

CII.—*Synthesis of Cyclic Compounds. Part V. The Catalytic and the Thermal Decomposition of some Normal Dibasic Acids. A Contribution to the Problem of the Ease of Formation of Simple Carbon Rings.*

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It has been shown (J., 1928, 2032) that suberone may be obtained in 40% yield by the dry distillation of a mixture of suberic acid and iron filings in the presence of a small quantity of baryta, although Easterfield and Taylor (J., 1911, 99, 2299) were unable to obtain satisfactory yields by a similar process. The advantages of this method are: (1) the ketone is prepared directly from the acid without previous preparation of a salt, (2) the distillation is carried out under atmospheric pressure, (3) the ketone is obtained in good yield, and (4) the cost is low (compare the dry distillation of thorium suberate under reduced pressure; Ruzicka and others, *Helv. Chim. Acta*, 1926, 9, 515). It was clearly desirable not only to investigate the mechanism of the reaction but also to extend it to other normal dibasic acids.

As a result of a series of comparative experiments in which suberic acid was heated with different quantities of iron filings and also baryta, full details of which will be found in the experimental section, it is concluded that an intermediate iron—most probably the ferrous—salt is formed at a relatively low temperature and then undergoes decomposition into the ketone at a somewhat higher temperature. When the quantity of iron present is less than that theoretically required for the formation of a ferrous salt, variable quantities of *n*-heptoic acid are formed; indeed, when no iron is present, *n*-heptoic acid forms the principal product of the reaction (*vide infra*). The use of small quantities of baryta facilitates the formation of the intermediate iron salt, lowers the decomposition temperature, and gives a purer product. Support for the view that an intermediate ferrous salt is formed is provided by the experiments of Easterfield and Taylor (*loc. cit.*), who found that the yields of

stearone obtained by the dry distillation of stearic acid with the equivalent quantity of iron for the formation of the ferrous salt (62%) and of ferrous stearate (60%) at 360° were practically identical.

The yields of ketone obtained from adipic and pimelic acids by the iron method (*i.e.*, the optimum conditions employed for suberic acid) were 51% and 56% respectively. Azelaic acid gave a 10% yield of *cyclooctanone*, and only methyl octyl ketone could be isolated from the distillation of sebacic acid and iron filings (compare Ruzicka and Brugger, *Helv. Chim. Acta*, 1926, 9, 389, who isolated 0.5% of suberone, 1.2—1.5% of *cyclononanone*, and 0.7% of methyl octyl ketone by the dry distillation of thorium sebacate). The formation and decomposition of the intermediate iron salt of azelaic acid is very much slower than that of suberic acid, so in the dry distillation of a mixture of suberic and azelaic acids under the conditions previously described (Vogel, *loc. cit.*), it is the iron salt of suberic acid which is preferentially formed and decomposed and hence only suberone is obtained. No appreciable quantity of ketone could be isolated from glutaric acid.

A summary of the results is given in Table I; the yields obtained from the calcium and thorium salts (Ruzicka and others, *Helv. Chim. Acta*, 1926, 9, 505) are appended for purposes of comparison. The last column represents the results obtained by the slow thermal decomposition of the acids (*vide infra*). It is evident from the table

TABLE I.

	Salt: Calcium.	Thorium.	Iron.	Acid.
Glutaric acid	0	0	<1%	0
Adipic ,,	45%	15%	51	80%
Pimelic ,,	40—50	70	56	52
Suberic ,,	35	40	40	<2
Azelaic ,,	5	20	10	<1
Sebacic ,,	<1	1.5	<1	<1

that the yields of ketone obtained by the dry distillation of the *salts* of the dibasic acids cannot be employed as an absolute index of ring-forming capacity, as these vary with the metal employed. In order, therefore, to obtain experimental evidence for the ease of formation of simple carbon rings, some other reaction must be employed. Before the method used in the present research is described, a critical discussion of the previous work on the subject must be given. The reaction chosen must satisfy at least two conditions: there must be (1) a main reaction involving the formation of the cyclic compound and (2) an alternative side reaction leading to an open-chain product. Ingold (J., 1921, 119, 305) studied the action of alkali under standard conditions on α -halogenated and

