

(b).—When 15 ml. of *o*-cresol methyl ether was added to 5.5 g. of diphenoyl chloride and 6.6 g. of aluminum chloride in 150 ml. of carbon disulfide as described in the preparation of IIa, the products were 2.6 g. of III, m.p. 193.5–194° and 4.6 g. of II, m.p. 125.5–126° (alcohol) and 139.5–140° (ether). The melting point and mixed melting point of the oximes obtained from these two forms of II was 141.5–142°.

Anal. Calcd. for $C_{22}H_{17}NO_3$: C, 76.95; H, 4.98. Found: C, 77.22; H, 4.81.

Reactions of Fluorenone Derivatives with Phenol Ethers.

—The reaction of *o*-cresol methyl ether (1 ml.), 0.24 g. of aluminum chloride and 0.2 g. of II in nitrobenzene yielded III, m.p. 193.5–194°.

4-(2,4-Dimethylbenzoyl)-fluorenone reacted with *o*-cresol methyl ether in nitrobenzene solution to form the corresponding 9,9-diaryl-4-aryloxyfluorene, m.p. 174.5–175°.

Anal. Calcd. for $C_{38}H_{34}O_3$: C, 84.73; H, 6.36. Found: C, 84.69; H, 6.54.

The reaction of veratrole and fluorenone under the same conditions yielded 9,9-bis-(3,4-dimethoxyphenyl)-fluorene, m.p. 224–225°.

Anal. Calcd. for $C_{28}H_{26}O_4$: C, 79.43; H, 5.98; mol. wt., 438. Found: C, 79.39; H, 5.94; mol. wt., 439, 429.

The methyl ester of fluorenone-4-carboxylic acid (1.5 g.), 2 ml. of *o*-cresol methyl ether and 1.8 g. of aluminum chloride in 10 cc. of tetrachloroethane yielded 1.5 g. of the methyl ester of 9,9-bis-(3-methyl-4-methoxyphenyl)-fluorene-4-carboxylic acid, m.p. 170–171°.

Anal. Calcd. for $C_{31}H_{28}O_4$: C, 80.14; H, 6.07. Found: C, 79.89; H, 6.26.

Reaction of the 9,9-Diaryl-4-aryloxyfluorenes with Sulfuric Acid.—Three grams of III was dissolved in 30 ml. of concd. sulfuric acid. The deep purple solution was allowed to

stand at room temperature for six hours and then poured onto 30 g. of crushed ice. The light blue solid which separated melted with decomposition and contained sulfur even after several washings. This solid was boiled for several hours with concd. sodium carbonate solution to yield a white solid IV, m.p. 186–187° (61%).

Anal. Calcd. for $C_{38}H_{34}O_3$: C, 79.70; H, 6.34. Found: C, 79.43; H, 6.54.

The yield of IVa (R = 3,4-dimethoxyphenyl) was 35%, m.p. 212–213°.

Anal. Calcd. for $C_{38}H_{34}O_3$: C, 73.53; H, 5.85. Found: C, 73.83; H, 5.65.

The yield of IVb (R = 2,4-dimethylphenyl, R₂ = 3-methyl-4-methoxyphenyl) was 35%, m.p. 164–165°.

Anal. Calcd. for $C_{38}H_{36}O_4$: C, 82.99; H, 6.52. Found: C, 82.35; H, 6.80.

Recyclization of IV (a) With Aluminum Chloride.—Aluminum chloride (0.4 g.) was added slowly and with stirring to 0.37 g. of IV dissolved in 10 ml. of nitrobenzene. The stirring was continued for 24 hours at room temperature and the product was isolated in the usual manner. A small amount of III, m.p. and mixed m.p. 192–193°, was isolated.

(b) **With 38% Hydrobromic Acid.**—Two-tenths of a gram of IV was dissolved in 20 ml. of glacial acetic acid and 5 ml. of 38% hydrobromic acid was added. The solution turned a deep red color and was warmed until it became colorless. The same amount of hydrobromic acid was added and the solution warmed until it remained colorless. Water was added to precipitate III, m.p. and mixed m.p. 191–192°.

