Since we had concluded that hydrogen crowding is the major factor causing cyclic monomers to polymerize,[1] it was of interest to examine a few of these compounds in the 1450 cm.$^{-1}$ region to see whether a correlation existed between these frequencies and polymerizability. Unfortunately, as the results in Table IV show, a multiplicity of absorption frequencies was observed and no basis for choosing particular ones was apparent. Therefore, this type of measurement cannot at present be used as a criterion of polymerizability.

Experimental

The absorption spectra were obtained from 0.1 or 0.01% solutions in carbon tetrachloride with a Perkin-Elmer single-beam double-pass spectrometer equipped with a calcium fluoride prism.

Cyclobutanone was obtained from the Aldrich Chemical Co. and was used as received. The other monocyclic ketones were redistilled commercial samples. The bi- and tricyclic ketones were the samples prepared in the preceding article.[10]

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[10] H. K. Hall, Jr., THIS JOURNAL, **82**, 1209 (1960).

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

Synthesis and Polymerization of Bridged Bicyclic Ethers[1]

BY EMERSON L. WITTBECKER, H. K. HALL, JR., AND TOD W. CAMPBELL

RECEIVED JULY 20, 1959

Polycyclohexylene ether has been prepared by an ionic polymerization of 7-oxabicyclo[2:2:1]heptane using catalysts suitable for the polymerization of tetrahydrofuran. This high melting (450°) polyether was obtained as a white powder which was insoluble in most solvents except phenols. The effect of catalyst concentration, temperature, polymerization time and copolymerization with tetrahydrofuran was investigated. *endo*- and *exo*-2-methyl-7-oxabicyclo[2:2:1]heptane polymerized to polyethers melting at 247 and 200°, respectively. Several other oxides of various ring systems were examined for polymerizability.

In the present paper we report an extension to bicyclic ethers of earlier studies[2,3] of the polymerization of atom-bridged bicyclic monomers.

Synthesis of Bridged Ethers.—Dehydration of suitable diols by alumina was used in almost all cases.

7-Oxabicyclo[2:2:1]heptane (I) was readily prepared by literature methods from hydroquinone. 2-Methyl-7-oxabicyclo[2:2:1]heptane was prepared similarly from 2-methylhydroquinone and the *endo*- III and *exo*-isomers II were separated by fractional distillation. Failures to prepare 6-oxabicyclo[3:1:1]heptane (IV) similarly have been recorded on three occasions[4-6] and we were also unsuccessful.

The adducts of butadiene and cyclopentadiene with quinone were hydrogenated and dehydrated similarly to provide in low yields 1,4-endoxodecalin(V) and 1,4-endoxo-5,8-methanodecalin (VI), respectively.

2,3-Benzo-7-oxabicycloheptane (VII) was prepared by adding furan to benzyne and hydrogenating the adduct.[7]

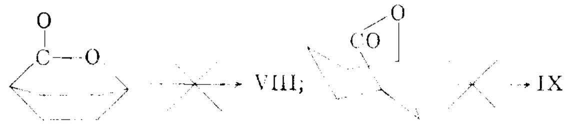
Dehydration of 3- and 4-hydroxycyclohexanemethanols gave other products than the desired 6-oxabicyclo[3:2:1]octane (IX) and 2-oxabicyclo-[2:2:2]octane (VIII), respectively.

7-Oxaspiro[5:3]nonane (X)[8] was not obtained by dehydration of 1,1-dimethylolcyclohexane over alumina, ketones and alcohols forming instead, but could be obtained in moderate yield by the alkaline hydrolysis of the corresponding ditosylate.

8-Oxabicyclo[4:3:0]nonane (XI) was obtained from 1,2-cyclohexanedimethanol. Dehydration of 1,3-cyclohexanedimethanol readily gave 3-oxabicyclo[3:3:1]nonane (XII), but similar treatment of the 1,4-isomer failed to give 3-oxabicyclo[3:2:2]-nonane (XIII). 6-Oxatricyclo[3:2:1:1^{3,8}]nonane (XIV) was prepared from bicyclo[2:2:1]heptene-5-methanol.[9]

In at least two cases oxides have been obtained from chlorohydrins, but not by dehydration of the corresponding diol. Clarke and Owen[15] prepared IX in this way and we obtained ether X similarly. Thus the dehydrohalogenation procedure may be more generally useful though less convenient.

