Pentachloroacetophenone.—Pentachlorophenyl methyl carbinol (118 g., 0.4 mole) was dissolved in one liter of glacial acetic acid, heated to the boiling point. Chromic anhydride (40 g., 0.4 mole) was added in three portions without further heating. The reaction mixture was left standing overnight and then poured into a large volume of water. The crude product was filtered and crystallized from ethanol to yield 97 g. (82.7%) of the ketone melting from 88–90°. A sample recrystallized from ethanol for analysis melted from 90–92°.

Anal. Calcd. for $C_8H_3OCl_5$: C, 32.81; H, 1.03. Found: C, 32.48, 32.60; H, 1.24, 1.16.

When pentachloroacetophenone in ether solution was added to an ether solution of methylmagnesium bromide no addition took place and the ketone was recovered unchanged.

Chlorinated Benzoic Acids.—The chlorinated benzoic acids were all prepared by oxidation of the corresponding aldehydes with alkaline potassium permanganate. In a typical experiment 2,4-dichlorobenzaldehyde (50 g., 0.285 mole), potassium permanganate (33.5 g., 0.194 mole) and sodium carbonate (60 g., 0.434 mole) in two liters of water was refluxed for three hours. The aqueous solution was filtered, cooled, extracted with benzene to remove unreacted aldehyde and finally acidified with sulfuric acid to yield the crude acid, having m. p. 158–160°. Recrystallization to a constant melting point from ethanol–water gave 40 g. (72%) of the acid melting at 160°. This agrees with the melting point of 159–160° previously reported by Cohen and Dakin[16] but Bornwater and Holleman[17] have reported the higher melting point of 164.3°. 3,4-Dichlorobenzoic acid was also crystallized from ethanol–water and melted from 207.5–209°. The highest previous melting point reported for this compound is 204.1°.[17] 2,6-Dichlorobenzoic acid, recrystallized by covering it with ligroin (b. p. 70–90°) and then adding benzene dropwise while boiling until the acid just went into solution, melted from 143–144°. Bornwater and Holleman[17] report a melting point of 143.7° for this compound. Pentachlorobenzoic acid was recrystallized from benzene and melted from 209.6–210.5°. Lock[1] has reported a melting point of 208° for pentachlorobenzoic acid. The absorption spectra in dioxane were measured by Dr. John D. Roberts using a Beckman spectrophotometer. Each sample was run at three concentrations and only those values of the transmission were retained which fell between 15 and 80%.

Summary

The ultraviolet absorption spectra of four chlorinated benzoic acids are reported. The decreased intensity, observed in the case of the di-ortho substituted acids, is attributed to suppression of the carboxyl group resonance.

[16] Cohen and Dakin, *J. Chem. Soc.*, **79**, 1129 (1901).

[17] Bornwater and Holleman, *Rec. trav. chim.*, **31**, 227 (1912).

NORTH ADAMS, MASS. RECEIVED JUNE 16, 1948

[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

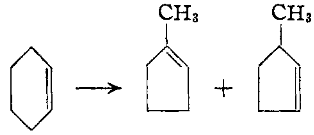
Isomerization of Cyclohexenes to Cyclopentenes: Oxidation of These Alkenes to Glycols and Acids

BY HOMER ADKINS AND ALAN K. ROEBUCK[1]

Zelinsky and Arabuzov[2] reported the isomerization of cyclohexene to methylcyclopentenes over alumina. The process seemed to offer a route for the preparation, from available cyclohexenes, of several cyclopentenes, glycols and acids, of possible value in organic syntheses. While our study was interrupted in the period 1942–1945, inclusive, several papers bearing on the subject appeared. Among these may be noted that of Block and Thomas[3] and an even more helpful publication by Scanlan, Swern, Billen and Findley.[4] The application of their method for oxidizing alkenes to glycols with hydrogen peroxide in formic acid has proven most useful.

We were fortunate in choosing as a catalyst pure alumina,[5] prepared from distilled aluminum isopropoxide, thus avoiding the multiplicity of reactions induced by the cracking catalyst used by Block and Thomas. The pure alumina catalyst was almost ten times as active per unit volume as one of the standard commercial alumina catalysts. The alumina *ex*-aluminum isopropoxide was quite active in isomerizing cyclohexenes to cyclopentenes. It was also active in establishing equilibrium between hydrocarbons differing only in the position of a double bond. The catalyst was not active, in converting cyclopentenes to cyclohexenes, to a significant extent, under the conditions described.

