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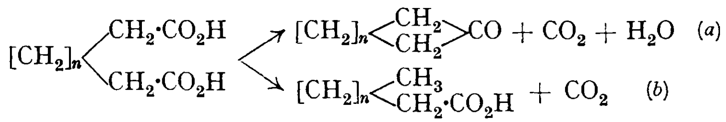
241. *Syntheses of Cyclic Compounds. Part X. The Thermal Decomposition of Substituted Glutaric Acids. Part I. ββ-Dimethylglutaric,* cyclo*Pentane- and* cyclo*Hexane-*1 : 1*-diacetic Acids, and the Mechanism of the Reaction.*

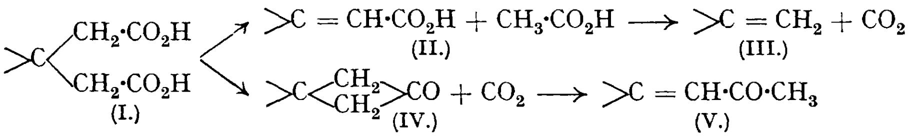
By Arthur I. Vogel.

In Part V of this series (J., 1929, 725) it was shown that the normal dibasic acids from glutaric to sebacic acid decompose on slow distillation in two directions :



$$\mathrm{[CH_2]_n}<\begin{matrix}\mathrm{CH_2\cdot CO_2H}\\\mathrm{CH_2\cdot CO_2H}\end{matrix}\begin{matrix}\nearrow \mathrm{[CH_2]_n}<\begin{matrix}\mathrm{CH_2}\\\mathrm{CH_2}\end{matrix}>\mathrm{CO + CO_2 + H_2O}\quad(a)\\\searrow \mathrm{[CH_2]_n}<\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_2\cdot CO_2H}\end{matrix}\mathrm{+ CO_2}\quad(b)\end{matrix}$$

and the reaction was employed to determine the ease of formation of the corresponding carbon rings. Glutaric acid yielded only butyric acid, and it was therefore of interest to investigate the effect of decreasing the tetrahedral angle between the two acetic acid residues by substitution. On slow thermal distillation, *cyclo*pentane-1 : 1-diacetic acid yielded *cyclo*pentylideneacetone, methylene*cyclo*pentane, and a small quantity of acetic acid. *cyclo*Hexane-1 : 1-diacetic acid behaved similarly, and ββ-dimethylglutaric acid was unaffected. The decomposition is simply interpreted by the following extension of the above mechanism, the difference being due to the greater proximity of the groups owing to valency deflexion :



$$\underset{\text{(I.)}}{>\mathrm{C}<\begin{matrix}\mathrm{CH_2\cdot CO_2H}\\\mathrm{CH_2\cdot CO_2H}\end{matrix}}\begin{matrix}\nearrow \underset{\text{(II.)}}{>\mathrm{C=CH\cdot CO_2H}}\mathrm{+ CH_3\cdot CO_2H}\longrightarrow \underset{\text{(III.)}}{>\mathrm{C=CH_2}}\mathrm{+ CO_2}\\\searrow \underset{\text{(IV.)}}{>\mathrm{C}<\begin{matrix}\mathrm{CH_2}\\\mathrm{CH_2}\end{matrix}>\mathrm{CO}}\mathrm{+ CO_2}\longrightarrow \underset{\text{(V.)}}{>\mathrm{C=CH\cdot CO\cdot CH_3}}\end{matrix}$$

The clue to the mechanism was provided by the isolation of acetic acid in poor yield, obviously owing to its decomposition in *statu nascendi* into volatile products at the high temperature of the reaction.

The relative yields of (III) and (V) provide a measure of the tendency for ring formation, and will be influenced by the magnitude of the tetrahedral angle between the two acetic acid residues.* In view of the ease of isolation and the small tendency to polymerisation and decomposition of the methylene-hydrocarbon, the yield of this compound is employed for the comparison of the effect of substitution. *cyclo*Hexane- and *cyclo*pentane-1 : 1-diacetic acids gave respectively a 33% and a 15%

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* For an alternative view, see Mills, *Rapports Institut Internat. Chimie Solvay*, 1931, **4**, 25 : this will be fully discussed when more data have been accumulated.