Attempts to reduce two bridged lactones directly to ethers failed. Lithium aluminum hydride gave exclusively diol, while copper chromite and hydrogen did not react.



Polymerization Results

7-Oxabicyclo-[2:2:1]heptane.—Alkyl, acyl, oxonium and hydrogen ions have been used to polymerize tetrahydrofuran.[10] These initiators were applied to 7-oxabicyclo[2:2:1]heptane to give a high melting (450°) polyether. Phosphorus pentafluoride[11] was also effective though slightly irreproducible and was much better than boron trifluoride. Much higher concentrations were re-

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[1] Presented in part at the 129th A.C.S. Meeting, Dallas, Tex., April, 1956, p. 8R of abstract; see also J. P. Wilkins, U. S. Patent 2,764,559 (1956).

[2] H. K. Hall, Jr., THIS JOURNAL, **80**, 6412 (1958).

[3] H. K. Hall, Jr., *ibid.*, **82**, 1209 (1960).

[4] M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 2103, 2108 (1950).

[5] R. B. Clayton and H. B. Henbest, *ibid.*, 1982 (1957).

[6] F. V. Brutcher, *et al.*, *Chemistry & Industry*, 1295 (1957).

[7] G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

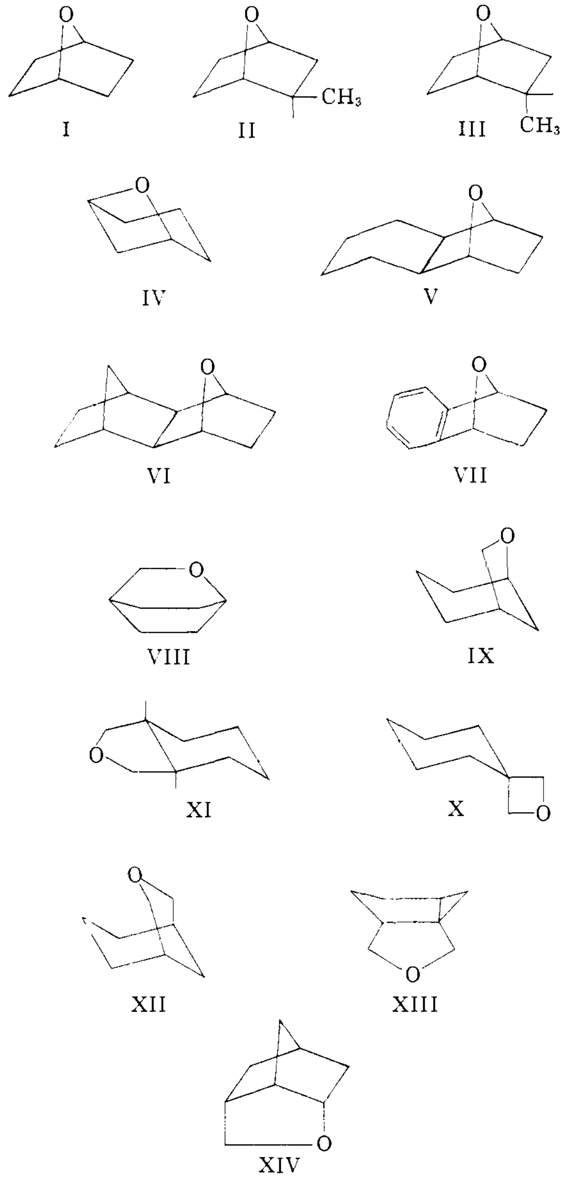
[8] This compound was recently reported by S. Searles, E. F. Lutz and M. Tamres, Abstracts of Spring, 1959, A.C.S. Meeting, Boston, Mass., p. 63-O.

[9] H. A. Bruson and T. W. Riener, U. S. Patent 2,440,220 (1948).

[10] Summarized by K. Hamann, *Angew. Chem.*, **63**, 236 (1951).

[11] T. W. Campbell, U. S. Patent 2,831,825 (1958).

TABLE I



quired for satisfactory rates of polymerization. Catalysts other than Lewis acids were completely ineffective. The following variables were investigated:

Catalyst concentration affected the rate and degree of polymerization (see Table II). As the catalyst concentration was increased, the polymerization time was decreased, but the intrinsic viscosity was little affected. Reproducibility was good in these experiments.

