50.5–51.5° (yield 73% of theory). The melting point of a mixture of this material with 1,2-diphenylcyclobutene was markedly depressed. The product was identical with an authentic sample of 1,4-diphenylbutane (melting point, mixture melting point, nmr.

1-Phenylnaphthalene (IX) and 1,3-Diphenylbutane (VIII) from Styrene.—Commercial styrene was washed with aqueous sodium hydroxide, water, then dried over sodium sulfate and distilled, bp 30–32° (10 mm). Iodine (0.030 g) was added to 15 ml of this material. The iodine–styrene solution was placed into four Pyrex glass tubes (6-mm outside diameter, 6 in. in length; 0.10 ml per tube). The tubes were cooled in liquid nitrogen, evacuated, sealed, and submerged in a metal bath (250°) for 0.5 hr. The tubes were cooled and then opened. Their contents were dissolved completely in benzene and combined. Vapor phase chromatography of the benzene solution showed the presence of four possible dimeric materials eluted at 30 (2.1%), 42 (66.3%), 58.5 (2.4%), and 101 cm (29.2%) from the air peak.

Material in the 42-cm peak was collected from the gas chromatographic column by condensation into a glass capillary tube. Its infrared and nmr spectra [$(CDCl_3)$ τ 2.80, 2.86 (10 H, phenyl groups), 7.08–7.70 (multiplet, 2.9 H, protons α to phenyl group), 7.87–8.36 (multiplet, 2.0 H, CH_2), 8.70 and 8.81 (doublet, 3.1 H, CH_3)] were identical with those of authentic 1,3-diphenylbutane.[15] Retention times of the two samples on gas chromatography were also identical.

The infrared spectrum of material corresponding to the 101-cm gas chromatographic peak was identical with the infrared spectrum of 1-phenylnaphthalene.[16] See Table I for vpc results.

TABLE I

VAPOR PHASE CHROMATOGRAPHIC RESULTS

Compound	Eluted, cm from air peak
1,2-Diphenylcyclobutene	32
cis-1,2-Diphenylcyclobutane	40
trans-1,2-Diphenylcyclobutane	52
1,4-Diphenylbutane	53
1,3-Diphenylbutane	42
1-Phenyltetralin	62
1-Phenylnaphthalene	101

Vapor Phase Chromatography.—The vapor phase chromatograms were run on an Aerograph gas chromatograph, Model A-90P. A 20% Apiezon L, 60–80 firebrick (5 ft × 0.25 in.) column was used throughout. Helium was used as the carrier gas at a pressure of 20 psi (91 ml/min). The chart speed was 1.7 cm/min. The following temperatures were used throughout: column, 200°; injector, 250°; collector, 220°; detector, 250°.

---

[15] We are indebted to Dr. Herman Pines, Northwestern University, for a sample of 1,3-diphenylbutane.

[16] Sadtler Standard Spectra, No. 21084, The Sadtler Research Laboratories.

Bridged Ring Compounds. VIII.[1] 1-Halobicyclo[2.2.2]octanes

ZENNOSUKE SUZUKI AND KEN-ICHI MORITA

The Basic Research Laboratories, Toyo Rayon Company, Ltd., Kamakura, Japan

Received September 9, 1966

Convenient syntheses of 1-chloro-, 1-bromo-, and 1-iodobicyclo[2.2.2]octanes are described. Reaction of 1-methoxybicyclo[2.2.2]octanes with acetyl halides in the presence of stannic chloride afforded 1-halobicyclo-[2.2.2]octanes in moderate yields. An analogous reaction of 4-methoxybicyclo[2.2.2]octan-2-ones with acetyl chloride afforded a mixture of 4-acetoxybicyclo[2.2.2]octan-2-ones and 4-chlorobicyclo[2.2.2]octan-2-ones. An acid-catalyzed reaction of 1-methoxybicyclo[2.2.2]octanes with acetic anhydride furnished 1-acetoxybicyclo-[2.2.2]octanes.