COLUMBIA, MISSOURI

[CONTRIBUTION NO. 834 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Chemistry of Allenic Acids. I. The Reaction of 1,2-Heptadiene-3-carboxylic Acid with Ethylmagnesium Bromide

BY JOHN H. WOTIZ AND JOSEPH S. MATTHEWS¹

The reaction of 1,2-heptadiene-3-carboxylic acid with ethylmagnesium bromide produced 2-butyl-3-ethyl-3-butenic acid in 85% yield. The mechanism of this reaction was studied and the structure of the product established.

Unpublished observations from this Laboratory dealing with the origin of the dimeric acid, $R_2C_7H_5O_2CO_2H$, found in the carbonation products of Grignard reagents from primary propargylic bromides, $R-C\equiv C-CH_2Br$,² showed it to be formed by the action of these Grignard reagents with the bromomagnesium salt of the allenic acid, $R-C=C=CH_2$ followed by carbonation and hydrolysis.

These findings suggested a novel reaction of Grignard reagents. In this paper we are reporting the reaction of ethylmagnesium bromide (I) with the allenic acid 1,2-heptadiene-3-carboxylic acid, $C_4H_9-C=C=CH_2$ (II).

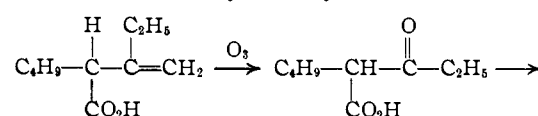
The Yield of Product.—A solution of a one molar quantity of II in ether was added to 2.5 molar quantity of I and the solution poured on Dry Ice. On hydrolysis and distillation a monocarboxylic acid, III, identified as $C_4H_9-CH-C=CH_2$, was

isolated in 85% yield. When a molar quantity of I was added to a molar ether solution of II, the yield depended upon the rate of addition and agitation. Since the first reaction is the formation of the bromomagnesium salt of the allenic acid, $C_4H_9-C=C=CH_2$ (IIMgBr), a slow addition with agitation did not yield any III, whereas a rapid addition produced III in 26% yield, owing to the formation of local high concentration of IIMgBr with which I reacted.

The acid III, $C_9H_{17}CO_2H$, on low pressure catalytic hydrogenation using Adams catalyst absorbed one mole of hydrogen. Its infrared spectrum (Fig. 1) indicates the presence of a terminal double bond by the strong absorption near 900 cm^{-1} and the absence of any starting allenic compound. When acid III was ozonized, ethyl *n*-amyl ketone was isolated.

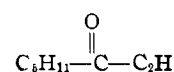
The Proof of Structure of III.—The acid III, $C_9H_{17}CO_2H$, on low pressure catalytic hydrogenation using Adams catalyst absorbed one mole of hydrogen. Its infrared spectrum (Fig. 1) indicates the presence of a terminal double bond by the strong absorption near 900 cm^{-1} and the absence of any starting allenic compound. When acid III was ozonized, ethyl *n*-amyl ketone was isolated.

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(1) Abstracted from the thesis of J. S. M. presented in partial fulfillment for the requirement for the degree of Master of Science.

(2) J. H. Wotiz, *THIS JOURNAL*, **72**, 1639 (1950).



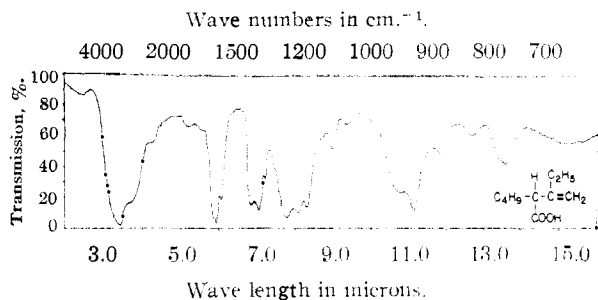
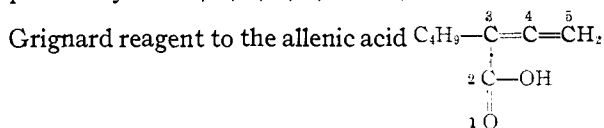


