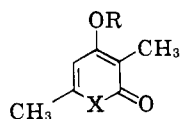


to be acetate derived,<sup>12</sup> and hispidin, isolated from *Polyporus hispidus*.<sup>13</sup> Compound Ia could be isolated in small quantity (ca. 6 mg./l.) from 4-day cultures of *P. stipitatum*, whereas stipitatic acid could not be detected until the seventh day. The possible role of Ia in the biosynthesis of stipitatic acid is therefore under further investigation.



- Ia, R = H; X = O  
 b, R = CH<sub>3</sub>; X = O  
 c, R = COCH<sub>3</sub>; X = O  
 d, R = H; X = N-CH<sub>3</sub>  
 e, R = H; X = N-H

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### Stable Carbonium Ions. VII.<sup>1</sup> Nuclear Magnetic Resonance Investigation of the Triphenyl-C<sup>13</sup>-carbonium Ion

Sir:

Recently we reported<sup>2</sup> on the nuclear magnetic resonance investigation of the trimethylcarbonium ion and were able to show that the C<sup>13</sup> resonance of 2-C<sup>13</sup>-2-methyl-2-chloropropane (1-C<sup>13</sup>-*t*-butyl chloride) is shifted by 273 p.p.m. downfield in the trimethyl-C<sup>13</sup>-carbonium ion, (CH<sub>3</sub>)<sub>3</sub>C<sup>13+</sup>, formed *via* complexing the halide with antimony pentafluoride. We expressed our view that the observed substantial shift is due both to the change of hybridization of the involved carbon atom from sp<sup>3</sup> to sp<sup>2</sup> and to the presence of positive charge on the carbon atom.

It was felt of interest to extend our investigations to the triphenyl-C<sup>13</sup>-carbonium ion, where charge delocalization through conjugative interaction with the three benzene rings was expected to decrease the C<sup>13</sup> chemical shift of the carbonium ion, as compared with that of the trimethylcarbonium ion.

Labeling the aliphatic carbon atom with C<sup>13</sup> (58%) allowed us to compare the nuclear magnetic C<sup>13</sup> shifts of the covalent, sp<sup>3</sup>-hybridized triphenyl-C<sup>13</sup>-methanol (in tetrahydrofuran solution) with that of the labeled triphenylcarbonium ion, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C<sup>13+</sup>-HSO<sub>4</sub><sup>-</sup> (triphenyl-C<sup>13</sup>-methanol in sulfuric acid solution). The data in Table I indicate a shift of 129.6 p.p.m. to less shielding in the triphenylcarbonium ion, as compared with the covalent triphenylmethanol.

In order to improve the signal-to-noise ratio the samples of enriched materials were put into 0.25-in. o.d. thin wall tubes and the spectra were recorded using the high resolution frequency-swept and proton

stabilized n.m.r. spectrometer of Baker and Burd<sup>3</sup> with the use of a frequency synthesizer. Using dispersion mode, rapid passage conditions spectra could also be obtained in standard size Varian sample tubes. Improved spectra were obtained using Overhauser enhancement by simultaneous H' irradiation.

TABLE I

(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C <sup>13</sup> OH (in THF) at 15.090646 Mc.
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C <sup>13</sup> -HSO <sub>4</sub> <sup>-</sup> (in H <sub>2</sub> SO <sub>4</sub> ) at 15.092603 Mc.
$\delta_{\text{C}^{13}(\text{C}_6\text{H}_5)_3\text{C}^+} - \delta_{(\text{C}_6\text{H}_5)_3\text{COH}} = 1957 \text{ c.p.s.} = -129.6 \text{ p.p.m. (CS}_2$
(reference) at 15.092330 Mc.)

The coupling with the ring protons is small which means that the spectra are concentrated essentially into a single line. There is however some coupling, about 5 c.p.s. to the *ortho* protons ( $J_{\text{CCCH}} = 5 \pm 0.2$  c.p.s.) and considerably less with the *meta* and *para* protons. The long range coupling with the *ortho* protons ( $J_{\text{CCCH}}$ ) is in accordance with similar observation of Frei and Bernstein<sup>4</sup> in the case of C<sub>6</sub>H<sub>5</sub>-C<sup>13</sup>OCl.

To assess, at least qualitatively, how much of the observed shift in the triphenylcarbonium ion is due to the change of hybridization from sp<sup>3</sup> to sp<sup>2</sup> and how much to the effect of the positive charge, a comparison of the chemical shifts of the triphenyl-C<sup>13</sup>-carbonium and trimethyl-C<sup>13</sup>-carbonium ions with their parent sp<sup>3</sup> hybridized, covalent precursors and with some C<sup>13</sup> compounds having sp<sup>2</sup>-hybridization is useful.

The C<sup>13</sup> shift of an uncharged sp<sup>2</sup>-hybridized compound is found around +45 to +70 p.p.m. (from CS<sub>2</sub> as reference).<sup>5-7</sup> The observed C<sup>13</sup> shift at -18.1 p.p.m. in the triphenylcarbonium ion shows the additional deshielding effect (about 60-80 p.p.m.) of the positive charge. As the positive charge is much more delocalized in the triphenylcarbonium ion than it is in the trimethylcarbonium ion, the larger deshielding effect observed in the case of the latter (-146.9 p.p.m. from CS<sub>2</sub>) is to be expected.

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### The Transition State in Methyl Radical Formation. The $\alpha$ -Deuterium Effect<sup>1</sup>

Sir:

The magnitude of the  $\alpha$ -deuterium isotope effect in many cases of "unimolecular" (*i.e.*, approaching limiting SN1) solvolyses is constant, about  $k_{\text{H}}/k_{\text{D}} = 1.15$  per deuterium atom, between ambient and 100°.<sup>2</sup>

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