$\alpha\alpha'$ -dihalogenated derivatives of dibasic acids, the side reaction being the replacement of the halogen atom by the hydroxyl group, and the progress of ring formation in competition with the side reaction being taken as a measure of the ease of production of the ring. It was shown that, whereas the yield of *cyclopropane* compound was about 50% in the glutaric acid series, only about 1% of *cyclobutane* compound was isolated in the adipic acid series (Ingold, J., 1921, 119, 951). For pimelic acid, Hassell and Ingold (J., 1926, 1465) state that "the ratio (ring formation) : (hydroxylation) is much greater than in any case previously investigated," but no quantitative figures are given. The reaction, as an index of ring-forming capacity, fails completely for suberic and azelaic acids owing to side reactions (Goss and Ingold, J., 1926, 1471), so that the experimental problem of the relative ease of formation of 5- and 6-membered rings must still be regarded as unsolved.

By assuming the value 115.3° as the angle between the carbon-to-carbon valencies in a polymethylene chain, calculated on the basis of the modified strain theory, and by employing Traube's relative atomic volumes for carbon and hydrogen (Ahren's Vorträge, 1899, 4, 255), Ingold computes the relative ease of formation of some simple carbon rings (Table II, A); the figures thus obtained exhibit

TABLE II.

	3-Ring.	4-Ring.	5-Ring.	6-Ring.	7-Ring.
Ease of ring formation	0.345	0.427	0.220	0.207	0.730 (A)
Stability	0.927	0.436	0.126	0.084	0.230 (B)
Angle of strain (Baeyer)	24.7°	9.7°	0.7°	-5.3°	-9.5° (C)
"Heat absorbed"					
(cals.) (S. and K.) ...	38.1	42.6	16.1	14.3	— (D)
Energy of C-C link					
(cals.) (Hückel)	127.2	130.1	136.5	137.5	138.5 (E)
Contribution (cals.) per					
CH ₂	168.5	165.5	159	158	158 (F)

a maximum at *cyclobutane*—in agreement with Ingold's own experimental results—and require the almost equal ease of formation of 5- and 6-membered rings. Ingold seeks to obtain further support for his theoretical calculations by comparing (A) with Stohmann and Kleber's thermal figures (D) (*J. pr. Chem.*, 1892, 45, 475). This comparison, however, is not justified, since thermal measurements must be compared not with ease of ring formation but with the *stability* of the ring, a quantity (Table II, B) which was also computed by Ingold (*loc. cit.*, p. 309) and exhibits no maximum at *cyclobutane* (compare Hückel, "Fortschritte der Chemie, Physik und Physikalischen Chemie," Bd. 19, Heft 4, 1927, s. 75). Hückel (*Ber.*, 1920, 53, 1281) states that the correct quantity to be employed for the comparison of the stability of ring systems by means of

thermochemical data is the energy of the C-C linking in the ring (Table II, E) or the contribution in cal. per CH₂ (*ibid.*, p. 11) (Table II, F): these exhibit no maximum at *cyclobutane*.

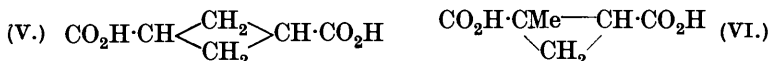
Examples such as (a) the greater yield of the *cyclobutane* compound (I) than of the *cyclopropane* compound (II) obtained by the condensation of trimethylene dibromide and ethylene dibromide,



respectively, with ethyl sodiomalonate (Perkin, J., 1885, **47**, 801; 1887, **51**, 1; Perkin and Prentice, J., 1891, **59**, 823), (b) the almost equal yields of *cyclobutane* (III) and *cyclopropane* (IV) compounds obtained in the condensation of ethyl $\alpha\alpha'$ -dibromoglutarate with



ethyl sodiomalonate in alcoholic solution (condensation in benzene solution gave a 70–80% yield of III; Ing and Perkin, J., 1925, **127**, 2387), and (c) the quantitative production of *cyclobutane-1:3*-dicarboxylic acid (V) and not the 3-membered ring compound



(VI) by the reduction of $\alpha\beta\delta$ -tribromobutane- $\beta\delta$ -dicarboxylic acid (Perkin and Simonsen, J., 1909, **95**, 1169) are difficult to correlate with Ingold's calculations and point unmistakably to the presence of polar and other factors which render comparison impossible.

