

TABLE I
 CYCLOHEXENE WITH NICKEL

T, °C.	n_D^{20}	Br no.	Liquid		Gas Liters (N. T. P.) per mole of C ₆ H ₁₀	
			C ₆ H ₁₂	C ₆ H ₆	H ₂	CH ₄
100	1.4463	191 ^a	0	0	0.04	0.3
125	1.4461	0.2	68	32	.04	.3
150	1.4459	.1	68	32	.1	.5
200	1.4462	.1	68	32	.1	1.2
250	1.4505	.1	62	38	.1	4.9
300	1.4553	.1	54	46	.4	10.2
350	1.4600	.1	48	52	.3	13.6
400	1.4610	.6	47	53	.0	16.0

^a Bromine number of original C₆H₁₀, 191.

Cyclohexene without Nickel.—The bomb was cleaned by wire-brushing followed by dilute hydrochloric acid and finally by steam. The cleaned bomb did not hydrogenate benzene at all in twelve hours at 350° under an initial hydrogen pressure of 100 kg./sq. cm. One hundred-cc. samples of cyclohexene were heated in this bomb for six hours at 200, 300, and 400°, and similar experiments were also made, using a glass liner with capillary glass stopper. Conversion was considerably less in the glass liner than in the steel bomb alone (Table II).

TABLE II

T, °C.	CYCLOHEXENE WITHOUT NICKEL			
	Bomb alone		Bomb plus glass liner	
	Liquid	Gas Liters (N. T. P.) /mole of C ₆ H ₁₀	Liquid	Gas Liters (N. T. P.) /mole of C ₆ H ₁₀
200	1.4463	187	0	0.8
300	1.4470	136	0.8	1.2
350
400	1.4540	0.8	5.2	0.4

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Preparation of Cyclic Ketones by Ring Enlargement

BY E. P. KOHLER,* M. TISHLER, H. POTTER AND H. T. THOMPSON

In response to a request from a group of physical chemists who are determining the heats of hydrogenation of unsaturated compounds¹ we have examined the feasibility of preparing a series of unsaturated cyclic hydrocarbons in sufficient quantity and of the unusual purity required for these physical measurements. The preparation of these compounds by methods based on ring closure appeared to us to be a hopeless undertaking because all of these methods fail almost completely in the case of compounds which have

* Due to the death of Professor Kohler, this manuscript was completed by his associates.

(1) Kistiakowsky, *et al.*, THIS JOURNAL, 60, 440 (1938), and previous papers.

Atmospheric Continuous

Cyclohexene with Nickel.—The yield of liquid product was practically quantitative. It was olefin-free. It contained benzene as shown by the formation of *m*-dinitrobenzene with nitrating mixture. The residue remaining after treatment with cold 15% fuming sulfuric acid was cyclohexane (n_D^{20} 1.4264–1.4266).

 TABLE III
 CYCLOHEXENE WITH NICKEL

Conditions	Liquid				Gas Liters (N. T. P.) per mole of C ₆ H ₁₀			
	T, °C.	C. T., sec.	Br no.	n_D^{20}	Wt. % C ₆ H ₁₂	Wt. % C ₆ H ₆	H ₂	CH ₄
	74	15	0.1	1.4458	68	32	0.2	0.04
	100	1	.1	1.4459	68	32	.2	.04
	102	4	.1	1.4460	68	32	.3	.02
	152	5	.2	1.4459	68	32	.5	.17

Cyclohexene without Nickel.—Cyclohexene was passed through a glass tube packed with glass rings at 97 and at 150°, the contact time being about thirty seconds. The product was unchanged cyclohexene: Br. no., 190, d^{20} , 0.811; n_D^{20} 1.4468.

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Summary

In the presence of nickel, both at superatmospheric and at ordinary pressure, cyclohexene is converted almost quantitatively into a mixture of cyclohexane (68% by weight) and benzene (32%).

