O
$\parallel$ ... $\xrightarrow{h\nu}$ ... $CH=CHCH_3$ +

10   cis and trans

O ... O ... HO

+ ... + ... + ... (5)

cis and trans

11

From these observations we conclude that the rearrangements of α-methylene ketones generalized in eq 3 and 4 involve singlet biradical intermediates.[11] For the γ-hydrogen abstraction leading to cyclobutyl ketones these intermediates must have a lifetime sufficient to permit the rotation about the α,β carbon–carbon bond required for ring closure. It is noteworthy in this regard that evidence is on record favoring short-lived biradical intermediates in the singlet γ-hydrogen abstraction reactions of saturated alkanones[12] and also implicating longer-lived singlet biradicals as intermediates in the related abstraction processes of β,γ-unsaturated ketones.[13,14]

(11) A theoretical discussion detailing the oversimplifications inherent in use of simple structures for such species is given by L. Salem and C. Rowland, *Angew. Chem.*, **84**, 86 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(12) L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *J. Amer. Chem. Soc.*, **93**, 1984 (1971); C. P. Casey and R. A. Boggs, *ibid.*, **94**, 6457 (1972).

(13) J. C. Dalton and H.-F. Chan, *J. Amer. Chem. Soc.*, **95**, 4085 (1973). See also P. S. Engel and M. A. Schexnayder, *ibid.*, **94**, 9252 (1972).

(14) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Russell A. Cormier, William C. Agosta*

Laboratories of The Rockefeller University
New York, New York 10021

Application of Spin Trapping to the Detection of Radical Intermediates in Electrochemical Transformations

Sir:

Radicals are postulated as intermediates in many electrochemical transformations.[1] Because many of the radicals so generated are too short-lived to be observed directly by electron spin resonance (esr) spectroscopy, most of these postulates are based upon n values and product analyses. We now report development of a new approach that permits direct spectroscopic detection and characterization of electrochemically generated free radicals and circumvents the laborious product analyses required in previous methods.

Janzen has reported that short-lived free radicals can be trapped by reaction with a nitrone to yield stable nitroxide radicals (eq 1) which can be identified by esr

$$R\cdot + C_6H_5CH=\overset{\uparrow}{N}C(CH_3)_3 \longrightarrow C_6H_5CH\overset{|}{N}C(CH_3)_3 \quad (1)$$

1   **2**
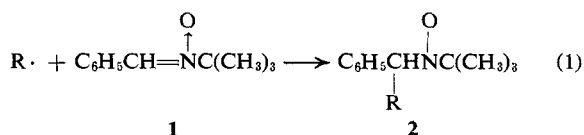
(1) A. P. Tomilov and M. Ya. Fioshin, *Russ. Chem. Rev.*, **32**, 30 (1963).

spectroscopy.[2] It appeared likely that this approach to spin trapping could be extended to electrochemically generated radicals assuming (1) that the technique was successful in solvents compatible with electrochemistry and (2) that the nitrone and nitroxides were electroinactive in useful potential ranges.

The potential of this trapping procedure was tested in an electrochemical environment by thermally decomposing phenylazotriphenylmethane, a source of the short-lived phenyl radical, in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP) and α-phenyl-N-tert-butylnitrone (PBN, **1**). A six-line esr spectrum was obtained (a_N = 14.72 G, a_H = 2.72 G) which closely matches that reported for **2** (R = C_6H_5) (a_N = 14.48 G, a_H = 2.17 G) in benzene.[3] The slightly larger coupling constants in acetonitrile are to be expected.[4] Spin trapping thus is feasible in an electrochemical solvent.

The electrochemical limits imposed by oxidation or reduction of PBN and the resulting nitroxide, **2**, are gratifyingly minor. Cyclic voltammetry indicated that PBN is electroinactive between 1.5 and -2.4 V (*vs.* sce). Although electrochemical data on the nitroxide **2** were not as definitive, cyclic voltammetry of solutions of it prepared in various ways as well as recent reports[5] indicated that the nitroxide resulting from phenyl radical trapping should be electroinactive between 0.7 and -2.0 V.[6]

The electrochemical reduction of aryl diazonium salts was chosen for our initial studies. This reaction has been postulated to proceed *via* a free-radical intermediate, using the criteria of n value and product analyses, both in aqueous[7,8] and in aprotic[9–13] media. For example, reduction of various diazonium tetrafluoroborates in sulfolane afforded n values near unity;[8] reduction in acetonitrile containing an aromatic substrate gave biaryls which had isomer ratios and partial rate factors which agreed well with those from thermal decomposition of benzoyl peroxide and N-nitrosoacetanilide, established sources of phenyl radical.[10]

Phenyldiazonium tetrafluoroborate (0.01 M) was reduced in acetonitrile containing 0.1 M TBAP at a stirred mercury pool cathode using a platinum auxiliary electrode (fritted compartment) and an aqueous sce reference electrode (fritted compartment) in the presence of PBN (0.01 M).[14] The solution was cooled in an

(2) E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971), and references cited therein.