In recent years functionally substituted bridgehead structures have been of interest in study of the theoretical organic chemistry and, as a result, a number of bridged bicyclic compounds have been prepared. This paper deals with the convenient syntheses of 1-halobicyclo[2.2.2]octane derivatives which are potentially useful starting material[2] for the preparation of bridgehead-substituted derivatives.[3]

1-Chloro- and 1-bromobicyclo[2.2.2]octanes have been obtained by rather difficult and multistep syntheses. Three approches have been used for the syntheses: (1) halogenation of bicyclo[2.2.2]octan-1-ol[4] or bicyclo[2.2.1]heptane-1-methanol[5] with Lucas reagent, (2) the Hunsdiecker reaction of bicyclo[2.2.2]-octane-1-carboxylic acid,[6] and (3) free-radical attack at the bridgehead hydrogen atom of a bicyclic hydrocarbon.[7]

Recently 1-methoxybicyclo[2.2.2]octanone derivatives (**1**) have become readily available.[8] Wolff–Kishner reduction of **1** gave 1-methoxybicyclo[2.2.2]-octanes (**2**). Reaction of **2a**, **2b**, and **2c** each with acetyl chloride in the presence of stannic chloride at room temperature afforded 1-chlorobicyclo[2.2.2]octanes in higher than 80% yield. An analogous reaction of **2a** with acetyl bromide and with acetyl iodide furnished 1-bromobicyclo[2.2.2]octane (**4**) and 1-iodobicyclo[2.2.2]octane (**5**),[9] respectively.[10] Thus, 1-halobicyclooctanes can be prepared from methyl vinyl ketone and 2-methoxy-1,3-butadiene in four steps in an over-all yield of about 50%. The infrared and nmr spectra of the halogenated products are consistent with the assigned structures (*cf.* Table I). These spectra

---

[1] Paper VII: K. Morita and Z. Suzuki, *Bull. Chem. Soc. Japan*, **39**, 1350 (1966).

[2] *Cf.* K. B. Wieberg and B. R. Lowry, *J. Am. Chem. Soc.*, **85**, 3188 (1963).

[3] For the syntheses of bridgehead-substituted bicyclo[2.2.2]octanes, see (a) K. Morita, *et al.*, *J. Org. Chem.*, **30**, 533 (1965); **31**, 229, 3106 (1966); (b) J. C. Kauer, R. E. Benson, and G. W. Parshall, *ibid.*, **30**, 1431 (1965), and literature cited therein; (c) H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **86**, 5183 (1964); (d) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

[4] A. A. Sayingh, thesis, Columbia University Libraries, 1952.

[5] W. P. Whelan, Jr., thesis, Columbia University Libraries, 1952.

[6] F. W. Baker, H. D. Holtz, and L. M. Stock, *J. Org. Chem.*, **28**, 514 (1963); see also ref 3d.

[7] A. F. Bickel, J. Knotnerus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960).

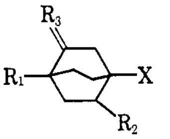
[8] K. Morita, M. Nishimura, and Z. Suzuki, *J. Org. Chem.*, **30**, 533 (1965); K. Morita and Z. Suzuki, *Tetrahedron Letters*, 263 (1964); K. Morita and T. Kobayashi, *J. Org. Chem.*, **31**, 229 (1966).

[9] An attempted preparation of iodobicyclooctane (**5**) by the Hunsdiecker reaction has been failed; *cf.* ref 6.

[10] Reaction of **2a** with acetyl fluoride in the presence of an acid catalyst afforded 1-fluorobicyclo[2.2.2]octane, mp, *ca.* 152° (most parts sublimes without melting). *Anal.* Calcd for $C_8H_{13}F$: F, 14.8; Found: 14.7. A detailed account of this interesting new fluorination reaction and its extention to other system will be reported shortly.