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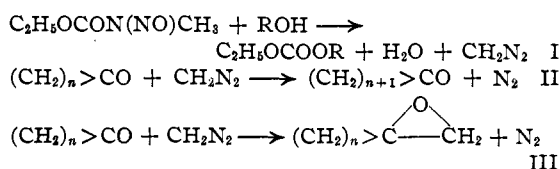
from nine to eleven members in the ring and even with the best of these methods² it would be a formidable task to secure cyclooctanone in sufficient quantity to prepare cyclooctatetrene. We have, therefore, confined our attention to methods based on ring enlargement, and particularly to the reaction between ketones and diazomethane. Mosettig and Burger,³ who were the first to apply this reaction to carbocyclic ketones, added cyclohexanone to a standardized solution of diazomethane in ether and methyl alcohol. During the course of our work the reaction was employed in

(2) Ziegler and Aurnhammer, *Ann.*, 513, 57 (1934).

(3) Mosettig and Burger, THIS JOURNAL, 52, 3456 (1930).

the same manner by Robinson and Smith and by Giraitis and Bullock.⁴ Meerwein⁵ patented a procedure which was far better for operating on a large scale because it obviated the necessity of manipulating large quantities of diazomethane and employing very large volumes of solvents. All of our experiments have been based on this procedure.

In Meerwein's mode of operation, nitrosomethylurethan is introduced at a suitable rate into a solution of a cyclic ketone in an alcohol which contains some alkaline catalyst. The principal reactions in the case of cyclic ketones may be represented by the following equations, although the actual intermediate may be other than diazomethane.



The rate at which the nitroso compound is introduced can be varied at will. The speed of the subsequent reactions depends on the temperature, the alcohol and the catalyst as well as on the concentration of diazomethane, but no variations in any of these factors had an appreciable effect on the relative amounts of cyclic ketone and spirocyclic oxide that were formed. The temperature was varied from 0 to 50° and potassium carbonate, barium oxide and magnesium methylate were used as basic catalysts in ethyl and butyl alcohols but no conditions were found more favorable than those described in the experimental part. It is possible to operate on any desired scale, but the reaction will become explosively violent if nitrogen-containing intermediates accumulate in the mixture.

Since the reaction does not stop with the introduction of one methylene group, the product is a mixture of ketones and oxides. The oxides may be removed without great difficulty, but isolation of pure ketones requires fractional distillation combined with recrystallization of the semicarbazones.

The ratio of ketone to oxide remains at about four to one as the reaction is applied to the series of ketones from cyclohexanone to cyclononanone, but the yield of ketone based on nitrosomethyl-

urethan falls from 63% in the preparation of cycloheptanone to 45% for octanone and to about 20% for nonanone and decanone. Unfortunately the reactivity of the carbonyl groups passes through a minimum at the ring size most difficult to prepare by ring closure methods.⁶ As a consequence larger proportions of nitrosomethylurethan are lost in side reactions. Ring enlargement again becomes the favored reaction when the method is applied to ketones having fifteen or more ring members.⁷

The preparation of cyclononanone and decanone suffers the further inconvenience that nitrogen is evolved from the mixture very slowly, hence addition of nitrosomethylurethan must be slow to avoid explosion.

Very recently Adamson and Kenner⁸ have investigated the action of a variety of aliphatic diazo compounds on carbonyl compounds. Our observations differ from theirs in that we did obtain ring enlargement by the Meerwein procedure applied to cyclooctanone and cyclononanone and further we isolated cyclononanone and cyclodecanone in appreciable amounts from the preparation of cyclooctanone.

Cycloheptanone and octanone were quantitatively reduced to the alcohols by catalytic hydrogenation. The alcohols dehydrated smoothly when heated in the presence of beta-naphthalene-sulfonic acid. Cycloheptene and cyclooctene were thus prepared in kilogram quantities without difficulty. Cycloheptene was converted to the conjugated diene and triene by the methods of Willstätter.⁹

In contrast with cyclopentadiene¹⁰ cycloheptadiene did not give gas when treated with methylmagnesium iodide at 100° in the Zerewitinoff apparatus.