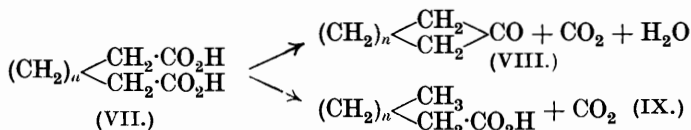
Reference must here be made to the important theoretical work of Wojnicz-Sianozencki (*Rocz. Chem.*, 1921, i, 244) on the ease of formation of simple carbon rings. The normal tetrahedral angle, $109^\circ 28' 24''$, in a polymethylene chain (compare Ingold, *loc. cit.*) forms the basis of the calculations and the whole conception is essentially a dynamic one; by applying the theory of probabilities and making certain plausible assumptions relative to the sphere of influence of the carbon atoms, the final result obtained is that

$$\eta_2 > \eta_5 > \eta_6 > \eta_7 > \eta_3 > \eta_4 > \eta_8$$

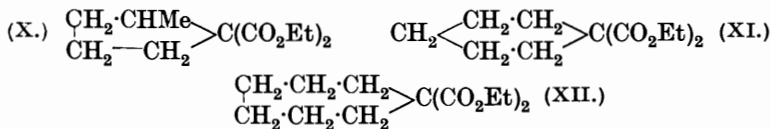
where η_n represents the probability of formation of an n -membered ring, *i.e.*, a double bond is formed more readily than a 5-ring, a 5-ring more readily than a 6-ring, etc. The points of particular interest are: (i) the greater ease of formation of a 3- than a 4-ring, a result in agreement with Ingold's calculations, and (ii) the 5-ring should be formed more readily than the 6-ring.

The reaction chosen by the author for the comparison of capacity

of ring formation, which satisfied the two conditions already mentioned and in which polar factors were reduced to a minimum, consisted in the slow thermal distillation of the normal dibasic acids (VII). Decomposition could occur in two ways: the first



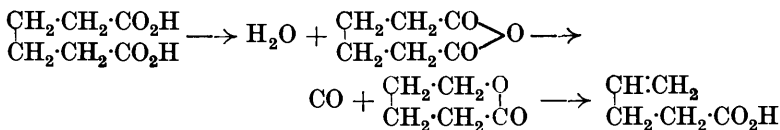
involves the loss of carbon dioxide and water with the production of the ketone (VIII); the second, the elimination of carbon dioxide only with the formation of a saturated monobasic acid (IX). The reaction products could be easily separated and weighed. Glutaric acid yielded only *n*-butyric acid, but the most interesting results were obtained with adipic and pimelic acids. The yields of *cyclopentanone* and *cyclohexanone* were respectively 80% and 52%, thus pointing to the conclusion that the *cyclopentane* ring is formed more readily than the *cyclohexane* ring, a result which is not in accord with the theoretical computations of Ingold (Table II, A) but is in agreement with the predictions made by Wojnicz-Sianozencki (*loc. cit.*). Further, the yield of monobasic acid was greater in the pimelic than in the adipic acid series. This observation is not an isolated one, for Perkin (compare *Ber.*, 1902, **35**, 2105) has found that $\alpha\delta$ -dibromopentane condenses more readily than $\alpha\epsilon$ -dibromopentane with ethyl sodiomalonate with the formation of the corresponding cyclic compounds (X) and (XI), and the 7-membered ring compound (XII) is formed with great difficulty from heptamethylene



dibromide and ethyl sodiomalonate. Suberic, azelaic, and sebacic acids gave good yields of *n*-heptoic, *n*-octoic, and *n*-nonoic acids and the yields of ketone in the first two cases did not exceed 2%. The yields of *cyclopentanone* obtained by the dry distillation of adipic acid (80%) and of adipic acid in the presence of 5% of baryta (78%) under comparable conditions are practically identical, so the reaction cannot be regarded as a catalytic one (D.R.-P. 256622; Roger Adams, "Organic Syntheses," 1925, **5**, 37); the effect of the baryta is to lower the decomposition temperature from 313—315° to 288—293° and slightly to accelerate the decomposition.

