with 5% alcoholic potassium hydroxide (400 ml.) for 1-hour. The potassium salt formed was filtered and converted into the free naphthol with acid. Crystallization from ethanol gave golden yellow crystals (16.5 g., 49%) melting at 183–183.5° dec.

Anal. Calcd. for $C_{16}H_{11}NO_2$: C, 77.09; H, 4.45; N, 5.62. Found: C, 77.04; H, 4.51; N, 5.29.

A solution of 4-phenyl-1-tetralone (IV) (3.0 g.) in ethanol (50 ml.) at 0° was treated successively with concentrated hydrochloric acid (1 ml.) and butyl nitrite (1.88 g.) in ethanol (25 ml.). The resulting solution was kept at 0° for one hour and then refluxed for 1.5 hours. Cooling of the resulting solution gave 2-nitroso-4-phenyl-1-naphthol (VI) (2.25 g.) (67%) melting at 182–3° dec.

2-Acetamido-4-phenyl-1-naphthyl Acetate (VIII).—2-Nitroso-4-phenyl-1-naphthol (VII) (2.5 g.) in acetic anhydride (150 ml.) was treated in the presence of platinum oxide (0.1 g.) with hydrogen at 40 p.s.i. at room temperature for five minutes. Removal of the solvent under reduced pressure gave 2-acetamido-4-phenyl-1-naphthyl acetate (VIII) (2.7 g.). One recrystallization from 75% acetic acid and one from benzene gave a white solid melting at 214°.

Anal. Calcd. for $C_{20}H_{17}O_3N$: C, 75.22; H, 5.37; N, 4.39. Found: C, 74.95; H, 5.30; N, 4.50.

2-Substituted aminomethyl-4-phenyl-1-tetralones (III).—4-Phenyl-1-tetralone (IV) (0.05 mole), paraformaldehyde (1.65 g.) and the amine hydrochloride (0.05 mole) were refluxed in absolute ethanol (20 ml.) under nitrogen for 5 hours and then poured into dilute hydrochloric acid. Extraction with ether gave a mixture of the unchanged tetralone and bis-(4-phenyl-1-keto-2-naphthyl)-methane. The latter after three crystallizations from ethyl acetate and one from a mixture of benzene and ethyl acetate melted at 213–215°. The amount isolated was 2 g. each for the dimethylamine and piperidine runs and 0.2 g. in the diethylamine preparation.

Anal. Calcd. for $C_{33}H_{28}O_2$: C, 86.84; H, 6.14. Found: C, 87.08; H, 6.30.

The hydrochloric acid solution was neutralized with sodium carbonate and extracted with ether. The ether extracted was dried and the amine hydrochloride formed with hydrogen chloride gas. The yields and physical properties for the various hydrochlorides are given in Table I.

TABLE I

2-SUBSTITUTED-AMINOMETHYL-4-PHENYL-1-TETRALONE HYDROCHLORIDES

$C_{16}H_{13}OCH_2NR_2\cdot HCl$		$R = CH_3$[a]	$R = C_2H_5$[b]	$R_2 = C_5H_{10}$[a]
M.p., °C.		182–185 dec.	144–147 dec.	177[f] dec.
Yield, %		15[c]	42[d]	28[e]
Formula		$C_{19}H_{22}ONCl$	$C_{21}H_{26}ONCl$	$C_{22}H_{26}ONCl$
Analyses, %				
Carbon	Calcd.	72.26	73.36	74.26
	Found	72.24	73.43	74.32
Hydrogen	Calcd.	6.97	7.57	7.31
	Found	7.25	7.58	7.43

[a] Three recrystallizations from acetone–absolute ethanol. [b] Four recrystallizations from absolute ethanol. [c] Ketone covered, 3.4 g. [d] Ketone recovered, 4.0 g. [e] Ketone recovered, 4.0 g. [f] Solid formed upon decomposition disappeared at 232°.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

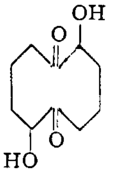
The Acyloin Reaction in the Closing of the Five-membered Ring[1]

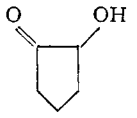
BY MARTIN CORDON, JACK D. KNIGHT AND DONALD J. CRAM[2]