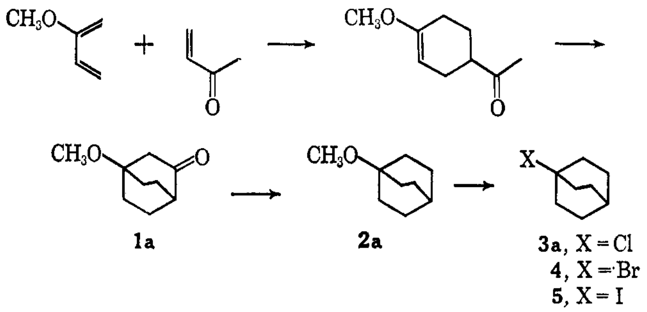
TABLE I

BRIDGEHEAD-SUBSTITUTED BICYCLO[2.2.2]OCTANE DERIVATIVES



Compd	R_1	R_2	R_3	X	Yield, %	Mp or bp (mm), °C	D at 20°	Infrared, ν (C=O or OMe), cm^{-1}	Nmr (CH$_3$), τ	Calcd, % C	Calcd, % H	Calcd, % Halogen	Found, % C	Found, % H	Found, % Halogen
3a	H	H	H_2	Cl	88	101.5–102.5^a	...	...	...	66.43	9.06	24.51	66.12	9.07	24.54
3b	CH_3	H	H_2	Cl	82	77.5–76.0	...	...	9.20^b	68.12	9.53	22.34	67.60	9.50	22.39
3c	CH_3	CH_3	H_2	Cl	90	An oil	...	...	9.16^b 8.79^c	69.54	9.92	20.53	69.35	9.95	20.50
3d	H	$<^{H}_{OAc}$	H	Cl	80	115–120 (15)	1.4883	...	...	59.26	7.46	17.49	59.71	7.61	17.52
4	H	H	H_2	Br	65	63.5–64.5^d	...	...	...	50.81	6.93	42.25	50.72	6.92	42.20
5	H	H	H_2	I	63	27.5–28.5	...	...	...	40.70	5.55	53.75	40.27	5.55	53.10
6a	H	H	=O	Cl	..	118–119	...	1731	...	60.57	6.99	22.35	60.74	7.09	22.13
6b	CH_3	H	=O	Cl	..	59.5–60.0	...	1728	9.08^b	62.61	7.59	20.54	62.71	7.59	20.50
6c	CH_3	CH_3	=O	Cl	..	119.5–120.5 (15)	1.4950	1729	9.12^{b,e}	64.34	8.10	18.99	63.76	8.13	18.97
2a	H	H	H_2	OCH_3	79	185–190 (760)	1.4748	2822 1116 1106	...	77.09	11.50	...	76.99	11.37	...
2b	CH_3	H	H_2	OCH_3	76	81–82 (17)	1.4658	2822 1104	9.23^b	77.86	11.76	...	77.58	11.70	...
2c	CH_3	CH_3	H_2	OCH_3	63	87–88 (12)	1.4665	2824 1101	9.24^b 9.10^b 9.10^f	78.51	11.98	...	78.31	12.01	...

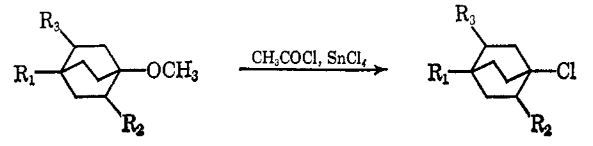
^{a} Lit. mp 103.5–104.5°.[6] ^{b} Bridgehead methyl protons. ^{c} Doublet (J = 7 cps). ^{d} Lit. mp 64–65°[3d] and 58.5–59.5°.[6] ^{e} Multiplet for R_2 methyl protons. ^{f} Doublet (J = 6 cps).



1a **2a** **3a**, X = Cl
4, X = Br
5, X = I

for **3a** and **4** were identical in all respects with the spectra of authentic specimens.[6]

Thionyl chloride and benzenesulfonyl chloride could be used in place of acetyl chloride for the cleavage of ethers. Thus reaction of 1-methoxy-4-methylbicyclo[2.2.2]octane (**2b**) with thionyl chloride in the presence of stannic chloride afforded 1-chloro-4-methylbicyclo[2.2.2]octane (**3b**) in 79% yield. An analogous reaction of **2b** with benzenesulfonyl chloride also furnished **3b**. Treatment of 3-acetoxy-1-methoxybicyclo[2.2.2]octane (**2d**) either with thionyl chloride or with acetyl chloride in the presence of stannic chloride gave 3-acetoxy-1-chlorobicyclo[2.2.2]octane (**3d**).



