The Synthesis of β-Ionylideneacetaldehyde

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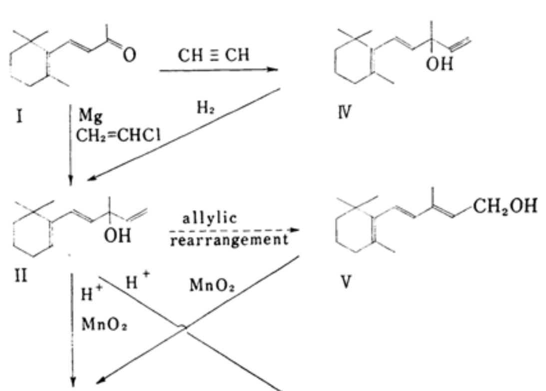
This paper will present a simple method to prepare β-ionylideneacetaldehyde, which is an important intermediate in the synthesis of vitamin A or its homologous compounds. *trans*-β-Ionylideneacetaldehyde (III) was obtained by the oxidation of vinyl-β-ionol (II) with manganese dioxide under an acidic condition. II was prepared by means of a Grignard reaction from β-ionone (I) and vinyl chloride.

II has been prepared by the reduction of ethynyl-β-ionol (IV)[1-4] derived from I and acetylene. Another method which utilizes the Grignard reaction of I with vinylmagnesium bromide has been reported,[4] but the yield of II is not so satisfactory (41%). The author obtained II in a 91% yield by means of the Grignard reaction of I with vinylmangnesium chloride.



The synthesis of vinylmagnesium chloride by means of Normant's method[5] and the continuous preparation of the chloride have been reported by Ramsden et al.[6] and by Reimschuessel[7] respectively. The present author applied Ramsden's method, but vinyl chloride gas was passed into tetrahydrofuran at 15～20°C as the reaction proceeded more rapidly. The Grignard compound of I with vinylmagnesium chloride was allowed to react as usual, and the product distilled to give II.[8]

III may be prepared by the oxidation of β-ionylideneethanol (V), the isomerization product of II. Because of the tendency to give a "*retro*-compound,"[11-14] it is very difficult to obtain V by the allylic rearrangement

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[1] K. Suga, Y. Ishikawa and S. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), to be published.

[2] R. G. Gould, Jr., and A. F. Thompson, Jr., *J. Am. Chem. Soc.*, **57**, 340 (1935).

[3] W. Oroshnik, G. Karmas and A. D. Mebane, ibid., **74**, 295 (1952).

[4] L. A. Yanovskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1435 (1960); *Chem. Abstr.*, **55**, 413e (1961).

[5] H. Normant, *Compt. rend.*, **239**, 1510 (1954); **241**, 1946 (1955).

[6] H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint and R. Cserr, *J. Org. Chem.*, **22**, 1602 (1957).

[7] H. K. Reimschuessel, ibid., **25**, 2256 (1960).

[8] Karrer et al.[9] reported that 1, 4-addition may occur in the Grignard reaction of I. On the other hand, Oroshnik et al.[10] described how the 1, 2-adducts were the main products of this reaction. In the present experiment the reaction product was proved to be II, and I was found to react normally with the Grignard reagent to give the 1, 2-adduct as a major product.

[9] P. Karrer, H. Salomon, R. Morf and O. Walker, *Helv. Chim. Acta*, **15**, 878 (1932).

[10] W. Oroshnik, G. Karmas and R. A. Mallory, *J. Am. Chem. Soc.*, **76**, 2325 (1954).

[11] A. F. Thompson, Jr., N. A. Milas and I. Rovno, ibid., **63**, 752 (1941).

[12] H. O. Huisman, A. Smit, S. Vromen and L. G. M. Fisscher, *Rec. trav. chim.*, **71**, 889 (1952).

[13] P. H. van Leeuwen and H. O. Huisman, ibid., **80**, 115 (1961).

[14] H. Pommer and W. Sarnecki, German Pat. 1059900, (1957).

of II in spite of the easier oxidation of V with manganese dioxide to III ;1) V has, therefore, usually been prepared by the reduction of β-ionylideneacetates. The author obtained *trans*-III in one step by treating II with manganese dioxide under an acidic condition.

To a solution of II in petroleum ether containing a small quantity of 50% sulfuric acid, manganese dioxide was added with vigorous agitation. The product was chromatographed on a silica-gel column. A hydrocarbon (A) and a carbonyl compound (B) were eluted with petroleum ether and benzene-ether (9 : 1) respectively. The properties of B agreed with the authentic data of *trans*-β-ionylideneacetaldehyde, which will be described later. The mechanism of this reaction is not clear as yet, but we can assume that as soon as II rearranges to V, oxidation occurs simultaneously.

The infrared absorption spectrum of A did not show the presence of either a hydroxyl or a carbonyl group. As the ultraviolet absorption spectrum shows the characteristic "*retro*-ionylidenetetraene" structure ($\lambda_{\max}$ 319 mμ ; ε, 52300), A may be considered to be, for the most part, "*retro*-compound (VI)."

Experimental15)

β-Ionone (I).—The properties of I used in this experiment were as follows : d_{25}^{25} 0.943 ; n_{D}^{20} 1.5198 ; Acid value 0.1 ; $\lambda_{\max}$ 296 mμ ; ε, 9900 (lit.,10) $\lambda_{\max}^{96\%\ \mathrm{ethanol}}$ 296 mμ ; ε, 10550) ; the 2, 4-dinitrophenylhydrazone, m. p. 125°C ; $\lambda_{\max}$ 389 mμ ; ε, 21000.