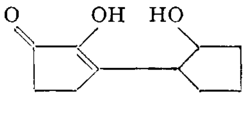
RECEIVED SEPTEMBER 4, 1953

The constitution of the major product of the acyloin reaction with dimethyl glutarate has been demonstrated to be either 3-(2′-hydroxycyclopentyl)-2-hydroxy-2-cyclopentenone (IIIA) or a tautomer. A number of reactions of the substance are described. Although analogous product could not be isolated from the acyloin reaction as applied to dimethyl pimelate, a condensation reaction between two molecules of 2-hydroxy-1-cycloheptanone occurred in the presence of base to give what is probably 2-(2′-hydroxycycloheptylidine)-7-hydroxycycloheptanone, or a tautomer.

As part of our study of the *trans*-annular electronic interactions in large rings[3] we desired to prepare as an intermediate 1,6-cyclodecandiol-2,7-dione (I). The low yield of 2-hydroxycyclopentanone (II) obtained from dimethyl glutarate under heterogeneous and high dilution conditions[4,5] coupled with the occasional isolation of dimeric cyclic acyloin[6] led to the hope that I could be obtained through the heterogeneous acyloin reaction with dimethyl glutarate under low dilution conditions. Although the isolation of neither I nor II was realized, a substance III whose properties are consistent with structure IIIA was isolated in about 40% yield from the reaction mixture.


I


II


IIIA

Compound III possesses the formula $C_{10}H_{14}O_3$, has weakly acidic properties, gives a deep purple color with ferric chloride, decolorizes bromine in carbon tetrachloride, and possesses infrared (see experimental) and ultraviolet absorption spectra (see Fig. 1) consistent with an α,β-unsaturated ketonic function. Furthermore, III consumes two moles of periodic acid, gives a negative acyloin test,[7] and forms derivatives that characterize the compound both as a diol (bis-*p*-nitrobenzoate and bis-*p*-toluenesulfonate) and a diketone (bis-oxime and bis-phenylhydrazone).

The chemical reactions that led to the structure of III are summarized in the formulations. Compound III absorbed hydrogen in the presence of palladium-on-charcoal to give IV if the reaction was interrupted after one mole of hydrogen was

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[1] This work was supported in part by the Office of Naval Research.

[2] Requests for reprints should be addressed to this author.

[3] (a) D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951); (b) H. Steinberg and D. J. Cram, *ibid.*, **74**, 5388 (1952); (c) D. J. Cram and N. L. Allinger, *ibid.*, **76**, 726 (1954).

[4] (a) J. C. Sheehan, R. C. O'Neill and M. H. White, *ibid.*, **72**, 3376 (1950); (b) J. D. Knight and D. J. Cram, *ibid.*, **73**, 4136 (1951).

[5] Good yields of five-membered ring product have been obtained with a homogeneous acyloin reaction (sodium and liquid ammonia) by J. C. Sheehan, R. C. Coderre, L. A. Cohen and R. C. O'Neill, *ibid.*, **74**, 6155 (1952).

[6] (a) M. Stoll and A. Rouve, *Helv. Chim. Acta*, **30**, 1822 (1947); (b) J. C. Sheehan and R. C. O'Neill, THIS JOURNAL, **72**, 4614 (1950).

[7] W. Rigby, *J. Chem. Soc.*, 794 (1951).