(3) A. L. Bluhm and J. Weinstein, *J. Org. Chem.*, **37**, 1748 (1972). The coupling constants originally reported by E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, **91**, 4481 (1969), have been corrected to give comparable values (E. G. Janzen, personal communication).

(4) Y. Takaya, G. Matsubayashi, and T. Tanaka, *Inorg. Chim. Acta*, **6**, 339 (1972). The coupling constants obtained by us for the trapping experiment in benzene are identical with those reported.[3] The increase is apparently due only to a solvent effect.

(5) M. Tsunga, C. Iwakura and H. Tamura, *Electrochim. Acta*, **18**, 241 (1973).

(6) Our data on 2,2,6,6-tetramethyl-4-acetamidopiperidine-1-oxyl agree with those for the unsubstituted compound.[5]

(7) J. K. Kochi, *J. Amer. Chem. Soc.*, **77**, 3208 (1955).

(8) R. M. Elofson, *Can. J. Chem.*, **36**, 1207 (1958).

(9) R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, **34**, 854 (1969).

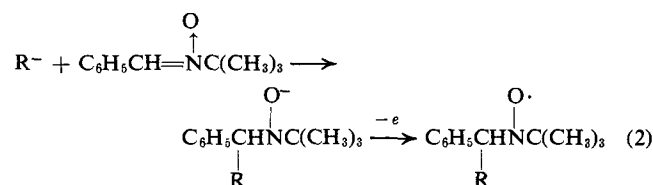(10) F. F. Gadallah and R. M. Elofson, *J. Org. Chem.*, **34**, 3335 (1969).

(11) R. M. Elofson, F. F. Gadallah, and K. F. Schulz, *J. Org. Chem.*, **36**, 1527 (1971).

(12) R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, **36**, 1769 (1971).

(13) F. F. Gadallah, A. A. Cantu, and R. M. Elofson, *J. Org. Chem.*, **38**, 2386 (1973).

ice bath, and the potential was maintained at -0.2 V for 5 min; an aliquot was removed by syringe under positive helium pressure. The aliquot was injected into an esr cell and was purged with nitrogen to remove traces of oxygen. This solution gave a very strong esr signal corresponding to the adduct 2 (R = C_6H_5) of phenyl radical with PBN. A control experiment run under identical conditions except that no current was passed gave no esr signal under very sensitive spectroscopic conditions. A subsequent 5-min electrolysis of this solution at -0.2 V gave the same strong signal observed before. In another control experiment, a solution was prepared as before except that no diazonium salt was present. This solution showed no esr signal after electrolyzing at -0.2 V for 5 or 35 min.

The formation of the nitroxide 2 (R = C_6H_5) during the reduction of the diazonium salt in the presence of PBN does not in itself conclusively require that electrochemical reduction of the diazonium salt gives phenyl radical as an intermediate. Another conceivable mechanism is an initial *two-electron* reduction of the diazonium salt to a phenyl anion which then adds to PBN to produce the anion of the corresponding hydroxyl amine (analogous to reaction of PBN with phenyllithium[2]). This anion could be oxidized to the nitroxide electrochemically or by diazonium ion (eq 2).[15]

$$R^- + C_6H_5CH=\overset{\overset{O}{\uparrow}}{N}C(CH_3)_3 \longrightarrow$$

$$C_6H_5\underset{\underset{R}{\mid}}{\overset{\overset{O^-}{\mid}}{CH}}NC(CH_3)_3 \xrightarrow{-e} C_6H_5\underset{\underset{R}{\mid}}{\overset{\overset{O\cdot}{\mid}}{CH}}NC(CH_3)_3 \quad (2)$$

It was felt that the phenyl anion, if formed, could be trapped by addition to CO_2. This process would result in an n value of 2 and in the isolation of benzoic acid as a product. The validity of this latter expectation was tested chemically by injecting a solution of phenyllithium into acetonitrile containing TBAP and saturated with CO_2. Surprisingly, analysis of this mixture showed no benzoic acid but did give acetophenone in 25% yield.[16] This product presumably arises by attack of phenyllithium on acetonitrile.