Aschan (*Annalen*, 1911, **385**, 58; *Ber.*, 1912, **45**, 1603) has described the distillation of adipic, suberic, and sebacic acids in a

current of carbon dioxide, but although he actually isolated only the ketones and monobasic acids, he expressed the view that unsaturated acids also are formed according to the scheme :



This view, which was unsupported by experimental evidence, is probably erroneous. Other relevant work is that of Blanc (*Bull. Soc. chim.*, 1908, **3**, 778), who found that the yields of ketones obtained by distillation of the anhydrides of adipic and pimelic acids at 200—220° (a temperature very much lower than that employed in the present research) were about 50%.

The work is being continued and will be extended to other normal and also to substituted acids.

EXPERIMENTAL.

Glutaric Acid.—The following modification of Wislicenus's method (*Annalen*, 1893, **275**, 309) for the preparation of glutaric acid was employed. One part of *cyclopentanone* was added during 2 hours to 10 parts of boiling dilute nitric acid (2 : 3), and the whole evaporated to dryness on the steam-bath. The residue was extracted twice with benzene-ether, the solvent removed, and the resultant glutaric acid recrystallised first from chloroform and then from benzene-ether. It melted at 97°. Yield: 280 g. of glutaric acid and 90 g. of succinic acid from 400 g. of *cyclopentanone* (two experiments).

A. Thermal decomposition. The apparatus employed consisted of a 500 c.c. Pyrex distilling flask furnished with a cork carrying a thermometer reaching to within 0.5 cm. of the bottom of the flask and connected to a long water-condenser and receiver. The flask, containing 100 g. of glutaric acid, was placed in a bath, the intervening space packed with copper turnings, and the whole gradually heated, the rate of distillation not exceeding one drop in several seconds. A small quantity of liquid passed over at 290—300° and the temperature then remained constant at 301—304° during the distillation, which lasted 20 hours. There was a carbonaceous residue. The distillate was taken up in ether, the ethereal solution was washed with excess of dilute aqueous sodium hydroxide and dried, and the ether evaporated. The neutral fraction (0.4 g.) did not give a semicarbazone on standing with semicarbazide acetate for some months and was therefore not further investigated. The alkaline washings were acidified with dilute sulphuric acid and

steam-distilled; from the steam-distillate, saturated with ammonium sulphate, ether extracted butyric acid, b. p. 160—162°/750 mm., $d_4^{19.9}$ 0.9595, $n_D^{19.9}$ 1.3978 (Found for the silver salt: Ag, 55.7. Calc.: Ag, 55.4%).

B. Catalytic decomposition. This term will be applied to the decompositions in which the proportion of iron and baryta was that which gave the highest yield of suberone from suberic acid (Vogel, *loc. cit.*). An intimate mixture of 50 g. of glutaric acid, 50 g. of iron filings, and 2.5 g. of crystallised baryta was slowly distilled exactly as described under (A): these were the standard conditions used throughout the work. There was some frothing at about 270°, some fuming above 290°, and a small distillate passed over at 290—380°. This was taken up in ether, washed with alkali, and recovered (1.5 g.). It distilled at 145—150°/758 mm. (*cyclobutanone* has b. p. 99—101°), and was not further investigated since it gave only a sticky semicarbazone.

Adipic Acid.—The adipic acid was obtained from the Deutsches Hydrierungs Akt. and had m. p. 152°.