Cyclohexene (I) was isomerized, over alumina at 470–480°, to 1-methylcyclopentene-1 (II) and 1-methylcyclopentene-2 (III), in a ratio of about 2.5 to 1. In a typical experimental 800 ml. of cyclohexene was passed over 120 ml. of the granular alumina catalyst at a rate of 60–70 ml. per hour. The reaction product (788 ml.) gave after fractionation 328 ml. of I, 273 ml. of II and 108 ml. of III.



I II III

Methylcyclohexene-1 (IV) was isomerized to 1,2-dimethylcyclopentene-2 (V) and 1-ethylcyclopentene-2 (VI). The yields of V and VI, on the basis of the amount of IV reacting, were 17 and 13%, respectively. The isomeric compounds with the unsaturation in the 1-position were also produced but the fraction containing them could not

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[1] Holder of a fellowship in 1946 and 1947 supported by the Standard Oil Co. of Indiana.

[2] Zelinsky and Arabuzov, *Compt. rend. acad. sci.* (*U. R. S. S.*), **23**, 794 (1939); *Chem. Abst.*, **34**, 3696 (1940).

[3] Block and Thomas, THIS JOURNAL, **66**, 1589 (1944).

[4] Swern, Billen, Findley and Scanlan, *ibid.*, **67**, 1786 (1945).

[5] Adkins, *ibid.*, **44**, 2179 (1922).

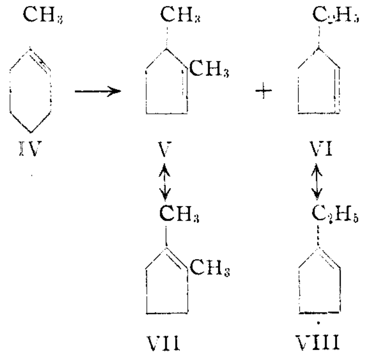
TABLE I

PROPERTIES OF CYCLOHEXENES AND CYCLOPENTENES

Name	B. p., °C. Reported	B. p., °C. Found	d^{25}_4 Reported	d^{25}_4 Found	n^{25}D Reported	n^{25}D Found	Mol. ref. Calcd.	Mol. ref. Found
Cyclohexene	83	82	0.809	0.806	1.4465(20°)	1.4435	27.24	26.81
1-Methylcyclohexene-1	109.2	109	.811	.806	1.4500(20°)	1.4480	31.86	31.93
1-Methylcyclohexene-2	104.5	103.5	.795	.796	1.4408(20°)	1.4400	32.86	31.86
1-Methylcyclohexene-3	102.3	102.1	.800		1.4419(20°)	1.4390		
1-Methylcyclopentene-1	75	75	.778	.787	1.4309(20°)	1.4300	27.24	26.91
1-Methylcyclopentene-2	65	65			1.4200(20°)	1.4198		
1,2-Dimethylcyclopentene-1	105	102.5			1.4447(13°)	1.4430		
1,2-Dimethylcyclopentene-2	95	92.5		.771	1.4290(20°)	1.4265	31.86	31.92
1-Ethylcyclopentene-1	108	104 103–105			1.4424(20°)	1.4425 1.4410[a]		
1-Ethylcyclopentene-2	99–103	96		.784	1.4310(20°)	1.4300	31.86	31.86

[a] Value for product of synthesis.

be separated into its components. The two compounds (V and VI) with unsaturation in the 2-position were isomerized separately over alumina to the corresponding 1,2-dimethylcyclopentene-1 (VII) and 1-ethylcyclopentene-1 (VIII). The inseparable mixture of isomers (VII and VIII) obtained directly from methylcyclohexene-1 (IV), was also isomerized in part back to V and VI.



At equilibrium the ratio of V to VII appeared to be about 3 to 2, while the ratio of VI to VIII was about 2 to 3. Although VII and VIII were not obtained in pure condition as the result of the isomerism of IV, each was obtained in a yield of about 7% of the theoretical from IV when V and VI were first isolated and then isomerized separately. The yields of 7 to 17% indicated above for each of the four isomers may be increased by reworking mixtures and products.