2a, $R_1 = R_2 = R_3 = H$
b, $R_1 = CH_3$; $R_2 = R_3 = H$
c, $R_1 = R_2 = CH_3$; $R_3 = H$
d, $R_1 = R_2 = H$; $R_3 = OAc$

3a, $R_1 = R_2 = R_3 = H$
b, $R_1 = CH_3$; $R_2 = R_3 = H$
c, $R_1 = R_2 = CH_3$; $R_3 = H$
d, $R_1 = R_2 = H$; $R_3 = OAc$

Reaction of 4-methoxybicyclo[2.2.2]octan-2-one (**1a**) with acetyl chloride in the presence of stannic chloride furnished at 1:1 mixture of 4-chlorobicyclo[2.2.2]octan-2-one (**6a**) and 4-acetoxybicyclo[2.2.2]octan-2-one (**7a**). An analogous reaction of 4-methoxy-1-methylbicyclo[2.2.2]octan-2-one (**1b**) with acetyl chloride gave a mixture of 4-chloro-1-methylbicyclo[2.2.2]octan-2-one (**6b**) and 4-acetoxy-1-methylbicyclo[2.2.2]octan-2-one (**7b**). Structure proof of the products was obtained by a combination of physical and chemical methods. Infrared spectra confirmed the absence of an ether group, and the existence of a carbonyl group. Nmr spectra are also consistent with the assigned structures (*cf.* Table I). Chloride **6b** derived from **1b** was identical in all respects with the sample derived from the reaction of 4-hydroxy-1-methylbicyclo[2.2.2]octan-2-one (**8b**)[8] and thionyl chloride.[11] Reaction of a pyridine solution of **8b** with thionyl chloride furnished sulfite **9** in 80% yield (see Scheme I). Table I lists physical constants of 1-halobicyclo[2.2.2]octan-2-ones.

Reaction of 1-methoxy-4-methylbicyclo[2.2.2]octane (**2b**) with acetic anhydride[16] in the presence of stannic chloride furnished 1-acetoxy-4-methylbicyclo[2.2.2]-

---

(11) It has been reported that reaction of 1-hydroxybicyclo[3.2.2]nonane[3d] and 1-hydroxyadamantane[12] with thionyl chloride afforded the corresponding chloro compounds, whereas 1-hydroxy-7,7-dimethylbicyclo[2.2.1]heptane was unaffected[13] under the similar but more enforced conditions. It has been suggested[14] that the mechanism of the reaction involves the formation of ion pairs as intermediates. The approximate relative rates[12b,15] of solvolyses of 1-bromobicyclo[2.2.1]heptane, 1-bromobicyclo[2.2.2]octane, and 1-bromoadamantane are 1, 10^6, and 10^{11}.

(12) (a) H. Stetter, M. Schwarz, and A. Hirschhorn, *Ber.*, **92**, 1629 (1959); H. Stetter and C. Wulff, *ibid.*, **93**, 1366 (1960); (b) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).

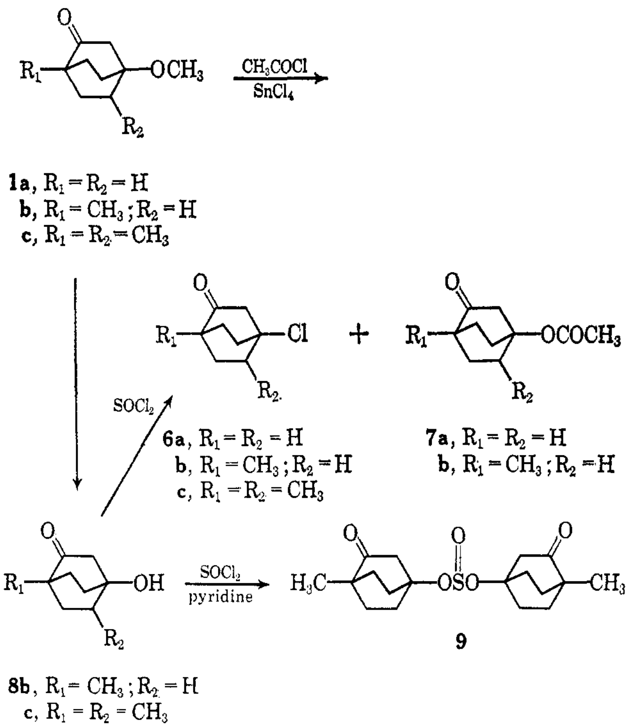
(13) P. D. Bartlett and L. H. Knox, *ibid.*, **61**, 3184 (1939).

