repeated recrystallization from alcohol gave orange plates, melting at 152–154° alone and on admixture with the cyclohexanone derivative.

Anal. Calcd. for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07; N, 20.13. Found: C, 51.88; H, 4.89; N, 20.23.

The recrystallized distillation residue was again recrystallized from alcohol to give colorless prisms of dimethylamine hydroiodide, m.p. 147–150°.

Anal. Calcd. for $C_2H_7N\cdot HI$: C, 13.87; H, 4.62; N, 8.08. Found: C, 13.60; H, 4.41; N, 8.21.

(b) **The Formation of VII from V.**—When 130 mg. of the freshly prepared free base V was heated in a sealed tube at 100°, the material first fused and then decomposed after 30 seconds. The resulting solid mass was washed with dry ether and distilled with aqueous alcohol. The distillate gave a 2,4-dinitrophenylhydrazone (yield 100%, m.p. 155–156°) which was identified as the cyclohexanone derivative by a mixed m.p. determination.

(c) **The Formation of VII and *dl-cis*-2-Chloro-N,N-dimethylcyclohexylamine (XII) from II-Hydrochloride.**—Dried II-hydrochloride (1.04 g.) in a sealed tube was heated in boiling xylene. It melted at once and then decomposed after about 7 minutes to give a solid mass, which was treated as described under (b). The 2,4-dinitrophenylhydrazone of cyclohexanone was obtained; yield 56%, m.p. and mixed m.p. 150°.

The distillation residue was dissolved in water. The oily layer which apeared on the addition of alkali was extracted with ether. The ether layer yielded a picrate (yield 24%, m.p. 145–150°) which was repeatedly recrystallized from ethyl acetate to give needles, m.p. 178°, which were identified as *dl-cis*-2-chloro-N,N-dimethylcyclohexylamine (XII) picrate by a mixed m.p. determination.

Anal. Calcd. for $C_8H_{16}NCl\cdot C_6H_3N_3O_7$: N, 14.35. Found: N, 14.47.

(d) **The Formation of VII and Crude *dl-trans*-2-Chloro-N,N-dimethylcyclohexylamine from V-Hydrochloride.**—V-Hydrochloride (40 mg.) was heated in a sealed tube at 125°. When the decomposed material was treated as described in (b), the 2,4-dinitrophenylhydrazone of cyclohexanone was obtained, m.p. and mixed m.p. 152–154°. When the decomposed material was dissolved in water and extracted with ether after the addition of potassium carbonate, the extract gave a picrate which contained halogen; yield 45%, m.p. 138–142°. This picrate showed no depression of melting point on admixture with an authentic sample of *dl-trans*-2-chloro-N,N-dimethylcyclohexylamine picrate and a depression of melting point on admixture with its *cis* epimer.

***dl-cis*-2-Chloro-N,N-dimethylcyclohexylamine (XII)** was prepared by the Mousseron procedure[15]; b.p. 100° (25 mm.). The hydroiodide, which melted at 168–169° after recrystallization from acetone–ether, was unchanged when heated in a sealed tube at 140°.

Anal. Calcd. for $C_8H_{16}NCl\cdot HI$: C, 33.16; H, 5.87; N, 4.83. Found: C, 33.28; H, 5.90; N, 4.65.

Intramolecular Interconversion of Halogen.—A solution of 1.07 g. of II-hydrochloride in 10 ml. of absolute ethanol was refluxed for 5 minutes and then kept at room temperature for 3 days. Ether (15 ml.) was added and the mixture kept for 50 days. During this interval colorless needles appeared (m.p. 150–155°, yield 520 mg.) which after three recrystallizations from ethanol melted at 156–157° alone and on admixture with the hydroiodide of II. The picrate was also identical with the picrate of II-HI.

Anal. Calcd. for $C_8H_{16}NI\cdot HI$: C, 25.17; H, 4.46. Found: C, 25.47; H, 4.58.

After 50 days different needles appeared (yield 120 mg.) which were recrystallized from ethanol as cubes, m.p. 184–185°.

Anal. Calcd. for $C_8H_{16}NCl\cdot HI$ (*dl-trans*-2-chloro-N,N-dimethylcyclohexylamine hydroiodide): N, 5.84. Found: N, 5.78.

The picrate (m.p. 166–168°) gave a positive Beilstein test for halogen, but contained no iodine. Since the melting point of the picrate was depressed on admixture with authentic *dl-cis*-2-chloro-N,N-dimethylcyclohexylamine (XII) picrate (m.p. 178°), it is probably the *trans* epimer.

