Tetrahedron Letters No. 26, pp 2179 - 2182, 1975. Pergamon Press. Printed in Great Britain.

# THE APPLICATION OF THE NEW TYPE GRIGNARD REAGENT DERIVED FROM ETHYL α-(tert-BUTYLSULFINYL)ACETATE TO THE SYNTHESIS OF α,β-UNSATURATED ESTERS.

Junzo Nokami, Norio Kunieda, and Masayoshi Kinoshita
Department of Applied Chemistry, Faculty of Engineering,
Osaka City University, Sumiyoshi-ku, Osaka, Japan

(Received in Japan 14 April 1975; received in UK for publication 12 May 1975)

Recently, we have reported that a new type Grignard reagent derived from ethyl α-phenylsulfinylacetate and alkylmagnesium halides has a good reactivity at the α-carbon atom toward aldehydes and ketones to give the corresponding addition products.1) In this communication, we wish to report an application of the Grignard reagent derived from ethyl α-(tert-butylsulfinyl)acetate(**1**) to the synthesis of α,β-unsaturated esters.

When **1** was treated with 1 equiv of an alkylmagnesium halides in ethyl ether or benzene at 0°C under nitrogen, the Grignard reagent **2** was produced as a milky precipitate. The following experiment is typical of the procedure employed for the preparation of α,β-unsaturated esters.2)

To a solution of **2** derived from 583 mg(3 mmol) of **1** and ethylmagnesium bromide(3 mmol) in 3 ml of ether was added 1 equiv of n-butyraldehyde at 0°C. The stirring was continued for 12 hr at room temperature. The reaction mixture was neutralized with a dilute solution of tartaric acid and extracted with chloroform. The extract was washed, dried and evaporated to leave 674 mg of crude needles of **3a** (84% yield), which was dissolved in 8 ml of carbon tetrachloride and treated with 413 mg(3 mmol) of sulfuryl chloride for 10 minutes at room temperature according to the method developed by Durst et al.3) The solvent was evaporated keeping the temperature below 40°C. The residual oil was passed through 15 g of alumina(200 mesh) with 30 ml of methylene dichloride to give 297 mg of (E)-ethyl 2-hexenoate(**4a**) (82% yield based on **3a**).

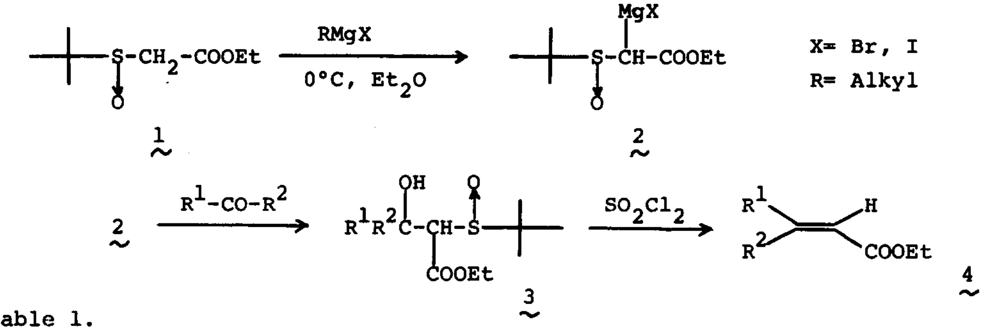
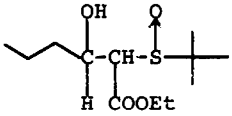
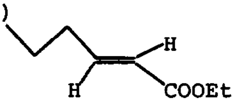
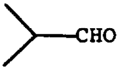
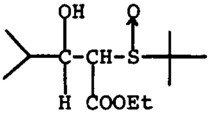
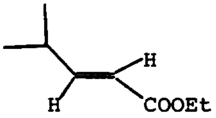
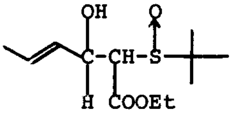
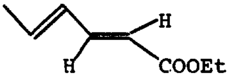
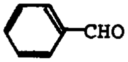
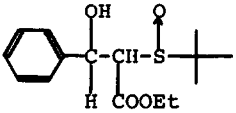
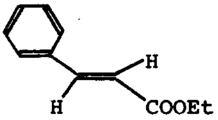
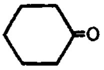
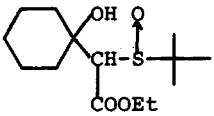
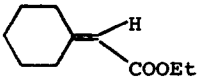
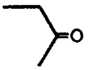
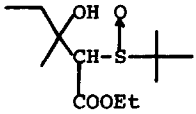
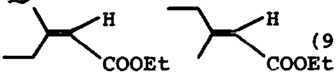