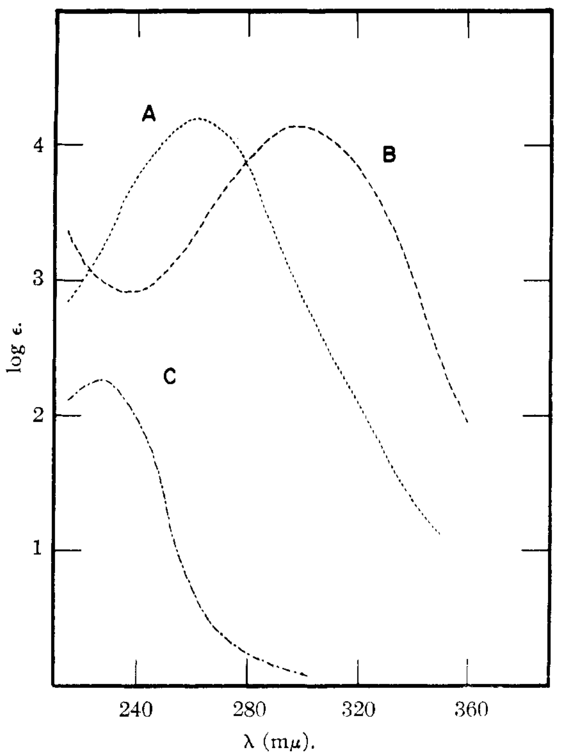
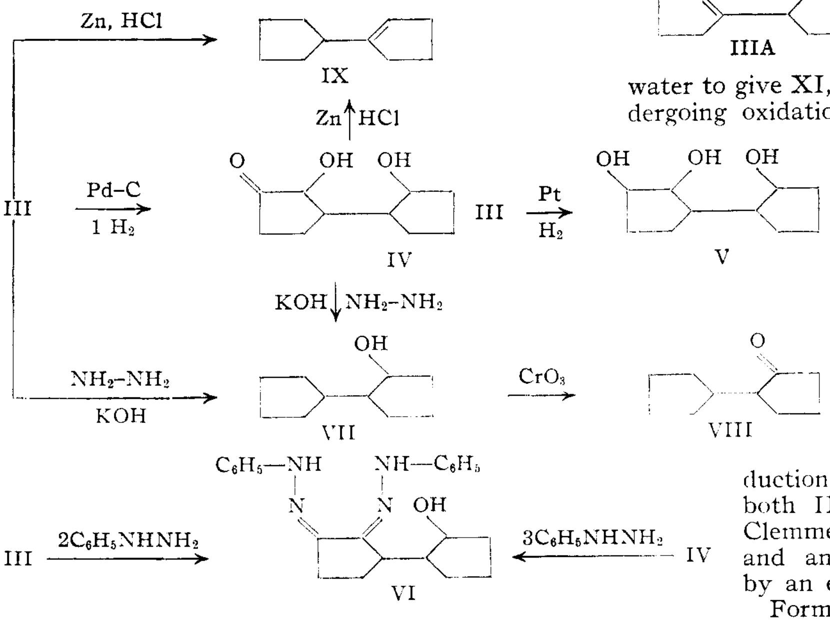


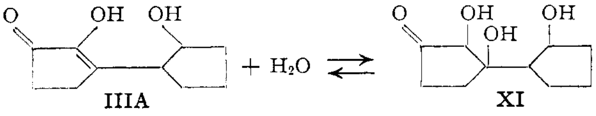
Fig. 1.—Ultraviolet absorption spectra (Cary Spectrophotometer, Model 11 PMS): A, compound III in 0.1 N hydrochloric acid; B, compound III in 0.1 N sodium hydroxide solution; C, compound XIII in 95% ethanol.

taken up, and V in the presence of platinum (two moles of hydrogen consumed). Compound IV was a neutral compound that gave an acyloin test[7] and reduced one mole of periodic acid. The substance was characterized as its semicarbazone, 2,4-dinitrophenylosazone and phenylosazone (VI), the last compound proving to be identical with the bis-phenylhydrazone derivative of III. Compound V appeared to be a mixture of isomers, only one of which was isolated in a pure state as its tris-p-nitrobenzoate.



When submitted to the reducing action of hydrazine and base,[8] both III and IV gave *trans*-2-cyclopentylcyclopentanol (VII) which was characterized as its urethan and p-nitrobenzoate. The melting points of these two derivatives correspond to those previously reported.[9] More convincing evidence for the structure of VII was obtained through its oxidation to VIII, whose semicarbazone and 2,4-dinitrophenylhydrazone were demonstrated to be identical with the same derivatives prepared from authentic 2-cyclopentylcyclopentanone.[9b] Similarly, both III and IV when submitted to a Clemmensen reduction gave an olefin whose properties correspond to those reported for IX, and which absorbed one mole of hydrogen in the presence of platinum.