Anal. Calcd. for $C_8H_{16}NCl\cdot C_6H_3N_4O_7$ (*dl-trans*-2-chloro-N,N-dimethylcyclohexylamine picrate): C, 43.02; H, 4.86; N, 14.35. Found: C, 43.25; H, 4.94; N, 13.95.

Acknowledgment.—The authors are indebted to the Service Center of Microanalyses of the Kyushu University and also to the Microanalytical Section of this Institute for the microanalyses.

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KATAKASU, FUKUOKA, JAPAN

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

Synthesis of Lactones[1]

BY PAUL S. STARCHER AND BENJAMIN PHILLIPS

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The use of peracetic acid in an inert solvent was investigated in the Baeyer–Villiger synthesis of lactones from cyclic ketones. Side reactions were minor with cyclopentanone and various cyclohexanones, and it was possible to isolate by distillation the corresponding δ-valerolactone and ε-caprolactones in high yield as stable monomeric compounds. Several previously unreported alkyl-substituted ε-caprolactones were prepared by this method. Extension of the reaction to cycloheptanone and cycloöctanone resulted in extensive ring cleavage to the corresponding dibasic acids.

A previous contribution[2] from this Laboratory described a new synthesis of peracetic acid—one which gave the product as a solution in an inert solvent. The present paper deals with the use of this reagent for the preparation of lactones by reaction with cyclic ketones.

The limitations which have made the Baeyer–Villiger reaction[3] and its various modifications unsatisfactory in the past for the preparation of many acid-sensitive products, such as δ-valerolactone and ε-caprolactone, have been noted.[4] High yields of these products were obtained in the present study, and this was attributed to the type of peracetic acid solution used. The absence of inor-

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TABLE I

OXIDATION OF KETONES, $(CH_2)_nC{=}O$, WITH PERACETIC ACID

Ketone, n	Molar ratio peracid/ketone	Reaction Time, hr.	Reaction Temp., °C.	Products	Yield, %	M.p. or b.p., °C. (mm.)	$n^{30}D$	Sapon. or neut. equiv. Calcd.	Sapon. or neut. equiv. Found	Hydrazide, m.p., °C. Found	Hydrazide, m.p., °C. Lit.
4	0.33	8	40	δ-Valerolactone	84	83 (4)	1.4540	100	101	105	105–106[10]
5	0.33	6.25	40	ε-Caprolactone	85	108 (10)	1.4605	114	113	116–116.5	114–115[25]
6	1.25	10	70	ζ-Enantholactone	29	70 (5)	1.4688	128	130	123.5–124	123[7]
				Pimelic acid	33	102	....	80.1	80.8		
7	1.25	8.5	70	η-Caprylolactone[a]	6	..	....				
				Suberic acid	59	137	....	87.1	87.5		

[a] Not isolated.

ganic impurities, notably water, hydrogen peroxide, mineral acids and salts, reduced polymerization to a minimum during the reaction step and avoided the formation of many of the by-products which plagued previous investigators.[5–12] Co-product acetic acid was the only significant initiator of by-product formation in the present synthesis. The problem of an acidic co-product is always encountered when any peracid is used in the Baeyer–Villiger reaction. Acetic acid is one of the least objectionable not only because it is a weak acid but also because its relatively low boiling point makes for its easier removal and facilitates subsequent recovery of the lactones by distillation under reduced pressure. The use of an excess of ketone or an azeotropic agent such as ethylbenzene also helps in the rapid removal of acetic acid.

The lactones obtained in this study are stable. Samples which were stored for three years at room temperature showed only slight changes in refractive index. Previous methods,[4–13] based on a variety of peracids, employed neutralization of the reaction mixture and extraction of the co-product acid and, in most cases, except for ε-substituted ε-caprolactones,[3,14,15] the products were primarily polymeric or polymerized during or after distillation.

In contrast to cyclopentanone and cyclohexanone, both of which reac trelatively rapidly with peracetic acid to give good yields of lactones, cycloheptanone and cyclooöctanone reacted very slowly with peracetic acid at moderate temperatures. This was in line with the earlier work of Friess,[7,16] who obtained lactone polymers from cycloheptanone and cyclooöctanone after treatment with perbenzoic acid but only after reaction times of 17 and 42 days, respectively, at room temperature. We found that at 70° both cycloheptanone and cyclooctanone reacted reasonably rapidly with peracetic acid, but the major products were not monomeric lactones. Cycloheptanone gave approximately equal amounts of ζ-enantholactone and pimelic acid while cyclooöctanone gave principally suberic acid. Cyclohexanone is much more resistant to ring cleavage than either cycloheptanone or cyclooöctanone. Oxidation of cyclohexanone with peracetic acid at 80° gave only a small amount (1%) of adipic acid.[17] Table I summarizes the data on the oxidation of these unsubstituted cyclic ketones.