(14) (a) D. J. Cram, *ibid.*, **75**, 332 (1953); (b) E. S. Lewis and C. E. Boozer, *ibid.*, **74**, 308 (1952); C. E. Boozer and E. S. Lewis, *ibid.*, **75**, 3182 (1953).

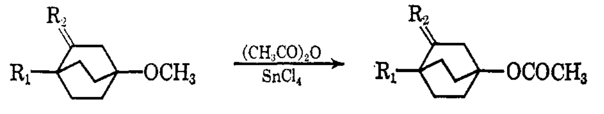
(15) R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); *J. Am. Chem. Soc.*, **86**, 4194 (1964).

(16) *Cf.* C. R. Narayanan and K. N. Iyer, *J. Org. Chem.*, **30**, 1734 (1965).

Scheme I

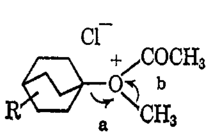


octane (10) in a quantitative yield. Reductive hydrolysis of 10 with lithium aluminum hydride gave 4-hydroxy-1-methylbicyclo[2.2.2]octane (11) which was identical with a sample prepared by Wolff–Kishner reduction of 4-hydroxy-1-methylbicyclo[2.2.2]octan-2-one (8b).[8] An analogous reaction of 4-methoxybicyclo[2.2.2]octan-2-one (1a) with acetic anhydride furnished 4-acetoxybicyclo[2.2.2]octan-2-one (7a).



1a, $R_1 = H; R_2 = O$ 7a, $R_1 = H; R_2 = O$
2b, $R_1 = CH_3; R_2 = H_2$ 10, $R_1 = CH_3; R_2 = H_2$

The mechanism of an acid-catalyzed cleavage of ethers with acyl halides has been suggested[17] which involves an oxonium ion such as 12 as an intermediate.



12

In contrast to the fission b which can proceed either by the S_N1 or S_N2 mechanism, the fission a can proceed only by the S_N1 mechanism. Since mass spectra infer[18] that a methyl carbonium ion is substantially less stable than a 1-bicyclo[2.2.2]octyl ion, it seems reasonable that the acid-catalyzed cleavage of 2 gave 1-halobicyclo[2.2.2]octanes (3) rather than 1-acetoxybicyclo[2.2.2]octanes (10).

The fact that the cleavage of 1 afforded 1-acetoxybicyclo[2.2.2]octan-2-ones (7) as well as 1-chlorobicyclo[2.2.2]octan-2-ones (6) can be rationalized by assuming the effect of the oxo group which destabilizes the carbonium ion formed at the bridgehead position. The electron-withdrawing inductive effects exerted by an oxo group β to the bridgehead position in the bicyclo[2.2.2]octane system have been found to reflect in the pK_a values of 1-bicyclooctylmorpholines. Thus, the introduction of an oxo group in the bicyclic ring resulted in a decrease of the basic strength of the tertiary amine by about 2 pK_a units.[19]

Experimental Section[20]

General Procedure for the Preparation of Substituted 1-Methoxybicyclo[2.2.2]octanes (2) from Substituted 4-Methoxybicyclo[2.2.2]octan-2-ones (1).—To a stirred solution of 19 g (0.34 mole) of potassium hydroxide and 16 ml (0.26 mole) of 80% hydrazine hydrate in 300 ml of diethylene glycol was added 0.1 mole of 4-methoxybicyclo[2.2.2]octan-2-one derivatives (1). After refluxing for 1 hr, the condenser was removed and the distillation apparatus was connected. The stirred mixture was then heated at 200° for 3 hr, during which time a distillate boiling at around 110° was removed. The cooled reaction mixture was poured into 1 l. of water and extracted three times with ether. The ether layer was combined with the extract from the distillate obtained above, washed with water, and dried over sodium sulfate. Ether was distilled through a 10-in.-long packed column. Distillation of the residue gave substituted 1-methoxybicyclo[2.2.2]octanes (2). Yields and physical constants are given in Table I.

