prior to use. 1,1′-Diethyl-[8] and 1,1′-dibenzylferrocene,[8] [3]ferrocenophane,[9] and [3][3]-1,3-ferrocenophane[9] were prepared by reported procedures.

Reductive Cleavage Reactions.—The usual procedure was to stir 3–5 g of the ferrocene derivative in 30 ml of *n*-propylamine with 1.0–1.6 g of Li wire cut into two or three pieces. Except in the case of **6**, each reaction mixture darkened and boiled spontaneously after a few minutes. Stirring was continued for several hours at room temperature; then the mixtures were diluted with benzene and poured into ice–water. The aqueous layer was added slowly to ice–water containing excess HCl and extracted twice more with benzene. The combined benzene solutions were dried ($MgSO_4$), treated with maleic anhydride, and slowly distilled to dryness on a steam bath to give a mixture of the Diels–Alder adduct and starting material. Separation and purification were accomplished in two different ways as described in the following paragraphs.

N-Phenyl-5-norbornene-2,3-dicarboximide (7) from Ferrocene (1).—The crude product obtained from **1** (3.00 g, 16.1 mmol), 1.63 g of Li, and 2.7 g of maleic anhydride was taken up in acetyl chloride, refluxed for 1 hr, and evaporated; the residue was dissolved in a small volume of benzene and then treated with 2.6 ml of aniline. After 1 hr at room temperature, the mixture was evaporated and the residue was heated for 0.5 hr on the steam bath with 30 ml of acetic anhydride and 2.9 g of anhydrous sodium acetate. This suspension was diluted with benzene, washed thoroughly with water, dried ($MgSO_4$), concentrated, and chromatographed on silica gel. The first fraction eluted with benzene was rechromatographed on Al_2O_3 and gave 0.70 g of **1** (23.3%) and 2.43 g of **7**. Following fractions after rechromatographing (Al_2O_3) yielded 2.19 g of **7**; the total yield of **7** was 4.62 g (59.8%). Recrystallization from methylene chloride–hexane gave pure **7** as white needles: mp 142.5–144.5° (lit.[10] mp 144°); ir (mull) 5.63, 5.82 μ (C=O); nmr τ 8.67–8.21 (m, 2, CH_2), 6.69–6.42 (m, 4, CH), 3.83–3.61 (m, 2, CH=CH), 2.98–2.40 (m, 5, C_6H_5).

1- and 5-Methyl-N-phenyl-5-norbornene-2,3-dicarboximide (8 and 9) from 1,1′-Dimethylferrocene (2).—From **2** (3.46 g, 16.2 mmol), 1.55 g of Li, and 3.0 g of maleic anhydride by the procedure described for **1** was obtained 8.78 g of a thin red oil which was chromatographed on SiO_2. Elution with hexane yielded starting material (1.03 g, 29.7%), with 1:1 hexane–benzene, N-phenylmaleimide, and with benzene, a mixture of **8** and **9**, whose separation required rechromatographing (Al_2O_3) several times followed by recrystallization from methylene chloride–hexane or hexane alone before reasonably pure materials could be isolated. Isomer **8** was isolated: mp 168–180° (lit.[11] mp 179–180°); ir ($CHCl_3$) 5.54, 5.77 μ (C=O); nmr τ 8.38 (m, 5, CH_2 and CH_3), 6.95–6.33 (m, 3, CH), 4.03–3.60 (m, 2, CH=CH), 2.99–2.34 (m, 5, C_6H_5) (lit.[11] τ 8.40, 3.93). The 5-methyl isomer, **9**, was isolated in approximately the same purity: mp 116–122.5° (lit.[11] mp 128–129.5°); ir ($CHCl_3$) 5.54, 5.76 μ (C=O); nmr τ 8.67–8.06 (m, 5, CH_2 and CH_3), 6.76–6.40 (m, 4, CH), 4.22 (m, 1, C=CH), 3.00–2.33 (m, 5, C_6H_5) (lit.[11] τ 8.18, 4.24).

