Anal. Calcd. for $C_{27}H_{28}O_{10}S_2$: C, 56.3; H, 4.90; S, 11.2. Found: C, 56.5; H, 5.03; S, 11.0.

Methyl 2-O-benzoyl-3,4-di-O-(*p*-tolylsulfonyl)-β-D-arabinopyranoside (IX) prepared by the same procedure had m.p. 160–161.5°, $[\alpha]^{21}\mathrm{D}$ −201° (*c* 0.981, chloroform).

Anal. Calcd. for $C_{27}H_{28}O_{10}S_2$: C, 56.3; H, 4.90; S, 11.2. Found: C, 56.2; H, 4.75; S, 11.2.

Methyl α-D-Ribopyranoside (VIII).—A solution of 2.88 g. (5 mmoles) of methyl 2-O-benzoyl-3,4-di-O-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (III) and 2.1 g. (50 mmoles) of sodium fluoride in 200 ml. of dry DMF was heated at reflux for 2 days. The reaction mixture was cooled to room temperature and then was stirred with 3 ml. of water for 4 hr. After evaporation to dryness *in vacuo*, the residue was partitioned between 40 ml. each of water and chloroform. The chloroform extract was evaporated to dryness *in vacuo* to give 1.9 g. of crude methyl 3(4)-O-benzoyl-α-D-ribopyranoside (VII) as a syrup which was free of sulfonate absorption at 8.5 and 12.3 μ in the infrared. Thin layer chromatography using chloroform–ethyl acetate (1:1) as the developing solvent showed two spots of equal intensities with R_f values of 0.34 and 0.28, probably the 3-O-benzoate and 4-O-benzoate (VII).

Treatment of crude VII with 0.5 ml. of 1 *N* methanolic sodium methoxide in 7 ml. of methanol at reflux for 1 hr. gave, after the usual work-up, 0.68 g. (83%) of methyl α-D-ribopyranoside (VIII) as a syrup: $[\alpha]\mathrm{D}$ +86° (*c* 1, water). Vapor phase chromatography[11] of the trimethylsilyl ether[14] of VIII showed a single peak with a retention time of 1.0 min.

Thin layer chromatography using 1-propanol–ethyl acetate–water (3:2:1) as the eluent, showed one main spot at R_f 0.42 assignable to VIII along with a trace of methyl β-L-lyxopyranoside at R_f 0.49.

Methyl α-D-ribopyranoside has $[\alpha]\mathrm{D}$ +103° (water).[15]

A solution of 100 mg. of methyl α-D-ribopyranoside (VIII) in 3 ml. of water which contained 0.7 ml. of 1 *N* aqueous hydrochloric acid was heated at reflux for 1.5 hr. The solution was cooled, neutralized with IR 45 (OH),[16] then evaporated to dryness to give 80 mg. of crude D-ribose as a yellow syrup. Paper chromatography of the crude product showed D-ribose as the predominant component, with a trace of lyxose as the only contaminant.

The phenylosazone[17] of the above material had m.p. 163–165° and was identical in all respects with the phenylosazone of authentic D-ribose.

Methyl α-L-ribopyranoside (X) was prepared from methyl 2-O-benzoyl-3,4-di-O-(*p*-tolylsulfonyl)-β-D-arabinopyranoside (IX) by an identical series of reactions and had $[\alpha]\mathrm{D}$ −83° (*c* 1, water). Hydrolysis of X in the manner described for D-ribose gave L-ribose as the predominant component contaminated with a trace of lyxose. The phenylosazone of L-ribose was identical spectrally with that of D-ribose and had m.p. 161–165°.

Acknowledgment.—The authors are indebted to Mr. O. P. Crews and his group for the preparation of quantities of certain of the intermediates and to Dr. Peter Lim and his staff for the infrared spectra, optical rotations, and paper chromatography. They also wish to thank Dr. Leon Goodman for his advice and encouragement throughout the course of this work.

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[15] C. T. Bishop and F. P. Cooper, *Can. J. Chem.*, **41**, 2743 (1963).

[16] A weak base anion-exchange resin manufactured by the Rohm and Haas Company, Philadelphia, Pa.

[17] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 132.