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yield of the corresponding methylene*cyclo*paraffin. In ββ-dimethylglutaric acid the two acetic acid residues are too far apart for reaction to occur when the acid is distilled alone. There is thus a profound difference in the effect of the *gem*-dimethyl group, the *cyclo*pentane and *cyclo*hexane rings upon the thermal decomposition of glutaric acids. The reaction is being extended to other substituent groups and ring systems.

The decomposition of these substituted glutaric acids in the presence of iron filings and a little baryta (Vogel, J., 1929, 721) was also investigated. All three acids decomposed to yield the hydrocarbon (III) and the ketone (V); the yields of (III) in the series *cyclo*pentane- and *cyclo*hexane-1 : 1-diacetic acids and ββ-dimethylglutaric acid were 29%, 38%, and 7% respectively. No acetone was isolated from any of the acids. The unsaturated ketones (V) isolated by simple fractionation from the thermal decomposition of the two cyclic acids possessed properties (b. p. and refractive index) which agreed well with those found by Dickins, Hugh, and Kon (J., 1928, 1630; 1929, 572) for the pure αβ-ketones. The densities, however, were appreciably lower. The ketones isolated from the catalytic decomposition consisted largely of the αβ-form, whereas distillation of the calcium salts yields chiefly the βγ-isomeride (Kon, J., 1921, **119**, 811).

Kon's explanation of the formation of the unsaturated hydrocarbon (III) by the hydrolytic action of water upon the unsaturated ketone (V) is highly improbable. It is suggested that his results can be readily interpreted by the mechanism put forward above by the present author.

EXPERIMENTAL.

The substituted glutaric acids were prepared by the condensation of the appropriate ketone with ethyl cyanoacetate in the presence of alcoholic ammonia at − 5°, the resultant dicyanoimides were hydrolysed with 60—70% sulphuric acid to the acids, which were freed from traces of imides by conversion into the sodium salts with sodium carbonate solution—the imides do not react—and then the acids were crystallised from dilute alcohol. ββ-Dimethylglutaric acid was isolated by ether extraction.

The apparatus employed for the thermal and catalytic decompositions was similar to that already described (Vogel, J., 1929, 726) except that two receivers in series were employed, both cooled in ice. In order to obtain reproducible results it is essential to adhere closely to the experimental conditions detailed below.

cyclo*Pentane*-1 : 1-*diacetic Acid.*—(A) *Thermal decomposition.* 40·0 G. of acid, m. p. 176°, were distilled from a 500-c.c. Pyrex flask during 11 hours. During the first 2 hours the temperature rose to 280° and only an aqueous distillate passed over. The temperature was then raised to *ca.* 300°, whereupon a hydrocarbon odour became apparent and an organic liquid distilled over; for the following 6 hours the temperature rose to 370°, the thermometer was then raised to the neck of the distilling flask, and the bath heated as strongly as possible by a large ring burner for a further 3 hours, a yellow viscid liquid then passing over. A black residue remained. The lower, aqueous layer of the distillate was separated, the " organic " layer washed with dilute ammonium hydroxide and then with water, the washings were added to the aqueous layer, dried with calcium chloride and distilled (rubber bungs were used since considerable losses of the hydrocarbon result with bark corks). The following fractions were collected at 764 mm.: (1) 70—100°, chiefly 79—84°, 2·6 g., $d_{4°}^{20°}$ 0·7793, $n_D^{20°}$ 1·4285 (Found: C, 87·5; H, 12·4. Calc. for C_6H_{10}: C, 87·9; H, 12·2%); no ketone was detected by treatment of this fraction with semicarbazide acetate. (2) 100—179°, 0·7 g., $d_{4°}^{20°}$ 0·8351, $n_D^{20°}$ 1·4507; the physical properties varied slightly in different experiments. (3) 180—215°, chiefly 183—185°, 1·0 g., $d_{4°}^{20°}$ 0·9091, $n_D^{20°}$ 1·4740 (Found: C, 77·2; H, 9·9. Calc. for $C_8H_{12}O$: C, 77·5; H, 9·8%). (4) 215—230°, 0·5 g. (Found: C, 80·6; H, 9·8. Calc. for $C_{16}H_{22}O$: C, 83·6; H, 9·7%). (5) A dark viscid residue (0·3 g.).

