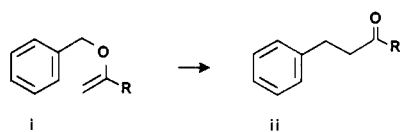


matropic rearrangement of 3-indoleglycolic acid derivatives as the key step in a general scheme for the total synthesis of indole alkaloids; further investigations concerning the use of the [3,3] sigmatropic rearrangement for the regiospecific synthesis of other substituted arenes are also in progress.

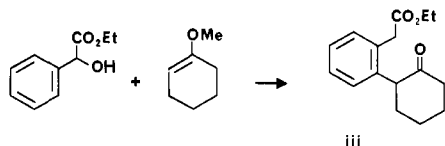
Acknowledgment. This research was supported in part by an M. J. Murdock Charitable Trust Grant of Research Corporation, and by the University of Washington Graduate School Research Fund.

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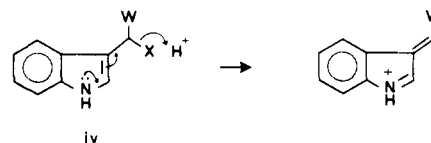
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- (5) It is noteworthy that, when W = carbonyl, 2 is vinylogously related to the cyclohexadienone which is initially formed in the [3,3] sigmatropic rearrangement of allyl phenyl ethers.
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 - (8) We have also effected Claisen rearrangement of ethyl mandelate with 1-methoxycyclohexene to give iii.



- (9) In marked contrast, reaction of benzyl alcohol with triethyl orthoacetate, under the same conditions used for ethyl mandelate, gave predominantly benzyl diethyl orthoacetate accompanied by small amounts of ethyl 3-phenylpropionate and ethyl *o*-methylphenylacetate (presumably via radical processes; cf. ref 4b-d).
- (10) (a) A typical experimental procedure follows. A solution of ethyl mandelate (2.00 mmol), triethyl orthoacetate (16 mmol), and hexanoic acid (0.20 mmol) in a 50-mL flask fitted with a 15-cm Vigreux column topped with a short-path distillation head was heated at 220 °C for 12 h in an argon atmosphere; ethanol was allowed to distil out of the reaction solution as it was formed. The Vigreux column was removed, the short-path distillation head was placed on the reaction flask, and heating was continued at 185 °C for 8 h. Excess ortho ester was removed (35 °C, 1 mm) and the residue was purified by chromatography on silica gel (30 g, hexane-ether eluent), followed by evaporative distillation (120 °C, 0.002 mm) to give diethyl *o*-benzenediacetate (6a) as a colorless liquid (210 mg, 84%): ¹H NMR (CCl₄) δ 1.15 (t, J = 7 Hz, 6 H), 3.60 (s, 4 H, ArCH₂-), 4.08 (q, J = 7 Hz, 4 H), 7.13 (s, 4 H); IR (neat) ν 1740 cm⁻¹. Anal. (C₁₄H₁₆O₄) C, H, O. Found *m/e* 250.1196. (b) All new compounds were fully characterized by spectroscopic methods. Yields are given for isolated products purified by column chromatography (silica gel) followed by evaporative distillation and are not optimized. The unrearranged mixed ortho ester of 4 and 5 (10–20%) and tarry polymers comprise the remainder of the mass balance; no other characterizable products were isolated. (c) Additional ¹H NMR data (CCl₄): 6b, δ 1.15 (t, J = 7 Hz), 1.23 (t, J = 7 Hz), and 1.46 (d, J = 7 Hz, CH₂CH) (total 9 H), 3.71 (AB, J = 16 Hz, Δν = 0.40 ppm, ArCH₂CO₂Et) and 3.95–4.40 (m) (total 7 H), 7.20–7.40 (m, 4 H); 6c, 1.08–1.36 (two overlapping t) and 1.28 (s) (total 12 H), 3.90–4.32 (m, 6 H), 7.38 (s, 4 H). ¹H NMR data (CDCl₃): 8a, δ 1.16 (t, J = 7 Hz) and 1.27 (t, J = 7 Hz) (total 6 H), 2.33 (s, 3 H, *p*-CH₃Ar), 3.67 (s, 2 H, 3-indolyl-CH₂CO₂Et), 3.9–4.4 (two overlapping q), and 4.20 (s, 2-indolyl-CH₂CO₂Et) (total 6 H), 7.0–8.2 (m, 8 H);

