The solids which remained suspended in the ether layers on hydrolysis were filtered off and dried. The ether layers were separated and dried over anhydrous sodium sulfate. Ether was removed by distillation. The products were identified by mixed melting point with an authentic specimen unless otherwise stated. All melting points are uncorrected.

Iodobenzene; **Tetraphenyltin.**—To 0.045 mole of triphenyltin-lithium was added 10.1 g. (0.0495 mole, 10% excess 0.045 mole) of iodobenzene dissolved in 40 ml. of ether. The reaction mixture was refluxed and hydrolyzed. The yellow solid recovered on hydrolysis was combined with the solid residue from the ether layer and crystallized from petroleum ether (b.p. 77–120°) to yield 12.7 g. (66.2%) of tetraphenyltin melting at 224–225°.

Benzyl Chloride; Triphenylbenzyltin.—To 0.045 mole of triphenyltin-lithium was added 5.7 g. (0.0495 mole) of benzyl chloride dissolved in 30 ml. of ether while the temperature of the reaction mixture was maintained at −35° in order to minimize possible side reactions. The suspension was stirred for 30 minutes at −35°, then for an additional 30 minutes while the temperature was permitted to rise to −10°. It was then hydrolyzed. The yellow solid recovered on hydrolysis was crystallized from petroleum ether (b.p. 77–120°) to yield 8.7 g. (60.0%) of tetraphenyltin melting at 224–225°. The ether layer yielded a yellow oil which partially solidified on cooling in an ice-bath. The solid was crystallized from ethanol to yield 4.6 g. (21.7%) of triphenylbenzyltin melting at 90–91°.

Ethyl Iodide; Triphenylethyltin.—To 0.045 mole of triphenyltin-lithium was added 7.7 g. (0.0495 mole) of ethyl iodide dissolved in 40 ml. of ether. The reaction mixture was refluxed and hydrolyzed. The yellow solid recovered on hydrolysis was crystallized from petroleum ether (b.p. 77–120°) to yield 3.9 g. (26.9%) of tetraphenyltin melting at 224–225°. The ether layer yielded a deep yellow solid which was extracted with 100 ml. of petroleum ether (b.p. 60–70°). On cooling the petroleum ether solution in an ice-bath a yellow solid precipitated. The solid was crystallized from a minimum amount of ethanol to yield 6.2 g. (36.4%) of triphenylethyltin melting at 56–58°.

Triphenyltin Chloride; Hexaphenylditin.—To 0.023 mole of triphenyltin-lithium was added 8.86 g. (0.023 mole) of triphenyltin chloride dissolved in 250 ml. of ether. The reaction mixture was refluxed and hydrolyzed. The white solid recovered on hydrolysis was combined with the solid residue from the ether layer and crystallized from an excess of petroleum ether (b.p. 77–120°) to yield 7.7 g. (52.8%) of hexaphenylditin melting at 229–231°.

Triphenylchlorosilane; Triphenylsilyl-triphenyltin.—To 0.045 mole of triphenyltin-lithium was added 13.3 g. (0.045 mole) of triphenylchlorosilane dissolved in 100 ml. of ether. The reaction mixture was refluxed for three hours and then hydrolyzed. The yellow solid recovered on hydrolysis was crystallized twice from a minimum amount of benzene to yield 19.5 g. (71.3%) of triphenylsilyl-triphenyltin melting at 289–291°. From the ether layer, 2.2 g. of unreacted triphenylchlorosilane was recovered.

Anal. Calcd. for $C_{36}H_{30}SiSn$: Si, 4.61; Sn, 19.48. Found: Si, 5.09; Sn, 19.61.

A mixed melting point with a specimen prepared by the reaction of triphenylsilyl-potassium with triphenyltin chloride showed no depression.[8]

---

(8) Unpublished work of T. C. Wu.