A Novel Cyclization of 4-Acetyl-1-methoxy-1-cyclohexene to 4-Alkoxybicyclo[2.2.2]octan-2-ones[1]

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An acid-catalyzed cyclization of 4-acetyl-1-methoxy-1-cyclohexene (**1**) in aprotic solvents such as benzene or tetrahydrofuran gave 4-methoxybicyclo[2.2.2]octan-2-one (**2**) in over 90% yields, whereas the analogous cyclization of **1** in alcoholic solvents furnished 4-alkoxybicyclo[2.2.2]octan-2-ones (**2–11**). Reaction of a methanol solution of 4-acetyl-1-cyclohexanones (**17**, **19**, and **22**) with trimethyl orthoformate in the presence of hydrochloric acid furnished 4-methoxybicyclo[2.2.2]octan-2-ones (**2**, **21**, and **23**), respectively.

It was demonstrated in previous papers[1,2] that acid-catalyzed cyclizations of 1-methoxy-4-(1-methoxyvinyl)-4-methyl-1-cyclohexene and 1-methoxy-4-methyl-4-vinyl-1-cyclohexene furnished 1,3-dimethoxy-4-methylbicyclo[2.2.2]oct-2-ene and 5-methoxy-2-methylbicyclo[3.2.1]oct-2-ene, respectively. The present paper describes the novel cyclization[3] of 4-acetyl-1-methoxy-1-cyclohexene (**1**) leading to 4-alkoxybicyclo[2.2.2]octan-2-ones (**2–11**).

Reaction of a tetrahydrofuran solution of 4-acetyl-1-methoxy-1-cyclohexene (**1**) with anhydrous ferric chloride or a benzene solution of **1** with anhydrous *p*-toluenesulfonic acid gave 4-methoxybicyclo[2.2.2]octan-2-one (**2**) in over 90% yields. The structure for **2** was established by the independent synthesis[4] of **2** from 1-methoxy-4-(1-methoxyvinyl)-1-cyclohexene (**12**)[5] utilizing the method already described[2] and by n.m.r. and infrared spectra. The n.m.r. spectrum confirmed the existence of a tertiary methoxyl group, τ 6.84, an isolated methylene group adjacent to a carbonyl group, τ 7.74, and a bridgehead hydrogen, τ 7.88. The infrared spectrum of **2** was also entirely consistent with the assigned structure. Bands for a methoxyl group were found at 2832 and 1112 cm.$^{-1}$, and that for a carbonyl group at 1729 cm.$^{-1}$.

When the cyclization of **1** was carried out in alcoholic solvents in the presence of hydrogen chloride or *p*-toluenesulfonic acid, alcohols were incorporated in the products and there were obtained 4-alkoxybicyclo[2.2.2]octan-2-ones (**2–11**). Treatment of a propyl alcohol solution of **1** with hydrogen chloride gave 4-propoxybicyclo[2.2.2]octan-2-one (**4**), whereas an analogous reaction of a methanol solution of 4-acetyl-1-propoxy-1-cyclohexene (**13**), derived from 2-propoxy-1,3-butadiene and methyl vinyl ketone, furnished 4-

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[1] Bridged Ring Compounds. IV. Paper III: K. Morita, M. Nishimura, and H. Hirose, *J. Org. Chem.*, **30**, 3011 (1965).

[2] (a) K. Morita, M. Nishimura, and Z. Suzuki, *ibid.*, **30**, 533 (1965); (b) K. Morita and Z. Suzuki, *Tetrahedron Letters*, **No. 6**, 263 (1964).

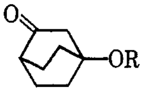
[3] The reaction is formally analogous to aldol condensation.

[4] K. Morita and Z. Suzuki, *J. Org. Chem.*, **31**, 233 (1966).

[5] I. N. Nazarov, G. P. Verkholetova, and L. D. Bergel'son, *Akad. Nauk SSSR, Otdl. Khim. Nauk*, 511 (1948); *Chem. Abstr.*, **43**, 2576*i* (1949).