It is clear that any one formula does not completely satisfy all of the above data, and that probably the system at hand when in solution in polar solvents is a mixture of tautomeric forms. Structure IIIA appears to be the tautomer that is the most consistent with the properties of III. Thus IIIA is an enol which is consistent with the weakly acidic properties of III and the color reaction with ferric chloride. Compound IIIA would not be expected to give an acyloin test but its reduction product IV should be a normal acyloin. A possible explanation in terms of structure IIIA for the consumption of two moles of periodic acid by III is that in acid solution the α,β-unsaturated ketonic linkage of IIIA undergoes a Michael-like addition of water to give XI, which is the species actually undergoing oxidation. Structure IIIA is also consistent with the fact that the same osazone is obtained by the reaction of either compound with phenylhydrazine. The reduction of IV to VII with the Wolff–Kishner reaction is reminiscent of the conversion of α-ketol linkages in the steroids to methylene groups,[10] whereas the reduction of III to VII probably involved the tautomerization of IIIA to the α-diketone structure which underwent reduction. The production of IX from both III and IV simply involves the Clemmensen reduction of an α-diketone and an α-ketol, respectively, followed by an elimination reaction.



Formula IIIA is also consistent with the ultraviolet (see Fig. 1) and infrared absorption spectra of III. The compound, 2-hydroxy-2-cyclo-

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[8] Huang-Minlon, This Journal, **68**, 2487 (1946).

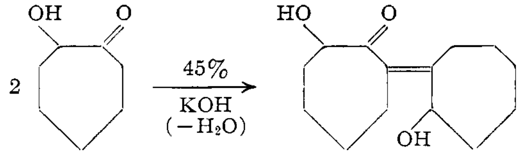
[9] (a) W. Hückel, O. Neunhoeffer, A. Gercke and E. Frank, *Ann.*, **477**, 99 (1929); (b) W. Hückel, A. Gross and W. Doll, *Rec. trav. chim.*, **57**, 555 (1938).

[10] D. H. R. Barton, N. S. Holness and W. Klyne, *J. Chem. Soc.*, 2456 (1949).

pentene-1-one serves as a model for IIIA, and has λ_{max} 252 mμ (95% ethanol), log ϵ 3.90, which when corrected for a β-substituent becomes 264 mμ.[11] Compound III has λ_{max} 264 mμ (95% alcohol), log ϵ 4.03. The infrared spectrum of III (Nujol mull) shows a split peak with strong absorption at 5.87, 6.05 μ, which is consistent with an α,β-unsaturated ketonic linkage subject to the constraints of a five-membered ring.[12]

Although it is difficult to ascertain the stage at which an aldol reaction between two moles of 2-hydroxycyclopentanone (II) actually occurred, some evidence indicates that the condensation reaction occurred during the decomposition of the disodium enediolate with acetic acid. Thus the yield of III decreased when the addition of acetic acid was carried out at 0°, whereas the best yield was obtained when the addition was carried out at about 40°. The yield dropped to less than 5% when sulfuric acid was substituted for acetic acid. These experiments suggest that sodium acetate is the condensing agent for 2-hydroxycyclopentanone (III) which undergoes aldolization very readily.

Although the seven-membered acyloin (2-hydroxycycloheptanone or XII) did not give a similar condensation product under the conditions of its isolation,[4b] a condensation reaction did occur when XII was subjected to the action of 45% potassium hydroxide solution. The product (unlike III) gave neither a ferric chloride test nor demonstrated any acidic properties, and therefore probably is XIII or some tautomerically related structure. The ultraviolet absorption spectrum of this substance (see Fig. 1) suggests the presence of an α,β-unsaturated ketonic function whose resonance is sterically damped. Molecular models of XIII indicate that the configuration in which the two double bonds are coplanar is rather constrained. The infrared spectrum of the condensation product shows absorption bands at 5.83 and 6.08 μ, which is consistent with the presence of an α,β-unsaturated ketonic linkage.



XII XIII

These results, particularly with respect to the acyloin reaction on dimethyl glutarate, point to the necessity of examining all of the products before coming to any conclusions regarding the relative ease of ring closure as a function of ring size in the heterogeneous acyloin reaction. In one case at least, the absence of α-ketol linkages in the polymer has been demonstrated.[3c] In some cases the polymer might be formed from material that has already cyclized. Thus the yield of isolated five-membered ring acyloin as compared to the yields of the larger ring compounds probably requires no special explanation[4a] with regard to the mechanism of the heterogeneous acyloin reaction, and the concept of high dilution at the sodium–solvent interface satisfactorily explains the high ratio of yield of ring to polymer in the preparation of large cycles.[13]