Table 1.

| Aldehydes and Ketones | Products $(\underset{\sim}{3})^{a)}$ | (yield %) | Products $(\underset{\sim}{4})^{a)}$ | (yield %) |
|---|---|---|---|---|
|  | (3a)  | (84) | (4a)  | (82) |
|  | (3b)  | (90) | (4b)  | (85) |
|  | (3c)  | (74) | (4c)  | (79) |
|  | (3d)  | (83) | (4d)  | (90) |
|  | (3e)  | (89) | (4e)  | (95) |
|  | (3f)  | (82) | (4f)  | (93)<sup>b)</sup> |

a) Satisfactory nmr, ir, and elemental analyses were obtained for all new compounds described here. b) The E/Z ratio was ca. 1.

Similarly, isobutyraldehyde, crotonaldehyde, benzaldehyde, cyclohexanone and ethyl methyl ketone readily react with **2** to yield the corresponding α,β-unsaturared esters(**4b**-f). The results are summarized in Table 1.

It is noteworthy that the α,β-unsaturated esters **4a**-d(except **4e**,f) obtained from this reaction possess the E-configuration. However, when ethyl methyl ketone was subjected to the same reaction, the Z-α,β-unsaturated ester was produced together with the E-ester(E : Z = ca. 1 : 1).4)

The assignment of E- and Z-configurations was based on nmr spectral data and gas chromatographical behavior. Further study on the application for organic syntheses of high stereospecificity in this reaction is in progress.

## Referrences and Notes

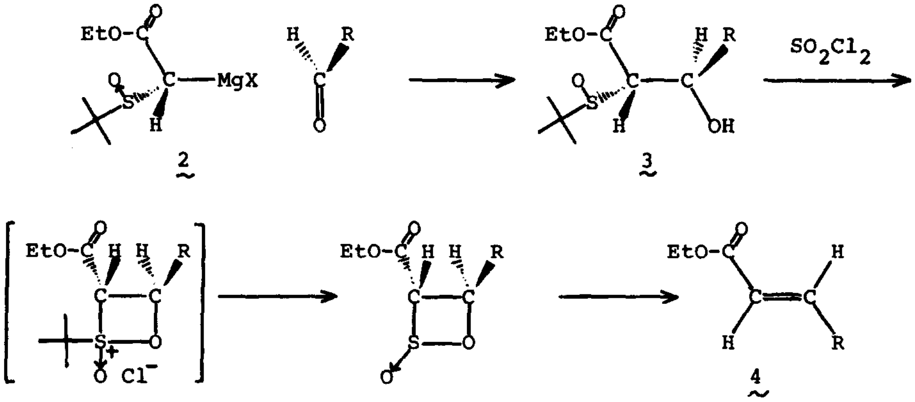
1) N. Kunieda, J. Nokami, and M. Kinoshita, Tetrahedron Lett., 3997(1974).

2) The synthesis of α,β-unsaturated esters by the alkylative elimination of the anion of methyl α-phenylsulfinylacetate has been reported. [B. M. Trost, W. P. Conway, P. E. Strege, and T. J. Dietsche, J. Amer. Chem. Soc., **96**, 7165(1974); B. M. Trost and T. N. Salzmann, ibid., **95**, 6840(1973)].

3) F. Jung, N. K. Sharma, and T. Durst, J. Amer. Chem. Soc., **95**, 3420(1973). They have reported that the E/Z ratio of the cis-elimination is generally not greater than 7 : 3.

4) Supposing the addition of the Grignard reagent(**2**) toward aldehydes obeys the model prediction proposed by Cram and Prelog5) in terms of the eclipsing effect of substituents at the reaction center, and further supposing the elimination of the adducts by treating with sulfuryl chloride (**3**→**4**) proceeds through the stereospecific cis-elimination via a β-sultine proposed by Durst et al.,3) a plausible stereochemical course for the reaction to yield the E-α,β-unsaturated esters preferentially is formulated as follows (Scheme 1), since the relative steric bulk of the substituents on the α-carbon atom of **2** is considered to be $\text{-H} < \text{-COOEt} < \text{-SO-Bu}^{t}$.

Scheme 1



5) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1971), and references therein.