

ion intermediate. Further work investigating substituent and medium effects is planned.

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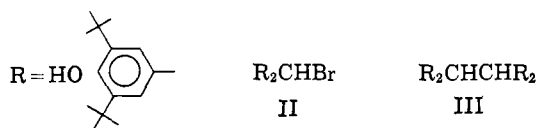
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RECEIVED DECEMBER 14, 1963

Bisgalvinoxyl,¹ a Stable Triplet

Sir:

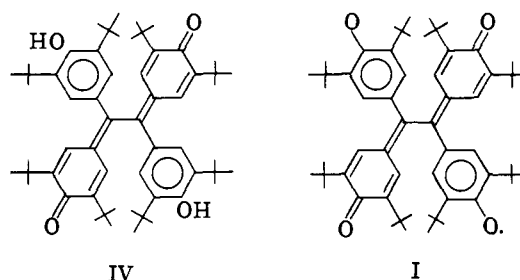
The study of interelectronic interactions in organic biradicals has been of interest in recent years.² We have been interested in systems containing individually stable radicals which may form a triplet electronic state rather than a chemical bond. An unusually stable type of radical has been studied by Coppinger.³ The synthesis⁴ and theoretical considerations⁵ of a potential triplet, based on Coppinger's galvinoxyl system, have been described but no further details have been published. We have synthesized bisgalvinoxyl (I) and found it to be a reasonably stable biradical. Its e.p.r. spectrum, in solid matrices at 77°K. and also in solution at room temperature, is interpretable as the spectrum of a biradical whose electrons are weakly coupled, resulting in a triplet electronic state.



Bromination of bis(3,5-di-*t*-butyl-4-hydroxyphenyl)-methane in benzene gave the benzhydryl bromide II. It was not isolated but its dehydrobromination product, the corresponding quinonemethide, could be obtained. Treatment of the crude benzene solution of II with finely divided copper metal gave the tetraphenylethane III in 70% yield. The assignment of structure III to the colorless crystalline reaction product, m.p. 330–332°⁶, rests on its elemental analysis,⁷ its infrared spectrum (hindered phenol at 2.7 μ , no bands other than CH below the weak phenyl band at 6.24 μ), and its ultraviolet spectrum⁸ ($\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ 276 μ (log ϵ 3.89), 283 (3.81)).

It was not possible to oxidize III to a single compound with any of the usual reagents for phenol oxidation. Bromination (8 moles of Br₂) of III in benzene followed by treatment of the reaction mixture with aqueous acidic stannous chloride gave the brick red bisquinonemethide IV (ca. 45% yield, erratic), m.p. 306–308°^{6,9}. The infrared (λ_{max} 2.75, 6.30 μ) and ultra-

violet spectra⁸ ($\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ 385 μ (log ϵ 3.48), 478 (4.26)) of the product are in accord with the assigned structure.



Oxidation of an ethereal solution of IV with aqueous alkaline ferricyanide followed by concentration under nitrogen gave bisgalvinoxyl (I) as a dark crystalline solid with a metallic luster. Iodometric titration of various samples of oxidized IV indicated that 1.8–1.9 equiv. of hydrogen had been removed from IV. The sole product of this reduction, isolated in 86% yield, was IV. The infrared spectrum of I has a strong band at 6.35 μ as does galvinoxyl itself.¹⁰ Its ultraviolet spectrum is quite complex and the absorption of a 10⁻³ *M* solution extends out to 1.2 μ .¹¹ The biradical is fairly stable as a solid but dilute solutions (10⁻³–10⁻⁴ *M*) in inert solvents are bleached by air in a few hours. The stability of I seems comparable to that of galvinoxyl. It is possible to write a singlet structure for I which requires the formation of a biscyclopropylidene group in the center of the molecule. However, the steric strain inherent in this structure would probably preclude its formation. The infrared spectrum of I rules out the presence of any appreciable amount of this tautomer.

The e.p.r. spectrum of I in several glasses at 77°K. (originally 10⁻² *M* solutions) clearly indicates that it is a triplet species. In 2-methyltetrahydrofuran, the medium which gave the best results, we were able to resolve lines of comparable intensity at ± 56 and ± 72 gauss, with respect to the strong $g = 2$ line (at 3280 gauss) of the remaining monoradical. There is also a weaker pair of lines at ± 110 gauss. The splitting of these $\Delta m = 1$ transitions, using a model of two point dipoles,¹² indicates that the average interelectronic distance in I is ca. 6 Å. The presence of several lines is a consequence of the asymmetry of the molecule.¹³ The spectrum also has a weak $\Delta m = 2$ line at 1635 gauss. Its low intensity is in accord with the weak interelectronic interaction deduced from the $\Delta m = 1$ region of the spectrum.

We followed the e.p.r. spectrum of a CH₂Cl₂ solution of IV as it was oxidized by PbO₂ in a sealed, degassed system. The five-line, cleanly resolved ($a = 1.23$ gauss) spectrum of the monoradical appeared immediately. As oxidation proceeded the line width increased and the hyperfine of the monoradical was superposed on a broad (ca. 40 gauss) absorption. This spectrum

(1) In choosing a name for this somewhat elaborate structure we have put aside the official (*Chemical Abstracts*) rules and followed the principle expressed by Professor Bartlett [P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962)].