TABLE I

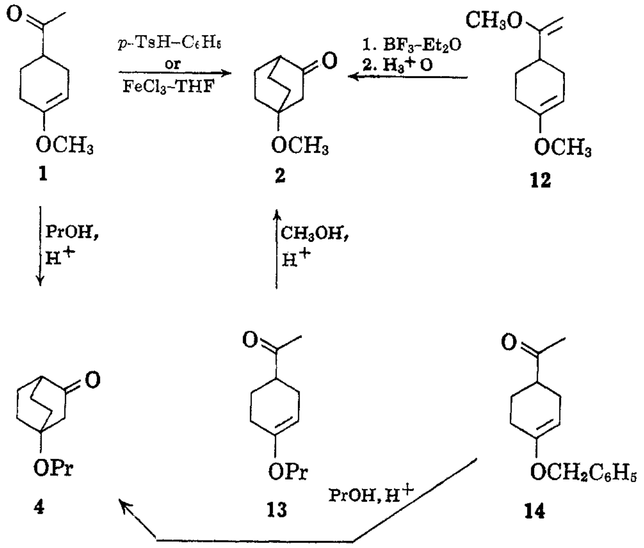
PHYSICAL CONSTANTS OF 4-ALKOXYBICYCLO[2.2.2]OCTAN-2-ONES



Compd.	R	B.p. (mm.) or m.p., °C.	$n^{20}D$	Infrared, $\nu_{C=O}^{film}$, cm.$^{-1}$	N.m.r., τ Adjacent to O	N.m.r., τ Adjacent to C=O	N.m.r., τ Bridgehead	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
2	CH_3	94–97 (4.0)	1.4880	1729	6.84[a]	7.74	7.88	$C_9H_{14}O_2$	70.10	9.14	69.95	9.35
3	C_2H_5	87–88 (0.7)	1.4815	1729	6.61[b]	7.72	7.90	$C_{10}H_{16}O_2$	71.39	9.59	71.10	9.52
4	n-C_3H_7	91–93 (0.6)	1.4775	1729	6.72[c]	7.73	7.88	$C_{11}H_{18}O_2$	72.49	9.96	72.79	9.96
5	i-C_3H_7	90–91 (0.6)	1.4760	1729	6.18[d]	7.71	7.90	$C_{11}H_{18}O_2$	72.49	9.96	72.28	9.98
6	n-C_4H_9	116 (3.0)	1.4775	1729	6.89[c]	7.72	7.90	$C_{12}H_{20}O_2$	73.43	10.27	73.41	10.29
7	i-C_4H_9	105–106 (0.4)	1.4760	1729	6.89[e]	7.72	7.89	$C_{12}H_{20}O_2$	73.43	10.27	73.15	10.11
8	sec-C_4H_9	109 (0.6)	1.4765	1729	6.41[f]	7.71	7.91	$C_{12}H_{20}O_2$	73.43	10.27	73.17	10.27
9	Cyclohexyl	64.5–65.5	. . .	1727[g]	6.55[h]	7.70	7.91	$C_{14}H_{22}O_2$	75.63	9.97	75.47	9.95
10	$CH_2CH{=}CH_2$	105–106.5 (1.5)	1.4972	1729	6.12[h]	7.69	7.89	$C_{11}H_{16}O_2$	73.30	8.95	73.10	8.98
11	$CH_2CH_2OCH_3$	121–123 (0.3)	1.4823	1729	6.60, 6.71[a]	7.70	7.88	$C_{11}H_{18}O_3$	66.64	9.15	66.75	9.05

[a] Singlet. [b] Quartet (J = 7 c.p.s.). [c] Triplet (J = 6 c.p.s.). [d] Heptet (J = 6 c.p.s.). [e] Doublet (J = 5 c.p.s.). [f] Quartet (J = 6 c.p.s.). [g] KBr pellet. [h] Multiplet.

methoxybicyclo[2.2.2]octan-2-one (**2**). Reaction of a propyl alcohol solution of 4-acetyl-1-benzyloxy-1-cyclohexene (**14**), prepared by thermal decomposition of 4-acetyl-1,1-dibenzyloxycyclohexane derived from **1** and benzyl alcohol in the presence of acid catalyst, also gave **4**. A variety of alcohol groups were thus introduced at C-4 of the bicyclo[2.2.2]octan-2-one structure by cyclizing **1** in various alcoholic solvents. Physical constants of the 4-alkoxybicyclo[2.2.2]octan-2-ones (**2**–**11**) are listed in Table I.



The exchange[6] of alkoxyl groups before cyclization suggested the possibility of formation of alkoxycarbonium ion **16**[7,8] and a protonated ketal **15** as intermediates. Reaction of ketal exchange and hydrolyses of ketals or vinyl ethers are formally analogous, and the mechanism of hydrolysis of ketals[13] or vinyl ether[14] has been suggested which involves alkoxycarbonium ions as an intermediate. Taft and Ramsey[15] found that alkoxycarbonium ions can generally be produced by addition of ketals to strong acids.

A mechanism illustrating the acid-catalyzed cyclization of **1** in alcoholic solvents can be depicted[16] as shown on p. 231, top of col. 1.