A. Thermal decomposition. 200 G. were distilled during 12 hours from a litre Pyrex distilling flask; the major portion passed over at 313—315°, but the temperature rose to 320° towards the end of the distillation. The distillate was treated with excess of dilute ammonia solution, the ammoniacal layer separated, and the residual liquid dried with calcium chloride and distilled. 92 G. of *cyclopentanone*, b. p. 131—132°, were obtained and there was hardly any residue of high boiling point. The excess of ammonia was evaporated from the ammoniacal washings, and from the neutral solution silver salts were precipitated (12.4 g. Found: Ag, 54.4%). These were decomposed with dilute sulphuric acid, and *n*-valeric acid, containing a little adipic acid in suspension, was obtained; it boiled at 183—185°/770 mm. (Found for the silver salt: Ag, 51.9. Calc.: Ag, 51.7%). The yield of ketone (80%) was unaffected if the distillation was carried out in lots of 50 g. from a 500 c.c. Pyrex distilling flask; the duration of the distillation was then 6 hours.

B. Decomposition in the presence of an equivalent quantity of iron. When 200 g. of adipic acid and 77 g. of iron filings were slowly heated, the temperature rose fairly rapidly to 250°, the ketone passed over mainly above 290°, and the temperature rose to 360° towards the end of the distillation. The yield of *cyclopentanone* was 70 g. or 61%.

C. Decomposition in the presence of 5% by weight of baryta. 200 G., mixed with 10 g. of crystallised baryta, were similarly heated. The distillate passed over at 288—293°/769 mm. and was worked up as

described under (A). The yield of *cyclopentanone* was 90 g. or 78%.

D. Catalytic decomposition. When a mixture of 200 g. of adipic acid, 200 g. of iron filings, and 10 g. of baryta was heated, after water had passed over, the ketone began to distil at 260° and most passed over at 290—300°; the temperature was finally raised to 360°. The yield of *cyclopentanone* was 59 g. or 51%; there was 10 g. of a product of high boiling point (compare the distillation of calcium adipate; Wislicenus, *Annalen*, 1893, **275**, 309; Wallach, *Ber.*, 1896, **29**, 2955) which probably contained some *cyclopentylidenecyclopentanone*.

Pimelic Acid.—This was prepared in fair yield by the condensation of $\alpha\gamma$ -dibromopropane and ethyl sodiomalonate (Perkin and Prentice, *J.*, 1887, **51**, 20; 1891, **59**, 823) and hydrolysis of the resultant ethyl pentanetetra-carboxylate with 50% sulphuric acid; a somewhat better yield was obtained by employing 4 mols. of ethyl sodiomalonate per mol. of $\alpha\gamma$ -dibromopropane (compare Baeyer, *Annalen*, 1894, **278**, 100). The most convenient method was the following one: $\alpha\epsilon$ -dibromopentane, b. p. 112—113°/22 mm. (Dox and Yoder, *J. Amer. Chem. Soc.*, 1921, **43**, 1366: it may now be prepared in good yield from ethyl glutarate; Müller and Rölz, *Monatsh.*, 1928, **50**, 105) was converted, by refluxing it with 2 mols. of alcoholic potassium cyanide, into the dinitrile, b. p. 164—165°/13 mm. (von Braun, *Ber.*, 1904, **37**, 3588, gives b. p. 171—172°/12 mm.; Hamonet, *Compt. rend.*, 1904, **139**, 59, gives b. p. 175—176°/14 mm.), and the latter hydrolysed by heating under reflux for 9 hours with 12—15 times its weight of 50% sulphuric acid; the pimelic acid separated as a crystalline solid from the cooled solution (yield, almost quantitative). The method of von Braun and of Hamonet (*loc. cit.*), involving the use of a sealed tube, is less convenient and is difficult to carry out with large quantities of material. On recrystallisation from benzene containing 5% of ether, the pimelic acid separated in prisms, m. p. 105—106°.