Like cycloheptadiene¹¹ cycloheptatriene combines with one mole of maleic anhydride at slightly elevated temperatures. Both addition products may be saturated completely by hydrogenation with Adams catalyst. The saturated anhydrides are isomeric. The nature of the isomerism and the structure of the product of addition to cycloheptatriene have not yet been determined.

(6) P. Pöhls, Dissertation, Marburg, 1932; O. Pauli, Dissertation, Marburg, 1932; Ruzicka and Buijs, *Helv. Chim. Acta*, **15**, 8 (1927); unpublished result from this Laboratory.

(7) Schroeder, Dissertation, Harvard University, 1939.

(8) Adamson and Kenner, *J. Chem. Soc.*, 182 (1939).

(9) Willstätter, *Ann.*, **317**, 223 (1901).

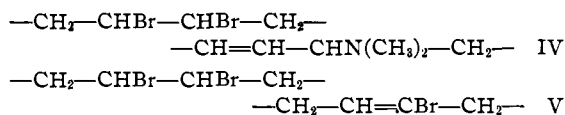
(10) Fischer and Walter, *Ber.*, **60B**, 1987 (1927).

(11) Koch, Dissertation, Kiel, 1932.

(4) Robinson and Smith, *J. Chem. Soc.*, 371 (1937); Giraitis and Bullock, *THIS JOURNAL*, **59**, 951 (1937).

(5) Meerwein, *Chem. Zentr.*, **104**, 11, 1758 (1933); (German Patent 579,309).

The conversion of cycloöctene to the diene by addition of halogen followed by removal of two molecules of hydrogen halide presented unexpected difficulty. When dibromocycloheptane was treated with dimethylamine, two concurrent reactions took place



The yield of the desired amine (equation IV) was 60%, but under the same treatment dibromocycloöctane gave only 10% yield of crude amine, the main product being the unsaturated bromide which could not be converted to anything useful for our purposes. Sodium ethylate and sodium *t*-amylate were equally unsatisfactory. With quinoline the product was mainly cycloöctene formed by debromination analogous to the reaction previously observed by Markownikoff.¹²

The preparation of more highly unsaturated compounds derived from cycloöctene will be presented in a subsequent publication.

Experimental Part¹³

The Seven-membered Ring—Cycloheptanone.—A two-liter three-necked flask fitted with an efficient stirrer, a thermometer, and a dropping funnel was charged with 500 cc. of cyclohexanone, 500 cc. of methanol and 1–2 g. of anhydrous sodium carbonate ground to an impalpable powder. About 10 cc. of nitrosomethylurethan was added all at once and after a variable induction period the reaction started as evidenced by a rise in temperature. Nitroso compound was then started dripping in at about 150 drops per minute and the reaction flask surrounded by ice water to maintain a temperature of 20 to 25° in the solution. The solution becomes pale yellow, but green or red tones indicate an unsafe concentration of explosive intermediates. The addition of 600 g. (4.55 moles) of nitrosomethylurethan requires about six hours. The mixture was stirred for at least thirty minutes after the addition was finished.

The methanolic solution was filtered and distilled. The products boiling above methanol and water were methyl ethyl carbonate, methylenecyclohexane oxide, cyclohexanone, cycloheptanone and a small amount of higher boiling material. The yield of cycloheptanone, b. p. 175–182°, was 63% and of the oxide, 15%.

Methylenecyclohexane Oxide, purified by redistillation, boiled at 148°, m. p. –38.3 to –40.5°. At room temperature 0.5% sulfuric acid converted it to the glycol which crystallized from petroleum ether in large, colorless, transparent crystals, m. p. 74°. Two other products were

formed in lesser and varying amounts: (1) Δ^1 -Cyclohexenylcarbinol, b. p. (15 mm.) 92–94°, which took up one mole of hydrogen with Adams catalyst to give cyclohexylcarbinol, identified by mixed melting point of its phenylurethan with a known sample. The unsaturated carbinol forms a phenylurethan, m. p. 96°, after recrystallization from ether–petroleum ether.