AMES, IOWA RECEIVED JUNE 29, 1951

[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

The Synthesis of Pimelic Acid from Cyclohexene-4-carboxylic Acid and its Derivatives

BY FRANK X. WERBER, J. E. JANSEN AND T. L. GRESHAM

Optimum reaction conditions for the alkaline isomerization and cleavage of cyclohexene-4-carboxylic acid to pimelic acid are presented. Evidence has been obtained showing that the intermediate cyclohexene-1-carboxylic acid undergoes attack by hydroxyl ion with displacement of a hydride ion to give cyclohexanone-2-carboxylic acid as a further intermediate; the latter is cleaved to pimelic acid or decarboxylated to cyclohexanone in relative amounts depending upon the reaction conditions. Hydrogen is formed in equivalent amounts, and hydrogenation is a side reaction. 3,6-Endomethylenecyclohexene-4-carboxylic acid does not undergo the new cleavage reaction. Cyclohexene-4-carboxaldehyde is partly cleaved to pimelic acid, and partly undergoes hydrogenolysis and aromatization.

Reports on a novel synthesis of pimelic acid and substituted pimelic acids, by cleavage of various cyclohexene derivatives, have recently appeared in the literature.[1,2] A study of this cleavage reaction was begun independently in this Laboratory prior to receipt of the German and U. S. publications, and the course of the reaction has been partly elucidated.

Unsaturated aliphatic acids are cleaved in fused alkali to acetic acid and a second saturated acid with two fewer carbon atoms than the starting material.[3,4] Extension of this reaction to cyclic unsaturated acids would lead one to expect cleavage to a single dibasic acid. Fusion of cyclohexene-4-carboxylic acid (I) in potassium hydroxide indeed gave pimelic acid in a yield of 33%. The reaction was further examined in aqueous solution under pressure and under a variety of conditions. Under the best conditions found, pimelic acid could be obtained in 78% yield. Complete conversions could be effected above 300° with reaction times up to 10 hours.

The gain of one carboxyl group in the reaction points to an oxidative process. Since oxygen is not freely available when the reaction is carried out in a sealed autoclave one would suspect dehydrogenation; actually, 0.85 mole of hydrogen per mole of I was found in the off-gases in one experiment (Burrell gasometric technique). Cyclohexanone (V) was a by-product of the reaction under all conditions; it was formed in yields varying from 3 to 24%.[5] This ketone is known to be the product of the "ketonic cleavage" of cyclohexanone-2-carboxylic acid (III), whereas pimelic acid is formed from III by the "acid cleavage," which usually required alkaline conditions.[6] It thus becomes rea-

---

(1) H. J. Pistor and H. Plieninger, *Ann.*, **562**, 239 (1949); see also USPB 25616, pp. 472–476 (U. S. Department of Commerce).

(2) H. deV. Finch, S. A. Ballard and T. W. Evans, U. S. Patent 2,454,047 to Shell Development Company; *C. A.*, **43**, 5416 (1949).

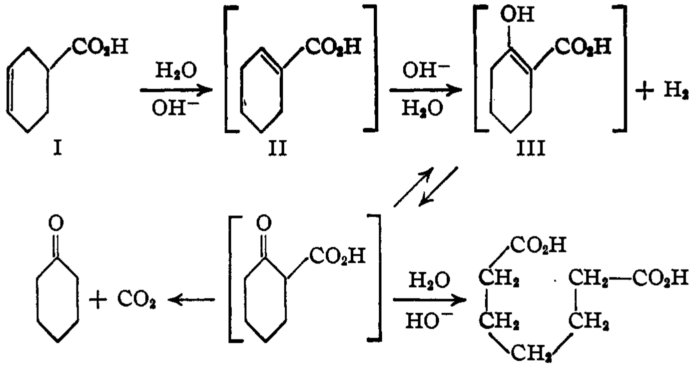
(3) F. G. Edmed, *J. Chem. Soc.*, **73**, 627 (1898); F. Varrentrap, *Ann.*, **35**, 196 (1840).

(4) F. Becker, *Ber.*, **11**, 1413 (1878).

(5) Cyclohexanone could also be formed by pyrolysis of disodium pimelate. In the presence of little water (5 moles per mole disodium pimelate) this became a serious reaction; however, under the conditions discussed above—large excess of water (22 moles per mole I)—the amount formed from disodium pimelate on heating at 350° was too small to be measured.

