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# NMR SPECTRA AND PROTOLYSIS OF STABLE SULFONIUM YLIDES

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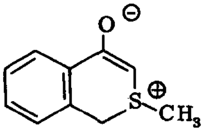
Several papers have appeared recently dealing with the nmr spectra and chemical exchange processes of phosphonium ylides (1, 2, 3, 4). The temperature dependence observed in the spectra of compounds of the type $(C_6H_5)_3\overset{\oplus}{P}\text{-CH=}\overset{O^{\ominus}}{C}\text{-R}$ has been identified with restricted rotation about the enolate C-C bond and/or protolysis reactions with trace amounts of acids present. We wish to report at this time the results of our work on the temperature dependence of related carbonyl-stabilized sulfonium ylide spectra. Several investigators have observed that line widths and chemical shifts of the methine proton resonances of ylides of the type $(CH_3)_2\overset{\oplus}{S}\text{-CH=}\overset{O^{\ominus}}{C}\text{-R}$ are temperature dependent (5, 6), and it has been suggested that this may reflect a rotational process interconverting cis and trans forms (5-8).

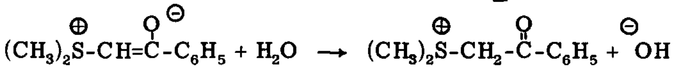
**1** $R_1 = R_2 = CH_3$, $R = C_6H_5$; **2** $R_1 = R_2 = CH_3$, $R = OCH_3$; **3** $R_1 = CH_3$, $R_2 = C_2H_5$, $R = C_6H_5$;
**4** $R_1 = CH_3$, $R_2 = (CH_3)_2CH$, $R = C_6H_5$; **5** $R_1 = CH_3$, $R_2 = C_6H_5CH_2$, $R = C_6H_5$;
**6** $R_1 = R_2 = R = C_6H_5$

While this interpretation must almost certainly be correct in several instances (6, 8), restricted rotation may not be the only source of the observed temperature dependence. For example, we recently prepared the cyclic sulfonium ylide **7** in which the S-C-C-O configuration is necessarily trans, yet we found that its nmr spectrum was temperature dependent. In $CDCl_3$, the methine proton resonance was broad ($\Delta\nu_{\frac{1}{2}}$ = 10 Hz, 3.5 ppm, 75°). On cooling, this resonance narrowed and shifted progressively downfield

7



($\Delta\nu_{\frac{1}{2}}$ = 4 Hz, 4.15 ppm, -40°) while other resonances in the spectrum of 7 remained essentially unchanged. Since rotation about the enolate bond is precluded in 7, an alternative rate process leading to nmr line broadening must exist for cyclic and, by inference, acyclic ylides. That this process is an intermolecular exchange reaction between ylide and trace amounts of water or other proton acids present (Equation-1) was demonstrated in several ways.



$$(CH_3)_2\overset{\oplus}{S}\text{-}CH{=}\overset{O^{\ominus}}{C}\text{-}C_6H_5 + H_2O \longrightarrow (CH_3)_2\overset{\oplus}{S}\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}C_6H_5 + \overset{\ominus}{O}H \qquad (1)$$

Preparation of ylides 1, 3, 4, 5 and 6 under strictly anhydrous conditions (from the corresponding sulfonium fluoroborate or bromide salts and NaH in dry THF) gave products which, on solution in ethanol-free $CHCl_3$ or dry $CH_3CN$, showed normal methine nmr line widths ($\Delta\nu_{\frac{1}{2}} \leqslant 1$ Hz, singlet; see Figure 1a). Addition of trace amounts of water, alcohols, or sulfonium salt produced dramatic line broadening (Figure 1b). This effect was studied in more detail using 1 in $CH_3CN$. The change in line shape of the methine resonance with concentration of added water may be related to the exchange rate constant $k_2$ by Equation 2 where $1/T_2$ is the natural line width (assumed equal to $\pi\Delta\nu_{\frac{1}{2}}$ of TMS).

$$k_2\,[H_2O] = \pi\,\Delta\nu_{\frac{1}{2}} - 1/T_2 \qquad (2)$$

A plot of the exchange broadening term ($\pi\Delta\nu_{\frac{1}{2}} - 1/T_2$) against $[H_2O]$ was linear of slope $k_2$ = 25 l. mole$^{-1}$ sec$^{-1}$. The dependence of line shape on temperature gave an estimate of $E_a$ as 5.5 kcal./mole (in moist $CHCl_3$).

A solution of 1 in $CHCl_3$ saturated with water gave the nmr spectrum of Figure 1b showing two broad resonances at 4.3 ppm and 2.7 ppm corresponding to methine and water protons, respectively. Saturation of the water resonance by irradiation at that frequency while sweeping the field resulted in complete disappearance of the methine resonance

