was unchanged at the lowest concentration at which it could be detected. The broad line may be attributable to $\Delta m = 1$ transitions in I which are broadened by incompletely averaged interelectronic interactions.[14]

We also investigated the e.p.r. spectrum of solutions of IV in acetic acid containing perchloric acid. The unalkylated bisquinonemethide system present in IV has been studied under these conditions by Wizinger,[15] who reported the formation of a diprotonated salt. We had previously repeated some of this work[16] and found that solutions containing the dication had strong e.p.r. absorption but we were unable to detect any hyperfine structure. Solutions of IV in acid exhibited a strong, nine-line ($a = 1.09$ gauss) e.p.r. signal. The spectrum was unchanged in AcOD, ruling out any splitting by OH groups. The species responsible for this spectrum is most likely cation radical V, containing eight equivalent protons, formed by a one-electron reduction of the dipositive ion.

V
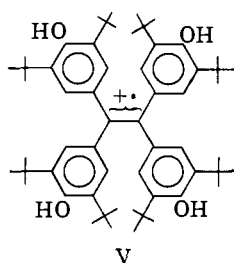
Acknowledgment.—We wish to thank R. M. R. Cramer and W. A. Yager for determining the e.p.r. spectra. We also wish to acknowledge several informative discussions of the e.p.r. spectra of triplets with Dr. E. Wasserman.

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Isolation and Structure of a Methyltriacetic Lactone from *Penicillium stipitatum*

Sir:

As part of a study[1] of the metabolic products of the tropolone-producing mole *Penicillium stipitatum* (NRRL 1006), we wish to report the isolation and identification of 3,6-dimethyl-4-hydroxy-2-pyrone. After 2 weeks growth on a previously described medium,[2] stipitatic acid was removed by concentration of the fermentation beer. The residue was subjected to chromatography on neutral alumina (Woelm, activity grade I). The acetone–ethanol (4:1) eluate was evaporated, and the residue was sublimed (120° at 0.3 mm.). The sublimate on recrystallization from acetone–petroleum ether (b.p. 60–90°) afforded Ia, m.p. 212–214°; yield, 45 mg./l.; $\lambda_{max}^{95\% \text{ EtOH}}$ 288 mμ (ϵ 8300), unchanged by the addition of mineral acid or base; λ_{max}^{KBr} 3.72, 5.99, 6.08, 6.31 μ; $[\alpha]D$ 0; pK = 5.05; neut. equiv. = 139; n.m.r. [$CDCl_3$–$(CD_3)_2SO$] τ 4.05, 5.06, 7.85, 8.25 p.p.m.,

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relative intensity 1:1:3:3.[3] *Anal.* Calcd. for $C_7H_8O_3$: C, 59.99; H, 5.75. Found: C, 59.91; H, 5.79. Control chromatographic experiments were run to demonstrate that Ia was a true mold metabolite and not an artifact formed during isolation.

Treatment of Ia with absolute methanol and sulfuric acid led to unchanged starting material, but Ia with ethereal diazomethane or dimethyl sulfate and potassium carbonate gave the methyl derivative, Ib, m.p. 83–84°, $\lambda_{max}^{H_2O}$ 297 mμ.[4] *Anal.* Calcd. for $C_8H_{10}O_3$: C, 62.50; H, 6.51; mol. wt., 154. Found: C, 62.51; H, 6.61; mol. wt. (Rast), 155. Reaction of Ia and acetic anhydride with sodium acetate, pyridine, or zinc dust produced the identical monoacetyl derivative, Ic, m.p. 83–84°, $\lambda_{max}^{H_2O}$ 293 mμ. *Anal.* Calcd. for $C_9H_{10}O_4$: C, 59.50; H, 5.51; acetyl, 23.0. Found: C, 59.51; H, 5.63; acetyl, 23.8. When Ia was heated with aqueous methylamine, a nitrogen-containing product was obtained, Id, m.p. 265° dec., $\lambda_{max}^{95\% \text{ EtOH}}$ 288 mμ, which underwent a hypsochromic shift to 279 mμ on the addition of sodium hydroxide. *Anal.* Calcd. for $C_8H_{11}NO_2$: C, 62.73; H, 7.24; N, 9.15. Found: C, 62.99; H, 7.37; N, 9.00.

The ultraviolet behavior of Ia and Id were as expected for these structures, since Berson, *et al.*,[5] showed that 4-hydroxy-2-pyrones and their corresponding pyridones have similar spectral properties and that addition of base produced appreciable hypsochromic shifts only with the nitrogen analogs.