Refractionation of (1) from sodium gave pure methylene*cyclo*pentane, b. p. 77—79°/767 mm., $d_{4°}^{20°}$ 0·7770, $n_D^{20°}$ 1·4320 (Wallach, *Annalen*, 1906, **347**, 325, gives b. p. 78—81°, $d^{19°}$ 0·78, $n_D^{19°}$ 1·4355). Refractionation of (3) from several experiments gave a small fraction, b. p. 68—73°/19 mm., a large fraction, b. p. 74—76°/19 mm., $d_{4°}^{20°}$ 0·9058, $n_D^{20°}$ 1·4793 (Found: C, 77·4; H, 9·9%), and a smaller fraction of higher b. p.

The aqueous distillate and ammoniacal washings were acidified with dilute nitric acid, extracted three times with ether to remove traces of unchanged diacetic acid, and the acid remaining in the aqueous solution converted into the silver salt *via* the ammonium salt; yield, 0·3 g. (Found: Ag, 64·5. Calc. for $CH_3\cdot CO_2Ag$: Ag, 64·7%).

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The physical properties of the ketone (V) prepared from the calcium salt are b. p. 181—184°, $d_{4^\circ}^{19\cdot4^\circ}$ 0·9332, $n_{\mathrm{D}}^{19\cdot4^\circ}$ 1·46728 (Kon, J., 1921, **119**, 823), and b. p. 66—70°/15 mm., $d_{4^\circ}^{19\cdot6^\circ}$ 0·93070, $n_{\mathrm{D}}^{19\cdot6^\circ}$ 1·46420 (Dickins, Hugh, and Kon, J., 1929, 578). Pure *cyclo*pentylideneacetone has b. p. 74—76°/14 mm. (by fractionation only) and b. p. 70°/12 mm. (from semicarbazone), $d_{4^\circ}^{16\cdot9^\circ}$ 0·94205, $n_{\mathrm{D}}^{16\cdot9^\circ}$ 1·47937; pure *cyclo*pentenylacetone has b. p. 72—74°/15 mm. (by fractionation only), $d_{4^\circ}^{17\cdot0^\circ}$ 0·95400, $n_{\mathrm{D}}^{17\cdot0^\circ}$ 1·46569, and b. p. 69—70°/16 mm. (from semicarbazone and aluminium amalgam reduction), $d_{4^\circ}^{20\cdot4^\circ}$ 0·93568, $n_{\mathrm{D}}^{20\cdot4^\circ}$ 1·46211 (Dickins, Hugh, and Kon, *loc. cit.*).

(B) *Catalytic decomposition.* An intimate mixture of 40·0 g. of the acid, 40 g. of iron filings, and 2 g. of finely powdered crystallised baryta was slowly distilled during 10 hours, exactly as described under (A). The whole was gently heated for the first 2 hours, the temperature not exceeding 200° at the end of this period—this allowed the intermediate formation of the iron salt. The temperature was then raised, and remained steady for the following 5—6 hours at 320—330°, rising to *ca.* 390° towards the end of this period. The final stage of the distillation was conducted as in (A) for a further 2—3 hours. The distillate was worked up as above and yielded the following fractions at 765 mm.: (1) 60—100°, chiefly 72—84°, 5·05 g., $d_{4^\circ}^{20^\circ}$ 0·7879, $n_{\mathrm{D}}^{20^\circ}$ 1·4287; this was clearly methylene*cyclo*pentane. (2) 101—160°, 0·3 g. (3) 161—210°, chiefly 176—186°, 2·2 g., $d_{4^\circ}^{20^\circ}$ 0·9368, $n_{\mathrm{D}}^{20^\circ}$ 1·4737 (Found: C, 77·3; H, 9·7%). (4) 211—250°, 1·1 g., $d_{4^\circ}^{20^\circ}$ 0·9947, $n_{\mathrm{D}}^{20^\circ}$ 1·4953 (Found: C, 80·1; H, 9·7%). (5) Dark residue, 0·5 g.