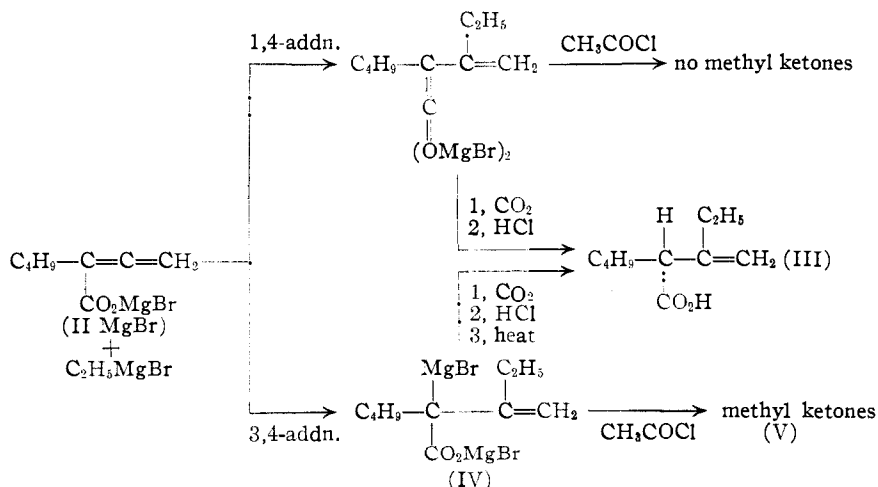
Fig. 1.

Its 2,4-dinitrophenylhydrazone did not depress the melting point of an authentic sample. On the basis of these findings we identify acid III as 2-butyl-3-ethyl-3-butenic acid.

The Mechanism of Reaction.—Nowhere in the literature were we able to find a reaction of Grignard reagents with an allenic acid, or even an α,β -unsaturated acid other than the reaction with its acidic hydrogen. We considered therefore the possibility of a 1,2-, 1,4-, 3,4- or 4,5-addition of the



(II) or its bromomagnesium salt, IIMgBr . However, the determination of the structure of acid III eliminated the possibility of 1,2- or 4,5-addition. A 3,4-addition would involve the addition of a Grignard reagent to an olefinic double bond. Such an addition was reported³ in the reaction of certain Grignard reagents with bidiphenylene-ethylene.



The reaction of primary Grignard reagents with 1-methylethylidenecyanoacetate to yield *l*-alkylcyanoacetates in 42–75% yields should also be mentioned.⁴ A 1,4-addition would be similar to the addition of a Grignard reagent to α,β unsaturated aldehydes, ketones or esters.⁵

To determine whether acid III was formed by a

(3) R. C. Fuson and H. D. Porter, *ibid.*, **70**, 895 (1948).

(4) E. R. Alexander, J. D. McCollum and D. E. Paul, *ibid.*, **72**, 4791 (1950).

(5) For a review of such additions see H. Gilman, "Organic Chemistry," second edition, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1938, pp. 672–674, 681.

1,4- or 3,4- addition a series of experiments were run which are outlined below.

A 3,4-addition would give another Grignard reagent, IV, which should yield a methyl ketone, V, by the reaction with acetyl chloride, and a malonic acid derivative by carbonation. The failure of these reagents to give such products is negative evidence for a 3,4-addition, but supports the hypothesis that the reaction proceeds by a 1,4-addition, and that the carboxy group in III is the same as in II. However, it seems possible that sterically hindered Grignard reagents or the ones formed from propargylic bromides may add differently to allenic acids.

Experimental

Preparation of 2-Butyl-3-ethyl-3-butenic Acid (III) (a).

A solution of 7 g. (0.05 mole) of 1,2-heptadiene-3-carboxylic acid (II) in 200 ml. of dry ether was added with shaking to 0.125 mole of ethylmagnesium bromide (I) in 100 ml. of ether. The resulting green solution was poured on 200 g. of powdered Dry Ice and upon coming to room temperature hydrolyzed with a saturated solution of ammonium chloride. The ether layer was extracted with three 50-ml. portions of saturated sodium carbonate. The aqueous basic extract was cooled with ice and acidified with cold, dilute hydrochloric acid and the liberated organic acids taken into ether. The ether solution was washed with a small portion of cold water, followed by saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. The ether was evaporated under vacuum at room temperature leaving 10.6 g. of a viscous liquid. Distillation yielded 7.2 g. (85% yield) of product boiling at 113–115° at 3 mm., n_D^{25} 1.4517. *Anal.* Calcd. for $\text{C}_{10}\text{H}_{18}\text{O}_2$: C, 70.6; H, 10.6; neut. equiv., 170. Found: C, 70.4; H, 10.4; neut. equiv., 172.⁷ Its infrared spectrum is in Fig. 1.⁸

(b).—The quantities of reagents and the procedure as described in part a was used except that the reaction product was not poured on Dry Ice. Distillation yielded 62% of product, b.p. 117–118° at 4 mm., n_D^{25} 1.4512.

