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,

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

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

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

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

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.

**Acknowledgment.**—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work through Grant 3031-A4.

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[4] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," New York, N. Y., Prentice-Hall, Inc., 1954, pp 7, 59 ff.

[5] M. Lepingle, *Bull. Soc. Chim. Fr.*, **39**, 741 (1926).

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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 $\alpha,\beta$-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.

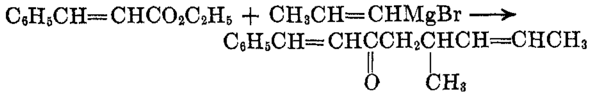
Kohler and coworkers extensively studied the reactions of methyl and ethyl cinnamate with phenylmagnesium bromide.[2] The products were predominantly (>80%) those from 1,4 addition, along with small amounts of ketone.

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

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

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.



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

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[1] J. W. McFarland and D. N. Buchanan, *J. Org. Chem.*, **30**, 2003 (1965).

[2] E. P. Kohler and G. Heritage, *Amer. Chem. J.*, **33**, 21 (1905).

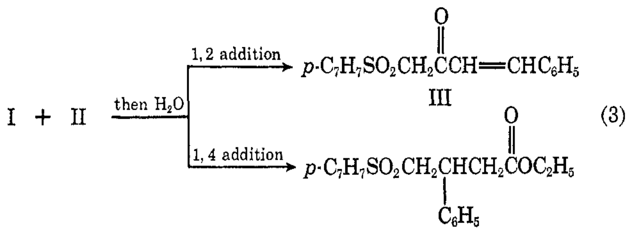
[3] E. P. Kohler and G. Heritage, *ibid.*, **34**, 568 (1906).

[4] G. P. Reynolds, *ibid.*, **46**, 198 (1911).

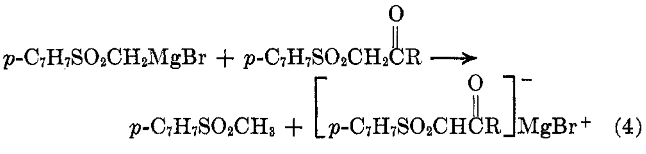
[5] I. N. Nazarov and A. I. Kakhniashvili, *Sb. Statei Obshch. Khim.*, **2**, 919 (1954); *Chem. Abstr.*, **49**, 6848*b* (1955).

[6] C. Lumbroso and P. Maitte, *Bull. Soc. Chim. Fr.*, **2**, 315 (1965).

Two distinct products would be possible from the reaction of I and II, one from a 1,2-addition reaction and the other from 1,4 addition. It was not expected that ketone III would add a molecule of I in the conventional sense because Field and coworkers[7] had shown that the following reaction takes place.



$$\mathrm{I} + \mathrm{II} \xrightarrow{\text{then } H_2O} \begin{cases} \xrightarrow{\text{1,2 addition}} p\text{-}C_7H_7SO_2CH_2\overset{O}{\overset{\|}{C}}CH{=}CHC_6H_5 \quad \mathrm{III} \\ \xrightarrow{\text{1,4 addition}} p\text{-}C_7H_7SO_2CH_2\underset{C_6H_5}{\underset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}OC_2H_5 \end{cases} \quad (3)$$



$$p\text{-}C_7H_7SO_2CH_2MgBr + p\text{-}C_7H_7SO_2CH_2\overset{O}{\overset{\|}{C}}R \longrightarrow p\text{-}C_7H_7SO_2CH_3 + \left[p\text{-}C_7H_7SO_2CH\overset{O}{\overset{\|}{C}}R\right]^- MgBr^+ \quad (4)$$

R = $C_6H_5$ or $CH_3$

In this paper we shown that the product from the reaction of I and II is always III. There was no evidence for 1,4 addition over a I/II ratio of 3:1 to 1:2 and a temperature range of 0–80°. Consistent with Field's results, the yield of III was less than the possible 50% when a 1:1 ratio of Grignard reagent and ester was used. Furthermore, one-half of the methyl *p*-tolyl sulfone and one-half of the ethyl cinnamate should be recovered. Our results approximated those predictions. The low yields of III in some cases may have been due to difficulty in the separation of mixtures. Fractional crystallization was found better for separating III from sulfone and unreacted II than was chromatography on alumina.