4-Acetyl-1-cyclohexanone (**17**) was usually formed as a by-product when cyclization of **1** was carried out in alcoholic solvents. On the other hand, only trace of **17** (if any) was produced when nonalcoholic solvents such as tetrahydrofuran, diethylene glycol diethyl ether, or benzene were employed. One might assume that the mechanism of formation of 4-acetyl-1-cyclohexanone (**17**) under anhydrous conditions involves reaction of an alkoxycarbonium ion **16** with alcohols.[7a] No study concerning the mechanism was carried out.

Reaction of 4-acetyl-1-methoxy-1-cyclohexene (**1**) with acetic acid at reflux furnished 4-acetyl-1-cyclohexanone (**17**), methyl acetate, and small amount of **2**. The reaction probably involves the addition of acetic acid to the enol ether double bond giving **18** which can decompose to **17** and methyl acetate.[17]

The assumption that the mechanism of cyclization of 4-acetyl-1-methoxy-1-cyclohexene (**1**) involves for-

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(6) For the ester exchange of enol ethers, see A. Ercoli and R. Gardi, *J. Am. Chem. Soc.*, **82**, 746 (1960); A. Ercoli, German Patent 1,068,256 (Nov. 5, 1959).

(7) For recent review of alkoxycarbonium ions and other ambident cations, see (a) S. Hunig, *Angew. Chem.*, **76**, 400 (1964); *Angew. Chem. Intern. Ed. Engl.* **3**, 548 (1964); (b) N. C. Deno, *Chem. Eng. News*, **42**, 88 (Oct. 5, 1964).

(8) Reactions of acetals or ketals with vinyl ethers,[9] vinyl acetates,[10] olefins,[11] or ketenes,[12] in the presence of acid catalysts, presumably proceed *via* alkoxycarbonium ions.

(9) R. I. Hoaglin and D. H. Hirsh, *J. Am. Chem. Soc.*, **71**, 3468 (1949). For a recent review of the reaction, see O. Isler and P. Schudel, *Advan. Org. Chem.*, **4**, 128 (1963).

(10) I. V. Machinskaya and V. P. Gorbunova, *Zh. Obsch. Khim.*, **34**, 1295 (1964).

(11) O. C. Dermer and J. J. Hawkins, *J. Am. Chem. Soc.*, **74**, 4595 (1952); R. Paul and S. Tchelitcheff, *Bull. soc. chim. France*, 1155 (1950).

(12) F. Sorm and J. Smrt, *Chem. Listy*, **47**, 413 (1953); *Chem. Abstr.*, **49**, 175*d* (1955); S. S. Vufit and V. F. Kucherov, *Izv. Akak. Nauk SSSR, Otd. Khim. Nauk*, 1658 (1960); *Chem. Abstr.*, **55**, 9273*h* (1961).

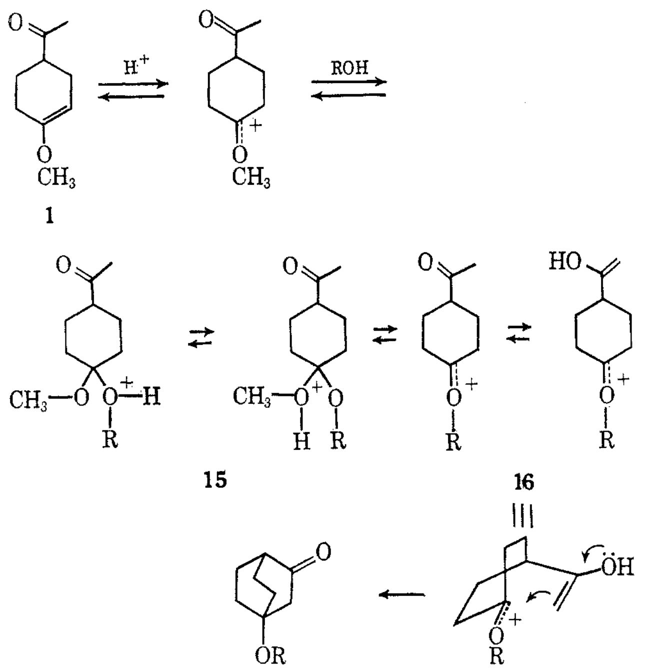
(13) (a) E. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 965 (1957); (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 334; (c) T. H. Fife and L. K. Jao, *J. Org. Chem.*, **30**, 1492 (1965); *cf.* R. H. DeWolfe and J. L. Jensen, *J. Am. Chem. Soc.*, **85**, 3264 (1963); C. A. Bunton and R. H. DeWolfe, *J. Org. Chem.*, **30**, 1371 (1965).

