ETHYL 1:2:3:6-TETRACARBETHOXY-5-METHOXY-$\Delta^{2:5}$-CYCLOHEXADIEN-1-ACETATE, A DERIVATIVE OF TRIETHYL ACONITATE.

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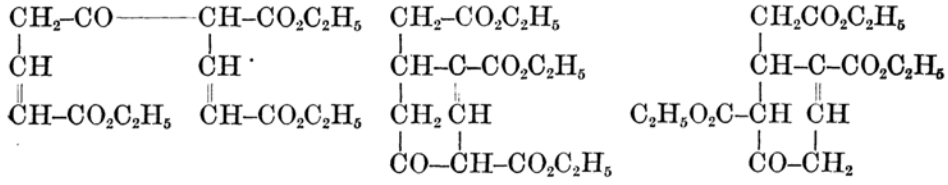
For a certain purpose the author tried the methylation of triethyl aconitate. A mixture of this ester and sodium ethylate in molecular proportion was heated on the water bath with an excess of methyl iodide in absolute alcoholic solution. As the reacting mixture was not brought to complete neutralisation in the course of one hour, it was heated at 115–120° under pressure. By this treatment the dark colour of the mixture faded to light brown. After concentrating the alcoholic solution, it was added to water

and extracted with ether. The ethereal extract gave a very viscous, fluorescent, slightly yellowish oil, which distilled at 225–230° under the pressure of about 1 mm.. It was purified by redistillation. 0.2220 Gr. of the substance gave 0.4632 gr. of CO_2 and 0.1340 gr. of H_2O ; 0.2929 gr. of the substance gave 0.6110 gr. of CO_2 and 0.1747 gr. of H_2O. (Found : C=56.92, 56.91 ; H= 6.75, 6.67%.) The numbers 491, 475, and 475 (mean 480) were obtained in the ebullioscopic determination of the molecular weight using acetone as the solvent. The analytical result corresponds to the formula $C_{23}H_{32}O_{11}$ which requires C=56.99, H=6.67%, and molecular weight=484. The obtained substance was not the methyl derivative of triethyl aconitate $C_{13}H_{20}O_6$ which requires C=57.31 ; and H=7.41%. If two molecules of triethyl aconitate $C_{12}H_{18}O_6$ split out one molecule of alcohol, and one hydrogen atom be substituted with a methyl group, that is, $2C_{12}H_{18}O_6 - C_2H_6O + CH_2$, the formula $C_{23}H_{32}O_{11}$ is obtained. Before entering the problem of the constitution of this substance, some statements on the condensation of diethyl glutaconate are indispensable.

E. E. Blaise[1] obtained a condensation product of diethyl glutaconate when he tried the methylation of this ester at a high temperature. He showed that this substance was formed by the action of sodium ethylate on the glutaconic ester, two molecules of the latter splitting one molecule of alcohol. He gave it formula I. To the same substance H. v. Pechmann, W. Bauer, and J. Obermiller[2] gave formula II, while R. Curtis and J. Kenner[3] accepted formula III.



I. II. III.

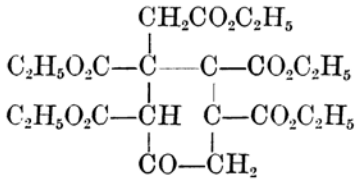
The last formula seems to be the most reasonable, and according to Curtis and Kenner this compound (in its enolic form) is called ethyl 2:6-dicarbethoxy-$\Delta^{2:5}$-cyclohexadien-5-ol-1-acetate. Blaise[4] tried the methylation of this compound and obtained a methyl derivative although not in a pure state.

In the present case, it is most probable that triethyl aconitate first gives the condensation product IV,[5] or, strictly speaking, its sodium derivative,

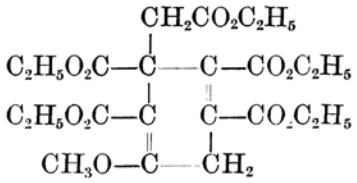
(1) *Bull. soc. chim.*, [3] **29** (1903), 1028.
(2) *Ber.*, **37** (1904), 2113.
(3) *J. Chem. Soc.*, **105** (1914), 282.
(4) Loc. cit.
(5) The mechanism of formation, cf. *Ber.*, **37** (1904), 2114.

and this is further methylated by the action of methyl iodide. Thus the compound with the formula $C_{23}H_{32}O_{11}$ is obtained. This substance does not dissolve in aqueous alkali, and gives no colouration on adding ferric chloride. It does not condense with phenylhydrazine by the same treatment as that which enabled Curtis and Kenner to obtain the phenylhydrazide of the compound represented by the formula III.[1]

This fact suggests that the methyl group in the compound $C_{23}H_{32}O_{11}$ is combined as a methoxy group, and that the intermediate product IV reacts in the enolic form, giving finally the methylated product V.



IV.



V.

Thus the constitution of the substance formed in the methylating reaction of triethyl aconitate at 115–120° is represented by the formula V, and may be called ethyl 1:2:3:6–tetracarbethoxy–5–methoxy–$\Delta^{2:5}$–cyclohexadien–1–acetate.

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(1) Blaise states that he obtained phenylhydrazone of the substance formed by methylating the condensation product of diethyl glutaconate, but the present author does not believe the correctness of Blaise's view.