1-Methylcyclohexene-3 (IX) apparently gave the same pentenes but not in the same proportions as did 1-methylcyclohexene-1. However, the reaction mixtures from the former could not be separated as definitively as was the case with the latter compound.

All of the unsaturated compounds (I to IX) referred to just above have been prepared and described previously. The structures assigned to VII and VIII are probable but not completely established. VIII was prepared by synthesis from cyclopentanone through the intermediate formation of 1-ethyl-pentanol-1, and the properties of the product found to be the same as the compound from isomerization. The boiling points, refractive indices, densities and calculated molecular refraction as found are given in Table I, as well as the values recorded by Egloff.[6] The values for 1-methylcyclohexene-2 (X) referred to below are also given in Table I.

All the alkenes, except 1,2-dimethylcyclopentene-1 (VII) and 1-ethylcyclopentene-1 (VIII) were converted to the corresponding glycols by oxidation with hydrogen peroxide in formic acid using the method of Scanlan, Swern, Billen and Findlay.[4] The yields and certain properties of the glycols obtained are given in Table II. The yields of glycols from the cyclohexenes were 70–80% while from the cyclopentenes they were about 60% in four cases and 30% in one. Two isomeric glycols, one a solid and the other a liquid, were obtained from 1-methylcyclohexene-2. The diacetates of the nine glycols were prepared in 80 to 95% yields. The results of the analyses of these diacetates, their molecular weight as calculated from quantitative saponification, and certain of their properties are given in Table III.

The cyclohexenes (I, IV and IX) and two of the cyclopentenes (II and V) were convertible in good to fair yield to keto or dibasic acids. Better yields of acids were obtained if the glycols were first prepared and then oxidized to the desired acid except in the case of the conversion of 1,2-dimethylcyclopentene-2 to 4-methyl-5-ketocaproic acid. Δ-Ketocaproic acid was obtained in 80% and β-methyladipic acid in 50% yields by the oxidation, with potassium permanganate in acetone, of 1-methyl-1,2-cyclohexanediol and 1-methyl-3,4-cyclohexanediol, respectively. The liquid and solid 1-methyl-2,3-cyclohexanediols were oxidized with chromic acid to dibasic acids melting at 76° and 54°, respectively. The structures of these acids have not been determined.

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[6] Egloff, "Physical Constants of Hydrocarbon," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940, pp. 324–328, 306–309.

TABLE II

GLYCOLS FROM CYCLOHEXENES AND CYCLOPENTENES BY OXIDATION WITH HYDROGEN PEROXIDE AND FORMIC ACID

Name	Yield, %	B. p., °C.	Mm.	M. p. or $n^{25}\mathrm{D}$	Carbon, %		Hydrogen, %		M. p. of derivative, °C.
					Calcd.	Found	Calcd.	Found	
1,2-Cyclohexanediol[7] (*trans*)	75	120–125	4	104					92[a] 178–9[b]
1-Methyl-1,2-cyclohexanediol[8]	73	105–108	2	84					192[b] 71[a]
1-Methyl-3,4-cyclohexanediol[9]	81	104	1	68					120–121[b]
1-Methyl-2,3-cyclohexanediol (liquid)	40	97–99	1	1.4838	64.58	64.28	10.84	10.79	185–186[b]
1-Methyl-2,3-cyclohexanediol (solid)	40	97–99	1	96	64.58	64.66	10.84	11.05	186[b]
1-Methyl-1,2-cyclopentanediol[10]	58	88–90	1	65					92[b]
1-Methyl-2,3-cyclopentanediol	65	95–97	1	1.4760					92–93[b]
1,2-Dimethyl-2,3-cyclopentanediol[11]	59	85–87	1	1.4755	64.58	64.65	10.84	10.89	
1-Ethyl-2,3-cyclopentanediol	30	90–115	1	1.4790	64.58	64.88	10.84	10.82	

[a] Dibenzoate. [b] Di-(3,5-dinitrobenzoate).