Experimental

Acyloin Condensation with Dimethyl Glutarate.—The apparatus employed has been described previously,[3a] and the general method is a modification of that reported by Sheehan.[4a] The proportions of reactants and solvent are as follows: 70.1 g. (0.437 mole) of dimethyl glutarate,[14] b.p. 95–96° (13 mm.), 41 g. (1.78 mole) of sodium and three liters of toluene distilled from sodium. The addition time was three hours, and the sodium was dispersed with a propeller turning at 6000 r.p.m. After the addition was complete the yellow mixture was stirred at reflux temperature for an additional 20 hours. The reaction mixture was cooled to 40° and 110 g. (1.83 moles) of glacial acetic acid was added dropwise with stirring, and the sodium acetate that separated was collected. The filtrate when cooled deposited white crystals which when recrystallized from chloroform amounted to 3.0 g. of III. The sodium acetate was returned to the reaction flask and stirred with four liters of refluxing benzene (in two portions), the sodium acetate was again collected, and the combined benzene and toluene filtrates were evaporated. The resulting mixture of oil and crystals was triturated with 100 ml. of cold chloroform and 11.3 g. of III was collected. The chloroform of the filtrate was evaporated, and the residual oil was flash-distilled at a pot temperature of 170–200° at 1 mm. to give 12.4 g. of a mixture of oil and solid. This mixture was triturated with cold benzene to give an additional 2.3 g. of III. Thus 16.6 g. (42% yield) of III was isolated from these various fractions, the melting points ranging between 144–149°. The combined material was recrystallized from chloroform (charcoal treatment) to give 12 g. of III (30% yield), m.p. 147–149°. An analytical sample was prepared by recrystallizing the material four times from chloroform, m.p. 149–150°.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74; mol. wt., 182. Found: C, 65.90; H, 7.57; mol. wt. (Rast), 218.

A dioxime of III was prepared from 100 mg. of material, 200 mg. of hydroxylamine hydrochloride and 2 ml. of 2% potassium hydroxide solution. The mixture was heated to 100° for four hours and cooled. The product that separated was recrystallized twice from 95% ethanol to give 73 mg. of white needles, m.p. 192–194°.

Anal. Calcd. for $C_{10}H_{16}O_3N_2$: C, 56.60; H, 7.59. Found: C, 56.32; H, 7.56.

The bis-phenylhydrazone of III was prepared from 75 mg. of III, 125 mg. of phenylhydrazine hydrochloride, 200 mg. of sodium acetate and 2 ml. of water. The product separated when the above mixture was heated at 100° for eight hours, and recrystallization of the material (twice) from 95% ethanol gave yellow prisms (120 mg.), m.p. 202–203° dec.

Anal. Calcd. for $C_{22}H_{26}ON_4$: C, 72.90; H, 7.24. Found: C, 72.76; H, 7.56.

The bis-*p*-nitrobenzoate of III was prepared in the usual way from 100 mg. of III, 215 mg. of *p*-nitrobenzoyl chloride and 1 ml. of dry pyridine. The product was recrystallized from 95% ethanol to give 155 mg. of light yellow needles, m.p. 157–158°.

Anal. Calcd. for $C_{24}H_{20}O_9N_2$: C, 59.99; H, 4.19. Found: C, 59.94; H, 4.42.

The bis-*p*-toluenesulfonate of III was prepared from 150 mg. of material, 330 mg. of *p*-toluenesulfonyl chloride and 2 ml. of dry pyridine. The above mixture was allowed to stand at room temperature for eight hours and poured into cold water. The product that separated was twice recrystallized from acetone–ether to give 90 mg. of small white needles, m.p. 163–165° dec.

Anal. Calcd. for $C_{24}H_{26}S_2O_7$: C, 58.74; H, 5.34. Found: C, 58.53; H, 5.35.

Wolff–Kishner Reduction of III to 2-Cyclopentylcyclopentanol (VII).—A mixture of 3.00 g. of III, 1.34 g. of potassium hydroxide, 3 ml. of 85% hydrazine hydrate and 12 ml. of diethylene glycol was held at reflux (125°) for three

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[11] The authors are indebted to H. J. Dauben and V. R. Ben (private communication) for these data.

[12] R. N. Jones, V. Z. Williams, M. J. Whalen and K. Dobriner, THIS JOURNAL, **70**, 2024 (1948).

[13] V. Prelog, *J. Chem. Soc.*, 420 (1950).