(14) M. D. Jones and N. F. Wood, *J. Chem. Soc.*, 5400 (1964).

(15) Work cited in ref. 7b.

(16) The mechanism illustrated may be compared with that of the ortho ester reaction involving ketones [J. P. Dusza, J. P. Joseph, and S. Bernstein, *J. Am. Chem. Soc.*, **86**, 3908 (1964)].

(17) *Cf.* O. L. Chapman and P. Fitton, *ibid.*, **85**, 41 (1963).



1

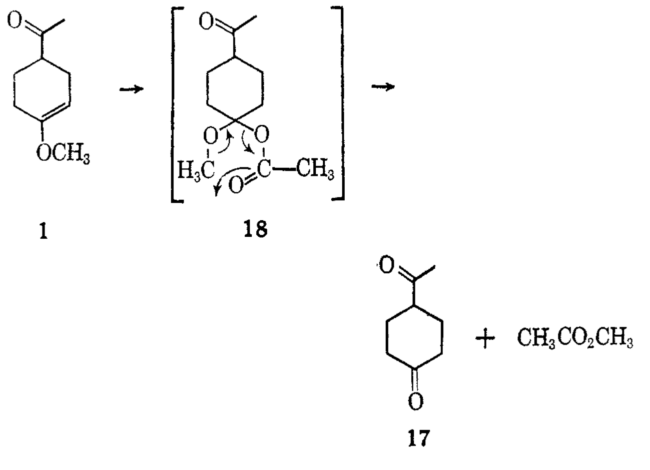
15

16

2-11

2, R = methyl
3, R = ethyl
4, R = *n*-propyl
5, R = isopropyl
6, R = *n*-butyl
7, R = isobutyl
8, R = *sec*-butyl
9, R = cyclohexyl
10, R = allyl
11, R = $CH_3OCH_2CH_2$

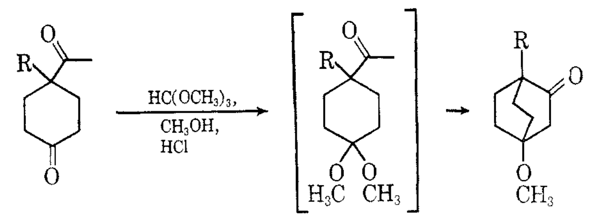
mation of a protonated ketal **15** as an intermediate led us to investigate cyclization of diketones such as 4-acetyl-1-cyclohexanone (**17**), 4-acetyl-4-methyl-1-cyclohexanone (**19**), and 4-acetyl-4-phenyl-1-cyclohexanone (**22**) under the conditions of ketal formation. Reaction of a methanol solution of 4-acetyl-4-methyl-1-cyclohexanone (**19**)[18] with trimethyl orthoformate in the presence of hydrochloric acid at reflux gave 4-methoxy-1-methylbicyclo[2.2.2]octan-2-one (**21**) in 91% yield. An analogous reaction of 4-acetyl-1-cyclohexanone (**17**) and of 4-acetyl-4-phenyl-1-cyclohexanone (**22**)[18] with trimethyl orthoformate gave 4-methoxybicyclo[2.2.2]octan-2-one (**2**) and 4-methoxy-1-phenylbicyclo[2.2.2]octan-2-one (**23**), respectively. Reaction of an ethanol solution of 4-acetyl-4-methyl-1-cyclohexanone (**19**) with triethyl orthoformate in the presence of hydrochloric acid at reflux afforded 4-ethoxy-1-methylbicyclo[2.2.2]octan-2-one.



1

18

17



17, R = H
19, R = CH_3
22, R = C_6H_5

20

2, R = H
21, R = CH_3
23, R = C_6H_5

Experimental Section

All boiling points and melting points are uncorrected. N.m.r. spectra were obtained with a Varian A-60 instrument using carbon tetrachloride as solvent and tetramethylsilane as the internal standard. Vapor phase chromatography was performed with a Yanagimoto GCG 220 using a polyethylene glycol 6000 column.