Anal. Calcd. for C₁₄H₁₇O₂N: C, 72.8; H, 7.36. Found: C, 72.9; H, 7.5.

(2) Dicyclohexyldioxane (?) boiled at 147.5–148° at 11 mm., refractive index 1.4432.

Anal. Calcd. for C₁₄H₂₄O₂: C, 75.0; H, 10.7; mol. wt., 224. Found: C, 74.9; H, 10.9; mol. wt., 232.

Cycloheptanol.—Cycloheptanone, b. p. 180–181°, was reduced by Raney nickel catalyst with hydrogen at 500 to 2000 lb./sq. in. (33 to 133 atm.) and 150 to 165°; 200 g. of heptanone diluted with 100 cc. of absolute ethanol was completely reduced in three to five hours. The catalyst was removed by filtration and a quantitative yield of cycloheptanol, b. p. 185–186°, obtained by distillation of the solution.

Cycloheptene.—Cycloheptanol with 1–2 g. of β -naphthalenesulfonic acid per mole was heated in a flask fitted with a fractionating column. The heat was applied by a bath at 180°, increasing to 250° as required to maintain distillation. The yield of cycloheptene was 80% at b. p. 112–116° and a small amount of cycloheptanol was recovered. Pure cycloheptene: b. p. (760 mm.) 114.38°; *n*_D²⁰ 1.4580. Cycloheptane with *n*_D²⁰ 1.4449 was obtained by gas phase hydrogenation (Willstätter, b. p. 114–115°).

1,2-Dibromocycloheptane.—With stirring and cooling, bromine in chloroform was added to 144 g. (1.5 mole) of cycloheptene. Because the product is unstable, the reaction was protected from air and moisture and kept below 0°. The solvent was removed under nitrogen at reduced pressure. The residue thus obtained was used without delay.

Δ^2 -Cycloheptenyldimethylamine.—The chloroform concentrate of dibromocycloheptane was cooled to 0° and excess anhydrous dimethylamine added (4 equiv., 270 g.). The two liquids were thoroughly mixed and cooled to –5°, then transferred to an autoclave which contained enough frozen benzene to bring the volume of the mixture to about 900 cc. The temperature was raised to 100° (inside) and maintained there for six hours. Longer periods of heating or higher temperatures darkened the reaction mixture but had no appreciable effect on the yield of amine.

When cooled to room temperature, no pressure remained; 300 g. of dimethylamine hydrobromide was removed by filtration, and the filtrate warmed to expel excess dimethylamine, then extracted with excess dilute hydrochloric acid. The acid extract was made strongly alkaline with sodium hydroxide. The free amine was taken up in ether, dried over barium oxide and distilled, finally from sodium. The yield of cycloheptenyldimethylamine, b. p. 184–187°, was 57–62% (Willstätter, b. p. 188°).

1-Bromocycloheptene.—The neutral benzene layer from the dimethylamine reaction was dried and distilled. A heavy, colorless liquid was obtained which contained halogen and became dark on standing: b. p. (13 mm.) 66.5–67.5°; b. p. (760 mm.) 191°.

(12) Markownikoff, *J. prakt. Chem.*, [2] 49, 430 (1894).

(13) Kistiakowsky and co-workers have determined the precise physical constants recorded here. Their investigation of heats of hydrogenation of the unsaturated compounds will be the subject of a later publication.

Anal. Calcd. for $C_7H_{11}Br$: C, 48.0; H, 6.28. Found: C, 48.15; H, 6.02.