Although no kinetic data are available on the reaction rates of various alkyl-substituted cyclohexanones with peracetic acid, a rough approximation of their relative reactivities may be obtained from Table II where the times and temperatures for a given yield are indicated. Cyclohexanone reacted more rapidly with peracetic acid than alkyl-substituted cyclohexanones. Increasing the number of substituents appeared to decrease the reaction rate: note methyl-, dimethyl- and trimethylcyclohexanones. An increase in the size of a substituent, particularly one in the 2-position, also appeared to decrease the rate. The position of substituents on the ring also appeared to affect the reaction rate. For example, 2,6-dimethylcyclohexanone reacts more slowly than the 3,5-isomer, probably because the methyl groups in the 2- and 6-positions tend to mask the carbonyl group. Except for 3- and 4-methylcyclohexanones, the above conclusions are in accord with studies[18] made on the stabilities of the cyanohydrins of alkyl-substituted cyclohexanones, where the steric concepts of "axial crowding" and "equatorial interference" were used to explain the relative stabilities of highly alkylated cyclohexanone cyanohydrins.

Several cyclohexanones substituted in the 2-position have been treated with peracetic acid and the resulting lactones obtained in very high yield (see Table II). Although two products are possible (equation, R′ = alkyl, R = H), only one product (I) was obtained. We were unable to find evidence of the alternate product II. Our results agree with those of Baeyer and Villiger[3] and with the generalization made by Doering[19] that secondary and tertiary groups migrate more

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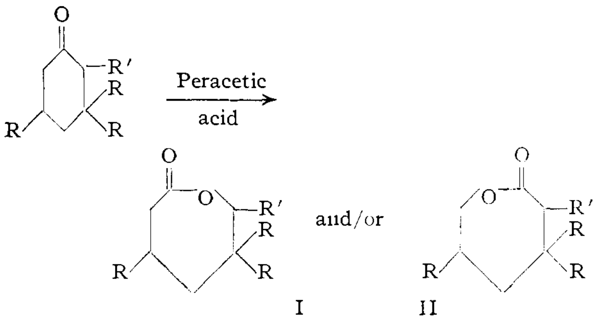
TABLE II: LACTONES FROM PERACETIC ACID AND CYCLOHEXANONES

Run	Substituents in cyclohexanone	Reaction[a] Time, hr.	Reaction[a] Temp., °C.	Substituents in ε-caprolactone	Yield, %	M.p. or b.p., °C. (mm.)	n^{30}D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sapon. equiv. Calcd.	Sapon. equiv. Found
5	None	6.5	40	None	90	108 (10)	1.4605					114	113
6	2-Methyl	8.5	40	ε-Methyl	92	94 (5)	1.4558	65.59	65.49	9.44	9.16	128	129
7	2-Isopropyl	9	50	ε-Isopropyl	84.5	107 (5)	1.4604	69.19	69.31	10.33	10.41	156	155
8	2-*sec*-Butyl	13	50	ε-*sec*-Butyl	91.6	113 (4)	1.4625	70.55	70.56	10.66	10.76	170	171
9	2-Cyclohexyl	10	50	ε-Cyclohexyl	82	154 (3.5)[c] 58	....	73.43	73.71	10.27	10.42	196	194
10	3-Methyl	11	40	β- and δ-methyl	81	87 (3)	1.4568	65.59	65.52	9.44	9.52	128	129
11	4-Methyl[b]	9.5	40	γ-Methyl	84	103 (5)	1.4558	65.59	65.46	9.44	9.52	128	128
12	3- and 4-methyl	11.25	40	β-, γ-, and δ-methyl	83	78–79 (2)	1.4576	65.59	65.87	9.44	9.49	128	128
13	3,4-Dimethyl	6.75	50	β,γ- and γ,δ-dimethyl	85	107–109 (5)	1.4603–10	67.57	67.51	9.92	9.89	142	140.5
14	3,5-Dimethyl	8.75	50	β,δ-Dimethyl	92	93 (2)	1.4548	67.57	67.35	9.92	9.86	142	143
15	2,6-Dimethyl	10	50–60	α,ε-Dimethyl	89	96–97 (5)	1.4558–64	67.57	67.75	9.92	10.10	142	142
16	3,3,5-Trimethyl	13	50	β,β,δ- and β,δ,δ-trimethyl	70	105 (4)	1.4565	69.19	69.29	10.33	10.43	156	154
17	2- and 4-octyl[d]	11	50	γ- and ε-octyl	80	132–155 (1.5)	1.4655–1.4760	74.28	74.70	11.58	11.76	226	225
18	Dimethyl[e]	6	50	Mixed dimethyl	94	95–96 (3)	1.456–7	...	...	...	...	143[h]	143
19	Mixed alkyl[f]	7.5	50	Alkyl	86	111–115 (5)	1.4590–9	...	...	...	...	144[h]	140
20	Mixed alkyl[g]	10	50	Alkyl	90	70–93 (1)	1.4561–84	...	...	...	...	146[h]	145