TABLE III

GLYCOL DIACETATES

Diacetate of	B. p., °C.	Mm.	$n^{25}\mathrm{D}$	Carbon, %		Hydrogen, %		Mol. wt.	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
1,2-Cyclohexanediol[12] (*trans*)	95–96	1	1.4419	...	...	..	..	200	202
1-Methyl-1,2-cyclohexanediol	90–92	1	1.4442	61.66	61.88	8.47	8.48	214	228
1-Methyl-3,4-cyclohexanediol[13]	88	1	1.4459	...	...	..	..	214	218
1-Methyl-2,3-cyclohexanediol (*ex*-liquid)	88–89	1	1.4464	61.66	61.50	8.47	8.74	214	222
1-Methyl-2,3-cyclohexanediol (*ex*-solid)	88–89	1	1.4458	61.66	61.76	8.47	8.70	214	220
1-Methyl-1,2-cyclopentanediol	69–70	1	1.4408	59.98	59.97	8.60	8.23	200	204
1-Methyl-2,3-cyclopentanediol	83–84	1	1.4380	59.98	59.77	8.06	8.06	200	204
1,2-Dimethyl-2,3-cyclopentanediol	83	1	1.4291	61.66	61.77	8.47	8.41	214	216
1-Ethyl-2,3-cyclopentanediol	83–84	1	1.4421	61.66	61.82	8.47	8.71	214	220

1-Methyl-1,2-cyclopentanediol was oxidized with potassium permanganate in acetone solution, giving a 43% yield of Δ-ketocaproic acid. 1-Methyl-2,3-pentanediol was oxidized to α-methylglutaric acid but in only a 6% yield with chromic in dilute sulfuric acid. The direct oxidation of 1,2-dimethyl-cyclopentene-2 with potassium permanganate in acetone gave a 46% yield of γ-methyl-Δ-ketocaproic acid. The same acid was obtained in a 43% yield from 1,2-dimethyl-2,3-cyclopentanediol. The direct oxidation with potassium permanganate in acetone of the compound believed to be 1,2-dimethyl-cyclopentene-1, gave a neutral compound which is apparently 2,6-heptanedione. The yield of crude product was about 30% of the theoretical but neither the oxidation product nor its bis-*p*-nitrophenylhydrazone could be obtained pure. However, the fact that the chief product of the oxidation was a non-acidic ketone is in harmony with the postulated structure for the dimethylcyclopentene. A dimethylcyclopentene having any structure other than VII should give an acid upon oxidation.

The names for alkenes in this paper have been used frequently in earlier publications and seem to give a clearer indication of the relationship of the compounds discussed than do other names. However, in certain cases another name is preferred in *Chemical Abstracts*: *i. e.*, 3-methyl-cyclopentene-1 for 1-methyl-cyclopentene-2, 2,3-dimethyl-cyclopentene-1 for 1,2-dimethyl-cyclopentene-2, 3-ethyl-cyclopentene-1 for 1-ethyl-cyclopentene-2, 3-methyl-cyclohexene-1 for 1-methyl-cyclohexene-2, and 4-methyl-cyclohexene-1 for 1-methyl-cyclohexene-3.

Experimental

Preparation and Isomerization of Cyclohexenes.—The cyclohexenes were prepared from cyclohexanol, 2-methylcyclohexanol or 4-methylcyclohexanol by dehydration over sulfuric acid.[14] The alkenes obtained were purified by fractional distillation. The methylcyclohexanols were prepared by the hydrogenation of the corresponding cresols over Raney nickel at 175° under a pressure of about 100 atm.

The alumina catalyst was prepared by pouring 180–200 g. of distilled aluminum isopropoxide into three liters of water rapidly stirred in a 4-liter beaker. The solid product was separated by filtration, washed with water until free of isopropanol, pressed as dry as possible, dried several days at room temperature and finally at 120°. The hard cake was then broken up and the part taken which would pass through a screen with 4 meshes, but not through one of 24 meshes per cm. There was thus obtained about 40 g.

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(7) Brunel, *Compt. rend.*, **137**, 63 (1903); Brunel, *Bull. soc. chim.*, [3] **29**, 884 (1903); Heilbron, "Dictionary of Organic Compounds," Vol. II, p. 68.

(8) Heilbron, *ibid.*, p. 655; Wilson and Read, *J. Chem. Soc.*, 1269 (1935).