(6) H. R. Snyder, L. A. Brooks and S. H. Shapiro, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 531.

sonable to assume that III is a precursor of pimelic acid in the present series of reactions, and the immediate product of the oxidative step



The variation in relative amounts of acid and ketone formed with varying reaction conditions bears out this point.

A decrease in the alkali concentration to a level lower than the excess theoretically required to neutralize the newly formed carboxyl group boosted the formation of cyclohexanone (Experiment 7, Table I). The average hydroxyl-ion concentration in the course of the cleavage of III would be much lower under these conditions than when excess alkali was used. Increased dilution (Experiment 10), and with it lowered hydroxyl-ion concentration, changed the ratio of products in a similar direction. Quite in keeping are the known facts of "acid cleavage"; the rate of acid cleavage is at least first-order with respect to hydroxyl ion concentration, while "ketonic cleavage" does not have such a dependence.[7] When the water concentration was cut to a bare minimum (Experiment 8) the yield of ketone rose to 24%, with a corresponding reduction in the formation of IV; as the medium assumes non-ionic character the hydroxyl-ion concentration is also reduced. Furthermore, since most of the water is in the vapor phase, the previously discussed alkali fusion conditions may have been duplicated. Complete absence of water suppresses even the isomerization of I to II; thus when the sodium salt of I was heated in dry xylene only starting material was recovered.

Conversion of I to II in itself required drastic temperatures. Although it has not been possible to isolate II in the pure state by this reaction, comparison of ultraviolet spectra has permitted at least a qualitative examination of the isomerization. Pure I did not exhibit a peak in the ultraviolet region, while II had a single, sharp peak at 218 mμ ($E_{\max}$ 76); the extent of absorption at 218 mμ of a mixture of cyclohexenecarboxylic acids recovered under a particular set of reaction conditions thus should furnish information on the relative proportions of I and II present.[8] Only starting material was recovered on treatment of I with alkali at 110° and 230°. Ninety per cent. of the material recovered from the reaction at 270° (54%) consisted of cyclohexenecarboxylic acids; the absorption peak at 218 mμ measured $E_{\max}$ 48, corresponding only to 60% II.[8] A small concentration of I was thus left unisomerized.

Alkali concentration is a factor also in the rate of "hydroxylation" of II to give III. A lowered alkali concentration gave less IV and V, but appreciable isomerized acid (II) was recovered (Experiment 7). The manner in which this "hydroxylation" takes place is not established. A mechanism involving the intermediate addition of water to II, giving a β-hydroxy acid which subsequently undergoes dehydrogenation to III, seems attractive. In none of our experiments, however, did we obtain any evidence for the recovery of unreacted material in the form of hexahydrosalicylic acid; moreover, when this hydroxy acid was heated in aqueous alkali at 250° only II was recovered.[1] We therefore prefer to view the reaction as a direct displacement of a hydride ion by a hydroxyl ion at the β-position of II; the hydride ion then reacts with water to give hydrogen and to regenerate the hydroxyl ion. Should there be an intermediate between II and III, it certainly has no more than a transitory existence.

Since it became obvious that the isomerization of I to II required an activation comparable to that of the "hydroxylation" step, it was thought advisable to study the cleavage of the conjugated acid II. Any difference in yields or necessary reaction conditions could then be attributed to the isomerization in the case of I. Accordingly, acid II was prepared from cyclohexanone cyanohydrin[9] by dehydration[10] followed by saponification of the unsaturated nitrile.[11] No significant differences were found in the maximum yield of pimelic acid obtainable, or in the temperature necessary to effect the conversion. In spite of the resistance of I to the influence of alkali at relatively high temperatures, the cleavage reactions (II to IV) still appear to be the rate-determining factor in the over-all transformation. Moreover, isomerization is a quantitative reaction and all losses must be accounted for in the subsequent steps.