In conclusion, sulfonyl Grignard reagents undergo only 1,2 additions to cinnamate esters. This behavior is analogous to the reactions of I with $\alpha,\beta$-unsaturated aldehydes and ketones. The sulfonyl Grignard reagent resembles vinyl Grignard reagents more than it does phenylmagnesium bromide in its reactions with cinnamate esters. The possible reasons for exclusive 1,2 addition have already been discussed.[1]

### Experimental Section

**Reaction of *p*-Tolylsulfonylmethylmagnesium Bromide (I) with Ethyl Cinnamate (II).**—The *p*-tolylsulfonylmethylmagnesium bromide (I) was prepared from 12.75 g (0.075 mol) of methyl *p*-tolyl sulfone[8] by the procedure used previously.[1] To the slurry of I in ether–benzene was added during 20 min at room temperature 13.47 g (0.077 mol) of II in 80 ml of dry benzene. After the mixture was stirred an additional 4 hr at room temperature, hydrolysis was effected with 100 ml of cold 1 *N* HCl solution. Removal of solvent *in vacuo* gave 22.7 g of greasy solid, mp 70–80°. Recrystallization from benzene–petroleum ether afforded 6.4 g (28.4%) of white needles, mp 115–119°. Further recrystallization gave 1-(*p*-tolylsulfonyl)-4-phenyl-3-buten-2-one (III) with constant mp 127–128°. Ir and nmr spectroscopy confirmed the structure of III.

*Anal.* Calcd for $C_{17}H_{16}O_3S$: C, 68.00; H, 5.33; S, 10.67. Found: C, 67.86; H, 5.21; S, 10.82.

The addition of 2 vol. of petroleum ether to the filtrate gave 6.60 g (51.8%) of recovered methyl *p*-tolyl sulfone, mp 73–78°. Recrystallization from ethanol-water gave pure sulfone, mp 85–86°, which did not depress the melting point of an authentic sample.

Removal of solvent and distillation of the residue afforded 9.28 g (68.5% recovery) of unreacted ethyl cinnamate (II), bp 66–69° (0.10 mm). The ir spectrum was identical with that of starting material.

In other reactions at various temperatures and I/II ratios, the maximum yield of III (86.6%) was obtained at room temperature with a I/II ratio of 2:1.

**Registry No.**—I, 3048-28-0; II, 103-36-6; III, 23042-70-8.

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[8] R. Otto, *Ber.*, **18**, 161 (1885).

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## Ring Inversion of Perfluoro-1,4-dithiane[1]

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Interconversion of chair conformations of six-membered rings containing two identical heteroatoms has been much studied by the nmr method,[3] with the exception of the 1,4-dithiane system. The results so far obtained for 1,2- and 1,3-dithianes in comparison with those of dioxanes and the corresponding diaza systems suggest that this barrier should be readily measureable by the nmr method. We are concerned here with the ring inversion of octafluoro-1,4-dithiane (**1**).

The $^{19}F$ nmr spectrum of **1**, kindly supplied by Dr. B. C. McKusick of the Central Research Department of E. I. du Pont de Nemours and Co., in 2:1 (v/v) acetone–chloroform at 70° is a single line of half band width of *ca.* 1.8 Hz, 71.8 ppm downfield from internal hexafluorobenzene. At −90°, the spectrum appears as an AB quartet, each line of which shows small additional splittings, centered 70.0 ppm downfield from internal hexafluorobenzene. The chemical-shift difference between the A and B parts is 15.02 ppm and $J_{AB}$ is 230 Hz. The quartet coalesces to a broad singlet at −32°. To gain information about the barrier to inversion, spectra were recorded at 23 temperatures between −62 and 17°.

A series of spectra, calculated as a function of $\tau$, the average lifetime spent in either chair confirmation, was generated by standard procedures[4] and compared with the experimental spectra to obtain a value of $\tau$ for each temperature. The variation of the rate constant $k_{inv}$ (= $1/\tau$) for interconversion of chair conformations with temperature gave the free energy of activation ($\Delta G^{\ddagger}$) as 10.05 ± 0.10 kcal/mol at −32°, the enthalpy of activation ($\Delta H^{\ddagger}$) as 9.74 ± 0.20 kcal/mol, and the entropy of activation ($\Delta S^{\ddagger}$) as −1.2 ± 1 eu.

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[1] Supported by the National Science Foundation.

[2] Harkness Fellow of the Commonwealth Fund of New York, 1966–1968. Chemistry Department, University College, Gower Street, London, W.C. 1.

[3] G. Binsch in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, Inc., New York, N. Y., 1968, p 97, provides an excellent review.

[4] J. T. Gerig and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 2791 (1966).