

nuclei such as  $^1\text{H}$  and  $^{15}\text{N}$  as well. Where these conditions are not met chemical synthesis of labeled peptides can be used. In either case, no method of assignment offers the substantial side benefits of  $^{13}\text{C}$  enrichment. The set of  $^{13}\text{C}$ -enriched peptides produced can be used in a variety of further studies. First, as mentioned above for gramicidin S-A, the substantial  $^{13}\text{C}$  satellites made visible in the proton spectrum can be used to confirm proton assignments. A proton difference spectrum between unenriched peptide and peptide labeled in one residue could be used in complex cases to bring out these satellites more clearly, allowing one in effect to study the proton spectrum of one residue at a time. Second, proton assignments could also be investigated by selective  $^1\text{H}$ - $^{13}\text{C}$  decoupling. This and all other studies involving measurement of the  $^{13}\text{C}$  spectrum are facilitated by the increased  $^{13}\text{C}$  signal intensity resulting from the enrichment. Third, relaxation time studies of poorly resolved carbons can be done separately using the enriched compounds. Fourth, binding studies involving interaction of the peptide with a high molecular weight species can be done with greater resolution and in higher dilution, as suggested in the preparation of a specifically active enriched fragment of the ribonuclease S-peptide which could be studied in its interaction with the S-protein.<sup>17</sup>

After completion of this manuscript, an article<sup>18</sup> appeared on the use of  $^{13}\text{C}$   $T_1$  values as indicators of intramolecular motion in gramicidin S. This article used the previous<sup>5</sup> nonrigorous  $^{13}\text{C}$  assignments in its discussion, which limited the certainty of some of the conclusions. Specifically enriched  $^{13}\text{C}$  compounds

(17) M. H. Freedman, J. S. Cohen, and I. M. Chaiken, *Biochem. Biophys. Res. Commun.*, **42**, 1148 (1971).

(18) A. Allerhand and R. A. Komoroski, *J. Amer. Chem. Soc.*, **95**, 8228 (1973).

would have aided the interpretation in two ways. First, unambiguous assignments would have been possible for peaks whose  $T_1$  values could be measured. Tentative assignments made in Figure 2 of the Allerhand and Komoroski article<sup>18</sup> are confirmed by our results except for Leu  $\alpha$  and Orn  $\alpha$ , which should be reversed. Second, accurate  $T_1$  values could have been obtained for unresolved peaks containing two resonances from different residues (as in Pro  $\beta$  + Orn  $\beta$ , and Pro  $\gamma$  + Orn  $\gamma$ ). The individual components of these unresolved peaks could have been studied in separate experiments.

### Conclusion

For peptides that can be produced chemically or biosynthetically from defined precursors available in  $^{13}\text{C}$ -enriched form, selective  $^{13}\text{C}$  incorporation provides a method for making unambiguous  $^{13}\text{C}$  chemical shift assignments and gives as a by-product a set of labeled compounds useful for a variety of other studies. This method, applied to the antibiotic gramicidin S-A, has allowed the establishment of all  $^{13}\text{C}$  chemical shift assignments, including those of the difficult to resolve carbonyl region.

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## Communications to the Editor

### Magnetic Circular Dichroism Studies. XXVIII.<sup>1</sup> Solvent Dependent Absorption and Magnetic Circular Dichroism Spectral Studies of Triphenylcarbenium Ion

Sir:

Triphenylcarbenium ion (**1**)<sup>2</sup> is the most-investigated carbocation and its propeller-shaped structure is well established.<sup>3</sup> The absorption spectrum of ion **1** has been previously studied by Gold,<sup>4</sup> Deno,<sup>5</sup> Evans,<sup>6</sup> Harmon,<sup>7</sup> Olah,<sup>8</sup> and others.<sup>9</sup> The results of these

(1) Part XXVII: Y. K. Mo, R. E. Linder, G. Barth, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, in press.

(2) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(3) H. H. Freedman in "Carbonium Ions," Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1973, p 1501.