Δ^2 -Cycloheptenytrimethylammonium Bromide.—A solution of 200 g. of methyl bromide in 500 cc. of acetone was cooled to below 0° . With stirring, 275 g. of cycloheptenyldimethylamine was added at such a rate that the temperature of the solution did not exceed 10° . (Seed crystals must be obtained before adding more than a small portion of the amine, otherwise sudden crystallization will liberate enough heat to cause loss of methyl bromide). The yield of white solid, m. p. 192 – 193° (dec.), was 90% (Willstätter used the iodide.)

Cycloheptadiene.—One hundred and seventeen grams of ammonium bromide was treated with potassium hydroxide in water, total volume 250 cc. The solution was distilled under nitrogen. The supernatant layer of the distillate was washed with dilute acid and dried over calcium chloride in the presence of hydroquinone, then distilled under nitrogen. The yield, b. p. 120 – 121.5° , was 85–90%. Pure cycloheptadiene: b. p. (758.3 mm.) 121.52° ; m. p. -110.42° (Willstätter, b. p. (724 mm.) 120 – 121°). When hydrogenated, this diene gave cycloheptane, m. p. -7.98° ; n_D^{20} 1.4449.

Cycloheptatriene.—To one mole of the diene in two volumes of dry chloroform at -5 to -10° , one mole of bromine in 500 cc. of chloroform was added drop by drop with vigorous stirring. The solution was concentrated under nitrogen at reduced pressure.

Under nitrogen, the chloroform concentrate was added drop by drop to 500 cc. of quinoline containing 1 g. of hydroquinone. The flask was heated in a bath at 140° and under pressure reduced almost to the boiling point of the quinoline. The distillate was collected in a well-cooled receiver. The product was washed with dilute acid, dried over calcium chloride in the presence of hydroquinone and distilled. The yield of crude material was 60 g. (86%).

The over-all yield of cycloheptatriene from 2100 g. of cycloheptanone was 265 g., b. p. 116 – 117° , which contained 5 to 10% cycloheptadiene. The diene was removed by careful fractionation by a very efficient still. Pure triene had the b. p. (760 mm.) 115.50° , m. p. -79.49 ; n_D^{20} 1.5243 (Willstätter, b. p. (724 mm.) 116°). It absorbed three equivalents of hydrogen and the heptane from gas phase hydrogenation showed n_D^{20} 1.4449.

Cycloheptatriene and Maleic Anhydride.—Twenty grams of cycloheptatriene with slight excess of maleic anhydride was boiled in xylene for five hours. The product was precipitated by hexane, which gave 34 g. of pale yellow solid, m. p. 93 – 98° . By recrystallization from carbon tetrachloride, thick, slightly yellow plates were obtained, m. p. 102 – 104° . From hexane the product separated as white needles of the same melting point.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.26; mol. wt., 190. Found: C, 69.7; H, 5.36; mol. wt., 196.

Hydrolysis by 10% sodium carbonate solution gave an acid, m. p. 170 – 174° , with evolution of gas.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.4; H, 5.77. Found: C, 63.6; H, 5.79.

Hydrogenation of the Addition Product.—Nine and one-half grams of the anhydride was dissolved in 40 cc. of acetic acid and 10 cc. of acetic anhydride and shaken

with hydrogen in presence of Adams catalyst. During seven hours the reaction stopped four times and was restarted by addition of fresh catalyst; 80% of two equivalents of hydrogen were absorbed and a solid crystallized. The solvent was evaporated under reduced pressure and the residue separated by crystallization from carbon tetrachloride and from hexane into 2 g. of the insoluble substance, m. p. 140° , and 5 g. of a more soluble compound that crystallized from hexane, m. p. 71 – 73° . The remainder of the material was a mixture of these two products.

Anal. 140° compound. Calcd. for $C_{11}H_{12}O_3$: C, 68.8; H, 6.25. Found: C, 69.1; H, 6.25. 73° compound. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.22. Found: C, 68.2; H, 7.12.

