

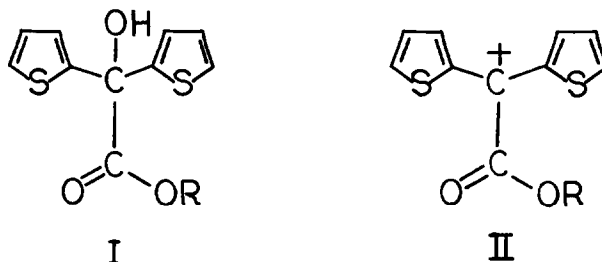
### OBSERVATION OF AN $\alpha$ -CARBOXYL CARBONIUM ION

George P. Nilles and Robert D. Schuetz<sup>1</sup>

Department of Chemistry and The Institute of Biology and Medicine  
Michigan State University, East Lansing, Michigan 48823

(Received in USA 26 May 1969; received in UK for publication 18 September 1969)

The serendipitous observation of a red coloration change during the product isolation from a preparation of 2,2'thenilic acid (2) (I, R=H) prompted us to investigate the spectral characteristics of this compound and its methyl ester I, (R=CH<sub>3</sub>) in a strong acidic medium. The experimental data clearly indicate the formation of the carbonium ion II (R=H, CH<sub>3</sub>) from I.



The visible spectrum (7) of I(R=H) in 50% (w/w) ClSO<sub>3</sub>H-CH<sub>2</sub>Cl<sub>2</sub> in Fig. 1 shows  $\lambda_{\text{max}} = 518$  nm.  $\log \epsilon = 4.52$ , indicative of carbonium ion formation (3).

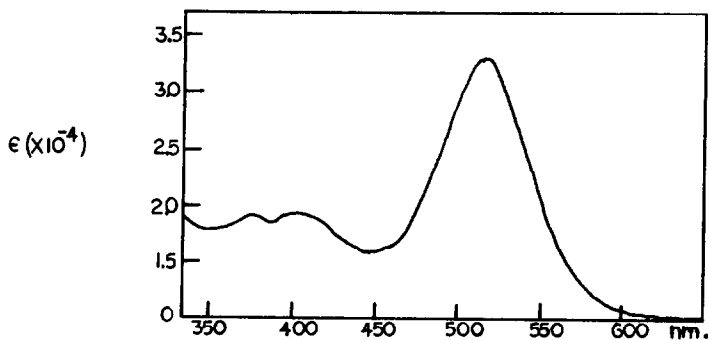


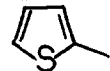
FIG. 1

The  $\text{ClSO}_3\text{H}$  concentration may be reduced to 1% (w/w) without affecting either the  $\lambda_{\text{max}}$  or  $\epsilon$ . Decomposition (indicated by loss of absorbance at 518 nm) is faster in 50%  $\text{ClSO}_3\text{H}$  < 1%. At 10%  $\text{ClSO}_3\text{H}$ , the absorbance @ 518 nm =  $A_0/2$  in 21 hours at  $25 \pm 2^\circ$  at an initial thenilic acid concentration of  $2 \times 10^{-5}$  M. This "half life" is a function of both the thenilic and  $\text{ClSO}_3\text{H}$  acid concentrations. The extinction coefficient is constant as a function of  $\text{H}_2\text{SO}_4$  ( $\log \epsilon = 4.32$ ) in sulfuric acid solutions down to 80% (w/w)  $\text{H}_2\text{SO}_4$  in  $\text{H}_2\text{O}$ .

The results of quenching the carbonium ion solution with anhydrous methanol or ethanol at  $-50^\circ$  are summarized in Table One, along with the nmr data of the starting materials and products. In all cases an instantaneous change from intense ruby red to colorless was observed. No decarboxylation of the acid or hydrolysis of the ester occurred under the experimental conditions. This was indicated by the constant appearance of the  $\text{CH}_3\text{-O-C}(=\text{O})$  singlet at  $6.25 \tau \pm 0.05 \tau$ . The resulting ester-ethers were obtained pure in better than 95% yield (8) by distillation.

TABLE ONE

Structure	Quenching Alcohol	Product	nmr <sup>7</sup> (in $\tau \pm 0.05$ )	m.p.
II, R=H	$\text{C}_2\text{H}_5\text{OH}^*$	$\begin{array}{c} \text{O} \quad \theta \\ \parallel \quad   \\ \text{CH}_3\text{OC}-\text{C}-\text{OC}_2\text{H}_5 \\   \\ \theta \end{array}$	2.7-3.3(m), 6.30(s), 6.65(q), 8.80( $\tau$ )	b.p. $110^\circ$ 0.3 torr
II, R= $\text{CH}_3$	$\text{C}_2\text{H}_5\text{OH}$	" "	2.7-3.3(m), 6.37(s), 6.67(q), 8.82( $\tau$ )	---
II R=H	$\text{CH}_3\text{OH}^*$	$\begin{array}{c} \text{O} \quad \theta \\ \parallel \quad   \\ \text{CH}_3\text{OC}-\text{C}-\text{OCH}_3 \\   \\ \theta \end{array}$	2.73-3.3(m), 6.25(s), 6.78(s)	---
I R=H	-	---	2.0-3.3(m)	$98-100^\circ$ dec
I R= $\text{CH}_3$	-	---	2.7-3.3(m), 5.51(s, -OH), 6.20(s)	$93^\circ$

\*treated with diazomethane after quenching work-up,  $\theta^2 =$  

Olah and Pittman (4) previously reported on the effect of an adjacent carbonium ion on the chemical shift of thienyl protons. The nmr spectrum appears to be considerably complicated by a coupling to a carbonium proton. In contrast, the nmr of II (R=H) as an 8% solution in 25% (w/w)  $\text{ClSO}_3\text{H}-\text{CH}_2\text{Cl}_2$  with tetramethyl ammonium tetrafluoroborate ( $\tau = 6.90$ ) (5) as a second

internal standard gave the very simple spectrum shown in Fig. 2 at  $-55^{\circ}$ .