Cyclohexancarboxylic acid and cyclohexanol have been isolated and identified as other side-reaction products, both in trace amounts of no more than 2 to 3%. Their formation is attributable to the hydrogenation of cyclohexenecarboxylic acids, either I or II, and of cyclohexanone under the catalytic influence of the iron wall of the reaction vessel.[12]

4-Cyanocyclohexene (VI) could be hydrolyzed, isomerized and cleaved to pimelic acid in the same yield as the free acid (I) under identical conditions.

---

[7] R. G. Pearson and E. A. Mayerle, THIS JOURNAL, 73, 926 (1951).

[8] This discussion has not taken into account the fact that the β,γ-unsaturated isomer undoubtedly is an intermediate in the reaction. E. J. Boorman and R. P. Linstead (*J. Chem. Soc.*, 258 (1935)) have shown, however, that this acid is readily equilibrated with II in alkaline solution in a ratio of 1:4; thus any reaction mixture containing II should have a concentration of the β,γ-unsaturated acid about one-fourth that of II. Since the peak at 218 mμ is in the region of absorption of the conjugated carbon–carbon double bond, cyclohexene-3-carboxylic acid, like I, may be assumed not to absorb at this wave length.

[9] L. Ruzicka and W. Bunger, *Helv. Chim. Acta*, 9, 399 (1926).

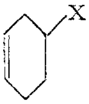
[10] B. K. Battacharya, *J. Indian Chem. Soc.*, 22, 85 (1945); *C. A.*, 40, 2139 (1946).

[11] E. J. Boorman and R. P. Linstead, *J. Chem. Soc.*, 258 (1935).

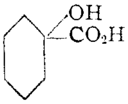
[12] Previous references to yields of "cyclohexanone" actually refer to mixtures containing a small percentage of cyclohexanol.

Cyclohexanol-1-carboxylic acid (VII) in accord with the findings of Pistor and Plieninger[1] gave pimelic acid in only 15% yield; 40% of the starting material was converted to cyclohexanone, presumably due to the instability of α-hydroxy acids in alkali.

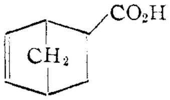
Any structural factor which interferes with the isomerization of the double bond into conjugation with the carboxyl group would be expected to interrupt the whole sequence of reactions and prevent cleavage to a dibasic acid. Application of Bredt's rule to 3,6-endomethylene cyclohexene-4-carboxylic acid (VIII),[13] would preclude isomerization. When VIII was subjected to the usual cleavage conditions only tars could be recovered.



VI, X = -CN
IX, X = -CHO



VII



VIII

The one-step cleavage of cyclohexene-4-carboxaldehyde[13] (IX) to pimelic acid was also attempted. Treatment with fused caustic at 250° transforms this aldehyde into a mixture of the corresponding carbinol and carboxylic acid, the latter predominating.[2] Since primary carbinols are also readily oxidized to the corresponding carboxylic acids it was hoped that a better over-all conversion to I, and from there to pimelic acid, would be effected by using aqueous alkali at 350°. Pimelic acid was actually formed in 42% yield. In addition, the neutral products of the reaction contained a hydrocarbon mixture of boiling point 100–110°. Comparison of the infrared spectrum with the spectra of toluene, methylcyclohexane and mixtures of these two hydrocarbons showed the unknown mixture to consist largely of toluene, in addition to about 10–15% of methylcyclohexane. Thus the carbinol immediately derived from IX underwent disproportionation followed by hydrogenolysis, or *vice versa*, under the influence of the hydrogen pressure in the bomb.

Experimental[14]

Cyclohexene-4-carboxylic Acid (I).—Although the reaction of acrylic acid with butadiene is mentioned in the classical paper of Diels and Alder,[13] experimental details were not given by these authors. Glacial acrylic acid, 144 g. (2.0 moles), 128 g. of butadiene (2.4 moles) and 2 g. of hydroquinone were placed in a one-liter stainless steel autoclave. The mixture was heated for one-half hour at 160–165°. The crude reaction products were subjected to distillation; after a forerun consisting of 4-vinylcyclohexene, 220 g. of cyclohexene-4-carboxylic acid (87% of theory) was collected, b.p. 126° (16 mm.), 123° (13 mm.) (lit.[15] 133° (20 mm.)), $n^{25}D$ 1.4780, $d^{25}{}_{.5}{}_4$ 1.0715.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99; neut. equiv., 126.2; bromine no., 126.9. Found: C, 66.74; H, 8.10; neut. equiv., 126.6; bromine no., 126.8.

