

structural proof of **6** (and thereby also of **5**) was given by the X-ray analysis of **12**. The crystal structure of **5** itself has not been solved so far.^{8b}

It is obvious that the present findings—besides being relevant to the problem of bicyclobutane hydrogenolysis—have several other points of interest. For example, an easy access to the novel, biologically active 8 α -methyleneestrane system is provided and the sequence exemplified by **9** \rightarrow **5** \rightarrow **6** \rightarrow **11** offers considerable potential as a method for introducing angular methyl (or CH₃-d₁₋₃) groups. Both the scope of this method as well as further aspects of the reactivity of **5** are under active investigation.

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* Address correspondence to this author.

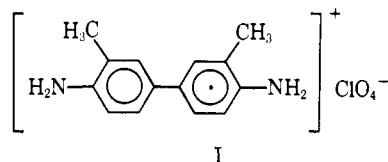
Eugene Galantay,* Nicholas Paoella
Sandor Barcza, Robert V. Coombs
Pharmaceutical Research, Sandoz-Wander, Inc.
Hanover, New Jersey 07936

Hans Peter Weber
Physicochemical Laboratories, Pharmaceutical Division
Sandoz A.G., 4000 Basle 13, Switzerland
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On the Electrogeneration and Characterization of a Stable, Solid, Ionic Free Radical

Sir:

We wish to report the direct electrogeneration of a stable, solid, ionic organic free radical. This entity is prepared in greater than 90% current yield by electrooxidation at a platinum anode of 3,3'-dimethyl-4,4'-diaminobiphenyl (*o*-tolidine) in methylene chloride containing tetraethylammonium perchlorate (TEAP). The blue-black electrolysis product of *o*-tolidine (*o*-T) under these conditions adheres tenaciously to the electrode surface as it is formed, yet does not "block" the electrode surface with respect to continued electrooxidation of *o*-T. The progress of the reaction is followed by spectral monitoring of the decrease of *o*-T or by the decrease in current under potentiostatic electrolysis conditions. Following exhaustive electrooxidation, the electrode product is mechanically removed from the anode. Elemental microanalysis of this material shows it to be the *o*-T analog of Wurster's Blue perchlorate, namely, **I** (*Anal.* Calcd for C₁₄H₁₆N₂O₄Cl: N, 9.00; Cl, 11.37. Found: N, 9.52;



Cl, 10.77). The composition of the electrolysis product is independent of the oxidation potential from +0.5 to +0.8 V *vs.* sce.

The electrochemistry of *o*-T was examined in a solvent in which compound **I** is soluble. Thus in acetonitrile (AN) containing TEAP, cyclic voltammetry at a platinum electrode shows that *o*-T is oxidized in two

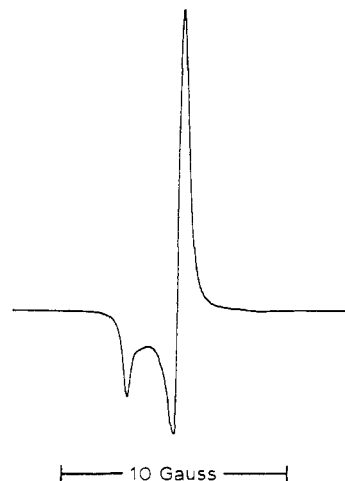
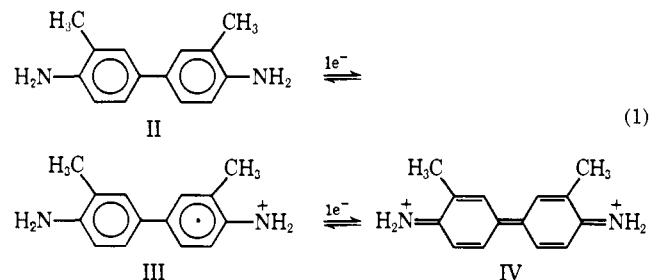


Figure 1. The esr powder spectrum of **I** in dry KCl; concentration is 0.32% by weight; temperature = 40°; $g_{||} = 2.0037$; $g_{\perp} = 2.0021$.

steps with peak potentials of 0.5 and 0.7 V *vs.* sce. Controlled-potential coulometry shows that each of these two steps involves the heterogeneous transfer of one electron per molecule, as has been observed for *o*-T in aqueous acidic medium,¹ corresponding to the



respective formation of the cation radical and diimine of *o*-T. The spectral characteristics of compounds **II**–**IV** are summarized in Table I. The hyperfine electron spin resonance (esr) spectrum of **III** is observed for both *in situ* and external electrooxidations of *o*-T in degassed AN containing TEAP. More than 60 lines are resolved with a total spectrum width of 38 G having $\langle g \rangle = 2.0023$.

Dissolution of the titled material (**I**) in AN gives rise to visible and hyperfine esr spectra which are identical with those obtained through direct electrooxidation of *o*-T in AN.