4-Acetyl-1-methoxy-1-cyclohexene (1).—A stirred solution of 160 g. (1.6 moles) of freshly distilled 2-methoxy-1,3-butadiene,[19] 182 g. (2.6 moles) of methyl vinyl ketone, and 0.5 g. of hydroquinone in 400 ml. of dry benzene was heated at 120° for 15 hr. under an atmosphere of nitrogen. Distillation of the reaction mixture gave 272 g. (86% yield based on methoxyprene) of **1**: b.p. 102–103° (8 mm.); n^{20}_{D} 1.4798; $\nu_{\max}^{\text{film}}$ 2850 (OMe), 1711 (C=O), 1672 cm.$^{-1}$ (C=C); lit.[20] b.p. 121.5–122° (20 mm.), n^{20}_{D} 1.4792.

4-Methoxybicyclo[2.2.2]octan-2-one (2). **A. With *p*-Toluenesulfonic Acid.**—To a vigorously stirred mixture of 1.3 g. (7.55 mmoles) of anhydrous *p*-toluenesulfonic acid and 0.1 g. of hydroquinone in 60 ml. of dry benzene was added a solution of 10 g. (64.85 mmoles) of 4-acetyl-1-methoxy-1-cyclohexene (1) in 80 ml. of dry benzene at reflux during a period of 6 hr. After the completion of the addition, the mixture was heated at reflux for 1 hr. more. The cooled mixture was neutralized with methanolic sodium methoxide, washed with water, and dried with anhydrous sodium sulfate. The product was collected by distillation to afford 9.1 g. of 2.[21]

B. With Ferric Chloride.—To a vigorously stirred mixture of 1.0 g. of anhydrous ferric chloride in 80 ml. of dry tetrahydrofuran was added a solution of 10 g. (64.85 mmoles) of 4-acetyl-1-methoxy-1-cyclohexene (1) in 80 ml. of tetrahydrofuran at reflux during a period of 7 hr. After the completion of addition, the mixture was heated at reflux for 1 hr. further. Tetrahydrofuran was evaporated *in vacuo* (bath temperature below 60°) and diluted with ether. The ethereal extract was washed with saturated sodium bicarbonate, dried over anhydrous sodium sulfate, and concentrated. The product was collected by distillation to furnish 9.2 g. of 2.[21] Similar results were obtained when diethylene glycol diethyl ether was used instead of tetrahydrofuran.

C. With Hydrochloric Acid.—To 180 g. of anhydrous methanol containing 21 g. of hydrogen chloride was added 10 g. (64.8 mmoles) of 4-acetyl-1-methoxy-1-cyclohexene (1) in 40 g. of anhydrous methanol at 0–5°. The mixture was then heated at reflux for 2 hr. and concentrated *in vacuo*. The residue was diluted with methylene chloride. The methylene chloride solution was washed with a small amount of aqueous sodium bicarbonate solution and water, dried over anhydrous sodium sulfate, and concentrated. The residue was distilled *in vacuo* to furnish 6.6 g. of a product, b.p. 94–105° (4 mm.), which was dissolved in a small amount of methylene chloride. The solution was put on 140 g. of alumina (100 mesh, Sumitomo Chemical Co.) packed in petroleum ether (b.p. 35–65°). Elution with petroleum ether and distillation gave 5.4 g. of 2.[21] Further elution with ether gave 0.7 g. of 4-acetyl-1-cyclohexanone (17). Identity of the latter product was established by the comparison of the infrared spectra and the retention time of vapor chromatography with that of material [b.p. 97–98° (3.5 mm.), n^{20}_{D} 1.4736; lit.[20] b.p. 141.5–142 (20 mm.), n^{20}_{D} 1.4732] prepared by hydrolysis of 4-acetyl-1-methoxy-1-cyclohexene (1) according to Petrov.[20]

Cyclization of 4-Acetyl-1-propoxy-1-cyclohexene in Methanol.—A stirred mixture of 24.5 g. (0.22 mole) of 2-propoxy-1,3-

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[18] J. Colonge and R. Vuillemet, *Bull. soc. chim. France*, 2235 (1961).

[19] A. A. Petrov, *Acta Univ. Voronegiensis*, **8**, 68 (1935); *Chem. Abstr.*, **32**, 6616^5 (1938).

[20] A. A. Petrov, *Chem. Abstr.*, **42**, 881*g* (1948).

[21] *Cf.* Table I.