8b, δ 1.18 (t, J = 7 Hz, 3 H), 2.30 (s, 3 H, *p*-CH₃Ar), 3.66 (s, 3-indolyl-CH₂CO₂Et) and 3.72 (s, CO₂CH₃) (total 5 H), 4.10 (q, J = 7 Hz, CO₂CH₂) and 4.20 (s, 2-indolyl-CH₂CO₂Me) (total 4 H), 7.1–8.2 (m, 8 H); 8c, δ 1.17 (t, J = 7 Hz) and 1.20 (t, J = 7 Hz) (total 6 H), 1.60 (d, J = 7 Hz, 2 H, CH₂CH<), 2.34 (s, 3 H, *p*-CH₃Ar), 3.68 (s, 2 H, 3-indolyl-CH₂CO₂Et), 3.8–4.3 (two overlapping q, 4 H), 4.95 (q, J = 7 Hz, 1 H, 2-indolyl-CH(CH₃)CO₂Et), 7.1–8.2 (m, 8 H); 8d, δ 2.35 (s, 3 H, *p*-CH₃Ar), 2.95 (br s, 6 H, N(CH₃)₂), 3.73 (two overlapping s, 5 H, 3-indolyl-CH₂CONMe₂ and CO₂CH₃), 4.20 (s, 2 H, 2-indolyl-CH₂CO₂Me), 7.1–8.2 (m, 8 H). Additional data: Anal. (C₁₅H₂₀O₄, 6b) C, H, O. Found *m/e* 264.1328. Anal. (C₁₆H₂₂O₄, 6c) C, H, O. Found *m/e* 278.1516.

- (11) Substituted ethyl mandelates may be prepared either from the corresponding cyanohydrins, which are, in turn, readily available from aromatic aldehydes, or by NaBH₄ reduction of ethyl phenylglyoxylates prepared from arenes by Friedel-Crafts acylation with ethyl oxalyl chloride.
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- (15) Prepared from ethyl 3-indoleglyoxylate or *N,N*-dimethyl-3-indoleglyoxamide by reaction with NaH-TsCl, followed by reduction with NaBH₄.
- (16) (a) The protection of the indole nitrogen with the electron-withdrawing tosyl group was found to be essential. Reaction of either ethyl 3-indoleglycolate (iv, W = CO₂Et) or 3-indolemethanol (iv, W = H) with triethyl orthoacetate



(30 equiv) and hexanoic acid (0.1 equiv) at 120 °C led to rapid and extensive decomposition, possibly by the pathway involving the unshared electrons on nitrogen which is depicted below (X = -OC(OEt)₂CH₃ or -OH). (b) For related pathways, see E. Leete, *J. Am. Chem. Soc.*, **81**, 6023 (1959), and references therein.

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- (18) ¹H NMR (CDCl₃): δ 1.53 (s, 3 H, CH₃C(OMe)₂OR), 2.28 (s, 3 H, *p*-CH₃Ar), 3.30 (s, 6 H, C(OCH₃)₂), 4.72 (s, 2 H, -CH₂O-), 7.0–8.2 (m, 8 H).

Stanley Raucher,* Alfred S.-T. Lui

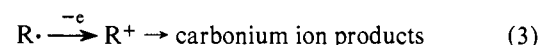
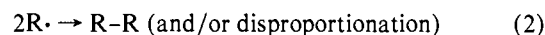
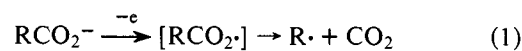
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Direct Observation of Radical Intermediates in the Photo-Kolbe Reaction—Heterogeneous Photocatalytic Radical Formation by Electron Spin Resonance

Sir:

Many electroinitiated chemical reactions are thought to proceed via radical intermediates. For example, the widely studied Kolbe reaction of carboxylates¹ is believed to follow the mechanism



The mechanistic details of this electrooxidative decarboxylation are still a matter of controversy.² Not only does the hypothetical primary product of electron transfer, the acyloxy radical (RCO₂·), rapidly split into CO₂ and a hydrocarbon