(9) Nametkin and Brussov, *Ber.*, **56B**, 1807 (1923).

(10) Böeseken, *Rec. Trav. Chim.*, **47**, 683 (1928).

(11) Godchot, Mousseron and Richaud, *Compt. rend.*, **200**, 1599 (1935).

(12) Brunel, *Ann. chim. phys.*, [8] **6**, 248 (1905).

(13) Stadnikow, *J. Russ. Phys. Chem. Soc.*, **36**, 484 (1904); Beilstein, Vol. VI, Springer, Berlin, 1923, p. 740.

(14) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 177.

(40 ml.) of the granulated alumina catalyst free of fine material.

The 120 ml. of alumina catalyst for isomerization was held in a flattened aluminum U-tube, 75 cm. in length and 50 × 6 mm. internal diameter in cross section, immersed in an electrically heated bath of sodium and potassium nitrates.[15] The compound to be isomerized was distilled into the catalyst chamber at a constant rate of 60–70 ml. per hour. The products were condensed in a water cooled condenser.

Separation of Products.—The products of isomerization were separated by fractionation through a Stedmann column[16] having a packed section of cones of stainless steel gauze, 90 cm. in length and 2 cm. in diameter. The column was provided with a partial reflux head, drip counter and electrically heated jacket. The heating of the jacket and the rate of boiling of the mixture was controlled by the use of variable transformers. The column was operated to deliver about 2 ml. of distillate per hour and is believed to have 60 theoretical plates. The distillation pot was a 1-liter round bottom flask surrounded by a glass heating mantle. The fractionation was followed by determining the refractive indices of successive fractions. After the first separation of a reaction mixture into fractions the process was repeated on successive fractions in the usual way. The reproducibility of results is shown by the fact that three different batches of the products from isomerization of 1-methylcyclohexene-1 gave the variation in yields indicated: 1,2-dimethylcyclopentene-2, 15.4, 15.4 and 14.8%; 1-ethylcyclopentene-2, 11.1, 11.7, and 10.1%; a fraction n^{25}D 1.4425, 24.8, 25.1 and 24.4%; and 1-methylcyclohexene-1, 10.8, 12.0 and 13.6%.

Results of Isomerization and Fractionation.—Cyclohexene was isomerized over 120 ml. of alumina, *ex*-aluminum isopropoxide, at 470–480°. The products were fractionated through the Stedmann column and the fractions, so obtained, refractionated. In a typical run there was obtained from 800 ml. of cyclohexene 273 ml. of 1-methylcyclopentene-1, b. p. 75°, n^{25}D 1.4300, 108 ml. 1-methylcyclopentene-2, b. p. 65°, n^{25}D 1.4198 and 328 ml. of cyclohexene, b. p. 82°, n^{25}D 1.4435. Since the fractionations were followed exclusively by determination of refractive indices the b. p. given in these summaries are only approximate and merely indicate the approximate boiling point range.

1-Methylcyclohexene-1 was isomerized and the products separated in the same way as those from cyclohexene. In a typical run there was obtained from 760 ml. of 1-methylcyclohexene-1, 59 ml. of material, b. p. 80–85°, n^{25}D 1.4200; 123 ml. of 1,2-dimethylcyclopentene-2, b. p. 92°, n^{25}D 1.4265; 91 ml. of 1-ethylcyclopentene-2, b. p. 96°, n^{25}D 1.4300; 55 ml. of 1-methylcyclohexene-2, b. p. 103°, n^{25}D 1.4390; 192 ml. of a fraction, b. p. 103–104.5°, n^{25}D 1.4410–1.4430; 26 ml. of a fraction, b. p. 106.7°, n^{25}D 1.4500+; and 82 ml. of 1-methylcyclohexene-1, b. p. 109°, n^{25}D 1.4480.

Similarly, the isomerization of 805 ml. of 1-methylcyclohexene-3 gave 59 ml. of a low boiling fraction, n^{25}D 1.4200; 85 ml. 1,2-dimethylcyclopentene-2, b. p. 92–93°, n^{22}D 1.4265; 175 ml. of a fraction, b. p. 96°, n^{25}D 1.4280–1.4310; 219 ml. of a fraction, b. p. 104°, n^{25}D 1.4400–1.4430; 54 ml. of a fraction, b. p. 106–107°, n^{25}D 1.4500+; and 105 ml. of 1-methylcyclohexene-1, b. p. 109–110°, n^{25}D 1.4480–1.4490.

