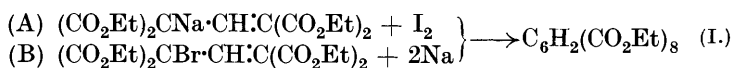


CCXI.—On the Spatial Configuration of the Single Valencies of Allene.

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WE have been engaged for several years in an investigation of a series of alidicyclic compounds, the parent of which was originally obtained by Guthzeit and Hartmann (*J. pr. Chem.*, 1910, **81**, 329) from ethyl dicarboxylglutaconate by the following methods *inter alia* :



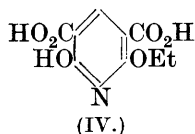
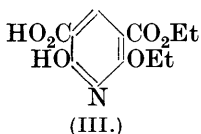
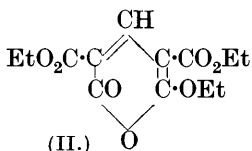
Our work is not yet finished, but the circumstances mentioned below have led to the publication of certain observations incidental to the main investigation.

In a series of researches on the preparation of allene derivatives (Faltis and de Roxas, *Monatsh.*, 1921, **42**, 459; Faltis and Pirsch, *Ber.*, 1927, **60**, 1621; Faltis, Pirsch, and Bermann, *Ber.*, 1930, **63**, 691), the claim has been made that allenetetracarboxylic esters can be prepared from bromodicarboxylglutaconic esters by treatment with silver oxide in hot alcohol or acetone. The objective before Faltis and his collaborators is the solution of the outstanding stereochemical problem of the isomerism of a "centro-asymmetric" allene derivative. When the second of the three papers appeared (1927), we strongly suspected that the compounds described as containing an allene nucleus were identical with substances, familiar to us, which undoubtedly possessed a different composition and constitution; but owing to the intervention of other interests the matter was not immediately pursued. When, however, in the present year, a substance was prepared and described as a diethyl di-*L*-menthyl allenetetracarboxylate, theoretically suitable for the demonstration of optical asymmetry in the allene structure, it seemed highly desirable to test our suspicions without further delay—the more so since Faltis and his co-workers used their study of the compound to support the unorthodox contention that the single valencies of an allene are coplanar.

Faltis and Pirsch's alleged ethyl allenetetracarboxylate was isolated by them from the product of the interaction of silver oxide with alcoholic ethyl bromodicarboxylglutaconate by two methods. In the first, the filtered solution was merely evaporated. The product was described as a crystalline ester, $\text{C}_{15}\text{H}_{20}\text{O}_8$, having m. p. 84° , and *M* (in camphor) corresponding to this formula (requires 328); the ester was stated to be extremely sensitive to neutral

permanganate. On repeating the work we obtained a crystalline ester, $C_{30}H_{42}O_{16}$, having m. p. 86° , and M (in camphor) 653, in agreement with the C_{30} -formula (requires 658); and our ester was saturated to neutral permanganate both in water and in acetone. Direct comparison of our product with Guthzeit and Hartmann's ester (I, m. p. 86°) established its identity therewith, and this was confirmed by hydrolysis of the product prepared by Faltis and Pirsch's method to two crystalline acid esters, $C_{26}H_{34}O_{16}$ and $C_{20}H_{26}O_{12}$, which were likewise identified with the similarly obtained products derived from Guthzeit and Hartmann's ester (I).

Faltis and Pirsch's second method involved a distillation under reduced pressure, and they appear to have assumed that the compound thus obtained is identical with that isolated by their first method. Now we have found that Guthzeit and Hartmann's ester, m. p. 86° , decomposes on distillation under diminished pressure, yielding, as a principal product, the ethyl ethoxypyronedicarboxylate $C_{13}H_{16}O_7$ (II) of Guthzeit and Dressel (*Ber.*, 1889, **22**, 1421; *Annalen*, 1891, **262**, 105), which, when pure, has m. p. 93° . Accordingly, on again repeating Faltis and Pirsch's preparation and isolating the product by their second method, we were not surprised to obtain, not the ester of m. p. 86° , but the pyrone ester, m. p. 93° . It was identified by direct comparison, by conversion, by means of dilute aqueous ammonia, and sodium hydroxide, into the pyridone acids (III and IV), and by hydrolysis with hydrochloric acid to glutaconic acid.



