(CD_3S{-}CH_2^+) = 10.96^{12} - 10.84^{11} = 0.12 \text{ eV}$$

from $CH_3OC_2H_5$ and $CD_3SC_2H_5$. Thus the difference between the appearance potentials of $CH_3OCH_2^+$ from analogous compounds is small, but such real difference as may exist seems to indicate that in $CH_3XCH_2^+$ greater charge stabilization is effected by sulfur than by oxygen. The gas-phase substituent stabilization order given by Taft, Martin, and Lampe[9] con-

flicts with the condensed phase order for several substituents in addition to $CH_3O$ and $CH_3S$, and they offer a rationalization as to why this might be occurring.

Other gas-phase considerations provide some information pertinent to the problem. The ionization potentials of sulfur compounds are always lower than their oxygen analogs. Thus, for example, $I(CH_3SCH_3)$ = 8.685 eV[13] whereas $I(CH_3OCH_3)$ = 10.00 eV.[13] The proton affinity of $H_2S$ is 170 ± 3 kcal/mol,[14] which is slightly higher than that of $H_2O$, 165 ± 3 kcal/mol,[14] and one would expect that a similar difference would exist between other sulfur compounds and their oxygen analogs. Both the ionization potential and proton affinity considerations show that the electrons in sulfur are more loosely bound than those of oxygen, which would permit a greater stabilizing interaction of a charged center with a sulfur-containing substituent than with its oxygen analog.

Our chemical ionization result that $CH_3SCH_2^+$ is formed more readily than $CH_3OCH_2^+$ is in accord with the inference to be drawn from the appearance potential, ionization potential, and proton-affinity evidence. Clearly, the differences in the appearance potentials of the $CH_3XCH_2^+$ ions are small and at the limit of accuracy of electron impact appearance potentials. However, energy differences of this order of magnitude will have important effects on the rates of decomposition under chemical ionization conditions. One calculates from the kinetic parameters given in Table III that if the activation energy for the formation of $CH_3SCH_2^+$ were 0.2 eV higher, the rate constant at 300°K would be about 4000 times smaller.

It is possible that the difference in the chemical ionization behavior of $CH_3COOCH_2OCH_3$ and $CH_3COOCH_2SCH_3$ is the result of differences in reaction mechanism rather than of differences in stabilization energy of the product ions. Our results provide no information on this point.

A continuing problem of importance is the relationship between ionic phenomena in the gas phase, where they are relatively uncomplicated, and those in condensed phase, where they are of practical importance; and in this light the apparent difference in behavior of the sulfur- and oxygen-containing compounds in the two phases is of much interest. We mention that in the chemical ionization kinetics studies made prior to this one, at least qualitative agreement has been found between the gas-phase and condensed-phase phenomena. A particularly pertinent example is that we found[1] the rate of production of $CH_3OCH_2^+$ by chemical ionization from $HCOOCH_2OCH_3$ to be twice as fast as that from $CH_3COOCH_2OCH_3$, whereas in condensed phase the difference in rates is a factor of three in the same direction.[1]

We believe that a fair conclusion to be drawn from the present work is that our chemical ionization result points up the fact that a significant discrepancy may exist between the gas-phase and condensed-phase behavior of the systems investigated. Further study of the phenomenon in both phases is indicated.

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## Experimental Section

The instrumentation and procedures of chemical ionization mass spectrometry have been described elsewhere.[2a]
Methylthiomethyl acetate and methylthiomethyl propionate were prepared by allowing dimethyl sulfoxide to react with acetic anhydride and propionic anhydride, respectively (Pummerer reaction).[16] Each was purified by preparative gas chromatography. Physical constants and spectral data agreed with literature[16] values.

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# Rates of Protodetritiation of Polycyclic Aromatic Hydrocarbons in Trifluoroacetic Acid[1]

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Abstract: Rates are reported for some or all of the positions of naphthalene, biphenylene, benzo[b]biphenylene, phenanthrene, chrysene, pyrene, fluoranthene, triphenylene, and perylene for protodetritiation in 96.9% trifluoroacetic acid–3.1% perchloric acid at 25° and in 98% trifluoroacetic acid–2% carbon tetrachloride at 70°. The results are compared with related results from Eaborn's research group and the two solvent systems are interrelated. The result is an extensive set of quantitative relative reactivities for aromatic substitution on polycyclic aromatic hydrocarbons suitable for testing various molecular orbital methods.

Aromatic substitution reactions and their orientation for specific positions in aromatic hydrocarbons have long been useful for testing theories of organic chemistry such as resonance theory and molecular orbital methods. Electrophilic hydrogen isotope exchange is an especially simple and convenient type of aromatic substitution and in the form of protodedeuteration or protodetritiation is particularly important because quantitative reactivities can thus be obtained for positions too unreactive for measurement by direct substitution.[3] Such protodetritiations were pioneered by Eaborn's research group, first in mixtures of trifluoroacetic acid with strong mineral acid such as perchloric acid at room temperature[4] and subsequently in trifluoroacetic acid alone at 70°.[5] Because of our own interest in applying molecular orbital methods to quantitative reactivities in aromatic substitution, we have applied Eaborn's approach to additional polycyclic aromatic hydrocarbons, first in a mixture of 96.9% trifluoroacetic acid–3.1% perchloric acid at 25° (I) and subsequently in trifluoroacetic acid at 70° (II). In this paper we summarize the results we have obtained for both solvent systems. These results taken together with the data of Eaborn allow a quantitative correlation of the two solvent systems and provide reactivity data for many individual positions of a wide variety of polycyclic aromatic hydrocarbons.

The tritiated hydrocarbons were generally prepared by treatment of the known bromo derivatives with butyllithium followed by quenching of the aryllithium with tritiated water. Most of the kinetic runs were worked up with the LSKIN program of DeTar and DeTar[6] or by Perrin's program.[7] The results are summarized in Table I and are discussed by individual systems as follows.

**Naphthalene.** The rate reported by Bott, Spillett, and Eaborn[8] for naphthalene-1-t in trifluoroacetic acid at 70° is 20% higher than our results. Our solvent generally contained about 2% of carbon tetrachloride in order to provide increased solubility for the higher polycyclic hydrocarbons. In Table II we summarize the effect of several solvent variations. It is seen that a small amount of water causes a substantial increase of rate whereas carbon tetrachloride has essentially no effect. Hence, the discrepancy of 20% still remains and is disconcerting because it would appear to lie outside the combined limits of experimental error. However, the discrepancy is not important compared with the total range of reactivity of $10^4$ measured in this work.

**Phenanthrene.** Our runs with solvent system I complement the results of Eaborn's group with trifluoroacetic acid at 70°.[9] We did not do the 4 position because of potential steric hindrance effects but for the remaining positions we obtain the same order of reactivity: $9 > 1 > 3 > 2$. Dewar and Warfield[10] obtained this same order in nitration of phenanthrene. The comparison of our results with Eaborn's helps to interrelate the two trifluoroacetic acid solvent systems (vide infra).

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