(c).—To 3.5 g. (0.025 mole) of II in 100 ml. of dry ether was added rapidly (10 ml. in one minute) 0.025 mole of I (in 10 ml. of ether). The product was worked up as described in part a. The total acidic product weighed 2.3 g. of which 1.3 g. (33%) was recovered acid II and 1.1 g. (26% yield) of acid III.

(d).—To a solution of 2.0 g. (0.0143 mole) of II in 100 ml. of dry ether was added with agitation over a period of 15 minutes 0.0143 mole of I in 4.1 ml. of ether. The product was worked up as described in part a. The total acidic product was 2.0 g. of the recovered acid II.

2-Butyl-3-ethyl-3-butenamide was prepared from acid III, thionyl chloride and ammonium hydroxide. Recrystallized from a mixture of petroleum ether (30–60°) and benzene it melted at 61–62°. *Anal.* Calcd. for $\text{C}_{10}\text{H}_{19}\text{ON}$: C, 71.0; H, 11.2; N, 8.3. Found: C, 70.9; H, 11.0; N, 8.2.

Hydrogenation of III was conducted in an all-glass semi-micro hydrogenation apparatus⁹ in absolute alcohol solution using Adams catalyst. Using a pressure of hydrogen slightly above atmospheric, 0.4987 g. (0.00293 mole) of acid III

(6) Microanalyses by the Microanalytical Laboratory of the University of Pittsburgh.

(7) Potentiometric titrations using a Beckman pH meter and 0.08 N sodium hydroxide.

(8) Infrared analysis by Dr. F. A. Miller at the Mellon Institute, Pittsburgh, Pa.

(9) L. M. Joshel, *Ind. Eng. Chem., Anal. Ed.*, **15**, 590 (1943).

absorbed 60.0 ml. (S.T.P.) of hydrogen (91% of theory) in 24 minutes.

Ozonization.—A solution of 2 g. of acid III in 100 ml. of redistilled carbon tetrachloride was cooled with an ice-salt cooling mixture while a mixture of oxygen and ozone of unknown concentration was passed through it. After 16 hours it was found that the oxygen-ozone mixture passing through the solution liberated iodine from a potassium iodide solution at the same rate as the oxygen-ozone mixture coming directly from the ozone generator. The carbon tetrachloride solution was then mixed with a 50% solution of acetic acid and zinc dust was added in parts. After the completion of the addition the solution was refluxed for one hour, the organic layer separated and the aqueous layer extracted with several portions of ether which were combined with the carbon tetrachloride solution and dried over magnesium sulfate. The solvents were removed by distillation and the residue treated with 2,4-dinitrophenylhydrazine to yield 0.5 g. of a yellow 2,4-dinitrophenylhydrazone. After two recrystallizations from alcohol it melted at 64–65° and did not depress the melting point of the 2,4-dinitrophenylhydrazone from ethyl *n*-amyl ketone.

Ethyl *n*-amyl ketone was prepared in 77% yields by the

method of Newman and Smith.¹⁰ Its 2,4-dinitrophenylhydrazone melted at 64–65°. *Anal.* Calcd. for C₁₄H₂₀O₄N₄: C, 54.5; H, 6.5; N, 18.2. Found: C, 54.8; H, 6.3; N, 18.2.

The Reaction of the Addition Product of I to the Acid II with Acetyl Chloride.—A solution of 3.5 g. (0.025 mole) of acid II in dry ether was added to a solution of 0.076 mole of I in ether. The solution was cooled in an ice-bath and 5.9 g. (0.075 mole) of freshly distilled acetyl chloride was added in parts. When the addition was about two thirds completed, the solution turned to a yellowish-green color and separated into two layers. Attempts to crystallize the addition product by cooling to Dry Ice temperature failed. It was therefore refluxed for one hour with a 10% solution of sodium hydroxide, the aqueous solution acidified with hydrochloric acid and extracted with several portions of ether, the ether solution dried with magnesium sulfate, and filtered. The filtrate was distilled at 2-mm. collecting four fractions, up to 107°, 107 to 112°, 112 to 116°, and 116 to 119°. None of the fractions yielded iodoform when treated with a 10% solution of sodium hydroxide and iodine-potassium iodide solution.