[a] Molar ratio of peracetic acid to ketone 1.25 except for runs 5 and 18 (1.2), 10 and 19 (1.1), and 9 and 20 (1.4). [b] Two attempts to prepare a lactone from this ketone are recorded in the literature.[3,10] [c] Reported b.p. 175° (12 mm.), m.p. 56°.[25] [d] 88% 4- and 12% 2-(α-methyl-α-ethylpentyl)-cyclohexanone. [e] Ketones derived from xylenols from coal hydrogenation. [f] Ketones derived from C_8-phenol fraction from coal hydrog. [g] Ketones derived from U. S. Steel's no. 1 cresylic acid. [h] Calcd. from ketone mixture equiv.wt.

readily to oxygen in this reaction[19a] than do primary groups.



A number of studies[19–24] on the course of the reaction of peracids with certain aromatic, aliphatic and aryl-alkyl ketones show that in some cases both possible products were obtained. In our work, we have assumed that mixtures of ketones were formed from cyclic ketones substituted in positions other than the 2-position. For example, when 3,3,5-trimethylcyclohexanone is treated with peracetic acid (Table II), two products are probable (equation, R′ = H, R = Me) because of the more subtle differences prevailing when the methyl groups are farther removed from the reaction site.

Large quantities of cresols, xylenols and higher phenols are available from coal tar and coal hydrogenation operations. Isolation of pure compounds from these mixtures is frequently difficult; however, fractions of relatively narrow boiling range are readily available. These mixtures are excellent starting materials for the synthesis of alkyl-substituted ε-caprolactones. Several of these phenols were catalytically hydrogenated to give mixtures of alkyl-substituted cyclohexanones. Treatment of these ketone mixtures with peracetic acid gave high yields of alkyl-ε-caprolactones (Table II). No attempts were made to isolate individual lactones from these mixtures.

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Experimental

Raw Materials.—The following ketones were obtained commercially and used without further purification: cyclopentanone from Arapahoe Chemicals, cyclohexanone from E. I. du Pont de Nemours and Co., cycloheptanone and cyclooöctanone from Fluka A. G. Chemische Fabricks Buchs/S. G., and 2-cyclohexylcyclohexanone from Dow Chemical Co. 2-Isopropyl- and 2-(*sec*-butyl)-cyclohexanones were prepared by vapor-phase dehydrogenation of the corresponding cyclohexanols obtained from Dow Chemical Co. 3,3,5-Trimethylcyclohexanone was prepared from isophorone by selective hydrogenation of the carbon–carbon double bond. The remaining alkyl substituted cyclohexa-

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[19a] It is interesting to note that the Beckmann rearrangement, which has sometimes been compared with the Baeyer–Villiger rearrangement, converts the corresponding oximes into a mixture of α- and ε-substituted ε-caprolactams; see Schäffler and Ziegenbein, *Chem. Ber.*, **88**, 1374 (1955).

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nones were prepared by standard preparative methods consisting of catalytic reduction of the corresponding substituted phenols to the corresponding alkylcyclohexanols followed by either catalytic dehydrogenation over a copper chromite catalyst or by oxidation with chromic acid. The properties agreed with those in the literature for the pure ketones. The mixtures of ketones were analyzed by the hydroxylamine method.

Peracetic acid was obtained by the acetaldehyde oxidation process[2] and consisted of 20–28% solutions of peracetic acid in acetone or ethyl acetate containing 3–6% acetic acid.

Preparation of ε-Caprolactones.—All of the lactones were prepared by essentially the same procedure. An excess of either the ketone or the peracetic acid was used, the choice depending somewhat on the ketone supply. The two examples of the preparation of ε-caprolactone illustrate these cases. The recorded yields are for isolated monomeric lactones and do not include polymeric lactone residues in any case. The boiling points and melting points are uncorrected. In one procedure, cyclohexanone (1764 g., 18 moles) was heated to 40° and treated dropwise with stirring with 1842 g. of a 24.8% solution of peracetic acid (6 moles) in acetone over a 4-hour period. The reaction was exothermic and required cooling during the addition period to maintain the temperature at 40°. After an additional 2.25-hour reaction period an analysis for peracetic acid indicated a conversion of 96%. The reaction mixture was distilled under reduced pressure using a glass column (36 × 1 inch) packed with two-turn glass helices. After removal of acetone, acetic acid and excess cyclohexanone there was obtained as a distillate 578 g. of ε-caprolactone, leaving a residue of 54 g. of the polyester of ε-caprolactone. The monomeric lactone had a freezing point of −1.3°, lit.[25] value −5°.