Hydrolysis of the compound melting at 73° by 5% sodium carbonate gave an acid, m. p. 146 – 147° , with gas evolved.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.55. Found: C, 62.28; H, 7.54.

The *trans*-Dibasic Acid.—Following the procedure of Koch,¹¹ 2 g. of the saturated anhydride was heated in a sealed tube with concd. hydrochloric acid at 180° for twenty-four hours. The resultant material was treated with charcoal in boiling water to remove a quantity of black tar. The aqueous filtrate gave 0.2 g. of acid, m. p. 205 – 210° , after recrystallization from water; mixed with Koch's *trans* acid (m. p. 220°), below 175° .

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.55. Found: C, 62.23; H, 8.03.

Cycloheptadiene and Maleic Anhydride.—By the same procedures described for analogous compounds derived from the triene, the series of compounds described by Koch¹¹ were prepared for comparison. The following materials were obtained:

Addition product m. p. 110 – 111° (Koch, 110 – 111°).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.8; H, 6.25. Found: C, 68.7; H, 6.10.

Hydrogenated anhydride m. p. 156 – 157° (Koch, 153°).

cis-Dibasic acid m. p. 132 – 134° (gas) (Koch, 138°).

trans-Dibasic acid m. p. 215 – 220° (Koch, 224 – 227°).

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.55. Found: C, 63.20; H, 7.70.

The Eight-membered Ring—Cycloöctanone.—Proceeding as in the preparation of cycloheptanone, to 336 g. of cycloheptanone in 300 cc. of methanol with 5 g. of powdered anhydrous sodium carbonate, 600 g. (1.5 equivalents) of nitrosomethylurethan was added at 30° . After standing overnight, the solutions from two such reactions were combined, filtered and fractionated, distillate being collected at ordinary pressure until the temperature reached 180° and the higher fractions at 100 mm. The products, after refractionation, were

83 g., b. p. 160 – 173° , methylenecycloheptane oxide

93 g., b. p. 173 – 185° , oxide and cycloheptanone

127 g., b. p. 185 – 200° , cycloheptanone and cycloöctanone

420 g., b. p. 200 – 202° , cycloöctanone m. p. above 33°

b. p. (100 mm.) 128 – 130°

41 g., higher boiling material containing higher ketones and oxides.

Cyclooctanone was converted to the semicarbazone by a methanol solution of semicarbazide. The semicarbazone was recrystallized from dioxane to m. p. 168–169°. The ketone was regenerated by hydrolysis with 15% sulfuric acid and the ketone steam distilled from the acid solution. The recovery of ketone from the semicarbazone was 95%, b. p. (60 mm.) 115–115.5°; m. p. 43.80°.

Cyclooctanol.—One hundred grams of the ketone in 150 cc. of absolute ethanol with 1.5 g. of Raney nickel catalyst was reduced at 140° with hydrogen at about 1800 pounds (120 atm.) pressure. The reaction was complete in four hours and the yield was 98%, b. p. (25 mm.) 111.3–111.7°, m. p. 25.06°.

Cyclooctene.—One hundred grams of cyclooctanol was heated with β -naphthalenesulfonic acid as described for cycloheptene; 80 g. (93%) of cyclooctene¹⁴ was obtained; b. p. (773 mm.) 143.8–144.5°; n_D^{20} 1.4693.

1-Bromocyclooctene.—Proceeding as described for the preparation of 1,2-dibromocycloheptane, 0.1 mole of cyclooctene was treated with one equivalent of bromine. The chloroform concentrate was treated with 13 g. (0.3 mole) of dimethylamine and 30 cc. of benzene in a sealed tube at 100° for nine hours; 14.2 g. of dimethylamine hydrobromide crystallized, equivalent to 56% of the bromine. By acid extraction only 1.7 g. of very crude high-boiling amine was obtained. Fractionation of the neutral benzene solution gave 13 g. of bromocyclooctene (70% yield), b. p. (23 mm.) 97–98°; n_D^{20} 1.5182. Oxidation converted it to suberic acid.

