Synthesis of 3,4-Methylenedioxyphenyl-glyoxal.*

By Sin'iti KAWAI and Koichi ASHINO.

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It is anticipated that the compound in the title will be obtained in yellow crystals or oil. Contrary to our expectation, when homopiperonal (I)⁽¹⁾ was oxidized with selenium dioxide in an alcoholic solution, colourless crystals with m.p. 107° were obtained. Further research upon the colourless compound revealed that it was nothing but the 3,4-methylenedioxyphenyl-glyoxal with one molecule of ethanol of crystallization (III). When the colourless compound was warmed with a boiling ethanol bath in Abderhalden's apparatus under reduced pressure (12 mm.) there remained a yellow oil (II).⁽²⁾ This yellow oil regenerated the colourless crystals (III) when treated with ethanol.

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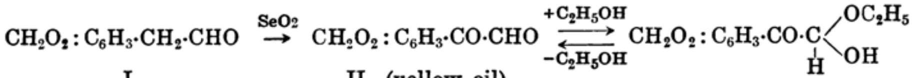
[*] The same contents will soon be published in Japanese in *J. Chem. Soc. Japan*, **59** (1938), No. 8.

(1) Prepared by the ozonolysis of safrol. Compare S. Nagai, *J. Faculty Eng., Tokyo Imp. Univ.*, **13** (1923), 189.

(2) Since a part of the yellow oil (II) volatilizes with the ethanol of crystallization, the exact content of the latter can not be estimated with this apparatus.



$$CH_2O_2:C_6H_3\cdot CH_2\cdot CHO \xrightarrow{SeO_2} CH_2O_2:C_6H_3\cdot CO\cdot CHO \underset{-C_2H_5OH}{\overset{+C_2H_5OH}{\rightleftarrows}} CH_2O_2:C_6H_3\cdot CO\cdot \underset{H}{C}{<}\begin{smallmatrix}OC_2H_5\\ OH\end{smallmatrix}$$

I II (yellow oil) III (colourless crystals)

The disappearance of the yellow colour, the sign of α-diketones, in compound III can probably be attributed to the transformation of one of the carbonyl groups into the hemi-acetal form.

When compound III was treated with more than two molecules of phenylhydrazine, it gave the corresponding mono-phenylhydrazone. *o*-Phenylene-diamine, when mixed with compound III, produced the corresponding quinoxaline-derivative.

Experimental.

Molecular Compound between 3,4-Methylenedioxyphenyl-glyoxal and Ethanol (III). An alcoholic solution of homopiperonal (3.3 g.) and selenium dioxide (4 g.) was refluxed on a steam-bath for two hours. After cooling the selenium which precipitated in the meanwhile was filtered off and the filtrate was concentrated to a small bulk. The colourless crystals mingled with selenium which appeared in the meantime was collected and recrystallized from ether. Colourless long prisms, m.p. 107°. Yield 1 g. Found(3): C, 58.30, 58.30; H, 5.62, 5.67. Calculated for $C_{11}H_{12}O_5$ (III): C, 58.48; H, 5.35%.) Fuchsine-sulphurous acid reaction was positive.

3,4-Methylenedioxyphenyl-glyoxal-mono-phenylhydrazone. Compound III (1 g.) and phenylhydrazine base (1.2 g.) were dissolved in glacial acetic acid which had been diluted with a little amount of water. Soon the mono-phenylhydrazone crystallized out, which was collected and recrystallized from ethyl alcohol, orange-yellow prisms, m.p. 140°. Yield 0.4 g. Found: N, 10.07. Calculated for $C_{15}H_{12}O_3$: N, 10.44%.

2-[3′, 4′-Methylenedioxyphenyl]-quinoxaline. Compound III (0.1 g.) and *o*-phenylene-diamine (0.6 g.) were dissolved in a small quantity of ethyl alcohol with gentle warming and then cooled. Soon the crystals of the quinoxaline derivative made their appearance, which were collected and recrystallized from ethyl alcohol, slightly yellow prisms, m.p. 167.5°. Yield 0.1 g. Found: C, 71.56; H, 4.07; N, 11.09. Calculated for $C_{15}H_{10}O_2N_2$: C, 71.99; H, 4.03; N, 11.20%.

Chemical Institute,
Tokyo-Bunrika University.

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(3) The microanalyses of this compound according to Pregl's method, prosecuted by Kisaburo Yamagami, were successful only when they were carried out first in nitrogen stream and then in oxygen. The ordinary method gave a little too small values of carbon and hydrogen since the ethanol of crystallization burned suddenly at the commencement of the analyses.