Alkali Reactions: Cleavage to Pimelic Acid.—In most of the high pressure experiments, a 1200-ml. autoclave (4³/₈ in. outside diameter, manganese steel, manufactured by American Instrument Company), was used. It had a pressure rating of at least 3500 p.s.i. at 350°. Agitation was provided by an Aminco shaker.

Cyclohexene-4-carboxylic Acid (I) (a) Caustic Fusion.—A mixture of 3.7 g. of cyclohexene-4-carboxylic acid and 15 g. of potassium hydroxide pellets (85%) was heated in a nickel crucible for 45 minutes at 360°. The cooled mixture was dissolved in water, acidified with concentrated sulfuric acid and exhaustively extracted with ether. The ether extract was concentrated and the residue recrystallized twice from benzene; the product weighed 1.55 g. (33% of theory) and melted at 102–104°, alone or mixed with a sample of pimelic acid (Eastman Kodak Co.) (lit.[6] 103.5–104°).

The *p*-bromophenacyl ester was prepared.[16] It melted at 137–138° (lit.[17] m.p. 137°). Mixed with the derivative prepared from an Eastman Kodak Co. sample it melted at 137.5–138.5°.

(b) **Aqueous Alkali–High Pressure.**—In a typical experiment (No. 1 in Table I) 63 g. (0.5 mole) of I, 46 g. (1.1 mole) of 97% sodium hydroxide pellets and 200 ml. of water were allowed to react in the autoclave at 350° for seven hours (reaction time does not include time required to heat and cool the mixture). Pressures up to 2600 p.s.i. developed in the bomb. The cooled reaction mixture was extracted continuously with ether for 8 hours to remove neutral products. It was then acidified with concentrated sulfuric acid and the mixture was again extracted continuously with ether overnight. The extract containing the liberated acids was evaporated down and the ether was replaced with excess benzene: benzene was continuously distilled off to remove water azeotropically and the solution was adjusted with benzene to a final volume of about 250 ml. The crystalline material which deposited on cooling and standing for several hours was collected and washed with 50 ml. of benzene. The dried material weighed 61.1 g. (76.4% of theory), m.p. 102–104°; the melting point was not depressed by admixture with Eastman Kodak Co. pimelic acid.

TABLE I

CLEAVAGE OF CYCLOHEXENE-4-CARBOXYLIC ACID

Expt. no.	Mole ratio acid:NaOH:H_2O	Bomb volume: reactant volume	Reaction temp., °C.	Reaction time, hr.	Yield pimelic acid, %
1	0.5:1.1:11	1220:290	350	7	76.4
2	0.5:1.25:28[a]		110	24	0
3	1.0:1.2:17	1220:450	230	10	0[b]
4	0.5:1.2:11	1220:290	270	10	31[c]
5	0.5:1.0:11	1220:280	320	10	65[d]
6	0.5:1.1:20	1220:430	400	3	67[e]
7	0.5:0.6:11	1220:270	350	5.3	*ca.* 30[f]
8	0.5:1.6:1.4	1220:115	350	4.5	39[g]
9	1.5:1.5:0	1220:300	350	6	0[h]
10	0.5:1.1:22	1220:490	350	6	62
11	0.5:2.0:11	1220:310	350	5	69

[a] Refluxed at atmospheric pressure; complete recovery of starting material. [b] 95% recovery of unchanged starting material. [c] 54% recovery of cyclic acids, bromine no. 113.6, $E^{217\,\mathrm{mm}}_{\mathrm{max}}$ 48, or containing 10% saturated acid and over 10% I. [d] At least 5% recovery of cyclic olefinic acid. [e] Product impure, 17–20% cyclohexanone formed. [f] 35% recovery of cyclic acids; bromine no. 118.8, $E^{218\,\mathrm{mm}}_{\mathrm{max}}$ 51, 14–18% cyclohexanone–cyclohexanol. [g] Product impure; 24% cyclohexanone. [h] Dry sodium salt heated in xylene suspension, 75% recovery of unisomerized acid.