General Procedure for Reaction of Substituted 1-Methoxybicyclo[2.2.2]octanes (2) with Acid Chlorides.—Typical examples are described. Analogous reactions were carried out by essentially the same way. Compounds 3a and 3b were isolated by sublimation or by recrystallization from methanol–water, and 3c and 3d by distillation. Physical constants are given in Table I. Yields are those of procedure A.

A. With Acetyl Chloride.—To a stirred mixture of 1.54 g (0.01 mole) of 1-methoxy-4-methylbicyclo[2.2.2]octane (2b) and 1.6 g (0.02 mole) of acetyl chloride was added 10 drops of stannic chloride with ice cooling. After stirring for 0.5 hr, the temperature was allowed to rise to 20 to 25° and stirring was continued at the same temperature for 3 hr. After cooling with ice, 10 ml of water was added and the mixture was stirred for 10 min. Then the mixture was poured into 50 ml of water and extracted twice with 50-ml portions of ether. The ether layers were combined, washed with aqueous sodium bicarbonate and water, and dried over sodium sulfate. Ether was distilled through a 10-in.-long packed column and the residue (1.5 g) was recrystallized from methanol-water to give 1.3 g of 1-chloro-4-methylbicyclo[2.2.2]octane (3b).

B. With Thionyl Chloride.—To a stirred mixture of 0.5 g (3.3 mmoles) of 2b and 2.0 g (16.8 mmoles) of thionyl chloride was added 10 drops of stannic chloride with ice cooling. After the usual work-up as described for procedure A, 0.4 g of 1-chloro-4-methylbicyclo[2.2.2]octane (3b) was obtained.

C. With Benzenesulfonyl Chloride.—To a stirred mixture of 0.4 g (2.6 mmoles) of 2b and 2.0 g (11.4 mmoles) of benzenesulfonyl chloride was added 10 drops of stannic chloride with ice cooling. After the usual work-up followed by distillation *in vacuo*, a mixture of 3b and methyl benzenesulfonate was obtained. Sublimation of the mixture afforded 0.3 g (1.9 mmoles) of 3b. Distillation of the residue of the above sublimation gave methyl benzenesulfonate: bp 130° (12 mm); ν_{max}^{film} 1365 (S=O), 1180 cm⁻¹ (OCH_3).

Reaction of 1-Methoxybicyclo[2.2.2]octane (2) with Acetyl Bromide or Acetyl Iodide. A. With Acetyl Bromide.—A mixture of 22.0 g (0.157 mole) of 2a and 35.0 g (0.284 mole) of acetyl bromide was treated in the same way as that described for the reaction with acetyl chloride. 1-Bromobicyclo[2.2.2]octane (4)[21]

---

[17] (a) R. L. Burwell, Jr., L. M. Elkin, and L. G. Maury, *J. Am. Chem. Soc.*, **73**, 2428 (1951); R. L. Burwell, Jr., *Chem. Rev.*, **54**, 615 (1954); (b) *cf.* G. Snatzke, *Ann.*, **686**, 167 (1965).

[18] J. L. Franklin, *J. Chem. Educ.*, **40**, 284 (1963). We are indebted to Professor Leon M. Stock who informed us of the reference.

[19] Reference 3a, p 3106.

[20] All melting and boiling points are uncorrected. Nmr spectra were obtained on a Varian A-60 spectrometer using carbon tetrachloride as a solvent and the infrared spectra were determined on a Perkin-Elmer Model 125 spectrophotometer.

[21] *Cf.* Table I.

was isolated by sublimation followed by recrystallization from methanol–water.