[14] The authors are indebted to the du Pont Experimental Station for generous samples of this material.

hours.[8] The mixture was then allowed to distil until the pot temperature rose to 220°, at which point the material was held for 20 hours. The mixture was then cooled and poured into 100 ml. of water, and the resulting mixture was extracted three times with 25-ml. fractions of ether. The ether solution was washed with water, dried, and evaporated to a dark oil which was distilled at a pot temperature of 145–150° at 21 mm. to give 2.17 g. (85% yield) of colorless oil, $n^{25}\text{D}$ 1.4850. Since analysis indicated this material VII to be impure, two derivatives were prepared.

The *p*-nitrobenzoate (90 mg.) was prepared in the usual way from 100 mg. of the above oil, m.p. 78–79° (white platelets from 95% ethanol), lit. m.p. 78–79°.[9]

Anal. Calcd. for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98. Found: C, 67.56; H, 6.72.

The phenylurethan (95 mg.) was prepared from 100 mg. of the oil, m.p. 90–91° (white needles from 95% ethanol), lit.[9] 92.5°.

Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.49. Found: C, 74.56; H, 8.17.

Oxidation of 2-Cyclopentylcyclopentanol (VII) to 2-Cyclopentylcyclopentanone (VIII).—To a solution of 350 mg. of the alcohol (see above) in 1 ml. of glacial acetic acid was added 187 mg. of chromic anhydride dissolved in 4 ml. of 50% aqueous acetic acid (the mixture was cooled to 0° before addition). The mixture was held at 0° for eight hours and at 25° for five hours, and was then poured into 30 ml. of water. The resulting mixture was extracted three times with 20-ml. portions of pentane, the pentane extracts were washed with water, sodium bicarbonate solution and again with water. The solution was dried and evaporated to a yellow oil that was distilled at a pot temperature of 100–110° (16 mm.) to give 210 mg. of colorless oil (VIII).

This ketone (100 mg.) was converted to its 2,4-dinitrophenylhydrazone in the usual way to give 90 mg. of small orange needles, m.p. 158–159°, m.m.p. with the 2,4-dinitrophenylhydrazone prepared from an authentic sample of 2-cyclopentylcyclopentanone,[15] 158–159°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.77; H, 6.07. Found: C, 58.02; H, 5.75.

The semicarbazone (65 mg) was prepared from the ketone (100 mg.) in the usual way, m.p. 200–206° dec., undepressed by admixture with an authentic sample.[16]

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.06; H, 9.17. Found: C, 62.87; H, 9.04.

Partial Hydrogenation of III to 3-(2-Hydroxycyclopentyl)-2-hydroxycyclopentanone (IV).—A mixture of 3.0 g. of III in 35 ml. of methanol and 0.47 g. of 10% palladium-on-charcoal was shaken in an atmosphere of hydrogen at atmospheric pressure and room temperature. A total of 1.18 moles of hydrogen was consumed (starting material = 1 mole). The mixture was filtered, and the methanol was evaporated from the filtrate to leave a yellow oil. This oil IV could not be crystallized and suffered extensive polymerization upon distillation. It gave an acyloin test,[7] no color reaction with ferric chloride, and consumed one atom of oxygen in a periodic acid titration.

From 100 mg. of oil, 110 mg. of a semicarbazone was obtained as white cubes from methanol, m.p. 195–196.5°.

Anal. Calcd. for $C_{11}H_{19}N_3O_3$: C, 54.76; H, 7.97. Found: C, 54.66; H, 8.05.

A 2,4-dinitrophenylosazone (50 mg.) was prepared[16] from 140 mg. of the oil, and the derivative formed red needles when crystallized from dimethylformamide, m.p. dec. started at 235°.

Anal. Calcd. for $C_{22}H_{22}N_8O_9$: C, 48.71; H, 4.09. Found: C, 48.76; H, 3.85.

The phenylosazone was prepared from the oil as follows. A mixture of IV (100 mg.), phenylhydrazine hydrochloride (300 mg.), sodium acetate (500 mg.) and 5 ml. of 95% ethanol was heated at 100° for 30 minutes. The resulting dark solution when cooled deposited a yellow solid which was recrystallized from 95% ethanol to give 50 mg. of small yellow prisms, m.p. 201–202°, undepressed by admixture with the bis-phenylhydrazone of III.