The isomerization of 330 ml. of 1-ethylcyclopentene-2 gave 53 ml. of a low boiling fraction, n^{25}D 1.4200–1.4270; 85 ml. of ethylcyclopentene-2, b. p. 96–97°, n^{25}D 1.4300, and 132 ml. of ethylcyclopentene-1, b. p. 103–104°, n^{25}D 1.4412–1.4432.

The isomerization of 550 ml. of 1,2-dimethylcyclopentene-2 gave 57 ml. of a fraction, b. p. 80–90°, n^{25}D 1.4485–1.4208, 230 ml. of 1,2-dimethylcyclopentene-2, b. p. 92–93°, n^{25}D 1.4265, and 142 ml. of 1,2-dimethylcyclopentene-1, b. p. 102°, n^{25}D 1.4423–1.4435. The intermediate fractions and residue amounted to 72 ml.

The isomerization of 800 ml. of the fraction, b. p. 103–104.5°, n^{25}D 1.4410–1.4430, from the isomerization of 1-methylcyclohexene-1, gave 39 ml. of a low-boiling fraction, n^{25}D approximately 1.4200; 88 ml. 1,2-dimethylcyclopentene-2, b. p. 92°, n^{25}D 1.4265; 138 ml. ethylcyclopentene-2, b. p. 96°, n^{25}D 1.4300, 256 ml. of a fraction, b. p. 102–104°, n^{25}D 1.4410–1.4425; and 56 ml. of 1-methylcyclohexene-1, b. p. 109°, n^{25}D 1.4495.

Preparation of 1,2-Cyclohexanediol from Cyclohexene.—Into a 3-neck, round-bottom flask equipped with a stirrer, thermometer, and a separatory funnel were placed 600 ml. (13.7 mole) of 88% formic acid and 140 ml. (1.4 mole) of 30% hydrogen peroxide. Eighty-two grams (1.0 mole) of cyclohexene was added during twenty to thirty minutes to the performic acid solution. When the temperature of the reacting mixture had reached 40°, the flask was surrounded with an ice-bath and the temperature was kept between 40 and 45° by controlling the rate of addition of the cyclohexene. When the exothermic reaction was over, the ice bath was removed, and the reaction mixture was stirred for one additional hour at 40°. The excess formic acid and water were removed by distillation from a steam-bath under a pressure of 50–20 mm. The liquid residue was cooled and neutralized by slowly adding a cold solution of 80 g. of sodium hydroxide in 150 ml. of water, keeping the temperature of the reaction mixture below 45°.[17]

The cyclohexanediol was extracted from the sodium hydroxide and sodium formate solution with one liter of ethyl acetate at 45°. The ethyl acetate layer was then washed with 100 ml. of water in two portions for the removal of sodium formate. The water extract was added to the solution of sodium hydroxide and sodium formate and the water solution extracted five times with ethyl acetate, using equal volumes of solution and ester in each extraction.

All the ethyl acetate extracts were combined and the solvent distilled off on the steam-bath. The residue was then distilled at 1–4 mm. using an all-glass condenser to facilitate handling the solid product. 1,2-Cyclohexanediol boiling at 120–125° (4 mm.), m. p. 100°, was obtained in a yield of 84–87 g. corresponding to 73–75% of the theoretical. A purer compound m. p. 104° was obtained by recrystallization of the product from ethyl acetate.

The procedure described above was also used for the preparation of the glycols listed in Table II.

Glycol Diacetates.—The glycol (0.1 mole) was refluxed with 200 ml. of acetic anhydride for eight hours. After distillation of acetic acid and excess acetic anhydride, the glycol diacetate was distilled as indicated in Table II in yields of 80–95%. The saponification equivalents of the diacetates (0.6 g.) were determined by saponification in 0.2 *N* sodium hydroxide for five minutes at reflux temperature and titration of the excess alkali.