Finally, a sealed tube reaction between Ia and concentrated aqueous ammonia at 120° produced the previously prepared compound, Ie, 3,6-dimethyl-4-hydroxy-2-pyridone, m.p. 268–270° dec., $\lambda_{max}^{95\% \text{ EtOH}}$ 288 mμ, $\lambda_{max}^{EtOH-NaOH}$ 278 mμ. Comparison with an authentic sample,[6] m.p. 272–273°, demonstrated that their infrared spectra were identical. Thus Ia is 3,6-dimethyl-4-hydroxy-2-pyrone.

The finding of this hitherto undescribed methyltriacetic lactone from *P. stipitatum* is in harmony with the acetate–methyl malonate condensation which has been found for the biogenesis of benzenoid[7] and troponoid[8] compounds by fungi. It is a structural analog of the dehydroacetic acid derivatives which recently have been suggested by Birch[9] as β-polyketomethylene intermediates in the biosynthesis of aromatic natural products, and it may represent a concrete example of the hypothetical triacetic acids proposed in the biosynthesis of alternariol and orsellinic acid.[10] Its finding also accords with observations on inhibition of synthesis of benzene derivatives in *P. urticae* by dehydroacetic acid.[11] Related substituted 4-hydroxy-2-pyrones may be alternaric acid, shown

(3) We wish to thank Dr. R. Breslow of Columbia University and Dr. D. P. Hollis of Varian Associates for the n.m.r. spectra obtained at 60 Mc. using tetramethylsilane = 10 as reference.
(4) This assignment of structure is based upon the spectral studies on 2-methoxy-4-pyrone and 4-methoxy-2-pyrone by I. Chmielewska, J. Cieslak, K. Gorczynska, B. Kantnik, and K. Pitakowska [Tetrahedron, **4**, 36 (1958)] and D. Herbst, W. B. Mors, O. R. Gottlieb, and C. Djerassi [J. Am. Chem. Soc., **81**, 2427 (1959)].
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to be acetate derived,[12] and hispidin, isolated from *Polyporus hispidus*.[13] 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.
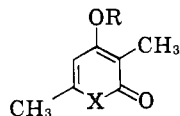
Ia, R = H; X = O
b, R = CH₃; X = O
c, R = COCH₃; X = O
d, R = H; X = N–CH₃
e, R = H; X = N–H

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Stable Carbonium Ions. VII.[1] Nuclear Magnetic Resonance Investigation of the Triphenyl-C¹³-carbonium Ion

Sir:

Recently we reported[2] on the nuclear magnetic resonance investigation of the trimethylcarbonium ion and were able to show that the C^{13} resonance of 2-C^{13}-2-methyl-2-chloropropane (1-C^{13}-t-butyl chloride) is shifted by 273 p.p.m. downfield in the trimethyl-C^{13}-carbonium ion, $(CH_3)_3C^{13}{}^+$, 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^3 to sp^2 and to the presence of positive charge on the carbon atom.

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

Labeling the aliphatic carbon atom with C^{13} (58%) allowed us to compare the nuclear magnetic C^{13} shifts of the covalent, sp^3-hybridized triphenyl-C^{13}-methanol (in tetrahydrofuran solution) with that of the labeled triphenylcarbonium ion, $(C_6H_5)_3C^{13}{}^+$-$HSO_4{}^-$ (triphenyl-C^{13}-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

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stabilized n.m.r. spectrometer of Baker and Burd[3] 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

$(C_6H_5)_3C^{13}OH$ (in THF) at 15.090646 Mc.

$(C_6H_5)_3C^{13}{}^+$–$HSO_4{}^-$ (in H_2SO_4) at 15.092603 Mc.

$\delta_{C^{13}(C_6H_5)_3C^+} - \delta_{(C_6H_5)_3COH} = 1957$ c.p.s. $= -129.6$ 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 ($J_{CCCH} = 5 \pm 0.2$ c.p.s.) and considerably less with the *meta* and *para* protons. The long range coupling with the *ortho* protons (J_{CCCH}) is in accordance with similar observation of Frei and Bernstein[4] in the case of C_6H_5-$C^{13}OCl$.

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

The C^{13} shift of an uncharged sp^2-hybridized compound is found around $+45$ to $+70$ p.p.m. (from CS_2 as reference).[5-7] The observed C^{13} 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_2) is to be expected.

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The Transition State in Methyl Radical Formation. The α-Deuterium Effect[1]

Sir:

The magnitude of the α-deuterium isotope effect in many cases of "unimolecular" (*i.e.*, approaching limiting S_N1) solvolyses is constant, about $k_H/k_D = 1.15$ per deuterium atom, between ambient and 100°.[2]

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.
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