Wolff–Kishner Reduction of IV to 2-Cyclopentylcyclopentanol (VII).—This procedure was identical to that employed for the reduction of III to VII. From 1.00 g. of IV was obtained 0.70 g. of VII as a colorless oil, b.p. (pot temperature) 95° (2 mm.). From 100 mg. of this oil was obtained 110 mg. of a *p*-nitrobenzoate derivative, m.p. 77–78.4°, undepressed by admixture with the *p*-nitrobenzoate of VII obtained directly from III.

Clemmensen Reduction of III to 1-Cyclopentylcyclopentene (IX).—Amalgamated zinc was prepared by shaking 30 g. of mossy zinc with 40 ml. of water, 4 ml. of concentrated hydrochloric acid and 2 g. of mercuric chloride for ten minutes. A solution of 5.07 g. of III in 50 ml. of water and 50 ml. of concentrated hydrochloric acid was held at reflux for 60 hours in contact with the zinc, a total of 30 ml. of concentrated hydrochloric acid being added at intervals in 2-ml. portions over that period. The yellow oil that separated was extracted with ether, the ether solution was washed with water and with sodium carbonate solution, and dried. The ether was evaporated, and the residual oil was distilled at a pot temperature of 95–100° at 13 mm. to give 2.51 g. of colorless oil. This material was distilled twice from sodium, $n^{25}\text{D}$ 1.4858 (reported for 1-cyclopentylcyclopentene, $n^{22.5}\text{D}$ 1.4863).[17]

Anal. Calcd. for $C_{10}H_{16}$: C, 88.18; H, 11.82. Found: C, 88.16; H, 11.83.

This oil gave the usual tests for unsaturation, and when hydrogenated in acetic acid with a platinum catalyst, 94% of the theoretical amount of hydrogen was consumed.

When submitted to the same procedure, compound IV (0.900 g.) gave 216 mg. of colorless oil (IX), $n^{25}\text{D}$ 1.4860.

Hydrogenation of III with Platinum Catalyst in Acetic Acid.—A mixture of 0.400 g. of III, 0.100 g. of prereduced platinum oxide and 10 ml. of glacial acetic acid was shaken in an atmosphere of hydrogen at atmospheric pressure and room temperature until no more hydrogen was absorbed (2.5 moles of hydrogen consumed if starting material equals 1 mole). The resulting mixture was filtered, the filtrate was evaporated, and the residual yellow oil was distilled at a pot temperature of 160–170° at 1 mm. to give 0.215 g. of colorless oil. This oil failed to yield a 2,4-dinitrophenylhydrazone and to decolorize bromine in carbon tetrachloride solution.

The *p*-nitrobenzoate derivative was prepared in the usual way (45 mg.) from 135 mg. of oil, m.p 215–217° (white needles from acetone).

Anal. Calcd. for $C_{31}H_{27}O_{12}N_3$: C, 58.77; H, 4.29. Found: C, 58.48; H, 4.59.

Condensation Reaction of 2-Hydroxycycloheptanone (XII).—A mixture of 0.50 g. of 2-hydroxycycloheptanone and 3 ml. of 45% potassium hydroxide was held at reflux temperature for 2.5 hours. Water (10 ml.) was then added, and the resulting mixture was acidified with 6 *N* sulfuric acid. This mixture was then extracted with ether, the extracts were washed with water, dried and evaporated to a volume of 15 ml. This solution was treated with charcoal, filtered and evaporated to a brown oil. When allowed to stand this oil deposited white plates which after recrystallization from ether amounted to 0.14 g., m.p. 140.4–141.5°. This solid was insoluble in water, dilute base, and did not decolorize bromine or permanganate solutions.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31; mol. wt., 238. Found: C, 70.32; H, 9.38; mol. wt., 199.

A mono-*p*-nitrobenzoate (10 mg.) of the above compound (54 mg.) was prepared by the usual method, m.p. 197–198° (four crystallizations from ether to give cream colored plates).

Anal. Calcd. for $C_{21}H_{25}O_6N$: C, 65.10; H, 6.54. Found: C, 65.67; H, 6.73.

LOS ANGELES, CALIFORNIA

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(15) J. von Braun, *Ber.*, **70B**, 1750 (1937).

(16) R. Shriner and R. Fuson, "The Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 170.

(17) C. Harries and H. Wagner, *Ann.*, **410**, 29 (1915).