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SYNTHESIS OF LEAF ALDEHYDE

U. Yu. Myaéorg and É. R. Myttus

UDC 547.381

The comparative oxidation of trans-hex-2-enol to leaf aldehyde has been effected with the aid of manganese dioxide, chromium oxide, and sodium dichromate in DMSO. It has been established that sodium dichromate in DMSO gives the best yield (not less than 80%) and a product of higher purity. It is a comparatively new reagent in organic synthesis. The use of sodium dichromate in DMSO is promising in the preparation of compounds requiring the use of mild conditions.

trans-Hex-2-enol and trans-hex-2-enal are extremely widespread in nature [1, 2]. Hex-2-enal is one of the components of the aroma of verdure, and therefore it has been called leaf aldehyde [3]. In addition to this, it is present in many other natural aromas, including the essential oil of tomatoes [4], olive oil [5], citrus leaves [9], and tea [7]. trans-Hex-2-enal is also present in the volatile components of many plants, such as oranges [8], hops [9], black currents [10], etc., usually together with trans-hex-2-enol. Leaf aldehyde has not been detected only in plants. It has been isolated from the scent glands of the nymph of *Ptermistria bispina* Stal. [11] and is one of the components of the pheromone of the silkworm [12]. It has also been isolated from the poisonous secretion of the insects *Eurycotis flori-*

Tartu State University. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 298-300, May-June, 1977. Original article submitted January 17, 1979.

0009-3130/79/1503-0257$07.50

dana W. [13] and *Crematogaster africana* Nayr [14]. It has been shown that allyl alcohol dehydrogenase from *E. coli* oxidizes the leaf alcohol cis-hex-3-enol to the leaf aldehyde trans-hex-2-enal [15].

Several methods of synthesizing trans-hex-2-enol and leaf aldehyde have been described in the literature [1, 2, 16-20], including the oxidation of hex-2-enol with hexavalent chromium oxide [18, 20]. We have performed the comparative oxidation of trans-hex-2-enol to leaf aldehyde with the aid of manganese dioxide, chromium(VI) oxide, and sodium dichromate in DMSO. This has shown that $Na_2Cr_2O_7$ in DMSO gives the best yield (not less than 80%) and a product of higher purity than manganese dioxide and chromium(VI) oxide. Sodium dichromate in DMSO is a comparatively new reagent in organic synthesis, but its use is promising in the preparation of compounds requiring the use of mild conditions.

EXPERIMENTAL

Hex-2-ynol. Hex-2-ynol was obtained in accordance with the equation

$$H-C_3H_7C\equiv C \xrightarrow[2)\ HCHO]{1)\ EtMgBr} H-C_3H_7C\equiv CCH_2OH$$

as in a published method [20, 22]. Paraformaldehyde was depolymerized by heating it with phosphorus pentoxide at 220°C. The gaseous formaldehyde was passed for six hours into the Iotsich reagent prepared from 136 g (2 moles) of pent-1-yne. After this, the mixture was boiled for another hour and was worked up in the usual way. The yield of product was 167 g (85.2%), bp 80-81°C/40 mm Hg, n_D^{20} 1.4541. The purity of the product according to GLC was 98%.

trans-Hex-2-enol. trans-Hex-2-enol was obtained with methanolic sodium in liquid ammonia, as in the standard method [23]. The yield was 44 g (87.8%), bp 75.5-76.2°C/ 38 mm Hg, $n_D^{19.5}$ 1.4380. The purity according to GLC was not less than 98%. In the IR spectra the absorption of a trans-HC= CH group appeared at 975 and 1680 cm^{-1} and of an –OH group at 3375 and 1035 cm^{-1}.

trans-Hex-2-enal. a) A solution of 8 g of the hexenol obtained above was shaken in 0.5 liter of dichloroethane with 100 g of active manganese dioxide prepared by Attenborrow's method for 2 h [24]. After this, the solid matter was separated off by filtration, the filtrate was evaporated, and the residue was distilled through a 20-centimeter Vigreux column. This gave 5.5 g of hex-2-enal having bp 66-68°C/40 mm Hg, n_D^{19} 1.4469. Yield 71% of theoretical; purity according to GLC not less than 85%.

b) The oxidation of 1 g of the hexenol obtained above in the manner described by Ohno [20] and distillation at 60-61°C/30 mm Hg yielded 0.8 g (82%) of leaf aldehyde with n_D^{19} 1.4442. According to GLC, the product contained 11% of the initial hexanol. The constants of the hexenal obtained by this method are not given by Ohno [20].

c) The hexenol obtained above (5 g) was added to a solution of 10 g of sodium dichromate dihydrate in 100 g of dimethyl sulfoxide. With stirring and water cooling, 7.2 ml of 96% sulfuric acid was added to this solution at such a rate that the temperature of the mixtur did not rise above 70°C. The mixture was stirred for another half-hour, and 300 ml of water with ice was added. The resulting aqueous solution was extracted with ether (3×100 ml) and the etheral extracts were combined and were washed with 50 ml of saturated sodium bicarbonate solution and with water and were dried over sodium sulfate. Evaporation of the solvent and distillation of the residue at 44-45°C/25 mm Hg yielded 3.9 g (80%) of trans-hex-2-enal with n_D^{19} 1.4467. The purity according to GLC was not less than 96.5%. The IR spectrum coincided with the published spectrum [20]. The UV region contained an absorption maximum at 22 nm (ε = 16,500) (in ethanol).

GLC analysis was performed in a 2 m×3 mm column. The liquid phase was 10% of Carbowax 20 M on Chromaton N-AW (80-100 mesh) at 105°C. Flame-ionization detector; carrier gas nitrogen (25 mm/min). The IR and UV spectra were taken on the prism instruments "Specord 71-IR" and "Specord UV-VIS," respectively.

SUMMARY

The comparative oxidation of trans-hex-2-enol to leaf aldehyde has been performed with the aid of manganese dioxide, chromium oxide, and sodium dichromate in DMSO. It has been found that Na_2CrO_7 in DMSO gives the best yield (not less than 80%) and a product of higher purity.

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DETERMINATION OF THE CONTENT OF HYDROXY GROUPS IN COTTONSEED OIL

S. G. Yunusova, F. M. Kantsepol'skaya,
E. L. Kristallovich, A. I. Glushenkova,
and A. U. Umarov

UDC 547.915:665.31

IR spectroscopy has been used to determine the content of hydroxy groups in cottonseed oil in relation to the periods of ripening. It has been found that the largest amount of hydroxy groups is present in the oil of the early stages of ripeness.

The oil of ripe cottonseeds contains a number of compounds with hydroxy groups, and observations have shown that their amount decreases as the seeds ripen. In view of this, the necessity arose for having available rapid and fairly accurate methods for the quantitative estimation of oxygen-containing compounds in the oil.

The present paper describes a method for determining hydroxy groups in the oil of cottonseeds during their ripening by IR spectroscopy.

The use of IR spectroscopy for the quantitative determination of hydroxy groups, ketones, and ether/ester groups in oxidized fatty esters and similar compounds has been reported previously [1, 2]. The method is based on finding the intensity of the characteristic absorption of the spectrum at the wavelength of the absorption maximum. It can be performed rapidly, requires only small amounts of sample (about 20 mg) and gives results agreeing well with lengthier chemical methods requiring considerably larger amounts of material. It is desirable to use the IR-spectroscopic method for the quantitative estimation of hydroxyl groups in cottonseed oils in relation to the vegetation periods when it is difficult to obtain the

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 300-303, May-June, 1979. Original article submitted January 26, 1979.

0009-3130/79/1503-0259$07.50