The temperature of the polymerization also affected the rate and degree of polymerization. Side reactions were decreased as the temperature was lowered and, therefore, higher molecular weights were obtained. The polycyclohexylene ether with the highest intrinsic viscosity was polymerized at −18°. The polymerization rate, however, was so slow that it was impractical to use temperatures much below 0°. The effect of temperature on the polymerization of 7-oxabicyclo[2:2:1]heptane is summarized in Table III.

TABLE II

POLYMERIZATION OF 7-OXABICYCLO[2:2:1]HEPTANE AT 0°

Catalyst	Mole %	Cocatalyst	Mole, %	Time, hr.	Yield, %	$[\eta_{inh}]$ (TCE–phenol)
$FeCl_3$	0.015	$SOCl_2$	0.62	70	45.4	0.56
$FeCl_3$	.0225	$SOCl_2$	0.93	23	33.2	.55
$FeCl_3$	.03	$SOCl_2$	1.24	18	36.6	.63
$FeCl_3$	.06	$SOCl_2$	2.48	7	41.6	.51
$FeCl_3$	.12	$SOCl_2$	3.96	5	29.8	.51
$SbCl_3$	.1	Epichlorohydrin	0.2	336	15.8	.61
$SbCl_3$	.2	Epichlorohydrin	.2	336	18.2	.50
BF_3	4.0	Epichlorohydrin	.1	72	4.4	.22
BF_3	0.2	Propylene oxide	.2	336	1.0	..
$SbCl_5$	.1	Propylene oxide	.2	40	22.0	.60
$SbCl_5$	.2	Propylene oxide	.2	40	12.4	.45
$SbCl_5$	.3	Succinic anhydride	1.0	72	29.4	.62
PF_5	12.0	[a]	..	102	58.8	.63
PF_5	..	[b]	..	92	81.0	1.04
$SnCl_4$	2.0	Acetyl chloride	1.0	120	5.6	..
$FeCl_3$	0.04	$SnCl_4$	0.1	72	18.0	0.56
$FeCl_3$	.03	Succinyl chloride	1.24	1168	51.2	.50
$FeCl_3$	.03	Succinyl chloride	0.62	45	36.2	.50
$FeCl_3$	.06	Succinyl chloride	1.24	48	46.8	.56
$FeCl_3$	.03	Succinyl chloride	0.62	132	32.6	.51

[a] 33% solution in ethylene dichloride at −30°. [b] 33% solution in nitrobenzene at −30°.

TABLE III

EFFECT OF TEMPERATURE

Catalyst was 0.03 mole % of $FeCl_3$ and 1.24 mole % of $SOCl_2$

Temp., °C.	Time, hr.	Yield, %	Intrinsic viscosity
21	0.5	75.8	0.23
0	22	27.0	.53
−18	312	25.6	.82

The rate of polymerization is dependent on catalyst concentration and temperature, but if these are kept constant the effect of time can be determined (see Table IV). The molecular weight as indicated by intrinsic viscosity reached a maximum in a relatively short time with a very low yield. The yield increased with time, while the intrinsic viscosity decreased very slightly.

TABLE IV

RATE OF POLYMERIZATION OF 7-OXABICYCLO[2:2:1]HEPTANE

Constant temp., 0°; constant catalyst, 0.03 mole % $FeCl_3$, 1.24 mole % $SOCl_2$

Time, hr.	Yield, %	$[\eta]$
2	2.8	0.73
5	12.0	.61
8	18.6	.62
24	48.2	.59
32	74.0	.56
96	74.0	.56

The fact that the molecular weight is not a function of conversion means that a chain reaction is occurring.

Properties of Polycyclohexylene Ether.—Polycyclohexylene ether melted between 430 and 450°, as observed both visually and by X-ray diffraction. It did not dissolve in *o*-cresol, anisole, dioxane, tetramethylene cyclic sulfone, tetrachloroethane, benzyl benzoate, *o*-dichlorobenzene, nitrobenzene, Dowtherm A, formic acid or other common solvents. The polymer is soluble in a mixture of 66 parts tetrachloroethane and 100 parts phenol. It is very slightly soluble in diphenyl ether and in phenol. An attempt to cast a film from tetrachloroethane–phenol gave an incoherent structure with the appearance of frosted glass.