Redistillation of fraction (1) from several experiments gave a large middle fraction, b. p. 76—78°, $d_{4^\circ}^{20^\circ}$ 0·7787, $n_{\mathrm{D}}^{20^\circ}$ 1·4350. No acetone could be detected with semicarbazide acetate. Redistillation of fraction (4) from several experiments gave a small amount, b. p. 69—70°/19 mm., a large fraction, b. p. 76—77°/16 mm., $d_{4^\circ}^{20^\circ}$ 0·9330, $n_{\mathrm{D}}^{20^\circ}$ 1·4752, and another slightly smaller fraction, b. p. 77—83°/16 mm., chiefly 82°/16 mm., $d_{4^\circ}^{20^\circ}$ 0·9448, $n_{\mathrm{D}}^{20^\circ}$ 1·4794.

cyclo*Hexane*-1 : 1-*diacetic Acid.*—(A) *Thermal decomposition.* 40·0 G. of acid, m. p. 180—181°, were distilled and worked up exactly as described under its *cyclo*pentane analogue. The following fractions were collected at 761 mm.: (1) 90—120°, chiefly 105—109°, 6·3 g., $d_{4^\circ}^{20^\circ}$ 0·8048, $n_{\mathrm{D}}^{20^\circ}$ 1·4486 (Found: C, 87·4; H, 12·6. Calc. for C_7H_{12}: C, 87·6; H, 12·5%). (2) 120—191°, 1·55 g., $d_{4^\circ}^{20^\circ}$ 0·8644, $n_{\mathrm{D}}^{20^\circ}$ 1·4694. (3) 190—215°, chiefly 202—208°, 1·1 g., $d_{4^\circ}^{20^\circ}$ 0·9155, $n_{\mathrm{D}}^{20^\circ}$ 1·4831 (Found: C, 78·0; H, 10·3. Calc. for $C_9H_{14}O$: C, 78·4; H, 10·2%). (4) A viscid high b. p. residue, 0·5 g.

When fraction (1) was distilled over sodium, the major portion boiled at 105—106°/770 mm., and consisted of pure methylene*cyclo*hexane, $d_{4^\circ}^{20^\circ}$ 0·8018, $n_{\mathrm{D}}^{20^\circ}$ 1·4486 (Wallach, *Annalen*, 1906, **347**, 329, gives b. p. 105—106°, d^{20° 0·8025, $n_{\mathrm{D}}^{20^\circ}$ 1·4501). This is probably the most convenient method for the preparation of this hydrocarbon. Fractions (3) from several experiments were combined and refractionated under 19 mm. Two large approximately equal fractions were obtained: (*a*) b. p. 80—93°, $d_{4^\circ}^{20^\circ}$ 0·9017, $n_{\mathrm{D}}^{20^\circ}$ 1·4824 (Found: C, 78·2; H, 10·1%), and (*b*) b. p. 97—98°, $d_{4^\circ}^{20^\circ}$ 0·8970, $n_{\mathrm{D}}^{20^\circ}$ 1·4869 (Found: C, 78·3; H, 10·2%). Fraction (*b*) consisted largely of *cyclo*hexylideneacetone, but no explanation can be given of the low density. Kon (J., 1921, **119**, 811) gives b. p. 202°/754 mm. (*ex* semicarbazone), $d_{4^\circ}^{24\cdot1^\circ}$ 0·9304, $n_{\mathrm{D}}^{24\cdot1^\circ}$ 1·4867, for the ketone derived from the calcium salt. Pure *cyclo*hexylideneacetone has b. p. 89°/12·5 mm., $d_{4^\circ}^{19\cdot0^\circ}$ 0·94931, $n_{\mathrm{D}}^{19\cdot0^\circ}$ 1·49128, when isolated by simple fractionation, and b. p. 95°/17 mm., $d_{4^\circ}^{17\cdot3^\circ}$ 0·94673, $n_{\mathrm{D}}^{17\cdot3^\circ}$ 1·48917, when purified through the semicarbazone; pure *cyclo*hexenylacetone has b. p. 83°/12 mm. (*ex* semicarbazone), $d_{4^\circ}^{18\cdot6^\circ}$ 0·93751, $d_{\mathrm{D}}^{18\cdot6^\circ}$ 1·47310 (Dickins, Hugh, and Kon, J., 1928, 1630).

