ART. X. — *On the Oxydation of Diamylene with Chromic Acid;* by J. WALZ, Ph.D.

AT the instigation of Prof. Erlenmeyer (in Heidelberg), who proposes to ascertain the relative constitution of Diamylene, I undertook the oxydation of this substance with chromic acid.

I used amylene which boiled between 35° and 40° C. This was polymerized rapidly and completely according to the method described by Erlenmeyer* and almost the whole of the product thus obtained, distilled at 153°–170° C. In order to test its purity it was treated with bromine in a narrow tube which was surrounded by cold water; the bromine was added gradually, every drop added causing a hissing sound and a considerable evolution of hydrobromic acid.† When the liquid had assumed a reddish-brown color it was purified, washed and dried according to the usual methods. The product thus obtained was not Bauer's bibromid ($C_{10}H_{20}Br_2$),‡ but the *monobromid of diamylene bibromid*, $C_{10}H_{19}Br_3$. It is an almost colorless oil, heavier than water and has a weak, but not disagreeable odor of camphor. It decomposes and turns brown at 100° C. It was analyzed with the following results:

* Verhandlungen des naturhistorisch medicin. Vereins, Heidelberg, vol. iii, 1865–6.

† Although the temperature of the liquid during the operation was about 15° C., no carbonization could be observed. Compare: Bauer, Sitzgsberichte der Wiener Akademie, xliii, 96.

‡ C=12, O=16, S=32, &c.

I. 0·2235 grms. of the substance furnished 0·2541 CO_2 and 0·1063 H_2O.

II. 0·2093 grms. furnished 0·2472 CO_2 and 0·1007 H_2O.

	$C_{10}H_{10}Br_2$ demands:	Found. I.	II.
C,	31·66	31·00	32·20
H,	5·01	5·28	5·34
Br,	63·33		
	100·00		

The oxydation.—At one time 14 grms. of diamylene were mixed with 100 grms. of bichromate of potassa, 150 of sulphuric acid (spec. gravity=0·1842) and 150 of water; in a second experiment 32 grms. of diamylene, 228 of the bichromate and 442 of sulphuric acid and of water, each, were employed, these quantities being required to supply 10 atoms of oxygen. This mixture was put into a spacious glass-balloon, which was connected with a reversed "Liebig's cooler" and was shaken until the substances began to act upon each other. The reaction soon became very intense, the liquid fairly boiling, and large quantities of carbonic acid being evolved. When the reaction had somewhat subsided, the oxydation was completed with the aid of a lamp; but in neither case was all the chromic acid reduced. The contents of the balloon were then diluted with water and distilled, furnishing a green oil and a few drops of an oily acid; the water which distilled over contained also a great deal of acid. A greenish resinous mass remained behind in the balloon, floating on the surface of the liquid.

The green oil.—Immediately after distillation this oil seems to hold some acid in solution; it was, therefore, neutralized with soda, washed with water and dried over chlorid of lime. In this way about 12 c.c. m. of the oil were obtained from 32 grms. of diamylene. It has no fixed boiling point, the thermometer rising from about 128° to 200° C. during its distillation. The following are the results of various analyses:

I. 0·1006 grms., taken from the entire quantity of the oil after drying with chlorid of calcium, yielded 0·2643 grms. CO_2 and 0·1206 H_2O.

II. 0·0996 grms., boiling at 140°–160° C., yielded 0·2690 CO_2 and 0·1236 H_2O.

III. 0·1646 grms., boiling at 160°–180° C., furnished 0·4552 grms. CO_2 and 0·1974 H_2O.

IV. 0·2016 grms. boiling at 180°–200° C., furnished 0·5667 CO_2. The determination of the water was lost.

	I.	II.	III.	IV.
C,	70·39	72·75	75·41	75·54
H,	13·30	13·75	13·32	....

			C.	H.
The formula	$C_7H_{14}O$	requires	73·68	12·28
" "	$C_8H_{16}O$	"	75·00	12·50
" "	$C_9H_{18}O$	"	76·05	12·67
" "	$C_{10}H_{20}O$	"	76·92	12·82

It would, consequently, appear most likely to consider this oil as a mixture of these various oxyds and as perhaps still containing diamylene which had not been attacked during the process of oxydation. It possesses a yellowish-green color, a penetrating odor of camphor and of mint; its specific gravity is less than that of water; it does not combine with bisulphite of soda and it is in no way affected by a temperature of 20° C. It appears to be difficult to dry it completely with chlorid of calcium, and sodium cannot be employed because it affects the oil chemically.

Hoping to obtain some farther information concerning the constitution of this substance, or, at least, to purify it by oxydizing the diamylene which it possibly still contained, I treated 6 grms. of the oil with 5 grms. of bichromate of potash, 8 grms. of concentrated sulphuric acid and 16 of water in a glass balloon connected with a reversed 'Liebig's cooler.' The course of this oxydation resembled exactly that of diamylene itself; the formation of acids, both oily and soluble in water, and of a resinous substance took place, while about 4 grms. of the oil, which still possessing the characteristic smell and color, now showed the following composition:

I. 0·0907 grms. of the substance yielded 0·2536 CO_2 and 0·1104 H_2O.

II. 0·1098 grms. of the substance yielded 0·3046 CO_2 and 0·1435 H_2O.

	I.	II.
C,	81·69	81·53
H,	13·52	13·53

This composition answers very nearly to the formula $C_{20}H_{40}O$ (which would be the oxyd of tetramylene) which requires 81·08 p. c. C, 13·51 H, and 5·41 O. Still it would seem as if merely a farther oxydation of the products intermediate between the diamylene and the acids described further on, had taken place in this instance, and, consequently, no definite formula can as yet be assigned to this oil.