B. With Acetyl Iodide.—A mixture of 4.5 g (0.032 mole) of **2a** and 10 g (0.059 mole) of acetyl iodide[22] was treated as described above and there was obtained a dark red liquid boiling at 120° (3 mm). When the liquid was decolorized with mercury, it crystallized to afford 4.7 g (0.020 mole) of colorless crystals of 1-iodobicyclo[2.2.2]octane (**5**). An analytical sample was recrystallized from methanol.

2-Acetoxy-4-methoxybicyclo[2.2.2]octane.—An ether solution of 4-methoxybicyclo[2.2.2]octan-2-one (**1a**) was treated with $LiAlH_4$ to give 2-hydroxy-4-methoxybicyclo[2.2.2]octane, bp 95–104° (1.5 mm). Acetylation with boiling acetic anhydride in pyridine gave 2-acetoxy-4-methoxybicyclo[2.2.2]octane: bp 135–140° (18 mm); $n^{20}D$ 1.4742; ν_{max}^{film} 1735 1245 (OAc), 2830, 1115 cm^{-1} (OMe); nmr τ 5.10 (one-proton sextet, J = 4.10 cps), 6.90 (three-proton singlet), 8.01 (three-proton singlet), 8.2–8.7 (11-proton broad multiplet).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.29; H, 9.13.

Reaction of Substituted 4-Methoxybicyclo[2.2.2]octan-2-ones (1) with Acetyl Chloride.—Reaction of 3.1 g (0.020 mole) of 4-methoxybicyclo[2.2.2]octan-2-one (**1a**) with 6.4 g (0.082 mole) of acetyl chloride in the presence of 10 drops of stannic chloride gave, after the usual work-up, 1.7 g of a mixture boiling at 100–105° (4 mm). The mixture was chromatographed on a column of alumina. Elution with petroleum ether (bp 35–65°) and recrystallization from petroleum ether gave 0.8 g (0.005 mole) of **6a**.[21] Fractions eluted with petroleum ether–ether (10:1) were combined and treated with hydroxylamine hydrochloride in ethanol to give 4-acetoxybicyclo[2.2.2]octan-2-one oxime: mp 109–110° (from ether); ν_{max}^{KBr} 3280, 1725, 1245 cm^{-1}.

Anal. Calcd for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.67; N, 7.10. Found: C, 60.94; H, 7.74; N, 6.94.

An analogous reaction of 4-methoxy-1-methyl bicyclo[2.2.2]octan-2-one (**1b**) with acetyl chloride gave a mixture of 4-chloro-1-methylbicyclo[2.2.2]octan-2-one (**6b**)[21] (see below) and 4-acetoxy-1-methylbicyclo[2.2.2]octan-2-one (**7b**). The structure of **7b** was assigned by infrared spectrum.

Reaction of 4-Hydroxy-1-methylbicyclo[2.2.2]octan-2-one (8b) with Thionyl Chloride. A.—A mixture of 20 g (0.126 mole) of **8b** and 45 g (0.378 mole) of thionyl chloride was heated at reflux for 5 hr. After cooling, the mixture was poured into 200 g of crushed ice and extracted twice with 100-ml portions of petroleum ether (bp 35–65°). Combined organic layer was washed with aqueous sodium bicarbonate and water, dried over sodium sulfate, and passed through a column of 30 g of alumina. Elution with petroleum ether (bp 35–65°) and recrystallization from petroleum ether gave 8.0 g (0.047 mole) of 4-chloro-1-methylbicyclo[2.2.2]octan-2-one (**6b**).[21] Identity was established by the comparison of infrared spectra and the mixture melting point.

B.—To a stirred solution of 15.4 g (0.10 mole) of **8b** in 50 ml of pyridine was added 14.2 g (0.12 mole) of thionyl chloride at 0° during a period of 30 min. The mixture was stirred for an additional 30 min and poured into cold water. Crystals were collected by filtration and washed with water. Recrystallization from ethanol gave 14.2 g (0.04 mole) of **9**, mp 146.5–147°.

Anal. Calcd for $C_{18}H_{26}O_5S$: C, 60.99; H, 7.39; S, 9.05; mol wt, 354. Found: C, 61.13; H, 7.40; S, 8.78; mol wt, 354 (osmometry).