Anal. Calcd. for $C_8H_{13}Br$: Br, 42.26. Found: Br, 42.25.

1,2-Dichlorocyclooctane.—Excess chlorine was passed into a chloroform solution of cyclooctene at –60°. The resulting solution was distilled: 16 g. (90%) of dichlorocyclooctane was obtained, b. p. (25 mm.) 130.4–130.6°, m. p. –5°, d_4^{20} 1.1620, n_D^{20} 1.5061.

Anal. Calcd. for $C_8H_{14}Cl_2$: Cl, 39.2. Found: Cl, 39.3.

1-Chlorocyclooctene.—Dichlorocyclooctane when treated with dimethylamine in the same manner as the corresponding bromine compound likewise gave no significant amount of amine, the product being 1-chlorocyclooctene, b. p. (19 mm.) 77–78°, 31 mm. 86–86.8°, n_D^{20} 1.4928.

Anal. Calcd. for $C_8H_{13}Cl$: Cl, 24.55. Found: Cl, 24.45.

The Nine- and Ten-membered Rings—Cyclononanone.—One hundred and thirty-five grams (1.3 equiv.) of nitroso-

(14) Willstätter and Waser, *Ber.*, **43**, 1176 (1910), cyclooctene b. p. (730 mm.) 143.5, n_D^{20} 1.4739.

methylurethan was added to 100 g. of cyclooctanone in 200 cc. of methanol with 3 g. of fine anhydrous potassium carbonate, operating in the usual manner. The temperature was maintained at 7° and the addition required thirty hours. The resulting mixture did not separate well on distillation, so each fraction was treated with a methanolic solution of semicarbazide and the semicarbazones separated by systematic fractional crystallization. The semicarbazones obtained were equivalent to 47.5 g. of cyclooctanone recovered, 24.7 g. cyclononanone and 2.2 g. of cyclodecanone.

Cyclodecanone.—Fifty grams of cyclononanone in 100 cc. of methanol at 20° with 2 g. of sodium carbonate was treated with 86 g. of nitrosomethylurethan. The addition required five days and twenty-four hours more elapsed before the reaction mixture became colorless and ceased giving off gas. The ketones were isolated from the reaction mixture as the semicarbazones and separated with difficulty by crystallization from methanol, in which the semicarbazone of decanone is less soluble. The semicarbazones isolated were equivalent to 16 g. of cyclononanone and 24 g. of cyclodecanone.

Hydrolysis of Cyclononanone Semicarbazone.—One hundred and fifty-six grams of the semicarbazone, m. p. 183–185°, was treated with 40 g. of sulfuric acid in 250 cc. of water. The ketone was removed from the acid solution by steam distillation and refractionated by means of an efficient adiabatic still at 22 mm. pressure. Of 97 g. of distillate, 79 g. boiled between 103 and 105°. From 11 g. of higher boiling point, 3 g. of semicarbazone of cyclodecanone was isolated. The best fraction of cyclononanone was 30 g., b. p. (22 mm.) 103.5–104.2°, m. p. 31–31.5°.

Hydrolysis of Cyclodecanone Semicarbazone.—Thirty grams of cyclodecanone semicarbazone, m. p. 210–211°, was treated with 30 g. of sulfuric acid in 200 cc. of water. Hydrolysis and steam distillation were noticeably slower than for the other ketones. The steam distillate was refractionated through a Podbielniak still to give 22.6 g., b. p. (8 mm.) 87.5–88°, m. p. 20–22°, and 2 g., b. p. (8 mm.) 88–89°.

Summary

Alicyclic ketones containing seven, eight, nine and ten carbon atoms have been prepared from cyclohexanone through successive ring enlargement by diazomethane.

Unsaturated cyclic hydrocarbons have been prepared from cycloheptanone and cyclooctanone.

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