Found : C, 61.40 ; H, 6.14 ; N, 15.21 ; Calcd. for $C_{19}H_{24}O_4N_4$: C, 61.29 ; H, 6.50 ; N, 15.05%.

Vinyl-β-ionol (II). — In a four-necked flask equipped with a thermometer, a dropping funnel, as gas inlet tube and a reflux condenser, 200 cc. of dry tetrahydrofuran, 13 g. (0.54 mol.) of magnesium, and a few crystals of iodine were placed. To this mixture 3.0 g. (0.03 mol.) of ethyl bromide was added drop by drop. When magnesium had been activated, the mixture was allowed to react with dry gaseous vinyl chloride at 40°C. After 30 min., the mixture was cooled to 15∼20°C and vinyl chloride was passed through for an additional 9 hr. The reaction mixture turned dark brown and viscous. After the completion of the reaction, the gas inlet tube was removed, and 60 g. (0.31 mol.) of I in 60 cc. of tetrahydrofuran was stirred into this solution at 5∼10°C. After having been stirred for another hour, the solution was heated to 40°C. The reaction mixture was decomposed with an ice-cooled ammonium chloride solution and extracted with ether. The ethereal layer was washed with a 2% aqueous solution of sodium hydrogen carbonate and water, and then dried over anhydrous sodium sulfate. Evaporation under reduced pressure gave 67 g. of a light yellow oil. By fractional distillation 57.4 g. of vinyl-β-ionol (II) was obtained (91.4% yield) : b. p. 113∼115°C/2 mmHg (lit., 113∼115°C/2 mmHg ;4) 91∼92°C/0.8 mmHg3)) ; n_{D}^{20} 1.5045 (lit., n_{D}^{20} 1.5702 ;4) 1.50223)) ; $\lambda_{\max}$ 237 mμ ; ε, 5700 (lit.,3) $\lambda_{\max}$ 235 mμ ; 5700).

Found : C, 81.35 ; H, 10.91 ; Calcd. for $C_{15}H_{24}O$: C, 81.76 ; H, 10.98%.

The infrared absorption spectrum showed the characteristic bands of a tertiary hydroxyl group (3400 and 1100 cm^{-1}) and of a vinyl group (920 and 990 cm^{-1}). The infrared and ultraviolet absorption spectra were identical with those of the partial reduction product of ethynyl-β-ionol derived from β-ionone and acetylene.1)

***trans*-β-Ionylideneacetaldehyde** (III). — To a solution of 5.00 g. (0.023 mol.) of vinyl-β-ionol in 150 cc. of petroleum ether, 1.3 cc. of 50% sulfuric acid and 50 g. of activated manganese dioxide were added under efficient agitation. The mixture was stirred for 72 hr. at room temperature. Upon the product had been worked up, 4.10 g. of a light yellow oil was obtained. This oil was chromatographed on a silica-gel column. From the petroleum ether-eluted fraction, a 0.69 g. of hydrocarbon (A) was obtained, while 1.77 g. (a 35.8% yield) of a carbonyl compound (B) was obtained from the benzene-ether (9 : 1).

The infrared absorption spectrum of B was super-imposable on that of the authentic sample ;1) 1670 and 965 cm^{-1}. The ultraviolet absorption spectrum : $\lambda_{\max}$ 275, 326 mμ ; ε, 11000, 14000 (lit.,16) $\lambda_{\max}$ 273, 326 mμ ε, 11800, 15600).

Semicarbazone.—Recrystallized from ethanol : m. p. and mixed m. p. 195°C ; $\lambda_{\max}$ 324 mμ ε, 34700 (lit.,17) m. p. 195∼196°C ; $\lambda_{\max}$ 323 mμ $E_{1\mathrm{cm}}^{1\%}$ 1330).

Found : N, 14.85. Calcd. for $C_{16}H_{25}ON_3$: N, 15.26%.

2, 4-Dinitrophenylhydrazone. — Recrystallized from chloroform-ethanol : m. p. and mixed m. p. 198°C ; $\lambda_{\max}$ 410 mμ ; ε, 40000 (lit.,16) m. p. 198°C ; $\lambda_{\max}$ 408 mμ ε 37000).

Found : C, 62.83 ; H, 6.35 ; N, 14.05. Calcd. for $C_{21}H_{26}O_4N_4$: C, 63.30 ; H, 6.58 ; N, 14.06%.

An attempt to isolate III by means of the addition product with sodium hydrogen sulfite12) was unsuccessful.

The ultraviolet absorption spectrum of A showed the characteristic "*retro*-ionylidenetetraene" structure at $\lambda_{\max}$ 319 mμ (lit., $\lambda_{\max}^{96\%\ \mathrm{ethanol}}$ 313 mμ ;12) $\lambda_{\max}^{\mathrm{ethanol}}$ 317 mμ18)), suggesting the formation of a retro-form unsaturated hydrocarbon. The isolated A changed to a gummy substance within a few hours and became insoluble in the usual solvents, so its structure was not identified.

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15) The UV absorption spectra were measured in ethanol, chloroform (the semicarbazone and the 2, 4-dinitrophenylhydrazone of (III)) or benzene (VI), and the IR absorption spectra, with liquid film. Elementary analyses were performed at the Institute of Physical and Chemical Research, Tokyo.

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17) N. L. Wendler, H. L. Slates. N. R. Trenner and M. Tishler, ibid., 73, 719 (1951).

18) W. Oroshnik, A. D. Mebane and G. Karmas, ibid., 75, 1050 (1953).

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