(10) M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948).

PITTSBURGH, PENNA.

RECEIVED AUGUST 3, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLORADO A. AND M. COLLEGE]

The Reaction of *p*-Methoxystyrene Oxide with Phenol¹

BY CYRUS O. GUSS

RECEIVED DECEMBER 20, 1951

The preparation of *p*-methoxystyrene bromohydrin by solvolysis of *p*-methoxystyrene dibromide provided an easy synthesis of *p*-methoxystyrene oxide. Reaction of the oxide with phenoxide ion gave the primary alcohol, but no secondary alcohol, and products of nuclear alkylation. The acid-catalyzed reaction of the oxide with phenol led almost exclusively to nuclear attack. These results further support the postulate of a unimolecular route to the primary alcohol in the ring-opening reactions of styrene oxides.

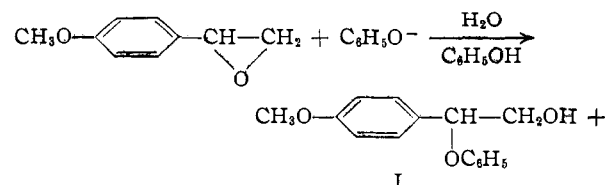
The effect of substituents in substituted styrene oxides on the direction of ring opening has been investigated recently^{2,3} in order to gain a better understanding of the mechanism of the reaction. Electron-attracting groups, as exemplified by the nitro group, favor the formation of the secondary alcohol in the reaction of the substituted styrene oxide with phenoxide ion, contrary to prediction based on inductive effects by which nitro groups would tend to lower the electron density on the α -carbon atom. On the other hand, if attack at the α -carbon involved a unimolecular ring opening, then the nitro group might well inhibit the formation of the primary alcohol³ and yet facilitate a bimolecular route to the secondary alcohol.⁴ A study of the ring-opening reactions of *p*-methoxystyrene oxide is an obvious source of supplementarily helpful data.

At least one attempt to make *p*-methoxystyrene oxide has been reported.⁵ Olefin oxides similarly activated have been found to be rather susceptible to thermal isomerization even when distilled at pressures down to around 1 mm.⁶ Therefore, the

first objective in the present work was to prepare *p*-methoxystyrene oxide in a sufficiently pure state without distillation or other heat treatment. Ordinarily the conversion of a bromohydrin to the corresponding oxide is rapid and quantitative. With this in mind, pure *p*-methoxystyrene bromohydrin was sought as a desirable precursor.

Among the methods investigated was the solvolysis of *p*-methoxystyrene dibromide to the bromohydrin as reported by Tutin, Caton and Hann.⁷ Eventually an acceptable modification of their procedure was developed which led to the bromohydrin in good yield and of analytical purity. The oxide was produced when the solvolysis was conducted in the presence of sodium hydroxide.

The reaction of *p*-methoxystyrene oxide with phenoxide ion was carried out at the same temperature and with the same concentration of components as was used with styrene oxide⁸ and the nitrostyrene oxides.^{2,3} As shown in the equation



(1) Scientific Series Paper No. 373 of the Experiment Station.

(2) C. O. Guss and H. G. Mautner, *J. Org. Chem.*, **16**, 887 (1951).

(3) C. O. Guss, *ibid.*, in press.

(4) G. Baddeley and G. M. Bennett, *J. Chem. Soc.*, 1819 (1935).

(5) E. D. Bergmann and M. Sulzbacher, *J. Org. Chem.*, **16**, 84 (1951).

(6) S. Winstein, T. L. Jacobs, R. B. Henderson, J. H. Robson and B. F. Day, *ibid.*, **11**, 157 (1946); G. P. Mueller and R. May, *THIS JOURNAL*, **71**, 3313 (1949).

(7) F. Tutin, F. W. Caton and A. C. O. Hann, *J. Chem. Soc.*, **95**, 2113 (1909).

(8) C. O. Guss, *THIS JOURNAL*, **71**, 3460 (1949).