The acid distillate.—The acid distillate, mentioned above, was neutralized with soda and evaporated to dryness. A considerable quantity of a salt, part of which proved to be deliquescent, was obtained in this way. It was decomposed with

sulphuric acid and distilled, furnishing an oily acid and water of a strongly acid reaction. The oily acid was separated and collected by itself and found to be a colorless syrup which shows no sign of crystallization at a temperature of 20° C. It was exactly neutralized with ammonia and precipitated with nitrate of silver. The precipitate formed a white, cheesy, voluminous mass, which is almost insoluble in water. Two analyses showed that the dry salt contained 40·66 and 40·88 p. c. of silver.

I. 0·1773 of the salt yielded 0·0721=40·66 p. c. Ag.
II. 0·1634 " " " 0·0668=40·88 " "

This composition would correspond to several salts, and we prefer, therefore, to leave the final decision to further investigations.

The water which distilled with the foregoing acid had a sour reaction and the smell pointed to the presence of acetic acid. It was several times partially neutralized with nitrate of silver, and the salts which crystallized out, were analyzed:

I. 0·1589 grms. of the dry salt left 0·1021=64·25 p. c. Ag.
II. 0·1698 " " " " 0·1086=63·95 " "
III. 0·1232 " " " " 0·0794=64·44 " "
IV. 0·2328 " " " " 0·1505=64·65 " "

Acetate of silver requires 64·67 p. c. Ag.

The salt analyzed under IV had been obtained as follows: the liquid was left in contact with the oily acid for several days, and shaken with it from time to time in order to dissolve as much of it as possible; it was then separated and subjected to a fractional distillation, which was suspended as soon as oily acid ceased to distil. The liquid which remained behind in the retort was neutralized with nitrate of silver while it was still hot, and on cooling down, a beautiful crystallization of acetate of silver was obtained. The purity of the salt, as disclosed by analysis, proves the absence of any acid intermediate between acetic acid and the one before described. I must mention yet that the amount of acetic acid formed is very large.

The tarry substance.—The tarry substance which I have mentioned above as having remained behind in the balloon after the distillation of the other products of oxydation, was boiled with dilute sulphuric acid and alcohol, the solution poured off and the chromium precipitated with soda. The solution was decanted from the precipitate* and evaporated to

* This precipitate was decomposed with sulphuric acid and a great deal of a tarry substance was thus obtained floating on the liquid. It is soluble in alcohol and ether, but insoluble in water. When the precipitate is boiled with a concentrated solution of pure potassa, sesquioxyd of chromium is precipitated and a yel-

dryness on the water-bath. A deliquescent salt remained behind which was decomposed with sulphuric acid and yielded an oily acid. This acid is a colorless syrup which does not crystallize at 50° C.; it possesses an agreeable fruit-like odor, is lighter than water, little soluble therein, and seems to have the formula $C_7H_{14}O_2$ (perhaps isomeric with œnanthylic acid). On account of the small quantity at my disposal I could not accurately determine its boiling point; but this seems to lie between 215°–225° C. The salts which this acid forms with the alkalies are very soluble in water and deliquesce in contact with the air.

The lime salt is very easily soluble in water; in the dessicator (over sulphuric acid) it dries up, forming a white, anhydrous, crusty mass, which is not deliquescent.

The silver salt is obtained as a flocculent white precipitate. Its composition was ascertained to be as follows:

I. 0·1471 of the dry salt left 0·0667=45·34 p. c. Ag.
II. 0·1078 " " " 0·0486=44·79 " "
III. 0·1727 " " " were subjected to combustion, furnishing 0·2245 grms. of CO_2 and 0·1046 H_2O.

Required by the formula $C_7H_{13}O_2$.			I.	II.	III.
C_7	84	35·44 p. c.	....	....	35·45
H_{13}	13	5·49 "	....	....	6·71
Ag	108	45·57 "	45·34	44·79	....
O_2	32	13·59 "	....	....	....
	237	100·00			

In conclusion, I beg leave to state that want of time and material prevented me from extending my experiments far enough to speak with greater certainty on many points touched upon in this article. Experiments in this direction will, however, be continued in the Laboratory of Prof. Erlenmeyer (Heidelberg), to whom I take this opportunity of expressing my heartfelt thanks for the kind interest and valuable advice which he bestowed upon me during the whole of my investigation.

New York, Nov. 18th, 1867.

lowish oily-looking substance appears which is easily soluble in water. Sulphuric acid decomposes it, and on distillation an oily acid is obtained which seems to be homologous to the above-mentioned acids. The quantity which I obtained of it was not sufficient for an analysis. These acids appear to me to be identical or isomeric with caprylic acid and its next higher homologues.