(4) (a) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952); (b) V. Gold and B. W. V. Hawes, *ibid.*, 2102 (1951).

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(7) (a) K. M. Harmon and A. B. Harmon, *J. Amer. Chem. Soc.*, **83**, 865 (1961); (b) K. M. Harmon and F. E. Cummings, *ibid.*, **87**, 539 (1965).

investigations (first eight entries in Table I) show that the absorption spectral parameters (both  $\lambda_{\text{max}}$  and  $\epsilon$ ) appear to be independent of medium or ion precursor. We would now like to report, for the first time, medium dependent absorption and magnetic circular dichroism (MCD)<sup>10</sup> spectroscopic studies of this ion.

Triphenylcarbinol (**2**) was ionized in four superacid systems (100%  $\text{H}_2\text{SO}_4$ ,  $\text{FSO}_3\text{H}$ , 20% oleum, and  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole)) at room temperature to give ion **1**.<sup>11</sup> The absorption and MCD spectra of the resulting solutions are shown in Figure 1 while the

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(9) (a) W. N. White and C. A. Stout, *J. Org. Chem.*, **27**, 2915 (1962); (b) B. A. Timimi, *Chem. Ind. (London)*, 2148 (1967).

(10) For a review of MCD see C. Djerassi, E. Bunnenberg, and D. L. Elder, *Pure Appl. Chem.*, **25**, 57 (1971).

(11) One milligram of **2** was dissolved in approximately 1 ml of each of the superacid solutions. In general, concentrations of the solutions were approximately  $10^{-3}$  M. All spectra were run in short path length (0.01 cm) quartz absorption cells. The absorption spectrum of  $\text{FSO}_3\text{H-SbF}_5$  (blank run) indicates there is essentially no absorption above 215 nm (a weak absorption tail begins at 205 nm). MCD and absorption spectra were immediately recorded in all cases and shown to be reproducible.