In an alternate procedure cyclohexanone (491 g., 5 moles) was heated to 40° and treated dropwise with stirring with 1790 g. of a 25.5% solution of peracetic acid in ethyl acetate (6 moles) over a 4-hour period with occasional cooling to maintain a temperature of 40°. After an additional 2.5-hour reaction period, analysis for peracetic acid indicated a conversion of 95%. Distillation of the reaction mixture under reduced pressure gave 512 g. of monomeric ε-caprolactone and 53 g. of the polyester of ε-caprolactone as a residue.

Reaction of Cycloheptanone with Peracetic Acid.—Cycloheptanone (448 g., 4 moles) was heated to 70°. To the stirred ketone was added dropwise, over a 2-hour period, 1787 g. of a 21.2% solution of peracetic acid (5 moles) in ethyl acetate. An additional 8-hour reaction period at 70° was required to consume 4 moles of the peracetic acid. The reaction mixture was introduced over a 3-hour period to a still kettle containing 1000 g. of ethylbenzene which was held under reflux at such a pressure as to keep a kettle temperature of 50°. The ethyl acetate, acetic acid and some ethylbenzene were removed continuously by distillation throughout the addition. After removal of the remainder of the ethylbenzene, the product was distilled rapidly through a one-plate column till the kettle temperature rose to 275° at 3 mm. pressure. The distillation residue weighed 70 g. A solid phase separated out of the distillate. Filtration gave 71 g. of a crystalline solid which, when recrystallized from isopropyl ether, was identified as pimelic acid, m.p. 102°. The mixed m.p. with an authentic sample showed no depression. The filtrate was fractionally distilled to give 148 g. of ζ-enantholactone (see Table I).

Reaction of Cyclooctanone with Peracetic Acid.—Cyclooctanone (126 g., 1 mole) was heated to 70°, and 455 g. of a 20.9% solution of peracetic acid (1.25 moles) in ethyl acetate was added dropwise over a period of 1.25 hours. An additional 6.75-hour reaction period was required to consume 1.03 moles of peracetic acid. The reaction mixture was diluted with 500 g. of ethylbenzene, and the ethyl acetate and acetic acid were removed by distillation under reduced pressure. When the kettle volume reached about 200 ml. a crystalline phase separated. The kettle material was cooled and filtered to obtain 35 g. of suberic acid, which had a melting point of 137° after two recrystallizations from water (recorded m.p. 140°).

The filtrate was concentrated by distillation to 96 g. No additional crystallization could be induced on cooling. Distillation through a small Vigreux column gave several fractions (b.p. range 58° (4 mm.) to 81° (3 mm.)) and 16 g. of apparently solid residue which was not investigated further. Analysis of the fractions by saponification indicated a total η-caprylolactone content of 8.5 g. (6% yield).

Proof of Structure of ε-Substituted-ε-caprolactones.—A 22.1-g. (0.1755 mole) sample of the lactone from run 6 (see Table II) was saponified with 63.1 g. of 10% aqueous sodium hydroxide solution (0.158 mole) by heating on the steam-bath. When a titration indicated complete consumption of the base, the reaction mixture was poured into 2 liters of acetone. The crystalline sodium salt of 6-hydroxyheptanoic acid was recovered by filtration, redissolved in water, reprecipitated by acetone, filtered, washed with cold acetone and dried; yield 21 g. (80%). Sodium 6-hydroxyhexanoate was prepared similarly from ε-caprolactone. Infrared absorption spectra of these salts exhibited a strong secondary OH band as a doublet at 8.82 and 9.1 μ for the salt from ε-methyl-ε-caprolactone and a strong primary OH band as a doublet at 9.3 and 9.45 μ for the salt from ε-caprolactone. The primary OH band from ε-caprolactone was not observed in the spectrum of the salt from ε-methyl-ε-caprolactone. The ε-methyl-ε-caprolactone gave a positive iodoform test. Its freezing point range (4 to 5°) was relatively narrow, further indicating a single compound.

The ε-cyclohexyl-ε-caprolactone prepared in run number 9 (Table II) was apparently the same compound obtained by Wallach[26] by cyclization of 6-hydroxy-6-cyclohexylhexanoic acid.

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