1-Ethyl-5-norborene-2,3-dicarboxylic Anhydride (10), 1-Ethyl-5-norbornene-2,3-dicarboxylic Acid (11), and 5-Ethyl-5-hydroxynorbornane-2,3-dicarboxylic Acid γ-Lactone (12) from 1,1′-Diethylferrocene (3).—Compound **3** (4.55 g, 18.8 mmol), 1.30 g of Li, and 3.0 g of maleic anhydride were allowed to react by the usual procedure to give the crude maleic anhydride adduct which was heated for 2 hr on the steam bath with 75 ml of 2 *N* Na_2CO_3 solution and then extracted three times with 100 ml of methylene chloride. From these extracts was recovered 3.01 g (66.2%) of starting material (chromatographed on Al_2O_3, eluted with hexane). After acidification with 4 *N* HCl, the clear aqueous solution was concentrated under vacuum and extracted three times with 100 ml of methylene chloride to give 5.01 g of crude products. These were separated by fractional crystallization from cyclohexane, cyclohexane–hexane, and methylene chloride–hexane into three components, **10**, **11**, and **12**. Characteristics of **10** follow: mp 64–66° (hexane) (lit.[12] mp 65–66°); ir ($CHCl_3$) 5.37, 5.61 μ (C=O); nmr τ 8.96 (t, 3, $C\mathbf{H}_3CH_2$), 8.67–7.66 (m, 4, $CH_3C\mathbf{H}_2$ and ring CH_2), 6.78–6.13 (m, 3, CH), 3.97–3.60 (m, 2, CH=CH). Those of **11** follow: mp 126–128.5° (methylene chloride–hexane or H_2O) (lit. mp 131–132°,[12] 136° [2]); ir ($CHCl_3$) 5.80 μ (C=O); nmr τ 9.25–7.90 (m, 7, CH_3CH_2 and ring CH_2; discernible are a triplet and quartet from the ethyl group, J = 7.3 Hz), 6.99–6.33 (m, 3, CH), 4.06–3.63 (m, 2, CH=CH), chemical shift variable with concentration (s, 2, OH); equiv wt (titration) 107, calcd 105. Those of **12** follow: mp 157.5–158°; ir (mull) 5.62 (C=O, lactone), 5.80 μ (C=O, acid); nmr (Na salt in D_2O) τ 9.07 (t, 3, $C\mathbf{H}_3CH_2$), 8.65–7.93 (m, 6, CH_2), 7.60–6.84 (m, 4, CH).

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71; mol wt, 210. Found: C, 62.48; H, 6.53; mol wt (titration), 205.

1-Benzyl-5-norbornene-2,3-dicarboxylic Anhydride (14) from 1,1′-Dibenzylferrocene (4).—Compound **4** (3.08 g, 8.4 mmol) and 0.92 g of Li wire were stirred for 7.5 hr in 30 ml of propylamine and subjected to the standard work-up. The resulting dried benzene solution containing benzylcyclopentadiene was treated with 1.5 g of maleic anhydride, concentrated on the steam bath, extracted five times with 50 ml of water (which yielded 0.57 g of maleic acid) and evaporated to dryness. The residue was heated 3.5 hr at 107° with 50 ml of 2 *N* Na_2CO_3 solution and the resulting suspension was extracted thoroughly with methylene chloride from which was recovered 1.63 g of **4** (52.9%). The alkaline solution was acidified with 2 *N* HCl and extracted with methylene chloride to give 2.14 g of crude acid (46.7%, calcd for benzylnorbornenedicarboxylic acid).

This acid was converted into its anhydride by refluxing for 1 hr with 25 ml of acetyl chloride. The solution was evaporated to dryness and the residue was extracted several times with hot hexane. The concentrated extracts, upon cooling, gave white crystals which were purified by recrystallization from ethyl acetate: mp 121–122.5° (lit.[13] mp 123°); ir ($CHCl_3$) 5.34, 5.58 μ (C=O); nmr τ 8.75–8.17 (m, 2, ring CH_2), 6.89–6.42 (m, 5, CH and benzyl CH_2), 3.88–3.60 (m, 2, CH=CH), 2.72 (s, 5, C_6H_5).

Attempted cleavage of [3]Ferrocenophane (5) and [3][3]-1,3-Ferrocenophane (6).—Attempted cleavage of **5** gave an intractable mixture whereas **6**, when subjected to similar reaction conditions, remained unchanged.

Registry No.—**1**, 102-54-5; **2**, 1291-47-0; **3**, 1273-97-8; **4**, 12114-61-3; **5**, 12402-44-7.

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Quantitative Deuteration of a Grignard Reagent. The Preparation of 2-Butene 2-d_1

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In connection with a recent study of a photocycloaddition reaction,[1] a sample of 2-butene-2-d_1 was desired in which the label was introduced not only specifically but quantitatively. Quenching of the appropriate Grignard reagent appeared a good method of preparation; however, in our hands other prepartions had given less than quantitative introduction of label.[2] Also, Pocker and Exner,[3] in a careful study, had noted that phenyl- and benzyllithium and magnesium com-

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pounds gave 75–95% deuteration when quenched with D_2O, depending on conditions. This note describes the preparation of the title compound in almost quantitative isotopic purity.

It has long been known[4] that there is some intermediate in the formation of Grignard reagents from halides that behaves like a free radical. Thus, coupling and disproportionation products arise in appropriate cases (eq 2 and 3). I suggest that the reaction of eq 4,

$$RX + Mg(s) \longrightarrow R\cdot \qquad (1)$$

$$2R\cdot \longrightarrow R_2 \qquad (2)$$

$$2RCH_2CH_2\cdot \longrightarrow RCH{=}CH_2 + RCH_2CH_3 \qquad (3)$$

$$R\cdot + (CH_3CH_2)_2O \longrightarrow RH + CH_3\dot{C}HOCH_2CH_3 \qquad (4)$$

abstraction of a hydrogen from ether, is the reaction that is primarily responsible for incomplete label introduction. I believe that in any event the isotopic contamination occurs prior to quenching, as implied by Pocker and Exner.[3] A simple solution to the problem then appeared: *the separation of the RH species from the Grignard reagent after formation but before quenching.*