The molecular weight of a sample with an inherent viscosity of 0.58 was calculated from the chlorine content (1.02%) to be 3800, assuming both terminal groups of the polymer chain to be Cl. An osmotic pressure determination indicated that the molecular weight of a sample with an inherent viscosity of 0.72 in TCE–phenol was in the 5,000–10,000 range. This inherent viscosity is comparable to those shown by polyamides of similar molecular weight.[12] In this case stiffness of the polymer chain, rather than hydrogen-bonding is the main factor in raising the inherent viscosity.

Copolymers.—In order to obtain lower melting, more soluble polyethers, 7-oxabicyclo[2:2:1]heptane was copolymerized with tetrahydrofuran. Copolymers melting below 250° were waxy while the higher melting ones were brittle. For example, starting with a 2-to-1 mole ratio of 7-oxabicyclo-[2:2:1]heptane and tetrahydrofuran, a 39% yield of a polymer with an inherent viscosity of 0.94 was obtained after polymerizing for 30 days at −18°. The polymer melted over the range 235–275°. Other copolymers prepared are listed in Table V. The melting points of copolymers prepared are listed in Table V. The melting points of copolymers were obtained by observing the powder in a capillary tube while heating it in a stirred liquid bath.

Table V

Copolymers of 7-Oxabicyclo[2:2:1]heptane and Tetrahydrofuran[a]

Epoxycyclohexane, mole	Tetrahydrofuran, mole	Temp., °C.	Time, hr.	Yield, %	Inherent viscosity	M.p., °C.
0.05	0.05	19	375	44.0	0.63	149–170
.05	.025	0	96	42.4	.55	220–275
.05	.0125	0	96	77.2	.47	286–305
.05	.005	0	96	50.8	.60	320
.05	.025	−18	480	38.8	.94	233–275[c]
.05[b]	.025	0	115	65.8	.75	250–294

[a] Catalyst used was 0.03 mole % of $FeCl_3$ and 1.24 mole % of $SOCl_2$. [b] Polymerization was run in *p*-dichlorobenzene. [c] X-ray m.p. 260°.

Other 7-Oxabicycloheptanes.—*endo*- and *exo*-2-methyl-7-oxabicycloheptanes polymerized well when treated with PF_5 in nitrobenzene or ethylene dichloride solution at −30°. In Table VI are given the best examples of these experiments. Again some difficulty with reproducibility was encountered, as is often the case with cationic polymerization. Addition of protonic compounds such as water, acetic acid, sulfuric acid or hydrofluoric acid, suppressed polymerization completely.

The methylcyclohexylene oxides were white polymers which, on heating, gave clear melts from which short fibers could be drawn. Films were melt-pressed from material having η_{inh} of 1.5 or more. They were cloudy and only moderately tough. A copolymer of η_{inh} 2.6 (TCE–phenol), cited in Table VI, was melt-spun to a clear bright monofilament. However, it had very low tenacity and could not be drawn.

The methylcyclohexylene ethers were soluble in phenol–tetrachloroethane (100:66 by wt.), *m*-cresol, trifluoroacetic acid, chloroform and chloroform–formic acid (60:40 by vol.). They were insoluble in 90 and 99% formic acids.

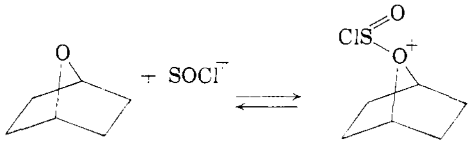
Ethers V and VI gave colored solutions with PF_5 in ethylene dichloride, but no viscosity change or other indication of polymerization was noted. Ether VII, 0.2 g., in 1.0 ml. of toluene at −80° polymerized when a trace of PF_5 was introduced. The solid white polymer, which was probably of low molecular weight, melted at 50° to a viscous liquid.

Other Ethers.—2-Oxaspiro[3:5]nonane polymerized readily when treated with PF_5; XI gave a thick sirupy polymer when treated with fluorosulfonic acid, a catalyst concentration of 3–12% giving a 40–50% yield of polymer of molecular weight 5700–9800 in 72 hours; XII and XIV failed to undergo polymerization.