A. Thermal decomposition. 50 G. were distilled during 6 hours exactly as described under adipic acid (A). The distillate, which passed over mostly at 334—336°, was mixed with pure ether and treated with an excess of dilute aqueous ammonia, the ethereal solution dried, and the ether slowly removed through a long column. The residual liquid had b. p. 155°/758 mm., $d_4^{15.2^\circ}$ 0.9489, $n_D^{15.2^\circ}$ 1.4521 (Vogel, *J.*, 1928, 2030, gives for *cyclohexanone* regenerated from the bisulphite compound, $d_4^{15.7^\circ}$ 0.9492, $n_D^{16.9^\circ}$ 1.4521) and gave a quantitative yield of *cyclohexanonesemicarbazone*, m. p. 166° (yield, 16.0 g. or 52%). From the ammoniacal washings, silver *n*-hexoate (4.3 g.) (Found: Ag, 48.9. Calc.: Ag, 48.5%) was obtained.

B. Catalytic decomposition. When 50 g. were heated during 6 hours, a pale yellow liquid distilled at 318—360° which gave 17.1 g. of cyclohexanone (yield, 56%) and 4.0 g. of a high-boiling product which was not investigated.

Suberic Acid.—This was prepared from castor oil (Baker and Ingold, J., 1923, **123**, 122; Vogel, J., 1928, 2032) and melted at 140°.

A. Thermal decomposition. 50 G. were distilled during 5 hours. The distillate, which passed over at 341—348°, was separated by means of ether and dilute sodium hydroxide solution into a neutral fraction (0.9 g.), which gave suberonesemicarbazone, and an acid fraction; the latter, after purification by steam distillation and treatment with ether, gave 15.5 g. of *n*-heptoic acid, b. p. 120°/18 mm., d_4^{25} 0.9212, n_D^{25} 1.4255 (Found for the silver salt : Ag, 45.7. Calc. : Ag, 45.6%).

B. Decomposition in the presence of 5% by weight of baryta. 50 G., mixed with 2.5 g. of crystallised baryta, were slowly distilled. A liquid passed over at 336—342° (mainly at 336—337°) and after being worked up as described under (A), gave a small quantity of suberonesemicarbazone (yield, >2%) and 12.9 g. of *n*-heptoic acid, b. p. 121°/18 mm., d_4^{25} 0.9231, n_D^{25} 1.4265.

C. Decomposition in the presence of 5% by weight of iron filings. This is the original "catalytic" process described in D.R.-P. 256622, for which an excellent yield of suberone is claimed. When 50 g. of suberic acid, mixed with 2.5 g. of iron filings, were distilled, a liquid passed over at 308—326°. The temperature was raised above 360° after 5 hours; considerable frothing and fuming set in and a further small quantity of liquid distilled over. The distillate was treated in the usual way. The neutral fraction yielded 2.5 g. of a liquid, b. p. 178—186°/769 mm., on distillation; treatment with semicarbazide acetate furnished an opaque granular semicarbazone, obviously impure, which after five crystallisations from dilute methyl alcohol melted at 162—163° and was identical with suberone-semicarbazone. The acid fraction gave 8.5 g. of *n*-heptoic acid, b. p. 121°/19 mm.

D. Decomposition in the presence of one-half the equivalent weight of iron filings. 50 G., mixed with 8.2 g. of iron filings (half the quantity required for the formation of a ferrous salt), were distilled during 6 hours. There was a small amount of frothing at first and a substance with a pungent acid odour passed over at 316—328°; when about half the total distillate has passed over, the odour of the distillate changed to a ketonic one, this process being accompanied by frothing and fuming in the flask. The temperature was raised towards the end of the decomposition until no further distillate was obtained. The distillate was worked up as detailed under (C) and

yielded 1.8 g. of *n*-heptoic acid and 7.7 g. of a ketonic fraction, b. p. 178—188°/766 mm., $d_4^{19.5}$ 0.9242, $n_D^{19.5}$ 1.4584, which afforded suberonesemicarbazone, m. p. 162—163°, after three crystallisations from dilute methyl alcohol.