It is not difficult to understand how, in Faltis and Pirsch's experiments, the silver oxide apparently acts as a reducing agent: in all our experiments by their method acetaldehyde was copiously evolved in the early stages of the reaction, and silver was deposited. Doubtless the silver acts like the sodium in Guthzeit and Hartmann's method (B) above.

In the experimental portion reference is made only to those observations which are necessary to refute the claims of Faltis and his co-workers: a constructive constitutional investigation will be published later. The present conclusion is merely that the evidence underlying the theory that the single valencies of allene are coplanar is untrustworthy.

E X P E R I M E N T A L.

Guthzeit and Hartmann's Ester.—The material, prepared in connexion with the investigation of which this work is a by-product, crystallised from ether-ligroin in rectangular plates, m. p. 86° (Found : *M*, in camphor, 650. Calc. for $C_{30}H_{42}O_{16}$: *M*, 658). It was stable to cold neutral or alkaline permanganate both in water and in aqueous acetone.

Faltis and Pirsch's Product (Evaporation Method).—Ethyl α -bromo- $\alpha\gamma$ -dicarboxyglutaconate was heated with freshly prepared silver oxide in alcohol, as recommended by Faltis and Pirsch. Acetaldehyde was evolved and silver deposited. The filtered solution on evaporation yielded a solid product which, after several crystallisations from ether-ligroin, had m. p. 86° (Found : *M*, in camphor, 653), was stable to cold permanganate in water or acetone, and did not depress the m. p. of Guthzeit and Hartmann's ester on admixture. Alkaline hydrolysis yielded the dibasic acid ester, $C_{26}H_{34}O_{16}$ (Found : *M*, by titration, 602; *M*, in camphor, 580, 601. Calc. : *M*, 602), which separated from ethyl acetate-ligroin in prisms, m. p. 192° (decomp.) alone or on admixture with a specimen similarly prepared from Guthzeit and Hartmann's ester (*loc. cit.*). Acid hydrolysis gave the dibasic acid ester, $C_{20}H_{26}O_{12}$, which crystallised from water as its trihydrate, m. p. 152° (Found : *M*, by titration, 520. Calc. : *M*, 512), which was identical with the trihydrate derived from Guthzeit and Hartmann's ester (*loc. cit.*). Both acid esters were stable to cold permanganate.

Distillation of Guthzeit and Hartmann's Ester.—The distillate was collected in two fractions, b. p. $200\text{--}220^{\circ}/11\text{--}12$ mm. and $230\text{--}245^{\circ}/12$ mm., decomposition taking place throughout the process. The second fraction, a viscous yellow oil, was not investigated, but the first, which solidified, was crystallised from ether-ligroin, and identified as ethyl 6-ethoxy- α -pyrone-3 : 5-dicarboxylate by its m. p. (93°), by analysis (Found : C, 55.1; H, 6.0; *M*, in camphor, 298. Calc. : C, 54.9; H, 5.7%; *M*, 284), by hydrolysis with hot hydrochloric acid to glutaconic acid (Found : C, 46.3; H, 4.2; *M*, by titration, 129; *M*, in camphor, 131. Calc. : C, 46.2; H, 4.6%; *M*, 130), by conversion, by cold dilute aqueous ammonia, into ethyl hydrogen 2-hydroxy-6-ethoxypyridine-3 : 5-dicarboxylate, m. p. $159\text{--}160^{\circ}$, and by hydrolysis of the last, by means of sodium hydroxide, to 2-hydroxy-6-ethoxypyridine-3 : 5-dicarboxylic acid, m. p. 182° (decomp.) (Guthzeit and Dressel, *loc. cit.*).

Faltis and Pirsch's Product (Distillation Method).—The directions of these authors were followed, and a liquid product was obtained

which on keeping largely solidified. After purification, the crystalline substance was identified as the pyrone ester by direct comparison and by conversion into the derivatives mentioned in the preceding paragraph.

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