TABLE II

ACID-CATALYZED CYCLIZATION OF 4-ACETYL-1-METHOXY-1-CYCLOHEXENE IN VARIOUS ALCOHOLS

1, g.	*p*-Toluenesulfonic acid, g.	Solvent (ml.)	Products, yield, g. (%)
3.0	0.15	Methyl alcohol (25)	**2**, 1.0 (34)
3.2	0.10	Ethyl alcohol (25)	**3**, 1.8 (57)
3.3	0.15	*n*-Propyl alcohol (30)	**4**, 1.8 (55)
6.0	0.30	Isopropyl alcohol (45)	**5**, 2.7 (38) **2**, 0.1 (2)
3.0	0.10	*n*-Butyl alcohol	**6**, 0.8 (33)
3.5	0.15	Isobutyl alcohol (30)	**7**, 3.4 (76)
3.0	0.15	*sec*-Butyl alcohol (20)	**8**, 1.25 (37)
3.0	0.13	Cyclohexanol (20)	**9**, 1.0 (23)
4.2	0.25	Allyl alcohol (50)	**10**, 1.3 (30) **17**, 1.5 (35)
3.0	0.07	Ethylene glycol monomethyl ether (30)	**11**, 1.3 (38)

butadiene,[19] b.p. 117–118°, 24.5 g. (0.35 mole) of methyl vinyl ketone, and 0.5 g. of hydroquinone was heated at 150° for 16 hr. under an atmosphere of nitrogen. The product was distilled, and the fraction boiling at 105–115° (4 mm.) amounted to 29.6 g. Redistillation gave 20.8 g. of **4-acetyl-1-propoxy-1-cyclohexene**: b.p. 85–89° (1.5 mm.); ν_{max}^{film} 1710 (C=O), 1671 cm.$^{-1}$ (C=C).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.28; H, 9.76.

To a solution of 80 g. of anhydrous methanol containing 20 g. of hydrogen chloride was added 5 g. (27.4 mmoles) of material obtained above in 40 g. of absolute methanol, and the mixture was heated at reflux for 3 hr. The mixture was then treated as described above and the fraction boiling at 95–105° (4 mm.) amounted to 3.1 g., which was found to consist of 92% of **2** and 8% of **17** by v.p.c. Pure **2** was isolated by chromatography on alumina as described above.

4-Acetyl-1-benzyloxy-1-cyclohexene (**14**).—To a stirred solution of 5.0 g. (32.4 mmoles) of 4-acetyl-1-methoxy-1-cyclohexene (**1**) in 35 g. of benzyl alcohol was added 10 g. of dry hydrogen chloride at 0–5°. The mixture was heated gradually. When the bath temperature reached 150°, benzyl alcohol was allowed to distil under reduced pressure. After the removal of benzyl alcohol, the mixture was heated at 210–220° for 2 hr. and distilled. The fraction boiling at 140–142° (0.3 mm.) amounted to 6.1 g. (82%), $n^{20}D$ 1.5419.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.11; H, 7.73.

Cyclization of 4-Acetyl-1-benzyloxy-1-cyclohexene (**14**) **in Propyl Alcohol**.—To a magnetically stirred solution of 4.5 g. (19.5 mmoles) of **14** in 50 g. of *n*-propyl alcohol was added 8 g. of dry hydrogen chloride at 0–5°. The mixture was heated at reflux for 30 min. After the removal of most of the hydrogen chloride and solvent *in vacuo*, the reaction mixture was neutralized with methanolic sodium methoxide and the mixture was distilled. The fraction boiling at 105–106° (0.4 mm.) amounted to 1.23 g., which was found to consist of 93.6% of **4-propoxybicyclo[2.2.2]octan-2-one** (**4**)[21] and 6.4% of **17** by v.p.c. Pure **4** was isolated by chromatography on alumina as described above.

An Acid-Catalyzed Cyclization of 4-Acetyl-1-methoxy-1-cyclohexene (**1**) **in Various Alcohols**.—A solution of **1** and *p*-toluenesulfonic acid in solvents specified in Table II was heated at reflux for 3 hr. and then distilled slowly to remove the solvent during a period of 3 to 4 hr. After the removal of the solvent, the product was collected by distillation. The distillate was chromatographed on alumina (100 mesh, Sumitomo Kagaku Co.). Material eluted with petroleum ether was collected and distilled. The results are listed in Table II. Although v.p.c. showed that each crude product was contaminated with some 4-acetyl-1-cyclohexanone (**17**), no attempt was made to isolate 4-acetyl-1-cyclohexanone (**17**), except in case of allyl alcohol as a solvent where a fairly large amount of **17** was formed.

2,4-Dinitrophenylhydrazones were prepared in a conventional way. Their physical constants are given in Table III.