E. Decomposition in the presence of an equivalent quantity of iron filings. 50 G., mixed with 16.5 g. of iron filings, were slowly distilled. There was considerable frothing and fuming at first, and some water distilled, followed by a colourless liquid of ketonic odour at 296—312° (chiefly at 296—298°); when the temperature was finally raised to about 400°, a small quantity of a blue liquid passed over. The distillate was mixed with ether, washed with dilute alkali solution and dried, and the ether removed; the residual liquid yielded on fractionation (1) a practically colourless liquid (8.0 g.), b. p. 177—185°/756 mm., chiefly at 179—180°/756 mm., $d_4^{19.5}$ 0.9259, $n_D^{19.5}$ 1.4580, which gave suberonesemicarbazone, m. p. 162°, after three crystallisations from dilute methyl alcohol, (2) a pale blue liquid (3.2 g.), b. p. 186—205°/756 mm., which became yellowish-brown on standing and contained some suberone, and (3) a dark-coloured liquid (3.0 g.), b. p. above 205°/756 mm., which was not investigated. The alkaline washings gave 0.1 g. of *n*-heptoic acid.

F. Decomposition in the presence of an equal weight of iron filings. 50 G., mixed with 50 g. of iron filings, were slowly distilled. There was a considerable amount of fuming and frothing while the temperature was 280—330°; the fuming then subsided, and a pale yellow liquid of ketonic odour passed over at 340—370°. The temperature was raised until no further distillate was obtained; the last fraction was bluish-green. After being worked up as detailed under (C), the distillate yielded 10.0 g. of a liquid, b. p. 180—182°/766 mm., $d_4^{19.4}$ 0.9326, $n_D^{19.4}$ 1.4582, which furnished suberonesemicarbazone, m. p. 162—163° after one crystallisation from dilute methyl alcohol; there was also a dark-coloured residue (0.9 g.).

The decomposition of suberic acid in the presence of an equal weight of iron filings and 5% by weight of baryta has previously been described (J., 1928, 2035), and that experiment and experiments C, D, E, and F indicate clearly that increasing the proportion of iron increases the purity of the resultant suberone, as evidenced by the boiling point, density, refractivity, and semicarbazone formation.

Azelaic Acid.—This was prepared by the oxidation of ricinoleic acid with potassium permanganate (Maquenne, *Bull. Soc. chim.*, 1899, 21, 1061) and after recrystallisation from benzene melted at 106—107°.

A Thermal decomposition. 50 G. were distilled during 8 hours.

The distillate, which passed over at 354—357°, was worked up as described under suberic acid (A). The neutral product gave the following fractions on distillation: (i) b. p. 85—155°, ca. 1 g., (ii) b. p. 180—230°, 1.4 g. Treatment of the latter with semicarbazide acetate yielded, after long standing, a semicarbazone the m. p. of which could not be raised above 105—110° after several crystallisations from dilute methyl alcohol; it was not further investigated owing to the small quantity available, but was clearly impure *cyclooctanonesemicarbazone*. The alkaline washings gave 5.0 g. of *n*-octoic acid, b. p. 129—130°/16 mm. (Found for the silver salt: Ag, 43.4. Calc.: Ag, 43.1%).

B. Catalytic decomposition. 80 G., mixed with 80 g. of iron filings and 4 g. of crystallised baryta, were slowly distilled. (The intermediate iron salt is only slowly formed and unless the following experimental conditions are maintained a very poor yield of ketone is obtained.) The temperature was slowly raised to 250°, kept at 250—300° for at least 2 hours, and then slowly raised. Some frothing and fuming occurred at 370—380° and a liquid with a ketonic odour distilled; the distillation was conducted very slowly at 370—390° during 20 hours until the liquid ceased to distil. The total duration of the distillation was 27 hours. The distillate gave by the usual treatment a neutral fraction, which was distilled under diminished pressure, the following fractions being collected: (i) up to 67°/17 mm., 3.7 g.; (ii) b. p. 67—74°/17 mm., 1.9 g.; (iii) 74—86°, chiefly 77—81°/17 mm., 2.8 g.; (iv) 86—130°/17 mm., 5.4 g. Each fraction was treated with semicarbazide acetate; fraction (iii) yielded a semicarbazone immediately, but fractions (i) and (ii) only after some time. The semicarbazone from fraction (iii) after recrystallisation from dilute methyl alcohol was caseous and melted at 95—120°; further recrystallisation from dilute methyl alcohol, followed by trituration with light petroleum (b. p. 60—80°) and recrystallisation from benzene and from dilute methyl alcohol, gave lustrous feathery plates, m. p. 166—167°, of *cyclooctanonesemicarbazone* (Found: C, 58.7; H, 9.3. Calc.: C, 59.0; H, 9.4%). The melting point of a mixture with an authentic specimen kindly supplied by Professor L. Ruzicka was 166—167.5°. The m. p.'s of mixtures with *cyclohexanonesemicarbazone* (m. p. 166°) and with *suberonesemicarbazone* (m. p. 162—163°) were respectively 139—149° and 149—156°. The semicarbazone derived from fraction (ii) behaved similarly, but was less pure. A poor yield of semicarbazone was obtained from fraction (i). The yield of *cyclooctanone* was about 10%.