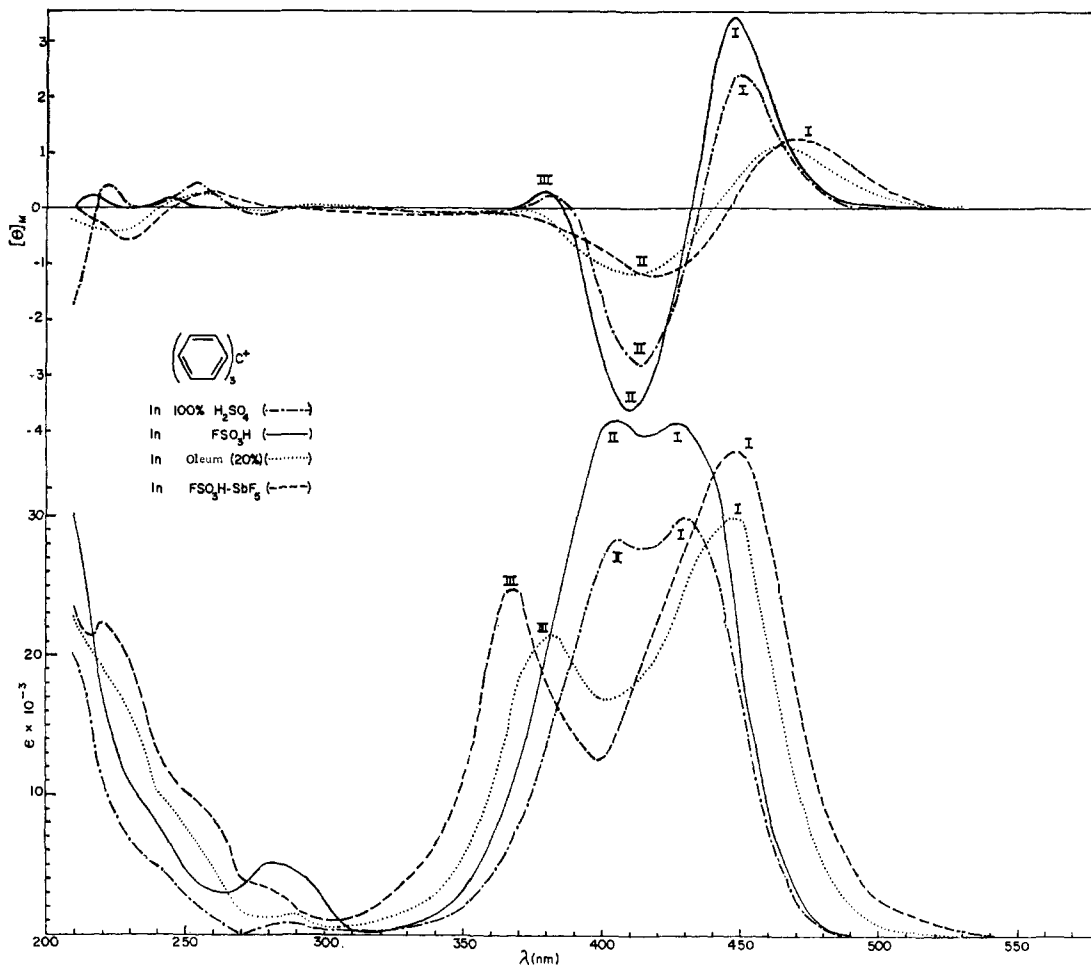


Figure 1. Absorption and MCD spectra of triphenylcarbenium ion in various superacids.

Table I. Variation in  $\lambda_{\max}(\epsilon)$  and  $\lambda([\theta]_M)$  with Ion Precursor and Solvent for Triphenylcarbenium Ion (1)

Source	Solvent	$\lambda_{\max}(\epsilon)^a$			$\lambda([\theta]_M)^b$			Ref
		Band I	Band II	Band III	Band I	Band II	Band III	
Ph <sub>3</sub> COH	>20% H <sub>2</sub> SO <sub>4</sub> in acetic acid	431 (37,360)	408 (36,400)					4
Ph <sub>3</sub> COH	Concd H <sub>2</sub> SO <sub>4</sub>	431 (39,800)	404 (39,800)					5
Ph <sub>3</sub> COH	FSO <sub>3</sub> H-SbF <sub>5</sub> in ethanol	430 (38,700)	403 (38,700)					8
Ph <sub>3</sub> Cl	96% H <sub>2</sub> SO <sub>4</sub>	432 (38,100)	404 (38,100)					7
Ph <sub>3</sub> C <sup>+</sup> BI <sub>4</sub> <sup>-</sup>	96% H <sub>2</sub> SO <sub>4</sub>	432 (35,800)	404 (35,800)					7
Ph <sub>3</sub> C <sup>+</sup> BBr <sub>4</sub> <sup>-</sup>	96% H <sub>2</sub> SO <sub>4</sub>	432 (38,400)	405 (37,300)					7
Ph <sub>3</sub> C <sup>+</sup> SbCl <sub>6</sub> <sup>-</sup>	H <sub>2</sub> SO <sub>4</sub>	430 (38,300)	410 (38,300)					9b
Ph <sub>3</sub> C <sup>+</sup> SbF <sub>6</sub> <sup>-</sup>	CH <sub>2</sub> Cl <sub>2</sub>	430 (38,250)	410 (38,250)					9b
Ph <sub>3</sub> COH	100% H <sub>2</sub> SO <sub>4</sub>	430 (29,200)	406 (28,300)		451 (2.39)	413 (-2.80)	380 (0.20)	This work
Ph <sub>3</sub> COH	FSO <sub>3</sub> H	429 (36,300)	404 (36,900)		447 (3.63)	409 (-3.04)	380 (0.29)	This work
Ph <sub>3</sub> COH	20% oleum	446 (29,700)		382 (23,300)	463 (1.10)	410 (-1.17)		This work
Ph <sub>3</sub> COH	FSO <sub>3</sub> H-SbF <sub>5</sub> (neat)	452 (34,600)		368 (24,500)	470 (1.24)	420 (-1.24)		This work
Ph <sub>3</sub> COH	100% H <sub>2</sub> SO <sub>4</sub> + 20% oleum	432 (31,300)	408 (30,600) <sup>c</sup>		450 (2.35)	411 (-2.80)	380 (0.13)	This work
Ph <sub>3</sub> COH	H <sub>2</sub> SO <sub>4</sub> + FSO <sub>3</sub> H	430 (34,100)	406 (32,800)		447 (2.75)	408 (-3.39)	378 (0.18)	This work
Ph <sub>3</sub> COH	FSO <sub>3</sub> H-SbF <sub>5</sub> + H <sub>2</sub> SO <sub>4</sub>	430 (32,100)	406 (32,100) <sup>c</sup>		448 (2.51)	410 (-3.15)	378 (0.10)	This work
Ph <sub>3</sub> COH	FSO <sub>3</sub> H + 20% oleum	446 (33,300)		382 (26,300)	463 (1.27)	412 (-1.51)		This work
Ph <sub>3</sub> COH	FSO <sub>3</sub> H-SbF <sub>5</sub> + 20% oleum	434 (37,600)	404 (35,400) <sup>c</sup>		447 (2.87)	408 (-3.58)	378 (0.18)	This work
Ph <sub>3</sub> COH	FSO <sub>3</sub> H-SbF <sub>5</sub> + FSO <sub>3</sub> H	445 (26,100)		375 (18,700)	465 (1.09)	415 (-1.12)		This work