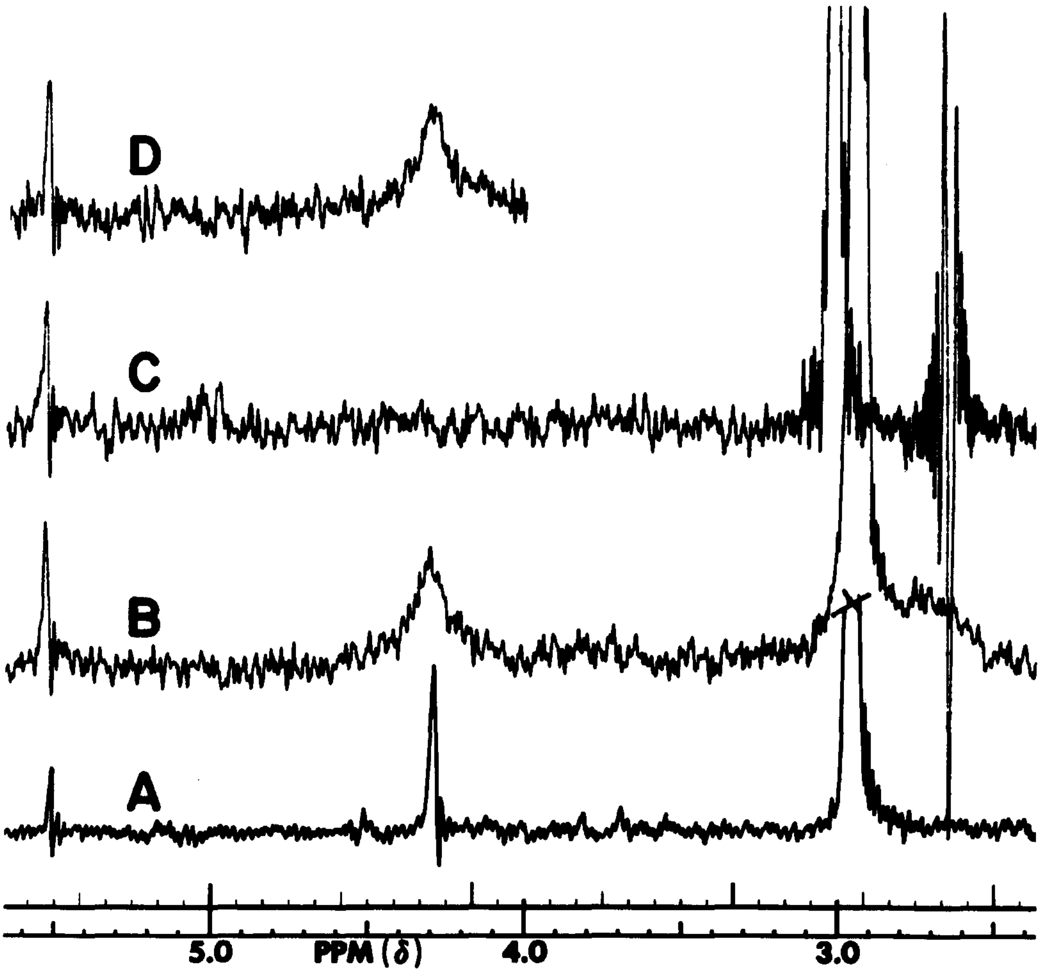
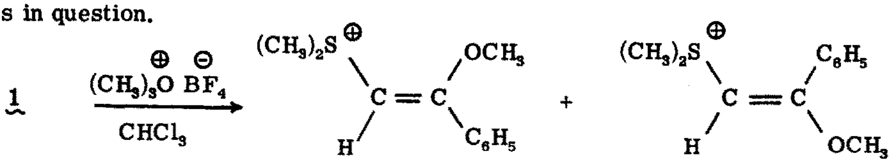


Figure 1. - Nmr of 1 in $CHCl_3$: A, anhydrous; B, saturated with water; C, on irradiation at the water resonance; D, after removal of irradiating signal. The phenyl and solvent resonances are not shown. The peak at 5.5 ppm is a solvent $^{13}C-H$ side band.

(Figure 1c). The signal reappeared when the irradiating frequency was displaced (Figure 1d). This result conclusively demonstrates that the broadening is due to protolysis, which must occur faster than spin relaxation of the methine proton (9, 10).

The nmr spectrum of anhydrous 1 in $CHCl_3$ (protolysis excluded) was found to be temperature invariant over the range -30 to 100°. This could mean that 1 is essentially frozen in one configuration, but we suggest that this is not the case on the basis of methylation experiments. Treatment of **1** with trimethyloxonium fluoroborate resulted in high yields of O-methylation products, **8** and **9**, in the ratio of 94:6. While the product composition does not necessarily reflect the starting isomer distribution, it does indicate that both cis and trans forms of **1** are present at room temperature. We are left with the conclusion that **1** is either rapidly rotating between cis and trans forms even at -30°, or that the nmr method is insensitive to the rate process in question.



**8** (94%) **9** (6%)

We wish to point out, however, that our results parallel those obtained for the phosphorus analog of **1**, $(C_6H_5)_3\overset{\oplus}{P}\text{-}CH\text{=}\overset{O^{\ominus}}{C}\text{-}C_6H_5$, for which no evidence was found for restricted rotation (1). The corresponding carbomethoxy derivatives, $(C_6H_5)_3\overset{\oplus}{P}\text{-}CH\text{=}\overset{O^{\ominus}}{C}\text{-}OCH_3$ and $(CH_3)_2\overset{\oplus}{S}\text{-}CH\text{=}\overset{O^{\ominus}}{C}\text{-}OCH_3$, both show restricted rotation at low temperatures (1, 2, 6). The reason for the dependence of the rotational barrier on the carbonyl substituent is not obvious, and we are presently investigating this point further.

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