The combined aqueous distillate and washings was acidified with dilute nitric acid and treated as described under *cyclo*pentane-1 : 1-diacetic acid, 0·4 g. of silver acetate being obtained (Found: Ag, 64·5%). This salt can also be isolated by diluting the aqueous distillate, steam-distilling it, concentrating the distillate after addition of excess of ammonium hydroxide, and then converting this into the silver salt.

(B) *Catalytic decomposition.* By using exactly the same quantities and procedure as for *cyclo*pentane-1 : 1-diacetic acid, the following fractions at 760 mm. were obtained in a typical experiment: (1) 80—120°, chiefly 104—108°, 7·2 g., $d_{4^\circ}^{20^\circ}$ 0·8105, $n_{\mathrm{D}}^{20^\circ}$ 1·4520. (2) 120—180°, 0·4 g. (3) 180—215°, chiefly 202—206°, $d_{4^\circ}^{20^\circ}$ 0·9452, $n_{\mathrm{D}}^{20^\circ}$ 1·4912 (Found: C, 78·0; H, 10·4%). Redistillation of fraction (3) gave a considerable portion, b. p. 88—90°/19 mm., $d_{4^\circ}^{20^\circ}$ 0·9385, $n_{\mathrm{D}}^{20^\circ}$ 1·4875.

ββ-*Dimethylglutaric Acid.*—(A) *Thermal decomposition.* 40·0 G. of acid, m. p. 100°, were heated in the usual manner for 9 hours. A small quantity of water passed over, but most of the acid (slightly discoloured) was recovered unchanged. The acid appeared to boil at about 290°; it solidified in the neck of the flask, and was melted out from time to time.

(B) *Catalytic decomposition.* The quantities and procedure were exactly as in the foregoing

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corresponding experiments, except that three boiling tubes connected in series and a final soda–lime guard tube were added after the two ice-cooled receivers. The first tube was empty and the next two each contained 3 c.c. of bromine and 5 c.c. of water. The temperature was raised during the first 1½ hours to 200°, during which there was considerable frothing and evolution of gas; the whole then became solid, and during the next 5 hours the temperature was gradually raised to 390°; the usual final distillation last for a further 3 hours. The distillate was dried with calcium chloride and fractionated. The following fractions were obtained: (1) up to 100°, 0·5 g. (2) 100—150°, over 50% at 130—140°, 1·5 g., $d_{4^\circ}^{20^\circ}$ 0·8598, $n_{D}^{20^\circ}$ 1·4266 (Found: C, 73·0; H, 10·2. Calc. for $C_6H_{10}O$: C, 73·5· H, 10·1%); this had the odour of mesityl oxide. (3) 150—190°, 0·85 g., $d_{4^\circ}^{20^\circ}$ 0·8953, $n_{D}^{20^\circ}$ 1·4491. (4) 190—220°, 1·0 g., $d_{4^\circ}^{20^\circ}$ 0·9460, $n_{D}^{20^\circ}$ 1·4869 (Found: C, 77·9; H, 10·0. Calc. for $C_9H_{14}O$: C, 78·5; H, 10·1%). No acetonesemicarbazone could be isolated from fraction (1). Analysis indicates that fractions (2) and (4) are mesityl oxide and isophorone respectively.

The bromine water was decolorised with sulphur dioxide, the heavy layer of dibromide separated, washed with dilute sodium hydroxide solution, and then water, dried with calcium chloride, and distilled. *iso*Butylene dibromide, b. p. 155—156°/758 mm., 4·0 g., was isolated (Found: Br, 74·0. Calc. for $C_4H_8Br_2$: Br, 74·3%), together with some higher b. p. products, which were not investigated.

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