Δ-Ketocaproic Acid.—1-Methyl-1,2-cyclopentandiol (11.6 g.) dissolved in 200 ml. of acetone, was oxidized a little above 0°, with 23 g. of potassium permanganate. The permanganate was added, to the rapidly stirred acetone solution, in 1–2 g. portions, allowing each portion to be decolorized before the next portion was added. After the completion of the oxidation the solid in the reaction mixture was separated by filtration and washed with 100 ml. of acetone. The solid was suspended in 200 ml. of water, a mixture of 40 ml. of sulfuric acid in 100 ml. of water was added slowly keeping the mixture at about room temperature. Sodium sulfite (about 20 g.) was then added in small portions at 30–40° until the reaction mixture was homogeneous. The solution was then extracted with 600 ml. of ethyl acetate in three portions. The ethyl acetate was distilled on the steam-bath and the Δ-ketocaproic acid (8.9 g.) distilled at 141–149° (2 mm.). The acetone solution obtained as described above was distilled and 2.5 g. of the diol recovered by distillation. The acid (neut. equiv. 131, calcd. 130) gave a hydrate m. p. 35–36°.[18] The yield was 68% of theoretical or 85% if allowance is made for re-

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[15] Adkins and Peterson, THIS JOURNAL, 53, 1513 (1931).

[16] L. B. Bragg, *Ind. Eng. Chem., Anal. Ed.*, 11, 283 (1939).

[17] Care should be taken to determine whether or not the concentration of peroxide has been reduced to a safe level before the mixture is heated.

[18] Vorländer, *Ann.*, 294, 273 (1896).

covered glycol. The acid was also obtained in 36% yield by oxidation of 1-methyl-1-cyclopentene following the procedure given above for the diol.

6-Ketoheptanoic Acid.[19]—This acid, b. p. 154–158° (2 mm.), (neut. equiv. 142, calcd. 144) was obtained in 57% yield, or 84% if allowance is made for recovered glycol, by the oxidation of 1-methyl-1,2-cyclohexanediol (13 g.) with permanganate in acetone as described for 5-ketohexanoic acid. The acid gave a semicarbazone, m. p. 144°,[20] a 2,4-dinitrophenylhydrazone, m. p. 82–83°, and a *p*-nitrophenylhydrazone, m. p. 112°.

4-Methyl-5-ketocaproic Acid.—This acid (neut. equiv. 145, calcd. 144), b. p. 120–130 (1 mm.), was obtained in 43–46% yield from 1,2-dimethyl-2,3-cyclopentene and from 1,2-dimethyl-2,3-cyclopentenediol using the permanganate in acetone procedure described above. The acid gave a semicarbazone, m. p. 168–169°.[21]

Oxidation of 1,2-Dimethyl-1-cyclopentene.—The application of the permanganate in acetone procedure to 1,2-dimethyl-1-cyclopentene (19.2 g.) gave a small amount of acids (2.4 g.) and neutral products (11.1 g.), b. p. 58–72°. The neutral product gave a *p*-nitrophenylhydrazone, m. p. 158–160°, and a 2,4-dinitrophenylhydrazone, m. p. 196–198°.

α-Methylglutaric Acid.—1-Methyl-2,3-cyclopentanediol (11.6 g.) in a mixture of 16 ml. of sulfuric acid and 200 ml. of water, was oxidized at about 0° with chromic acid. Chromic anhydride (20 g.) was added in 1–2 g. portions, allowing time for the decolorization of one portion before the next was added. The reaction mixture was warmed up to 40° after the addition of the last portion of the oxidizing agent and extracted with a liter of ethyl acetate in five portions. The ethyl acetate was distilled and the residue extracted with a solution containing 8 g. of sodium hydroxide in 60 ml. of water. The unoxidized glycol (4 g.) was extracted with ethyl acetate. The alkaline solution was made acid with sulfuric acid and the organic acid extracted with ethyl acetate. After distillation of ethyl acetate the acids were distilled at 150–180° (2 mm.). The distillate crystallized in part when stored at about 0°. After recrystallization from ethyl acetate 0.6 g. of α-methylglutaric acid, m. p. 75–76°, neut. equiv. 74 (calcd. 73) was obtained.[22]

β-Methyladipic Acid.—1-Methyl-3,4-cyclohexanediol (13 g.) was oxidized in the manner described above with chromic acid to give 8.5 g. of crude β-methyladipic acid, m. p. 88°; after recrystallization, 4 g. of acid, m. p. 93–94°, (neut. equiv. 81, calcd. 80) was obtained.[23]