(2) S. I. Weissman, *Ann. Rev. Phys. Chem.*, **12**, 151 (1961); E. A. Chandross and R. Kreilick, *J. Am. Chem. Soc.*, **85**, 2530 (1963); **86**, 117 (1964).

(3) G. M. Coppinger, *Tetrahedron*, **18**, 61 (1962).

(4) N. C. Yang and A. J. Castro, *J. Am. Chem. Soc.*, **82**, 6208 (1960).

(5) D. Kearns and S. Ehrenson, *ibid.*, **84**, 739 (1962).

(6) Melting with decomposition in an evacuated capillary, uncorrected.

(7) *Anal.* Calcd. for C₂₈H₃₆O₄: C, 82.15; H, 10.23. Found: C, 82.46, 82.44; H, 10.27, 10.33.

(8) Extinction coefficient recorded as log ϵ .

(9) *Anal.* Calcd. for C₂₈H₃₂O₄: C, 82.60; H, 9.80; mol. wt., 843. Found C, 82.23, 82.02; H, 10.30, 10.47; mol. wt., 830.

(10) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957).

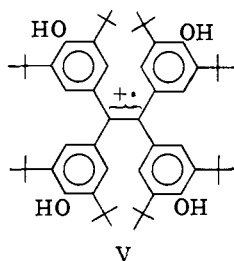
(11) The spectrum shows λ C₆H₁₂ 265 sh μ (log ϵ 4.0), 302 (4.2), 335 sh (4.1), 387 (4.5), 410 sh (4.5), 435 (4.7), 565 (4.0), and 800–900 (3.0). The bands at 410 and 435 μ may be due to monoradical; for the spectrum of galvinoxyl see the paper quoted in ref. 1.

(12) For the analogous case in n.m.r. see G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).

(13) The interpretation of the spectrum is based on the lines at ± 56 and ± 110 gauss. For the related spectrum of triplet naphthalene in a randomly oriented sample see W. A. Yager, E. Wasserman, and R. M. R. Cramer, *ibid.*, **37**, 1148 (1962). The lines at ± 72 gauss may be due to another conformation of the molecule which has been trapped in the glass.

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 work¹⁶ 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.



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.

(14) S. I. Weissman, *J. Chem. Phys.*, **29**, 1189 (1958).

(15) R. Wizinger, *Ber.*, **60**, 1377 (1927).

(16) Unpublished work with A. M. Trozzolo.

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RECEIVED DECEMBER 30, 1963

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

Sir:

As part of a study¹ 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 m μ (ϵ 8300), unchanged by the addition of mineral acid or base; $\lambda_{\max}^{\text{KBr}}$ 3.72, 5.99, 6.08, 6.31 μ ; $[\alpha]_D^{20}$ 0; pK = 5.05; neut. equiv. = 139; n.m.r. $[\text{CDCl}_3-(\text{CD}_3)_2\text{SO}] \tau$ 4.05, 5.06, 7.85, 8.25 p.p.m.,

(1) S. W. Tanenbaum, E. W. Bassett, and M. Kaplan, *Arch. Biochem. Biophys.*, **81**, 169 (1959).

(2) P. V. Divekar, P. E. Brenneisen, and S. W. Tanenbaum, *Biochim. Biophys. Acta*, **60**, 588 (1961).

relative intensity 1:1:3:3.³ *Anal.* Calcd. for $\text{C}_7\text{H}_5\text{O}_3$: 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°, $\lambda_{\max}^{\text{H}_2\text{O}}$ 297 m μ .⁴ *Anal.* Calcd. for $\text{C}_8\text{H}_{10}\text{O}_3$: 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°, $\lambda_{\max}^{\text{H}_2\text{O}}$ 293 m μ . *Anal.* Calcd. for $\text{C}_9\text{H}_{10}\text{O}_4$: 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 m μ , which underwent a hypsochromic shift to 279 m μ on the addition of sodium hydroxide. *Anal.* Calcd. for $\text{C}_8\text{H}_{11}\text{NO}_2$: 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 m μ , $\lambda_{\max}^{\text{EtOH-NaOH}}$ 278 m μ . 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 benzenoid⁷ and troponoid⁸ compounds by fungi. It is a structural analog of the dehydroacetic acid derivatives which recently have been suggested by Birch⁹ 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)].

(5) (a) J. A. Berson, *ibid.*, **74**, 5172 (1952); (b) J. A. Berson, W. M. Jones, and L. F. O'Callaghan, *ibid.*, **78**, 622 (1956).

(6) V. Prelog and S. Szpilvogel, *Helv. Chim. Acta*, **25**, 1306 (1942). We wish to thank Prof. V. Prelog for an authentic sample of 3,6-dimethyl-4-hydroxy-2-pyridone.

(7) F. Lynen and M. Tada, *Angew. Chem.*, **73**, 513 (1961).

(8) S. W. Tanenbaum and E. W. Bassett, *Biochim. Biophys. Acta*, **59**, 524 (1962).

(9) A. J. Birch, D. W. Cameron, and R. W. Rickards, *J. Chem. Soc.*, 4395 (1960). For an early suggestion to this type of compound see J. N. Collie, *ibid.*, 1806 (1907); and for other recent chemical analogies to fungal aromatic syntheses see J. R. Bethell and P. Maitland, *ibid.*, 3751 (1962).

(10) R. Thomas, *Biochem. J.*, **78**, 748 (1961).

(11) G. Ehrensvar, *Exptl. Cell. Res. Suppl.*, **3**, 192 (1955).