<sup>a</sup> Wavelength in nm; molar extinction coefficient in  $M^{-1} \text{ cm}^{-1}$ . <sup>b</sup> Molecular magnetic ellipticity in  $\text{deg dl dm}^{-1} \text{ mol}^{-1} \text{ G}^{-1}$ . <sup>c</sup> Spectral changes were observed when the solution was warmed to 60° for 10 min; see text.

spectral parameters are summarized in Table I. The absorption and MCD spectra of ion 1 in 100% H<sub>2</sub>SO<sub>4</sub> and in FSO<sub>3</sub>H solutions are similar but differ from those in 20% oleum and in FSO<sub>3</sub>H-SbF<sub>5</sub> (1:1 mole:mole) solutions. The separation of the absorption

bands (depicted as band I and band III, bottom traces in Figure 1) as well as the separation of the large positive and negative MCD bands (depicted as band I and band II, upper traces in Figure 1) is large in the latter medium. Our absorption spectrum of ion 1 in 100%

$\text{H}_2\text{SO}_4$  (or in  $\text{FSO}_3\text{H}$ ) is similar to those reported previously.<sup>4-9</sup> However, it should be noted that the absorption spectrum of ion **1**, measured at  $-60^\circ$  in  $\text{FSO}_3\text{H-SbF}_5$  (9:1 mole:mole)-ethanol solution,<sup>8</sup> differs significantly from that obtained by us at room temperature in  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) solution (without ethanol).

The present observations of triphenylcarbinol (**2**) in 20% oleum and in  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) solution may indicate the formation of (i) sulfonation (fluorosulfonation) products, (ii) a solvent-separated ion pair ( $\text{Ph}_3\text{C}^+\text{Y}^-$ , or (iii) an associated ion pair ( $\text{Ph}_3\text{C}^+\text{Y}^-$ ).<sup>12</sup> The formation of sulfonation products was ruled out because on quenching with water-ice, all the solutions gave a quantitative yield of starting material **2** (see also subsequent discussion). It is unlikely that solvent-separated ion pairs are formed in neat  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) because a previous nmr study has shown that such species are not found under similar experimental conditions.<sup>13</sup> We thus favor the formation of associated ion pairs ( $\text{Ph}_3\text{C}^+\text{Y}^-$ ) in both 20% oleum and in  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) solutions and cannot rule out the formation of such species in 100%  $\text{H}_2\text{SO}_4$  and in  $\text{FSO}_3\text{H}$ .