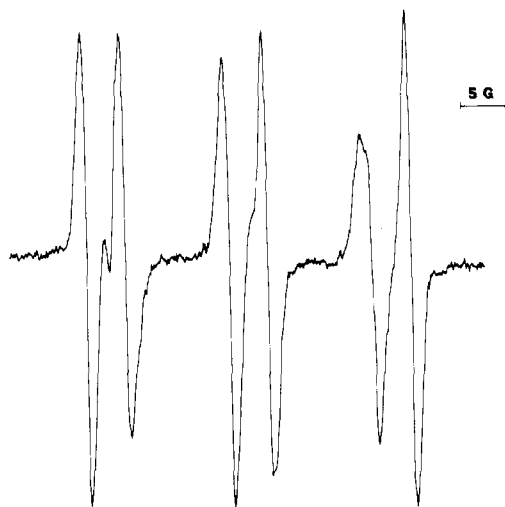
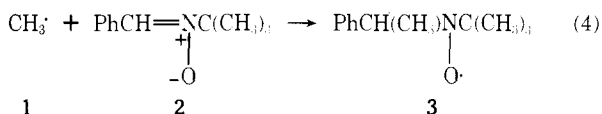


Figure 1. ESR spectrum observed during illumination of a degassed suspension of TiO_2 powder in acetic acid containing 0.02 M α -phenyl-*n*-tertbutylnitron (PBN): the methyl radical adduct with PBN.

radical, $\text{R}\cdot$, but the secondary radical $\text{R}\cdot$ also has only a transient existence. In fact neither radical has been observed directly in electrochemical Kolbe reactions,³ although the isolation of dimers, $\text{R}-\text{R}$, and the similarity of product distributions in preparative homogeneous radical initiated and electroinitiated decarboxylations⁴ strongly point to the intermediacy of $\text{R}\cdot$ as a transient free solution species. Our recent discovery of a heterogeneous, photoassisted decarboxylation of acetate ions to yield ethane at an illuminated TiO_2 electrode, the "photo-Kolbe reaction",⁵ and the closely related studies of the photocatalytic decomposition of acetic acid solutions to form methane and CO_2 on illuminated TiO_2 powder⁶ provided a completely new type of oxidative decarboxylation reaction. We proposed that these reactions occurred via the formation of intermediate radicals and, to test this reaction sequence, sought direct confirmation by electron spin resonance (ESR) spectroscopy. We report here the first observation of radical intermediates ($\text{R}\cdot$) in a Kolbe-type reaction by ESR.

Two carboxylic acids, acetic and triphenylacetic acid, were decarboxylated via the photo-Kolbe reaction to yield a highly reactive methyl and a persistent triphenylmethyl radical, respectively. While the former was detected using the spin trapping technique^{7,8} as an adduct with a nitron (eq 4), the latter could be observed directly as a free radical. Experi-



mentally a flat quartz ESR cell which had a two-compartment side arm was used. Approximately 200 mg of photoplatinized TiO_2 ⁹ powder was placed in one compartment. The other compartment contained the reaction solution consisting of 0.02 M α -phenyl-*N*-tert-butyl nitron (PBN) in glacial acetic acid. The cell was degassed several times and filled with prepurified helium (~ 600 Torr). First, only the reaction solution was poured from its compartment into the flat ESR cell, which was then inserted into the cavity of the ESR spectrometer (Varian E9). A (dark) background spectrum of this solution taken at the highest receiver gain showed no ESR spectrum. The sample was illuminated with a 400-W tungsten lamp. Two glass filters, (1) Oriel G-772-4750, 50% transmittance (T) at 500 nm and $<1\%$ T at 465 nm, and (2) Oriel G-772-3900, 50% T at 395 nm and $<1\%$ T at 360 nm, were used in all experiments. In addition to the filters, the light was focused through the metal grid of the ESR cavity which passed $\sim 40\%$ of the light. Illumination of the reaction solution through either filter 1 or 2

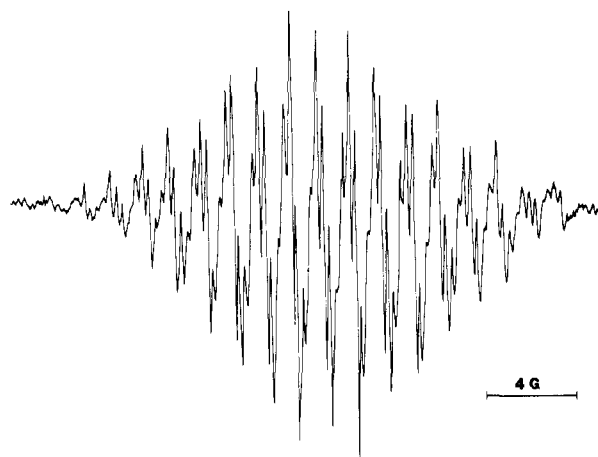


Figure 2. ESR spectrum of triphenylmethyl radical produced by heterogeneous photocatalytic decarboxylation of tetra-*n*-butylammonium triphenylacetate on TiO_2 powder.