Reaction of 4-Hydroxy-1,5-dimethylbicyclo[2.2.2]octan-2-one (8c) with Thionyl Chloride.—A mixture of 5.0 g (0.030 mole) of **8c** and 10 g (0.084 mole) of thionyl chloride was treated similarly and there was obtained 2.7 g (0.015 mole) of 4-chloro-1,5-dimethylbicyclo[2.2.2]octan-2-one (**6c**).[21]

4-Hydroxy-1,5-dimethylbicyclo[2.2.2]octan-2-one (8c).—A mixture of 3 g (1.8 moles) of 4-methoxy-1,5-dimethylbicyclo[2.2.2]octan-2-one (**1c**) and 100 g of anhydrous pyridine hydrochloride was vigorously stirred at 200–220° for 5 hr in an atmosphere of nitrogen. After cooling at 130° (pyridine hydrochloride solidifies below 130°), 200 ml of water was added slowly in order to dissolve pyridine hydrochloride. The mixture was cooled at room temperature and extracted three times with 100-ml portions of ether. The ether extracts were combined, washed with water, and dried over sodium sulfate. Evaporation of ether and distillation of the residue gave 4-hydroxy-1,5-dimethylbicyclo[2.2.2]octan-2-one (**8c**): bp 105–108° (0.9 mm); $n^{22}D$ 1.4932; ν_{max}^{film} 3440, 1720 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.58. Found: C, 71.41; H, 9.58.

Reaction of 4-Methoxy-1-methylbicyclo[2.2.2]octane (2b) with Acetic Anhydride.—To a stirred mixture of 0.5 g (3.3 mmoles) of **2b** and 1.5 g (15 mmoles) of acetic anhydride was added 7 drops of stannic chloride with ice cooling. After stirring at room temperature for 2 hr, water was added and the mixture was extracted with ether. The ether layer was shaken with aqueous sodium bicarbonate and water and dried over sodium sulfate. Distillation of the residue gave 0.6 g (3.3 mmoles) of 4-acetoxy-1-methylbicyclo[2.2.2]octane (**10**), bp 100–102° (15 mm). Reductive hydrolysis of an ether solution of **10** with $LiAlH_4$ gave 1-hydroxy-4-methylbicyclo[2.2.2]octane: mp 101–101.5° (from petroleum ether); ν_{max}^{KBr} 3250, 1087 cm^{-1} (OH).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.20; H, 11.50.

Preparation of 4-Hydroxy-1-methylbicyclo[2.2.2]octane from 8b.—To a stirred mixture of 24 ml (0.39 mole) of 80% hydrazine hydrate, 10 g (0.18 mole) of potassium hydroxide, and 100 ml of diethylene glycol was added 10 g (0.065 mole) of 4-hydroxy-1-methylbicyclo[2.2.2]octan-2-one (**8b**). The mixture was heated at reflux for 1 hr and treated further as described above. The reaction mixture was cooled, poured into 700 ml of water, and extracted three times with 100-ml portions of ether. The combined ether extract was washed with water and dried over sodium sulfate. Evaporation of ether and recrystallization from petroleum ether gave 4.5 g of crystals melting at 100–101°. This material was identical in all respects with a sample obtained above.

Reaction of 4-Methoxybicyclo[2.2.2]octan-2-one (1a) with Acetic Anhydride.—To a stirred mixture of 1.54 g (0.01 mole) of **1a** and 4.0 g (0.039 mole) of acetic anhydride was added 10 drops of stannic chloride with ice cooling. Stirring was continued for 2 hr at room temperature. The mixture was poured into water and extracted with ether. The ether layer was washed with aqueous sodium bicarbonate and water and dried over sodium sulfate. Ether was evaporated and an ethanol solution of the residue was treated with hydroxylamine hydrochloride in a conventional way to afford an oxime of **7a**, mp 110–111°. The oxime was identical in all respects with a sample derived by the reaction of **1a** with acetyl chloride.

Acknowledgment.—The authors wish to thank Professor Leon M. Stock for the identification of **3a** and **4**.

---

[22] J. Thiele and H. Haakh, *Ann.*, **369**, 145 (1909).