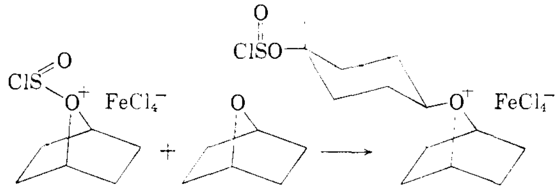
Discussion

Mechanism.—A direct displacement mechanism as

Initiation:

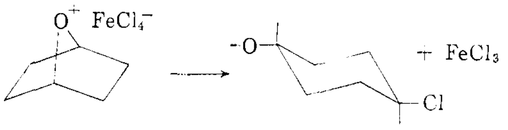


Propagation:



seems reasonable for the polymerizations described here. Termination involves collapse of ion pair to chloroether, since the polymer contains chlorine

Termination:



Analogous mechanisms have been proposed for polymerization of other cyclic ethers.[13]

Polycyclohexylene ether is undoubtedly an all-*trans* polymer, as evidenced by its extremely high melting point. This fact strongly supports the above mechanism. A carbonium ion process would give a mixed *cis–trans* polymer.

Polymerizability and Conformation.—Conformational analysis has been used previously to account for the polymerizability of cyclic carbonyl compounds.[2,3] It also is useful in the case of cyclic ethers. Cyclopentane is known to be strained to the extent of 6 kcal. per mole owing to H–H crowding. Tetrahydrofuran with almost the same bond angles is also strained by 2.9 kcal.,[14] which ac-

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[12] (a) G. B. Taylor, This Journal, **69**, 635 (1947); (b) J. R. Schaefgen and P. J. Flory, *ibid.*, **70**, 2709 (1948).

[13] J. B. Rose, *J. Chem. Soc.*, 546 (1956).

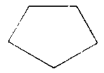
[14] R. C. Cass, S. E. Fletcher, C. T. Mortimer, H. D. Springall and T. R. White, *ibid.*, 1406 (1958).

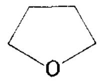
TABLE VI

POLYMERIZATIONS OF 2-METHYL-7-OXABICYCLO[2:2:1]HEPTANES[a]

Monomer, g.	Solvent, ml.	Temp., °C.	Time	Yield, %	M.p., °C.	[η]inh (TCE-phenol)
endo, 26.0	Ethylene dichloride, 50	25	4	95.4	234	0.53
3.0	Nitrobenzene, 9	0	22	90.7	247	0.73
endo, 15 unsubst., 15	Nitrobenzene, 45	−30	120	45.7	260	2.64
exo, 26.0	Ethylene dichloride, 30	−30	90	66.5	200	0.67
exo, 15.0	Ethylene dichloride, 15	−30	100	78.0	200	0.80
exo, 15.0	Ethylene dichloride, 30	−30	100	37.4	200	1.06
exo, 15.0	Ethylene dichloride, 60	−30	100	16.9	200	1.05

[a] Catalyst, gaseous PF_5.

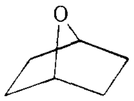




counts for its polymerizability.

7-Oxabicycloheptane exists in the boat form

or



Here angle strain as well as H–H crowding is relieved on polymerization. A single methyl or benzo substituent does not suppress polymerization but a fused cyclohexane or bicycloheptane ring does so.

Ethers VIII, IX and XIII should be polymerizable. Ether XII, however, with two fused chair forms, should be stable as observed.

Acknowledgments.—We are indebted to the following and their associates: Dr. J. P. Wilkins for the original suggestion, Mr. I. D. Plank for the microanalyses, Dr. H. E. Cupery for the hydrogenations, Mr. H. Thielke for vapor-phase chromatograms, Dr. R. Zbinden for infrared spectra, Dr. P. W. Morgan for helpful encouragement, and Mr. C. Mardecz and Mr. G. Elechko for technical assistance.

Experimental

Diols.—Cyclohexane-1,4-diol and 2-methylcyclohexane-1,4-diol were prepared by hydrogenation of the corresponding hydroquinones in ethanol solution over ruthenium dioxide.

3-Hydroxycyclohexanemethanol was prepared by lithium aluminum hydride reduction of 6-oxabicyclo[3:2:1]octan-7-one. It had b.p. 129–132° (1.5 mm.) (lit.[15] b.p. 117–125° (0.5 mm.)). 4-Hydroxycyclohexanemethanol was prepared similarly from 2-oxabicyclo[2:2:2]octan-3-one, b.p. 122° (1.0 mm.) (lit.[16] b.p. 135–147° (3 mm.)). No trace of bicyclic ether was obtained in either reduction. Attempted hydrogenolysis of the latter lactone over copper chromite failed, no hydrogen being absorbed and only starting material being recovered.

Cyclohexane-1,1-dimethanol was supplied by the Polychemicals Department, E. I. du Pont de Nemours & Co., Inc.