produced no ESR spectrum. Next, the platinumized TiO_2 powder was mixed with the reaction solution and the mixture poured into the ESR cell. A (dark) background spectrum of this suspension showed only a very broad structureless peak associated with the doped anatase powder (centered around $g = 2.00 \pm 0.05$, with a line width of 500 ± 25 G). When the scan range was reduced to 100 G, this background signal was relatively flat. Illumination of the sample using filter 1 gave no ESR spectrum. Upon illuminating using filter 2, however, the typical six-line spectrum of a nitroxide radical (3) appeared slowly and reached a photostationary intensity after several minutes. The signal decayed slowly when the illumination was turned off. The spectrum (Figure 1) shows coupling constants, $a_{\text{N}} = 15.85 \pm 0.1$ G and $a_{\text{H}} = 4.75 \pm 0.1$ G, which are slightly larger ($\sim 8\%$) than those reported for 3 in benzene ($a_{\text{N}} = 14.79$ G and $a_{\text{H}} = 3.73$ G).¹⁰ The slightly larger values are consistent with the known dependence of N and β -H coupling constants on solvent and can be attributed to the effect of hydrogen bonding in HOAc on the spin density in nitroxide radicals.¹¹ Illumination of only PBN in benzene under the same experimental conditions gave no ESR spectrum. The reported photochemical oxidation of PBN by ultraviolet irradiation^{12,13} does not appear to occur under our experimental conditions. Thus the previously postulated intermediacy of methyl radicals^{5,6} in the photo-Kolbe reaction of acetate appears established.¹⁴

In another series of similar experiments, the reaction solution consisted of a saturated solution of triphenylacetic acid and tetra-*n*-butylammonium triphenylacetate (TBATPA)¹⁵ (1:1, total ~ 3 M) in acetonitrile (ACN). No ESR spectrum was observed for the reaction in the dark or upon illumination with the 400-W tungsten lamp using filters 1 or 2 in the absence of the TiO_2 . Again a suspension of platinumized TiO_2 powder in this reaction solution showed only the previously described broad structureless background signal in the dark.¹⁶ Upon illumination with the 400-W tungsten lamp and filter 1, no ESR spectrum was observed. Illumination of the sample using filter 2 resulted in a signal that could be assigned to the triphenylmethyl radical, $\text{Ph}_3\text{C}\cdot$. After ~ 30 min the spectrum was relatively stationary in intensity and clearly discernible (Figure 2). This spectrum closely matches that reported for $\text{Ph}_3\text{C}\cdot$ in benzene¹⁷ and is practically undistinguishable from the spectrum of this radical obtained previously in this laboratory^{3b} by a two-step (oxidation + reduction) electrolysis of triphenylacetic acid in ACN. When a saturated solution of triphenylacetic acid and TBATPA in acetonitrile containing 0.02 M PBN was illuminated with a 450-W xenon lamp, a weak set of signals appeared, apparently consisting of the superposition of two spectra, probably a nitroxide radical and the

triphenylmethyl radical. Only a short illumination (10 min at $\leq 50^\circ\text{C}$) with a more powerful light source, a 2500-W xenon lamp (operated at 1600-W), filtered through Pyrex, brought about a dramatic intensification of the signals. Again signals from two species were found; one (of stationary intensity) could be assigned to $\text{Ph}_3\text{C}^\cdot$, while the other (which decayed in the dark at room temperature) showed the typical six-line pattern of a spin adduct on the nitron (PBN).¹⁸ Irradiation of a sample that did not contain TiO_2 and PBN using both the 2500 and 450-W xenon lamps produced no ESR spectrum. The photo- and thermal decomposition of triphenylacetate¹⁹⁻²¹ does not occur under the given experimental conditions.