Electrochemical reduction of phenyldiazonium tetrafluoroborate in the presence of CO_2 using both TBAP and $LiClO_4$ as supporting electrolytes gave *no* detectable amounts of either benzoic acid or acetophenone. The products consist of unidentified tarry material and mercury-containing compounds as observed by Kochi.[7] Benzene is formed in 35–40% yield. Coulometry gave n values of 1.15 and 1.28 for two experiments. In the absence of CO_2, the n value for the reduction was 1.24.

We feel, therefore, that observation of 2 (R = C_6H_5) is a consequence of reaction between PBN and phenyl

(14) Cyclic voltammetry of phenyldiazonium tetrafluoroborate in acetonitrile containing 0.1 M TBAP at a platinum cathode indicated that electrode fouling occurred after a single scan. This problem prevented our reductions being done at a platinum working electrode. Employing a hanging mercury drop electrode, cyclic voltammetry showed a poorly defined reduction peak at approximately -0.2 V vs. sce. This evidence as well as literature reports[9] indicated that the reductions could be carried out satisfactorily at -0.2 V.

(15) The anionic mechanism is compatible with an overall n value of 1 although the initial reduction is a two-electron process.

(16) Use of phenylmagnesium bromide in place of phenyllithium resulted in isolation of benzoic acid in 85% yield.

radical and not phenyl anion and demonstrates the applicability of spin trapping to detection of electrochemically generated free radicals. The technique appears to be suitable for electrochemical reactions occurring over the approximate range of 0.7 to -2.0 V. We are planning to extend this procedure to other systems in which free-radical intermediates are generated as a result of electrochemical processes.

Allen J. Bard,* John C. Gilbert,* Richard D. Goodin
*Department of Chemistry, University of Texas
Austin, Texas 78712*

Stereoselective Formation of the anti-7-Benzonorbornadienyl Grignard Reagent

Sir:

Both cycloaddition of benzyne to cyclopentadienylmagnesium bromide[1] and reaction of anti-7-chlorobenzonorbornadiene (1)[2] with magnesium turnings in tetrahydrofuran followed by deuterolysis give benzonorbornadiene-7-d (2) with >90% of the D at the anti position. These highly stereoselective formations
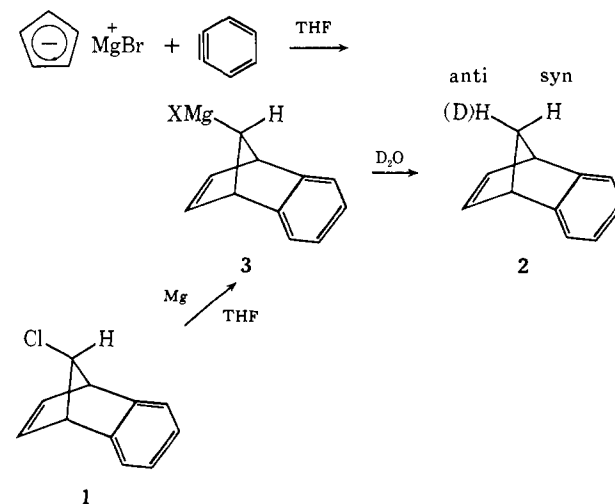
and deuterolyses of the anti-7-benzonorbornadienyl Grignard reagent (3)[3] could be due to (a) stereoselective formation and configurational stability of 3, (b) equilibration of 3 and its syn isomer to a mixture of isomers containing >90% 3, or (c) selective destruction of the syn isomer. Because no Grignard reagent

(1) (a) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958); (b) W. T. Ford, R. Radue, and J. A. Walker, *Chem. Commun.*, 966 (1970); (c) W. T. Ford, *J. Org. Chem.*, **36**, 3979 (1971).

(2) M. E. Brennan and M. A. Battiste, *J. Org. Chem.*, **33**, 324 (1968).

(3) The configuration of 3 is assigned by assuming that deuterolysis proceeds with retention of configuration. Carbonation,[4-6] bromomercuration,[4] and deuterolysis[7] of other Grignard reagents have been determined to proceed with retention.

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(5) (a) H. M. Walborsky and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3288 (1964); (b) H. M. Walborsky and M. S. Aronoff, *J. Organometal. Chem.*, **51**, 31 (1973).

(6) G. J. Martin and M. L. Martin, *Bull. Soc. Chim. Fr.*, 1636 (1966).

(7) T. Yoshino, Y. Manabe, and Y. Kikuchi, *J. Amer. Chem. Soc.*, **86**, 4670 (1964).