Reaction of 4-Acetyl-1-methoxy-1-cyclohexene (**1**) **with Acetic Acid**.—**1** (3.0 g., 19.45 mmoles) was dissolved in 10 ml. of glacial acetic acid, and acetic acid was slowly distilled during a period of 4 hr. Careful redistillation of the distillate gave 0.3 g. of methyl acetate. Distillation of the residue *in vacuo* gave 1.53 g. of a product, b.p. 95–96° (3.5 mm.), which was found to consist of 81% of **4-acetyl-1-cyclohexanone** (**17**), 5% of **4-methoxybicyclo[2.2.2]octan-2-one** (**2**), and 14% of unidentified material by v.p.c.

TABLE III

PHYSICAL CONSTANTS OF 4-ALKOXYBICYCLO[2.2.2]OCTAN-2-ONE 2,4-DINITROPHENYLHYDRAZONES

Parent ketone	2,4-Dinitrophenylhydrazone m.p., °C.	Formula	Calcd., %			Found, %		
			C	H	N	C	H	N
2	141.5–142.5	$C_{15}H_{18}N_4O_5$	53.88	5.43	16.76	53.97	5.46	16.78
3	152.5–153.5	$C_{16}H_{22}N_4O_5$	55.16	5.79	16.08	55.07	5.77	16.12
4	142–144	$C_{17}H_{22}N_4O_5$	56.34	6.12	15.46	56.24	6.10	15.37
5	178–179	$C_{17}H_{22}N_4O_5$	56.34	6.12	15.46	56.16	6.13	15.35
6	106–107	$C_{18}H_{20}N_4O_5$	57.43	6.43	14.89	57.53	6.42	14.85
7	139.0	$C_{18}H_{20}N_4O_5$	57.43	6.43	14.89	57.33	6.38	14.81
8	134–135	$C_{18}H_{20}N_4O_5$	57.43	6.43	14.89	57.35	6.49	14.75
9	169–170	$C_{20}H_{26}N_4O_5$	59.69	6.51	13.92	59.70	6.37	13.70
10	140.5–142.0	$C_{17}H_{22}N_4O_5$	56.66	5.59	15.55	56.71	5.58	15.50
11	171–174	$C_{17}H_{22}N_4O_6$	53.96	5.86	14.81	54.19	5.95	14.85

4-Methoxy-1-methylbicyclo[2.2.2]octan-2-one (**21**).—To a solution of 24 g. (0.156 mole) of 4-acetyl-4-methyl-1-cyclohexanone (**19**) and 52 g. (0.49 mole) of trimethyl orthoformate in 160 ml. of absolute methanol was added 10.3 g. of hydrogen chloride at 0–5°, and then the mixture was heated at reflux for 30 min. Most of the methanol and hydrogen chloride were removed *in vacuo*, and the residue was neutralized with methanolic sodium methoxide and diluted with ether. The ethereal extract was washed with water, dried over anhydrous sodium sulfate, and distilled. There was obtained 23.5 g. (91%) of **21**, b.p. 118–119° (15 mm.). The identity was established by the comparison of the infrared spectrum and v.p.c. retention time with those of authentic **21**.[2a]

An analogous reaction of 3 g. (21.4 mmoles) of 4-acetyl-1-cyclohexanone (**17**), 2.73 g. (25.7 mmoles) of trimethyl orthoformate, and 2.1 g. of hydrogen chloride in 20 ml. of absolute methanol afforded, after chromatographic purification, 2.3 g. (76%) of **4-methoxybicyclo[2.2.2]octan-2-one** (**2**).

4-Ethoxy-1-methylbicyclo[2.2.2]octan-2-one.—A mixture of 3 g. (19.5 mmoles) of 4-acetyl-4-methyl-1-cyclohexanone (**19**), 6.5 g. (43 mmoles) of triethyl orthoformate, and 20 ml. of absolute ethanol was treated as described above and the product was distilled. The fraction boiling at 127–128° (20 mm.) amounted to 3.1 g. (87%), $n^{20}D$ 1.4750.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.23; H, 9.97.

4-Methoxy-1-phenylbicyclo[2.2.2]octan-2-one (**23**).—A mixture of 2 g. (9.3 mmoles) of 4-acetyl-4-phenyl-1-cyclohexanone (**22**), 3.2 g. (33 mmoles) of trimethyl orthoformate, and 20 ml. of methanol was treated as described above. The residue was recrystallized from benzene–petroleum ether to furnish 1.7 g. of crystals, m.p. 82.5–83.5° (lit.[2a] m.p. 82.5–83.5°). The identity was established by the comparison of their infrared spectra and by the mixture melting point.