In addition, we have studied (Table I) the absorption and MCD spectra of ion **1** in mixed superacid systems (1:1 v:v). The separation of the two absorption bands of ion **1** in 100%  $\text{H}_2\text{SO}_4$  + 20% oleum and in 100%  $\text{H}_2\text{SO}_4$  +  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) solutions, prepared either by treating **2** with the superacid mixtures or by adding 20% oleum or  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) solution to ion **1** in 100%  $\text{H}_2\text{SO}_4$  was small. The spectra were similar to those observed in 100%  $\text{H}_2\text{SO}_4$  and in  $\text{FSO}_3\text{H}$  where bands I and II were observed. When these solutions were warmed to  $60^\circ$  for 10 min, the separation of the two bands increased and the spectra were similar to those observed in 20% oleum and in  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) solutions. On the other hand, when an equal volume of 100%  $\text{H}_2\text{SO}_4$  was added to ion **1** in 20% oleum or  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) solution and held at  $60^\circ$  for 20 min, the separation of the two bands remained unchanged (bands I and III were observed). These results indicate that a thermodynamically stable species, an associated ion pair ( $\text{Ph}_3\text{C}^+\text{Y}^-$ ), was formed in 20% oleum and  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) solutions at room temperature and in 100%  $\text{H}_2\text{SO}_4$  + 20% oleum and 100%  $\text{H}_2\text{SO}_4$  +  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) superacid mixtures at higher temperature ( $60^\circ$ ). Further, the gegenion is relatively tightly bound and does not perceptibly exchange with the solvent at  $25^\circ$ .

It is interesting to note that the absorption spectrum of ion **1** in 20% oleum +  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) superacid system at room temperature is similar to that observed in 100%  $\text{H}_2\text{SO}_4$  but is different from that observed in each individual superacid system. However, it slowly changes to that observed in either 20% oleum or  $\text{FSO}_3\text{H-SbF}_5$  (1:1 mole:mole) solution by warming the solution at  $60^\circ$  for 10 min. The unusual behavior of ion **1** in this superacid mixture may be explained by

(12) Free ions (or nonassociated ions) can only be observed in the gas phase (in a mass spectrometer). Ions formed in solution phase are always associated with the medium (or the gegenions) to a certain degree. In the lowest nucleophilicity superacid system, these associations are weak.

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the fact that reaction between  $\text{FSO}_3\text{H-SbF}_5$  and 20% oleum occurs prior to the ionization of **2** and thus changes the nature of the gegenion. The chemistry of this superacid system has been reviewed recently by Gillespie and Peel.<sup>14</sup>

It seems clear, therefore, that the propeller-shaped structure of ion **1** is very sensitive to the nature of the gegenions. The degree of interaction between ion **1** and the gegenions or the ability to form an associated ion pair,  $\text{Ph}_3\text{C}^+\text{Y}^-$ , depends on the nature of the gegenions. Consequently the propeller-shaped structure of ion **1** is directly related to such interaction and thus alters the absorption and the MCD spectra. In summary, we have observed significant changes in the absorption and MCD spectra of ion **1** in various superacid media and have found three MCD bands in the near-uv and visible spectrum of ion **1**. It should be noted that Nemcova, Malat, and Zahradnik,<sup>15</sup> in calculating the excitation energies and oscillator strengths of ion **1** using the semiempirical LCAO-SCF-CI method of Pariser, Parr, and Pople, found only two absorption maxima in the long wavelength region when they assumed that ion **1** has a planar confirmation.

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### Observation of a Second Wien Effect in Nonaqueous Solutions of Dichloro-1,1,7,7-tetraethyldiethylenetriaminenickel(II) and of Sodium Tetraphenylborate

Sir:

The enhanced dissociation of weak electrolytes by high electric fields, known as the second Wien or dissociation field effect,<sup>1</sup> was first accounted for theoretically by Onsager,<sup>2</sup> and the principal features of this theory have been verified by the available experimental data,<sup>3</sup> most of which relate to simple inorganic salts in aqueous solution.<sup>4,5</sup> Detailed investigations of the effect in nonaqueous media are rather rare.<sup>2,6</sup> As well as being of interest from an electrochemical standpoint, the second Wien effect is the basis of the electric field-

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