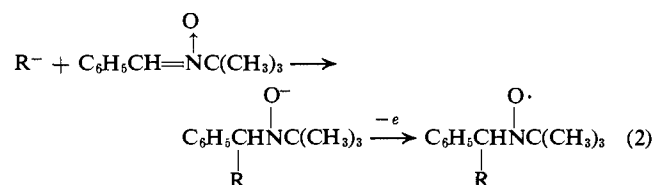ice bath, and the potential was maintained at -0.2 V for 5 min; an aliquot was removed by syringe under positive helium pressure. The aliquot was injected into an esr cell and was purged with nitrogen to remove traces of oxygen. This solution gave a very strong esr signal corresponding to the adduct 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]

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

$$C_6H_5\underset{\underset{R}{|}}{\overset{\overset{O^-}{|}}{C}HNC(CH_3)_3} \xrightarrow{-e} C_6H_5\underset{\underset{R}{|}}{\overset{\overset{O\cdot}{|}}{C}HNC(CH_3)_3} \quad (2)$$

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.

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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
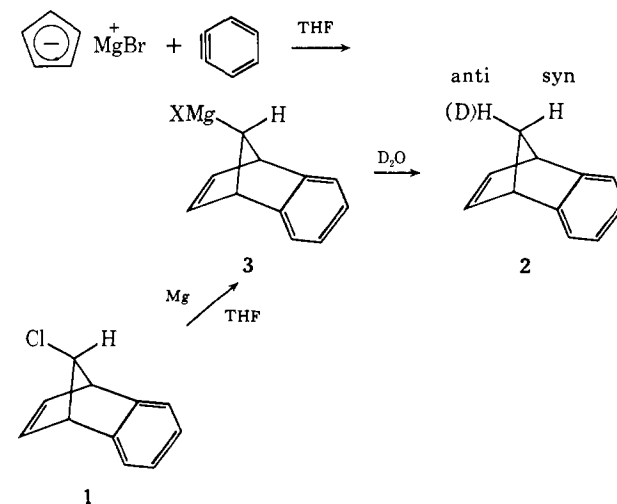
and deuterolyses of the anti-7-benzonorbornadienyl Grignard reagent (3)[3] could be due to (a) stereoselective formation and configurational stability of 3, (b) equilibration of 3 and its syn isomer to a mixture of isomers containing $>90\%$ 3, or (c) selective destruction of the syn isomer. Because no Grignard reagent

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(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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before has been prepared so stereoselectively from magnesium metal and an alkyl halide at saturated carbon,[4,5,8] we sought to determine why **3** was formed from **1**.

Results of preparations and deuterolyses of 7-benzonorbornadienyl Grignard reagents are in Table I.

Table I. Stereochemistry of 7-Benzonorbornadienyl Grignard Reagent Formation and Deuterolysis in THF

Reaction	% yield of 2	Atom excess D in 2 anti	syn
C₆H₅MgBr + benzyne[a]	29	0.91	0.00
1 + Mg	86	0.48	0.05
1 + MgCl₂ + NaNaph[b]	93	0.35	0.28
(a) 1 + Mg, (b) NaNaph	81	0.31	0.00
1 + NaNaph	66	0.00	0.00
4 + Mg[c]	43	0.05	0.03
4 + MgCl₂ + NaNaph[b]	34	0.64	0.26

[a] References 1b,c. [b] Average of two runs. [c] Average of three runs.

In all cases the yield of benzonorbornadiene was determined by glpc, and the amount and location of deuterium (estimated to be ±0.05 atom excess D at each position) were determined from the relative areas of pmr signals of the Diels–Alder adduct of benzonorbornadiene and diphenylisobenzofuran.[9] By the same procedure used with **1**, treatment of syn-7-chlorobenzonorobornadiene (**4**)[10] with Mg turnings in THF

4
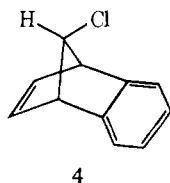
at reflux followed by deuterolysis incorporates little or no D at either position in **2**. Addition of a 15% excess of sodium naphthalenide (NaNaph) in THF to a solution of **1** or of **4** at 25° in THF which contains a 30% excess of anhyd MgCl₂[11] followed by deuterolysis leads to deuteration at both the syn and anti positions of **2**. Reaction of **1** with NaNaph in the absence of MgCl₂ followed by deuterolysis gives **2** containing no detectable D, demonstrating that organomagnesium rather than organosodium compounds are the species which react with D₂O in the NaNaph–MgCl₂ experiments. Excess NaNaph does not isomerize Grignard reagent **3** once it is formed, because successive preparation of **3** from **1** and Mg, addition of NaNaph, and deuterolysis place D only in the anti position of **2**.

Since Grignard solutions prepared by different methods do not incorporate D with the same stereoselectivity, once they are formed the syn- and anti-7-benzonorbornadienyl Grignard reagents must be configurationally stable for hours in THF at 25°. Tests of the stability of the Grignard solution prepared from **1**, MgCl₂, and NaNaph by refluxing in THF lead to no deuteration, probably because the Grignard reagents

react with a carbon acid formed in side reactions of NaNaph. This complication prevents rigorous proof of the configurational stability of **3** and its syn isomer at 65°, but previous reports that 2-norbornyl[4] and 1-methyl-2,2-diphenylcyclopropyl[5] Grignard reagents are configurationally stable on a laboratory time scale in ethyl ether or THF and that several secondary alkyl Grignard reagents are configurationally stable at >100° on the nmr time scale[12,13] suggest that **3** and its syn isomer are unlikely to interconvert in refluxing THF. The syn isomer might be destroyed selectively, but there is no reason to expect that a syn/anti equilibrium mixture would be >90% anti. Therefore, the anti-7-benzonorbornadienyl Grignard reagent **3** apparently is formed >90% stereoselectively by two different routes.

Two disturbing features of our results are the formation of substantial undeuterated benzonorbornadiene in most experiments and the low yields of benzonorbornadiene from **4**. Experiments designed to determine the sources of these problems are in progress.

anti-7-Chlorobenzonorbornadiene forms a Grignard reagent at saturated carbon with Mg more stereoselectively than any other alkyl halide known to us.[4,5,8] This might be explained by an electron transfer–free radical surface mechanism[5,14] of Grignard reagent formation and substantial barriers to pyramidal inversion of 7-benzonorbornadienyl free radicals and carbanions, but we defer further discussion to a full paper.

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(15) National Science Foundation Predoctoral Fellow, 1971–present.

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Influence of Geometry on Cyclopropyl Participation in the Thermolysis of Azo Compounds. A Photoelectron Spectroscopic Rationalization[1]

Sir:

Recent work[2,3] has shown that the reactivity of thermal decomposition grows substantially for the azo compounds (**1–4**) with increasing dihedral angle between the plane of the cyclopropane ring and the rest of the structure. Below we present a rationalization of this phenomenon by means of the photoelectron (pe) spectra of **1** and **2**.

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