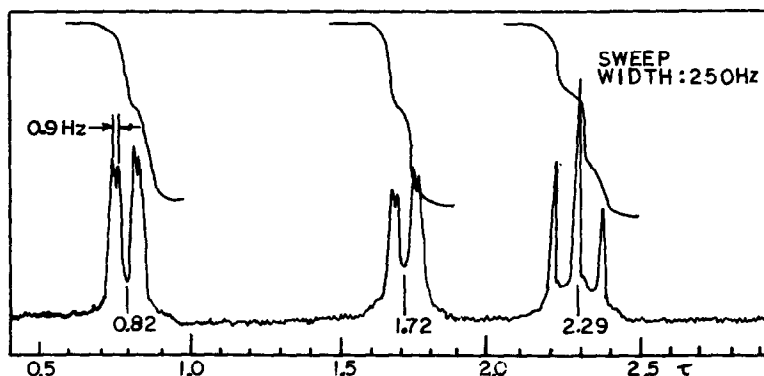
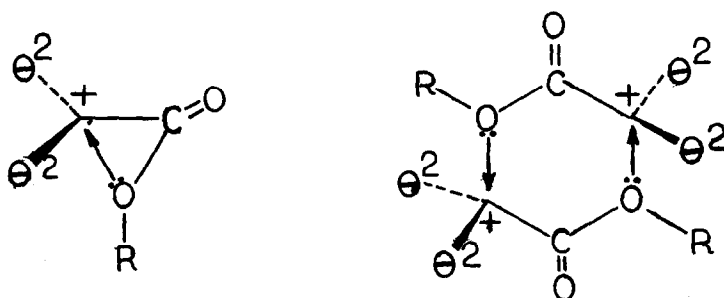


FIG. 2

The nmr spectrum of II ( $R=CH_3$ ) was virtually identical,  $\tau = 0.82$  (d of d), 1.72 (d of d), 2.30 (t) and 5.71 (s,  $CH_3O^-$ ). The large downfield shift of the thienyl protons, together with the simple spectrum may be taken as evidence for considerable and symmetrical participation by the thiophene rings in stabilizing the carbonium ion. The triplet ( $J = 4.65$  Hz) is readily explainable since  $J_{34}=J_{45}=4.65$  Hz. Although ion II ( $R=H$ ) was rapidly resinified at room temperature, the nmr of ion II ( $R=CH_3$ ) could be determined at  $+30^{\circ}$  and showed virtually no change from the low temperature spectrum,  $\tau = 0.83$  (d of d), 1.72 (d of d), 2.35 (t) and 5.78 (s,  $CH_3O^-$ ).

No protonation of the ester function could be detected despite scanning the nmr spectrum out to  $-7 \tau$ . While we cannot rule out small rapid reversible protonation of the ester function, it may be noted that no quenching of any such protonated form by ethanol occurred, *i.e.*, no ethyl esters were noted from either II,  $R=CH_3$  or  $R=H$ . The downfield chemical shift of the methoxy protons of II,  $R=CH_3$  compared with methyl 2,2-thienilate is probably due to the inductive effect of the adjacent carbonium ion (6).

There is also the possibility that the carbonium ion may be stabilized by some participation of the type shown below. In either the monomeric or dimeric form, the methyl group should be more effective in stabilizing the positive charge than hydrogen and this may explain the observed greater thermodynamic stability of II,  $R=CH_3$  *vs.* II,  $R=H$ .



1. To whom all correspondence should be addressed at The Institute of Biology and Medicine or the Department of Chemistry.
2. Preparation of this compound has been reported previously [S. Z. Cardon and H. P. Lankelma, *J. Am. Chem. Soc.*, 70, 4248 (1948)] but no coloration was reported on work-up. Also the compound is stable for several months at  $-20^{\circ}$  in contrast to its reported instability at room temperature. However, 2,2'-thenilic acid as well as the alkoxy dithienyl acetic acids were unstable at room temperature. They were converted to their methyl esters with diazomethane for elemental analysis.
3. George A. Olah, Charles U. Pittman, and Martyn C. R. Symons in "Carbonium Ions" by George A. Olah and Paul von R. Schleyer, John Wiley & Sons, New York, 1968, p. 156.
4. C. U. Pittman, Jr. and G. A. Olah, *J. Am. Chem. Soc.*, 87, 5123 (1965). The value given for the thienyl protons in thienyl cyclopropyl carbinol is a printing error. The chemical shift should be 2.05 $\tau$  -2.57 $\tau$ . Personal communication to the authors from George A. Olah, 1969.
5. N. C. Deno, J. S. Lin, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *J. Am. Chem. Soc.*, 87, 3000 (1965).
6. There is the possibility that some of this difference may be due to a solvent effect. Use of external TMS as a standard, in general gave chemical shifts 0.2 ppm lower field than internal tetramethylammonium tetrafluoroborate.
7. Visible spectra were determined on a Cary 14 spectrophotometer and the nmr spectra on a Jeolco C60-H instrument.
8. Products resulting from quenching, and methyl 2,2'-thenilate gave correct elemental analyses.