Cyclohexane-1,2-dimethanol was prepared by copper chromite reduction of diethyl cyclohexane-1,2-dicarboxylate, in turn prepared from diethyl phthalate by hydrogenation over ruthenium dioxide. It had b.p. 125–130° (3.0 mm.) (lit.[17] b.p. 110–130° (0.3 mm.)). Cyclohexane-1,3-dimethanol, b.p. 120–122° (0.25 mm.) (lit.[18] b.p. 112–114° (0.1 mm.)) was prepared similarly from dimethyl isophthalate. The 1,4-isomer was prepared analogously from dimethyl terephthalate.

Cyclopentanediol, b.p. 115–133° (11 mm.) (lit.[19] b.p. 115° (6 mm.)), was prepared by hydrogenation of cyclopentenediol (Columbia–Southern Co.) over ruthenium dioxide. The infrared spectrum showed a trace of carbonyl, owing to ready autoxidation, but no olefinic linkage.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.8; H, 9.9. Found: C, 58.3; H, 9.7.

1,5-Naphthalenediol was recrystallized twice from nitromethane and hydrogenated over ruthenium dioxide in ethanol. The product crystallized well: crop 1, m.p. 163–205° (mostly at 186°); crop 2, m.p. 136–163° (mostly at 145°).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.5; H, 10.7. Found: C, 70.7, 70.8; H, 10.5, 10.8.

Monocyclopentadienequinone, m.p. 73–74° (lit.[20] m.p. 77–78°), and monobutadienequinone, m.p. 56–57° (lit[21] m.p. 58°), were prepared by literature methods. Hydrogenation over ruthenium dioxide in ethanol proceeded smoothly. Filtration and evaporation left the diols as colorless viscous glasses.

Bicyclohept-5-ene-2-methanol, b.p. 95–97° (14 mm.), $n^{25}D$ 1.4981 (lit.[22] b.p. 92–95° (13 mm.)), was obtained by the addition of allyl alcohol to cyclopentadiene.

Oxides.—Dehydrations of the diols were accomplished by heating with an equal weight of alumina (Alcoa Activated Alumina, Grade F-20) to 250–320° until distillation ceased. For most small-scale reactions this required 1–2 hours, while the large-scale preparations were allowed to distil overnight. Pressure was maintained at 150 mm. in the distillation of the high boiling fused-ring oxides. The distillate was dried and subjected to a preliminary vacuum distillation through a Claisen head, and was then fractionated in a spinning band column.

7-Oxabicyclo[2:2:1]heptane, obtained in 34% yield, had b.p. 119.0–119.5° (lit.[23] b.p. 117–118°), $n^{25}D$ 1.4469 (lit.[24] $n^{20}D$ 1.4477).

Similarly, a mixture of *exo*- and *endo*-2-methyl-7-oxabicyclo[2:2:1]heptanes was obtained by heating 2-methylcyclohexane-1,4-diol with alumina. These were separated in a 125-cm. Podbielniak column by Dr. H. Eatough and the purity of each was established as <99.9% by vapor phase chromatography.

Isomer A, b.p. 133.0–134.0°, $n^{25}D$ 1.4449, was obtained in 24.4% yield on a 2-kg. scale.

Anal. Calcd. for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 75.2, 74.8; H, 11.0, 10.8.

Isomer B, b.p. 138.5–140.0°, $n^{25}D$ 1.4497, was obtained in 5.5% yield on the same scale.

Anal. Found: C, 75.0, 74.8; H, 11.0, 11.0.

A 14.8% yield of intermediate fraction consisting of mixed isomers was also obtained.

According to Allinger's rule,[25] isomer A is *exo*-2-methyl-7-oxabicyclo[2:2:1]heptane, while isomer B is the *endo* compound.

---

(15) M. F. Clarke and I. N. Owen, *J. Chem. Soc.*, 2108 (1950).

(16) L. N. Owens and P. A. Robins, *ibid.*, 326 (1949).

(17) G. A. Haggis and L. N. Owen, *ibid.*, 389 (1953).

(18) G. A. Haggis and L. N. Owen, *ibid.*, 399 (1953).

(19) L. N. Owen and P. N. Smith, *ibid.*, 4035 (1952).

(20) W. Albrecht, *Ann.*, **348**, 31, 47 (1906).

(21) O. Diels and K. Alder, *Ber.*, **62**, 2361 (1929).