These experimental results clearly establish the existence of methyl and triphenylmethyl radicals as heterogeneously (on TiO_2) photogenerated radical intermediates in the photo-Kolbe reaction. As expected,^{5,6} there is a close mechanistic parallel between the oxidation step in the photo- and electrochemical-Kolbe reactions. However, the generally high current densities and oxidation potentials in the latter reactions, as well as the possible strong adsorption of the radicals on the solid electrodes, have not allowed their detection by ESR up until now.³ On the other hand, the low surface density of the photogenerated radicals on the TiO_2 powder, together with the unimportance of follow-up oxidations in these reactions (because two-hole oxidations are improbable), permits the detection of the intermediate radicals here. Since many photoinduced oxidation reactions are known on n-type semiconductor materials, such as n- TiO_2 , the study by ESR of photogenerated intermediate radicals on partially platinized semiconductor powders should provide a useful tool in the investigation of photoredox processes on these materials.²²⁻²³ Moreover, heterogeneous photocatalysis could provide a generally useful method for generating reactive radicals for study by ESR.²⁴

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- Produced by mixing equimolar amounts of triphenylacetic acid (Aldrich Chemical Co.) in methanol and tetra-*n*-butylammonium hydroxide (Southwestern Analytical Chemicals), evaporation of solvents at room temperature, and drying at room temperature for 1 week under high vacuum.
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- This nitroxide spectrum, with $a_N = 14.88 \pm 0.1$ G and $a_H = 2.75 \pm 0.1$ G, resembles the reported spectrum for the acetoxy adduct ($a_N = 13.88$ G, $a_H = 1.99$ G).¹⁰ Trapping of the triphenylacetoxy radical is thus possible

as the alternative, trapping of trityl radical by PBN, has been shown not to occur.⁷

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- The support of this research by the Schweizerische Nationalfonds zur Foerderung der wissenschaftlichen Forschung (to B.K.) and by the National Science Foundation and the Robert A. Welch Foundation is gratefully acknowledged.

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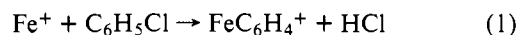
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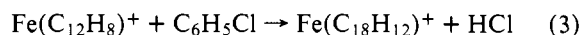
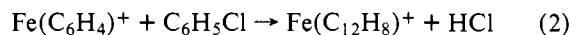
Fe^+ Induced Dehydrohalogenation and Polymerization of Phenyl Halides in the Gas Phase

Sir:

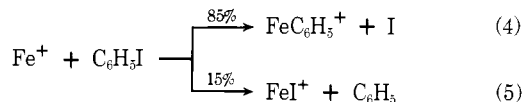
In the gas phase atomic transition metal ions react with a number of alkyl halides by insertion into the carbon-halogen bond.^{1,2} If the alkyl group has β -hydrogen atoms, the metal insertion complex loses HX to form a metal ion-olefin complex. In the case of methyl halides, however, M^+ reacts to form MCH_3^+ and MX^+ .^{1,2} It might be expected that aryl halides would react as the methyl halides do since elimination of HX from an aryl halide is a very high energy process. We wish to report, however, the following reaction between Fe^+ and chlorobenzene:



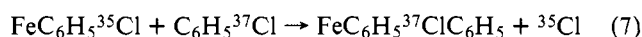
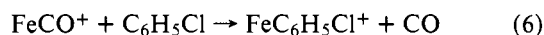
The Fe^+ is formed by electron impact on $\text{Fe}(\text{CO})_5$ and the reactions observed at low pressures ($\sim 10^{-6}$ Torr) in an ion cyclotron resonance spectrometer.³ Double-resonance techniques establish³ that reaction 1 is a bimolecular process between the indicated reactants. The mass of the product of the analogous reaction of $\text{C}_6\text{D}_5\text{Cl}$ verified the hydrogen content of the product. The rate constants for the reaction are within an order of magnitude of the reactant collision frequencies ($\sim 10^{-9}$ cm^3 molecule⁻¹ s⁻¹). Furthermore, the following reactions succeed reaction 1.



Reactions of fluorobenzene and bromobenzene are analogous to reaction 1. Iodobenzene, however, reacts according to



The products of reactions 4 and 5 are most readily rationalized in terms of a metal insertion followed by cleavage of either the metal-carbon bond or metal-iodine atom bond. The possibility that metal insertion plays a role in the mechanism of reaction 1 is suggested by the following series of reactions:



Double resonance establishes that the indicated isotopic variants of the reactants of reaction 7 give only the indicated isotopic variants of the products. If the product of reaction 6 is envisioned as $\text{C}_6\text{H}_5\text{-Fe-Cl}^+$, then elimination of a Cl atom