C. Catalytic decomposition of "azelaic acid" isolated from "mixed acids" (compare J., 1928, 2035). The acid was isolated from the

mother-liquor of the suberic acid preparation and melted at 105—106° after several crystallisations from benzene. An intimate mixture of 100 g. of the acid, 100 g. of iron filings, and 5 g. of crystallised baryta was slowly distilled from a 2-litre Pyrex distilling flask. Considerable frothing and fuming took place at 200—260°, the distillate passed over chiefly at 325—340°, and the distillation was stopped at 360°. The product was worked up exactly as described under B and gave the following fractions on distillation : (i) b. p. 62—70°/13 mm., d_4^{27} 0.9133, n_D^{27} 1.4571, 6.7 g., (ii) b. p. 70—80°/13 mm., d_4^{27} 0.9293, n_D^{27} 1.4611, 3.1 g., (iii) b. p. 80—130°/13 mm., 2 g. Fractions (i) and (ii) yielded only suberonesemicarbazone on treatment with semicarbazide acetate. A minute quantity of the cyclooctanone fraction was isolated by Ruzicka and Brugger's sodium bisulphite method. Suberone is therefore the main product.

Sebacic Acid.—Boot's pure sebacic acid, m. p. 130°, was employed.

A. Thermal decomposition. 50 G. were distilled during 8 hours. The distillate, which passed over at 359—364°, was separated into a neutral fraction (0.9 g.), which gave a poor yield of a sticky semicarbazone on long standing with semicarbazide acetate, and an acid fraction consisting of *n*-nonoic acid (7.0 g.), b. p. 142—143°/16 mm., d_4^{20} 0.9096, n_D^{20} 1.4343 (Found for the silver salt : Ag, 41.1. Calc. : Ag, 40.8%).

B. Catalytic decomposition. 75 G. of sebacic acid, mixed with 75 g. of iron filings and 3.5 g. of crystallised baryta, were slowly distilled until nothing further passed over. The distillate (yield, relatively small) gave a neutral fraction which was separated by distillation under reduced pressure into (i) 3.5 g., b. p. 46°/15 mm.—80°/12 mm., (ii) 1.7 g., b. p. 80—92°/12 mm., (iii) 1.3 g., b. p. 92—100°/12 mm., (iv) a blue liquid (2.2 g.), b. p. 100—120°/12 mm. All the fractions were treated separately with semicarbazide acetate; a crystalline semicarbazone was obtained immediately and in excellent yield from fraction (iii), but only slowly from fractions (i) and (ii). The semicarbazone from (iii) after three crystallisations from dilute methyl alcohol melted at 122—123°, the m. p. being unaffected by further crystallisation from the same or other solvents; it was clearly methyl octyl ketone semicarbazone (Found : C, 61.7; H, 10.8. Calc. : C, 62.0; H, 10.9%) (Ruzicka and Brugger, *Helv. Chim. Acta*, 1926, 9, 397, give m. p. 120°; Pickard and Kenyon, *J.*, 1911, 99, 57, give m. p. 121°). The semicarbazones from fractions (i) and (ii) melted at 116° after three crystallisations from dilute methyl alcohol and were shown by mixed m. p. determinations and analyses to be identical with the semicarbazone from fraction (iii). No other semicarbazone was isolated.

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