(22) K. Alder and E. Windemuth, *ibid.*, **71B**, 1939 (1938).

(23) E. A. Fehnel, S. Goodyear and J. Berkowitz, THIS JOURNAL, **73**, 4978 (1951).

(24) R. C. Olberg, H. Pines and V. N. Ipatieff, *ibid.*, **66**, 1096 (1944).

(25) (a) N. L. Allinger, *ibid.*, **79**, 3445 (1957); (b) *Experientia*, **10**, 328 (1954).

2-Oxaspiro-(3:5)-nonane.—Forty-three grams of cyclohexane-1,1-dimethanol in a mixture of 100 ml. of pyridine and 100 ml. of chloroform was mixed at 0° with 114 g. of toluenesulfonyl chloride in 200 ml. of 1:1 chloroform–pyridine over a period of one hour. The mixture was allowed to warm at room temperature and then warmed overnight gently. The mixture was poured into water and the chloroform removed on the steam-bath and the coarse crystalline solid was filtered and dried. The solid was mixed intimately with 50 g. of potassium hydroxide and 50 g. of sodium hydroxide and heated at 250–300° in a vacuum. The distillate consisted of essentially pure cyclic ether containing less than 20% of unsaturated compound. This liquid was dried and distilled through a micro spinning band column, b.p. 64° (14 mm.). The yield of analytically pure material was 6.9 g. A vapor phase chromatogram indicated purity of greater than 99.7%, while the infrared spectrum showed no detectable impurities.

Anal. Calcd. for $C_8H_{14}O$: C, 76.2; H, 11.1. Found: C, 76.1; H, 11.4.

Treatment with PF_5 at 0° caused a white polymer to form slowly.

8-Oxabicyclo[4:3:0]nonane: the method of Haggis and Owen[17] gave an 84% yield of oxide, b.p. 69.5° (21 mm.) (lit. b.p. 65–66° (9 mm.)).

2,3-Benzo-7-oxabicyclo[2:2:1]heptane was prepared according to Wittig and Pohmer.[7,26]

3-Oxabicyclo[3:3:1]nonane.—The crude distillate obtained from 70 g. of cyclohexane-1,3-dimethanol and 70 g. of alumina (4 hours at 250–300°, 150 mm.) was taken up in ether, dried and evaporated. The oily residue was extracted four times with 150-ml. portions of hexane. The hexane extracts were filtered through Celite and evaporated to a small volume whereupon crystallization occurred. Cooling and filtration gave 9.0 g. (14.7%) of white crystals, m.p. 135–138° (sealed capillary) (lit. m.p. 113–114°,[17] 120°.[27] The infrared spectrum showed the absence of unsaturation, carbonyl and hydroxyl groups.

6-Oxatricyclo[3:2:1:1]$^{(3,8)}$nonane was obtained as described by Bruson and Riener,[9] m.p. 111–113° after crystallization from hexane at −80° (lit.[9] m.p. 100–105°) (sealed capillary).

1,4-Endoxo-5,8-methanodecalin.—This crude oxide obtained from 86 g. of diol and processed as described above was distilled in a spinning band column to give an inhomogeneous yellow product, b.p. 89–115° (16 mm.), 17.9 g. This material, 13.5 g., was dissolved in 75 ml. of acetone and treated with 230 ml. of a solution prepared from 20 g. each of potassium permanganate and magnesium sulfate in 750 ml. of water. A permanent purple coloration was observed at this point. The reaction mixture was decolorized with SO_2 and extracted with hexane. The hexane extracts were washed with 5% sodium hyroxide, water, and distilled in a semi-micro spinning band column. After a forerun, b.p. 78–91° (17 mm.), 2.7 g., the colorless pure bridged oxide, b.p. 91° (17 mm.), 4.7 g., $n^{25}\mathrm{D}$ 1.5081–1.5098, stereochemistry unknown, was collected. It had a sharp penetrating odor. The infrared spectrum showed the absence of unsaturation, carbonyl and hydroxyl groups, and was consistent with the assigned structure.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83; O, 9.74. Found: C, 80.57, 80.58; H, 9.97, 9.88; O, 9.27.