The ether extracts containing neutral products from a number of experiments were dried and combined for work-up. Removal of solvent left a sweet-smelling liquid. Trial distillation showed most of the material to boil at 155–158° (cyclohexanone b.p. 157°). Vigorous oxidation with potassium permanganate gave adipic acid (m.p. and mixed m.p. 152–153°). The liquid readily formed a 2,4-dinitrophenylhydrazone[18] (m.p. 158–159°; mixed with the 2,4-

---

[13] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

[14] Analyses by A. K. Kuder and J. Kubik. Ultraviolet and infrared spectra were determined by John Efroymson and J. J. Shipman, respectively.

[15] W. H. Perkin and G. Tattersall, *J. Chem. Soc.*, **91**, 490 (1907).

[16] R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 157.

[17] T. L. Kelly and P. A. Kleff, THIS JOURNAL, **54**, 4444 (1932).

[18] R. L. Shriner and R. C. Fuson, ref. 16, p. 170–171.

dinitrophenylhydrazone of cyclohexanone of m.p. 160°, it melted at 159–160° (lit. m.p. 162°[19]). Since the liquid also gave a positive reaction with the ceric nitrate reagent[20] another portion was treated with 3,5-dinitrobenzoyl chloride,[21] and a crystalline ester was obtained with some difficulty. It melted at 113–114° after two recrystallizations from ethanol; mixed with an authentic sample of cyclohexyl 3,5-dinitrobenzoate (m.p. 114–115°) it melted at 113.5–114.5° (lit.[22] m.p. 112–113°).

The mother liquors from a number of pimelic acid recrystallizations were combined, the benzene was removed and the residue was subjected to distillation. The major portion (about 80%) of the residue distilled at 100–132° (11 mm.). Redistillation of this fraction gave a narrower cut, b.p. 125–131° (11 mm.), n^{25}D 1.4592, m.p. 10–18°, of sharp, fecal odor (cyclohexanecarboxylic acid, lit.[23] b.p. 121° (14 mm.), n^{22}D 1.4599, m.p. 30–31°). The amide,[24] recrystallized twice from ethanol, melted at 185–186°, alone or mixed with an authentic sample of cyclohexane carboxamide (lit.[25] m.p. 185–186°). The infrared spectrum was identical with that of the authentic material.

Table I outlines variations in the experimental conditions. Unless a statement regarding the yield of cyclohexanone appears, the combined yield of this ketone and cyclohexanol was 3–6%, work-up procedure was the same in each case as outlined above, except where otherwise indicated.

Cyclohexene-1-carboxylic Acid (II).—The acid was prepared from cyclohexanone through the cyanohydrin[9] which in turn was dehydrated by the method of Battacharya,[10] using the sequence of thionyl chloride and pyridine. Hydrolysis of 1-cyanocyclohexene gave an equilibrium mixture of II and cyclohexene-3-carboxylic acid as indicated by Linstead and Boorman,[11] which could be partially separated by distillation. Approximately one-half of the crude reaction product was obtained as a soft solid, b.p. 135 139° (11 mm.), m.p. 30–34° (lit. m.p. 38°) which undoubtedly was contaminated with the β,γ-unsaturated isomer. The ultraviolet spectrum of this material showed a single peak at 218 mμ ($E_{\max}$ 76).

Due to the limited quantity of II available all experiments were carried out in a 180-ml. autoclave. In all cases 12.6 g. (0.1 mole) of II, 9.5 g. (0.23 mole) of sodium hydroxide and 80 g. (4.45 moles) of water were used, and reaction products were purified on a scale proportional to that described above for the cleavage of I. All results are to be compared with those of Experiment No. 10 in the cleavage of I.

