

CCLXIII.—*Syntheses of Cyclic Compounds. Part IV.*
The Catalytic Decomposition of Suberic Acid and
the Preparation of Suberone directly from Mixtures
of Suberic and Azelaic Acids.

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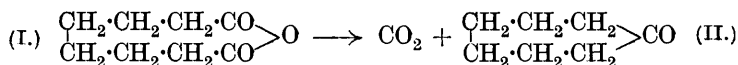
It is proposed to investigate the decomposition, in the presence of various catalysts, of both simple and substituted dibasic acids in order (1) to develop simple methods for the preparation of cyclic ketones and (2) to study the effect of substituents on this method of ring formation. The present communication is concerned with suberic acid. The only previous work on this subject (D.R.-P. 256622) was the alleged production of suberone in good yield by the dry distillation of suberic acid in the presence of 5% by weight of iron filings; Aschan (*Ber.*, 1912, **45**, 1603), however, isolated a small quantity of suberone by the dry distillation of the acid. Day, Kon, and Stevenson (*J.*, 1920, **117**, 639) were unable to obtain satisfactory results by this catalytic process and reverted to the dry distillation of the calcium salt as a method for the preparation of suberone.

The author finds that if an intimate mixture of suberic acid, an *equal weight* of iron filings (a quantity considerably greater than the equivalent quantity), and 5% by weight of crystallised baryta be subjected to dry distillation, a yield approaching 40% of suberone is obtained. The crude product is an almost colourless, mobile liquid with a characteristic ketonic odour in contrast with the practically black liquid, contaminated with suspended matter and having a characteristic "hydrocarbon" odour, obtained from either the calcium or the thorium salt.

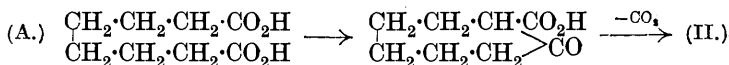
The mixture of azelaic and suberic acids obtained by the oxidation of ricinoleic acid with nitric acid (Day, Kon, and Stevenson, *loc. cit.*; Baker and Ingold, *J.*, 1923, **123**, 122) also gives a good yield of

suberone, together with a relatively small quantity of a liquid the exact composition of which has not yet been elucidated. This liquid boils at about the same temperature as suberone but can readily be separated from it, as the latter reacts immediately with a saturated aqueous or preferably aqueous-alcoholic sodium bisulphite solution, whereas the former gives no solid derivative.

The formation of suberone by the catalytic decomposition of suberic acid probably takes place in two stages, involving the formation of the anhydride (I) and the subsequent elimination



of carbon dioxide (compare Blanc, *Bull. Soc. chim.*, 1908, **3**, 778). Two other mechanisms are possible, one represented by (A) (compare Aschan, *loc. cit.*) and the other involving the intermediate formation of an iron salt.



It is extremely difficult to prepare pure azelaic acid in quantity from the mixed acids obtained by the oxidation of ricinoleic acid with nitric acid; although a product, m. p. 106°, may be obtained by fractional crystallisation from solvents, this contains a considerable quantity of suberic acid, as was shown by analysis and by the production of suberone by its catalytic decomposition. Pure azelaic acid is best prepared by the oxidation of ricinoleic acid with potassium permanganate (Maquenne, *Bull. Soc. chim.*, 1899, **21**, 1061): this melted at 107° and no suberone was obtained by its catalytic decomposition.

EXPERIMENTAL.

Preparation of Suberic Acid.—Castor oil, in lots of 25 kg., was hydrolysed by alcoholic sodium hydroxide to ricinoleic acid, and the latter oxidised by nitric acid to a mixture of azelaic and suberic acids (Baker and Ingold, J., 1923, **123**, 122). The two acids were separated from each other by means of a mixture of benzene and ethyl alcohol in proportion intermediate between those described by Baker and Ingold (*loc. cit.*) and by Day, Kon, and Stevenson (*loc. cit.*); rectified spirit was substituted for absolute ethyl alcohol. The acid which first separated melted at 135–138° and after two crystallisations from water melted sharply at 140°.

Catalytic Decomposition of Suberic Acid.—An intimate mixture of 100 g. of suberic acid (m. p. 140°), 100 g. of iron filings, and 5 g. of finely powdered, crystallised barium hydroxide was placed in a

2-litre Pyrex distilling-flask fitted with a thermometer, reaching to within 0.5 cm. of the bottom, and connected with a long water-condenser and a receiver. The mixture was slowly heated in an air-bath, the space between the sides of the flask and the bath having been packed with copper turnings. Considerable frothing took place at about 235° and water distilled over : a mobile, slightly coloured liquid with a ketonic odour passed over at 280—290°. The ketone was separated from the water in the distillate, the aqueous layer was extracted twice with ether, and the combined extracts and ketone were washed with alkali and dried with anhydrous potassium carbonate. The ether having been removed through a long fractionating column, the residue was separated under reduced pressure into the following fractions : (1) a small head fraction, b. p. 63—65°/15 mm., n_D^{20} 1.4595, d_4^{20} 0.9378; (2) a main fraction, b. p. 65.5—66°/15 mm., n_D^{20} 1.4611, d_4^{20} 0.9467; (3) a small tail fraction, b. p. 67—70°/15 mm., n_D^{20} 1.4627, d_4^{20} 0.9458. The residue weighed less than 1 g. and the total yield of distillate was 24 g. All the fractions were colourless mobile liquids, and remained so after being kept for 6 months (compare the product from calcium or thorium suberate which rapidly darkens on keeping), and on treatment with aqueous semicarbazide acetate and methyl alcohol gave immediate precipitates of semicarbazones which melted at 162—163°, either alone or when mixed with an authentic specimen of suberone semicarbazone prepared from thorium suberate, after one crystallisation from dilute methyl alcohol. No other semicarbazone could be isolated and it was evident that the ketone was practically pure *cycloheptanone*. It could be obtained perfectly pure by regeneration from the bisulphite compound.

Preparation of Suberone from Mixtures of Suberic and Azelaic Acids.—The crude mixture of acids must first be recrystallised from benzene. An intimate mixture of 300 g. of the mixed acids, 300 g. of iron filings, and 15 g. of finely ground, crystallised barium hydroxide was distilled from a 4-litre Pyrex distilling flask as described for suberic acid. (The heating must be very gradual, as there is considerable frothing and evolution of fumes in the early part of the reaction—temperature 200—250°. Indeed, this part of the process may be conducted in the open on a large iron plate : the intimate mixture is gently heated until the evolution of steam and other fumes has ceased, and the cold dark-coloured product is broken up and transferred to the distilling flask.) The rate of heating was such that the liquid distilled at the rate of about one drop per second; the final temperature was 360—400°. The product was isolated as described under suberic acid and distilled, and the fraction, b. p. 62—75°/14 mm., collected; the yield averaged

90 g. from 600 g. of the mixed acids. This fraction was added to a saturated aqueous-alcoholic sodium bisulphite solution, and the crystalline bisulphite compound, which was immediately precipitated, was filtered off, well washed with alcohol and ether, and decomposed with sodium hydroxide, and the ketone isolated by ether extraction. Further small quantities of suberone may be obtained by treating the high-boiling fractions with sodium bisulphite.

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