1,4-Endoxodecalin.—The crude oxide obtained from 100 g. of butadienequinone was dried and extracted twice with hexane. The hexane extracts were filtered through Celite and distilled in a spinning band column to give an inhomogeneous yellow product, b.p. 72–126° (16 mm.), 31.9 g. A center fraction, b.p. 97–115° (16 mm.), 9.84 g., was decolorized with 175 ml. of permanganate solution as described above. Distillation of the final product in a semi-micro spinning band column gave, after 2.9 g. of forerun, the colorless oxide, b.p. 84° (17 mm.), 3.1 g., $n^{25}\mathrm{D}$ 1.4889–1.4908. It had an intensive sharp odor.

Anal. Calcd. for $C_{10}H_{16}O$: O, 10.5. Found: O, 10.36.

The infrared spectrum showed that unsaturation, carbonyl and hydroxyl groups were absent and was consistent with the assigned structure.

Other Dehydrations.—The following diols underwent dehydration to form mixtures of products from which no bridged oxides could be isolated: cyclopentanediol, 3- and 4-hydroxycyclohexanemethanols, and cyclohexane-1,1- and 1,4-dimethanols. The following diols were recovered largely unchanged: decalin-1,5- and 1,8-diols and bicycloheptanediol.

Also, 3-cyclohexenol, b.p. 70–72° (13 mm.), $n^{25}\mathrm{D}$ 1.4832, and 3-cyclohexenemethanol, $n^{25}\mathrm{D}$ 1.4750, gave no bridged oxides when distilled from alumina.

Polymerizations.—The monomer, 5–25 g., was cooled to 0 or −30° and the catalyst was added. The flask was stopped and left in the refrigerator. When the polymerization was completed, as evidence by a solid plug or no further solidification, the polymer was ground up, slurried in ether, washed with water and acetone, filtered and dried. The ether slurry washed the polymer free of excess catalyst, unpolymerized 7-oxabicyclo[2:2:1]1-heptane and low molecular weight materials. No polymerization went entirely to completion. The yields ranged from 0–77.6%; the average polymer was obtained in 45–50% yield.

Analysis of a sample of polycyclohexylene ether with an intrinsic viscosity of 0.58 gave: C, 71.85; H, 10.39; Cl, 1.02. Calcd. for $(C_6H_{10}O)n$: C, 73.5; H, 10.2. Theoretical values do not take end groups into consideration.

In the catalyst complex ferric chloride–thionyl chloride, both of which were added as 10% solutions in ether, the ferric chloride was used successfully in quantities ranging from 0.015 mole % to 0.12 mole % and the thionyl chloride from 0.62 mole % to 3.96 mole %. No polymerization took place when the catalyst was cut below these minimum amounts. A 20–1 ratio of thionyl chloride to ferric chloride proved to be the most favorable ratio. A 5–1 ratio did not cause polymerization. The polymerization results were satisfactorily reproducible.

Phosphorus pentafluoride was used in either of two ways. Gas from a cylinder was bubbled into a solution of the monomer with swirling at −5 to 30° until a faint yellow-orange persisted. More intensely colored solutions led to lower molecular weight. Alternatively, benzenediazonium hexafluorophosphate, Phosfluorogen A (Ozark–Mahoning Co.) was heated in a distillation setup at 150–160° and the PF_5 was swept over 1–2 hours into the monomer solution with dry nitrogen. The salt was used in 3–12-g. (1.3–5.3 g. of PF_5) quantities for 25 g. of monomer. Polymerization was somewhat erratic, certain runs failing to develop color or to polymerize. Nevertheless, PF_5 usually gave higher molecular weight products than the chloride catalysts and was much better than BF_3.

Best results were obtained by conducting the reaction in 33% solution at −30°. The results in the various solvents were: nitrobenzene = ethylene dichloride > 2,4-dimethyl-sulfolane > no solvent. Polymerization was accompanied by the appearance of deeply colored solutions which were immediately decolorized by water or alcohol. The polymers were always pure white.

Other Catalysts.—7-Oxabicyclo[2:2:1]heptane containing a little lithium aluminum hydride gave no polymer after several weeks at room temperature. Dr. R. Taylor found that sodium cyclohexyl oxide was also ineffective. At 100° calcium or barium carbonate was without effect after 100 hours. The isomeric methyl 7-oxabicyclo[2:2:1]heptanes were not polymerized by powdered KOH after 100 hours at room temperature.

WILMINGTON, DEL.

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(26) We are indebted to Dr. H. E. Simmons for a sample of the benzyne–furan adduct.

(27) A. T. Blomquist and J. Wolinsky, THIS JOURNAL, **79**, 6025 (1957).