Oxidation of 1-Methyl-2,3-cyclohexanediol.—The oxidation of the isomeric glycols by the chromic acid procedure just described, gave dibasic acids of different properties. The solid isomer gave an acid, m. p. 51–52°, while the liquid isomer gave an acid, m. p. 75–76°. Each of the acids showed a molecular weight of 166 as compared with a calculated value of 160 for a seven carbon atom saturated dibasic acid. The yield of solid acids was only about 10% of the theoretical but the loss in obtaining the crystalline acids was considerable.

Summary

Cyclohexene is isomerized over pure alumina at 470–480° to methylcyclopentene-1 and -2. Methylcyclohexene-1 is isomerized over pure alumina to 1,2-dimethyl- and ethyl-cyclopentenes as indicated in formulas V to VIII, inclusive. The four cyclopentenes have all been isolated in yields which make them available for synthesis. The method of oxidation using hydrogen peroxide in formic acid has been used quite effectively for the conversion of cyclohexene, three isomeric methylcyclohexenes and four cyclopentenes to the corresponding glycols. These glycols have been oxidized further with potassium permanganate or chromic acid to various dibasic and keto acids.

MADISON, WISCONSIN RECEIVED JUNE 14, 1948

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[19] Perkin, *J. Chem. Soc.*, **57**, 229 (1890).

[20] Wallach, *Ann.*, **329**, 377 (1903).

[21] Chiurdoglu, *Bull. soc. chim. Belg.*, **47**, 363 (1938); *Chem. Abstr.*, **32**, 9052 (1938).

[22] Mulliken, "Identification of Organic Compounds," Vol. I, p. 41.

[23] Heilbron, "Dictionary of Organic Compounds," Vol. II, p. 608.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

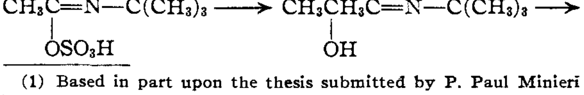
A New Reaction of Nitriles. I. Amides from Alkenes and Mononitriles[1]

BY JOHN J. RITTER AND P. PAUL MINIERI

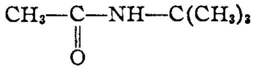
It has been found in this Laboratory that interaction of alkenes with nitriles occurs in the presence of concentrated sulfuric acid. Hydrolysis of the reaction product by simple dilution with water yields an amide, I. This reaction has been accomplished with nitriles generally and a number of active alkenes, and appears to be of wide applicability. Amide formation from these reactants seems explainable as follows, formulated for acetonitrile, isobutene and sulfuric acid:

$$(CH_3)_2C{=}CH_2 + H_2SO_4 \longrightarrow (CH_3)_3C{-}OSO_3H$$

$$(CH_3)_3C{-}OSO_3H + CH_3C{\equiv}N \longrightarrow$$



$$\underset{\displaystyle OSO_3H}{CH_3C}{=}N{-}C(CH_3)_3 \xrightarrow{H_2O} \underset{\displaystyle OH}{CH_3CH_3C}{=}N{-}C(CH_3)_3 \longrightarrow$$



$$CH_3{-}\underset{\displaystyle \overset{\|}{O}}{C}{-}NH{-}C(CH_3)_3$$

I

Experiments under identical conditions with substitution of acetamide for acetonitrile gave no reaction product, setting aside the possibility of addition of an amide, or its equivalent in sulfuric acid solution, to the olefinic double bond.

Confirmation of the identities of these compounds was reached through synthesis of N-*t*-butyl acetamide by an authentic method as well as by hydrolysis of N-*t*-amyl acetamide and N-*t*-octyl acetamide (Tables II, III) to *t*-amylamine and *t*-octylamine, respectively. N-*t*-butyl acetamide was obtained previously[2] by Beckmann rearrangement of pinacolone oxime; the product of the acetonitrile–isobutene reaction was identical with this compound, thus establishing the reac-

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[1] Based in part upon the thesis submitted by P. Paul Minieri in May, 1948, to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] R. Scholl, *Ann.*, **338**, 16 (1905).