The solid-state esr spectrum of polycrystalline **I** in dry KCl is shown in Figure 1. The temperature dependence of this magnetic resonance spectrum of 1.0×10^{-4} M **I** in KCl is shown in Figure 2. This change in paramagnetism with temperature is analogous to that found in the case of Wurster's Blue (WB) perchlorate²⁻⁷ with the "transition temperature" of **I** occurring at *ca.* 335°K as opposed to 186°K for WB perchlorate. These results suggest that a dimerization of **I** occurs in the solid state as reported by McConnell,

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Table I. Absorption Maxima in Acetonitrile^c

Compd	λ , Å	$10^{-4}\epsilon$	λ , Å	$10^{-4}\epsilon$	λ , Å	$10^{-4}\epsilon$	λ , Å	$10^{-4}\epsilon$	λ , Å	$10^{-4}\epsilon$
II	2860 (2820)	3.2 (2.9)								
III	3660 ^a (3650) ^a	0.9 ^b (4.8)	4255	1.0 ^b	4450	1.2 ^b	4565	1.3 ^b	6400 ^a (6300) ^a	0.5 ^b (2.8)
IV	4400 (4370)	6.2 (6.2)								

^a Dimer bands as discussed in text. ^b Relative molar absorptivities at 25° where the equilibrium constant, K , for the disproportionation process $II + IV \rightleftharpoons 2III$ has a value of 3.2×10^3 . ^c Parenthetical values are for *o*-T in aqueous solution, ref 1.

et al.,⁸⁻¹⁰ and others¹¹⁻¹³ for WB perchlorate. In 2:1 ethanol-ether solution, the hyperfine esr spectrum of I (the cation radical of *o*-T) was examined as a function of temperature. This dependence is shown in Figure 2. This behavior is also analogous to the WB perchlorate case as reported by Kawamori, *et al.*,¹⁴ and suggests a

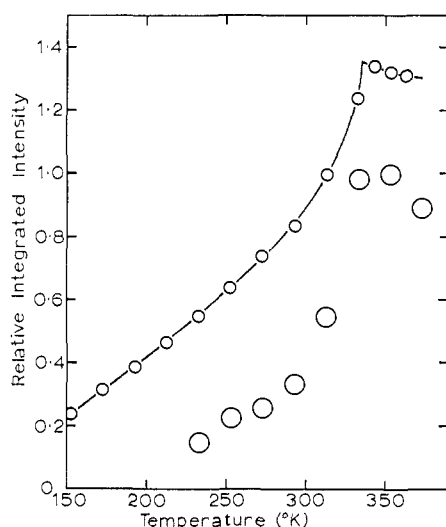


Figure 2. Temperature dependence of the integrated esr spectral intensities for $1.0 \times 10^{-4} M$ I in dry KCl (small circles) and $6 \times 10^{-4} M$ I in 2:1 ethanol-ether (large circles).

dimerization of the cation radical of *o*-T. Further evidence in support of this suggestion is provided by the concentration and temperature dependence of the visible spectrum of either I or electrogenerated *o*-T⁺ in both AN and ethanol-ether, the bands shown in Table I at 3660 and 6400 Å decreasing with both increasing temperature and decreasing concentration. The solution dimerization of *o*-T⁺ has also been observed in aqueous acidic medium, and a solid electrolysis product (presumably dimer) has also been noted.¹ The nature of the solution dimerization process is quite probably the formation of a charge-transfer complex.^{15,16}

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Assuming a dimerization mechanism, the temperature dependence of the integrated esr spectral intensities indicates that the enthalpy of the dissociation process is approximately 4 kcal mol⁻¹ for I both in solid KCl and in ethanol-ether solution.

The electropreparation and chemical and structural characterization of a series of these solid, stable, ionic free radicals are in progress.

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* Address correspondence to this author at the Department of Chemistry, The University of Delaware, Newark, Del. 19711.

Henry N. Blount,* Theodore Kuwana

Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

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Synthesis of Aldehydes and Secondary Amines from Carboxylic Acids via Imines¹

Sir:

Burgstahler, Worden, and Lewis² have reported the reduction of carboxylic acids with lithium in ethylamine to a mixture of alcohols and aldehydes, the latter having been isolated in most cases as their 2,4-dinitrophenylhydrazone derivatives. They made no effort to develop this reaction as a general synthetic route to aldehydes. Since it has been shown in these laboratories that the reduction of carboxylic acids can be stopped cleanly at the aldehyde stage,³ it was felt that further investigation of the reaction for use as a synthetic method was warranted.

Multigram quantities of carboxylic acids were used and the aldehydes were isolated in pure form rather than as derivatives. Glpc of the reduction product showed that little if any alcohol was present. A significant result of the investigation was the identification of an imine⁴ formed during the product isolation

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(3) This material was presented in part at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, and the 21st Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., Nov 1969.

(4) Imines had previously been isolated from lithium-methylamine reductions of furans in this laboratory (A. O. Bedenbaugh, J. H. Bedenbaugh, J. D. Aakins, and W. A. Bergin, *J. Org. Chem.*, **35**, 543 (1970)).