The preparation of 2-butenylmagnesium bromide in tetrahydrofuran was effected by standard procedures. The reaction mixture was then heated until a few milliliters of the solvent had distilled out, and with it any 2-butene that had been formed. Quenching of the reaction mixture then gave evolution of 2-butene-2-d_1 as a mixture of 90% *trans* and 10% *cis*, which could be trapped at −80°. It was analyzed by nmr as 100 ± 2% monodeuterated in the vinyl position (relative to 6 H in the methyls) and as 99.03% d_1, 0.81% d_0, and 0.16% d_2 by mass spectrometry at low voltage. Since the D_2O used was 99.82 at. % deuterated, and a small isotope effect on quenching can be expected,[3] only about 0.5% adventitious unlabeled material was present.

The present preparation suggests that development of separation procedures will enable quantitative deuteration of liquids and solids as well. The separation is, however, particularly simple for gaseous products.

Experimental Section

Bromine (40 g) in methylene chloride (75 ml) was stirred at 0° and gaseous *cis*-2-butene (Matheson CP, 99% *cis*, 1% *trans*) was added until decolorization occurred. The solvent was removed on a rotary evaporator and the crude dibromobutane was added to 100 ml of ethylene glycol containing the theoretical amount of 85% KOH (16.5 g). The solution was heated in a round-bottom flask to which a small Vigreux column was attached. Reaction occurred, and a mixture of the desired 2-bromo-2-butene and water distilled over. The material boiling below 95° was dried over anhydrous potassium carbonate and redistilled. A center cut, bp 82–86° (lit.[5] bp 85.55° for *trans*-2-bromo-2-butene), weighed 16.3 g (48%) and was used immediately in the next step.

Tetrahydrofuran (50 ml) was distilled from ethylmagnesium bromide directly into a dropping funnel and a three-necked flask. Formation of the Grignard reagent from the 2-bromo-2-butene under nitrogen in the standard manner required some heating until initiation occurred. At the end of the reaction, the mixture was again brought to reflux and several milliliters of the reaction mixture distilled out. The vessel was then fitted with a series of two dewar condensers, the first filled with an ice water bath and the second with Dry Ice–acetone. Deuterium oxide was added, and the condensate from the second dripped into a receiver cooled with Dry Ice–acetone. Removal from residual solvent by bulb-to-bulb distillation from Dry Ice–acetone to liquid nitrogen on a vacuum line afforded 2-butene (about 7 ml of liquid at 0°, 65%) that was free of any impurity detectable by nmr. It was analyzed by vpc on a 10% $AgNO_3$–15% benzyl cyanide column as 90% *trans*–10% *cis*.

Registry No.—2-Butene-2-d_1, 23042-68-4.

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Reaction of *p*-Tolylsulfonylmethylmagnesium Bromide with Ethyl Cinnamate

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In a previous paper from this laboratory, it was shown that *p*-tolylsulfonylmethylmagnesium bromide (I) added 1,2 but not 1,4 to a variety of α,β-unsaturated aldehydes and ketones.[1] To test the generality of 1,2 addition of sulfonyl Grignard reagents, the reaction of I and ethyl cinnamate (II) was studied. Some reactions of I with the methyl ester of cinnamic acid were also carried out and the results were similar.

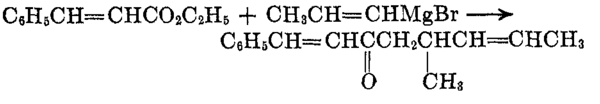
Kohler and coworkers extensively studied the reactions of methyl and ethyl cinnamate with phenylmagnesium bromide.[2] The products were predominantly (>80%) those from 1,4 addition, along with small amounts of ketone.

$$C_6H_5CH{=}CHCO_2R + C_6H_5MgBr \longrightarrow (C_6H_5)_2CHCH_2CO_2R + (C_6H_5)_2CHCH_2COC_6H_5 \qquad (1)$$

$$R = CH_3 \text{ or } C_2H_5$$

The addition of phenylmagnesium bromide to other esters has also been shown to give 1,4-addition products.[3,4] Methylmagnesium iodide, however, gave 1,2 addition to methyl cinnamate, affording the unsaturated tertiary alcohol.[2]

Allyl Grignard reagents have been reported to give low yields of tertiary alcohols arising from 1,2 addition.[5] Apparently other products were not isolated. The esters used were of the acrylate and crotonate types. Vinyl Grignard reagents were found to react with ethyl cinnamate giving ketone from 1,2 addition, followed by 1,4 addition of a second molecule of organometallic.[6] The reported yields were low.



$$C_6H_5CH{=}CHCO_2C_2H_5 + CH_3CH{=}CHMgBr \longrightarrow C_6H_5CH{=}CH\underset{\underset{O}{\|}}{C}CH_2\underset{\underset{CH_3}{|}}{C}HCH{=}CHCH_3 \qquad (2)$$

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