TABLE II

	Reaction		
Expt. no.	Temp., °C.	Time, hr.	Yield of pimelic acid, %
1	350	6	60
2	300	10	63
3	280–285	10	45[a,b]
4	260–270	10	27.5[c]

[a] The figure represents conversion. [b] Recovery of starting material 34%, yield 69%. [c] Recovery of starting material 69%, yield 89%.

4-Cyanocyclohexene.—The starting material was readily prepared from acrylonitrile and butadiene.[26] The cleavage was carried out by the method used in the cleavage of I. 4-Cyanocyclohexene, 55.5 g. (0.5 mole), was treated with alkali as described above for I, allowing a five-hour reaction time. The resulting alkaline reaction mixture was boiled for 30 minutes to remove most of the liberated ammonia, extracted with ether, and acidified and worked up as previously described. Pimelic acid was isolated in 75% yield.

Cyclohexanol-1-carboxylic Acid.—This acid was prepared by hydrolysis in acid of the corresponding cyanohydrin.[9] The acid, 41 g. (0.284 mole), was heated in the bomb with 25 g. of sodium hydroxide and 200 ml. of water for seven hours at 325–335°. The resultant reaction mixture was extracted continuously with ether to remove all insoluble neutral material; from the ether extract 11 g. (40% of theory) of cyclohexanone was isolated. The aqueous layer was worked up as before; 5.5 g. (15%) of crude pimelic acid was obtained.

Cyclohexene-4-carboxaldehyde.—The reaction again was carried out using the described procedure; 55 g. (0.5 mole) of cyclohexene-4-carboxaldehyde was used, and the reaction time was five hours. The crude alkaline reaction product had a strong aromatic odor, and the neutral material was separated by extraction with ether. From the aqueous layer 30.5 g. (38%) of pimelic acid was obtained by the previously described isolation method. The neutral extract was dried (sodium sulfate) and the solvent was removed; the residue, 15 g., was subjected to distillation at atmospheric pressure. The following cuts were obtained: (1) b.p. 99–109°, n^{25}D 1.4650, about 4 g.; and (2) b.p. 110–130°, n^{25}D 1.4641, 3 g. The infrared spectrum of cut I was compared with those of toluene, methylcyclohexane and mixtures of the two hydrocarbons. All characteristic peaks of the toluene spectrum were present in the spectrum of cut I; the peaks of methylcyclohexane were all present, but quite evenly subdued in proportion to their size in the spectrum of the pure sample. Size of the peaks indicated cut I to contain approximately 10–15% methylcyclohexane, and over 60% toluene.

3,6-Endomethylenecyclohexene-4-carboxylic Acid.[13]—Conditions tried were those found to be optimum in the case of the cleavage of I. Following is a summary of the reaction conditions; 69 g. (0.5 mole) of VIII, 46 g. (1.1 moles) of sodium hydroxide, 200 ml. of water; reaction time, five hours; temperature, 350°. The crude reaction product contained a copious sediment of tarry polymer; filtration of this polymer and acidification of the filtrate gave only more tarry material. Efforts to extract the acidified mixture with ether and to isolate possible monomeric products met no success.

Acknowledgment.—We thank Mr. Harry Davis and associates for carrying out the high pressure experiments. The technical assistance of Mr. M. T. Nolt is highly appreciated.

BRECKSVILLE, OHIO RECEIVED JULY 9, 1951

---

[19] Campbell, *Analyst*, **61**, 393 (1936); E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 383.

[20] R. L. Shriner and R. C. Fuson, ref. 16, p. 96.

[21] *Ibid.*, p. 165.

[22] T. Reichstein, *Helv. Chim. Acta*, **9**, 802 (1926).

[23] N. Zelinsky, *Ber.*, **35**, 2687 (1902).

[24] R. L. Shriner and R. C. Fuson, ref. 16, p. 157.

[25] W. Markownikov, *Ber.*, **25**, 3355 (1892).

[26] A. A. Petrov and N. P. Sopov, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 2228 (1947), *C. A.*, **42**, 4957 (1948).