Polymerization was observed as an increase in viscosity of the molten lactam or as formation of a glass or a solid mass. The tubes were cooled, broken, open, extracted with water and acetone and dried.

The following lactams and amides were unchanged under the polymerization conditions except for darkening. No viscosity increase or formation of solid or glass were observed, and the products always dissolved readily in acetone–water mixtures; II, IV, VI, VIII, X and XXI.

The inherent viscosity is defined as ($\ln \eta_{rel})/c$, where c is 0.5 g. of polymer per 100 ml. of solution, or 2 in η_{rel}. The polymer melting temperature was determined approximately by pressing a small portion of polymer firmly with a spatula and moving it along a calibrated heated bar. The temperature at which the turbid, opaque trail on the bar gave way to a clear melt was taken as the melting point.

The polymers of Table IV were all soluble in sulfuric acid, *m*-cresol, 90 and 99% formic acids, chloroform–formic acid (60:40 by vol.) and trifluoroacetic acid, except that the polymer from XXVI gave two liquid phases in the last solvent.

Spectra.—The infrared spectra of all compounds encountered in this investigation were measured routinely and supported the proposed structures. In particular, all of the nortricyclene derivatives absorbed at 12.3–12.4 μ, as first noted by Roberts, *et al.*[19]

WILMINGTON, DEL.

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

Infrared Carbonyl and Carbon–Hydrogen Frequencies in Bridged Bicyclic Ketones

BY R. ZBINDEN AND H. K. HALL, JR.

RECEIVED JULY 20, 1959

Infrared measurements of the C=O and C—H stretching frequencies of monocyclic and bridged bicyclic ketones have been made. The frequencies have been correlated with ring size and geometrical structure of the molecules.

In this paper we report infrared absorption measurements on the C=O and CH_2 stretching vibrational bands of monocyclic and bridged bicyclic ketones. The frequencies are correlated with ring size and geometrical structure of the molecules. The experimental results are summarized in Table I.

C=O Stretching Frequencies.—The discussion of the C=O stretching frequencies is straightforward in view of the results on other cyclic carbonyl compounds described in a previous paper,[1] wherein references to earlier work are given (see also ref. 2). The carbonyl frequency is known to increase with decreasing ring size by going from an open chain or 7-membered ring to a six-, five- and four-membered ring. The frequencies listed in Table II show that the same is true for bi- and tricyclic ketones, where the C=O frequency is determined by the size of the smallest ring (*cf.* ref. 1).

The frequency shifts are due to bond angle deformations. Halford[3] has given a formula for the frequency ν as a function of substituent bond angle φ

$$\nu(\text{in cm.}^{-1}) = 1278 + 68k - 2.2\,\phi \text{ in degrees}$$

where k is the carbonyl stretching force constant for an aliphatic ketone. He showed that $k = 10.2 \pm 0.3$ practical units ($= 10^{-5}$ dynes/cm.) and is almost independent of the bond angle φ. This means that the linear relationship can be used to calculate the bond angle φ from the observed frequencies. The results of such a calculation are listed in Table II in parenthesis behind the frequency values. The absolute error in ϕ is ±9° due to the uncertainty in k. However, the difference between any two angles listed in Table II should be much more precise.

CH_2 Stretching Vibrations.—Similarly, the CH_2 stretching frequencies can be correlated with ring size, more specifically with the bond angle of the CH_2 group substituents. This particularly has been noticed for cyclopropane rings[1,4,5] where this bond angle is reduced from 109 to 60°. Similar band shifts have also been observed for unsaturated CH stretching vibrations due to bond angle deformations.[6–8]

First we want to point out that the difference Δ (Table I) between the asymmetric and symmetric CH_2 stretching frequency is approximately constant and has a value between about 60 and 90 cm.$^{-1}$. This was also true for a number of compounds previously analyzed.[1] In some cases this rule of constant difference was actually used as a guide for band assignments. A qualitative explanation can be given as follows: Consider the two CH bonds in a CH_2 group as two coupled dipoles of the same frequency. Such a system has two normal vibrations, a symmetric and an antisymmetric one. The frequencies will split due to vibrational interaction. Reduction in substituent bond angle increases the force constant of both dipoles but does not change their interaction appreciably which means that the two components shift by about the same amount toward higher frequencies. For this reason the symmetric or the antisymmetric vibrational frequency could be used as a measure for bond angle deformations. In this work we have chosen to use their average (Table I) to get slightly better accuracy. It is the shift of this $\nu_{av.}$ which will be discussed in the following paragraphs.

We assume a linear relationship between the substituent bond angle and the average CH_2 frequency in analogy to the carbonyl band shifts. The

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[1] H. K. Hall, Jr., and R. Zbinden, THIS JOURNAL, **80**, 6428 (1958).

[2] T. Burer and H. H. Gunthard, *Helv. Chim. Acta*, **39**, 356 (1956).

[3] J. O. Halford, *J. Chem. Phys.*, **24**, 830 (1956).

[4] R. N. Jones and C. Sandorfy in "Technique of Organic Chemistry," Vol. IX, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 444–459.

[5] J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5030 (1951).

[6] K. W. F. Kohlrausch, R. Seka and O. Tramposch, *Ber.*, **75**, 1385 (1942).

[7] N. L. Allinger, THIS JOURNAL, **80**, 1953 (1958).

[8] P. von R. Schleyer, *ibid.*, **80**, 1700 (1958).

TABLE I

CARBONYL AND C-H STRETCHING VIBRATIONS IN MONOCYCLIC AND BRIDGED BICYCLIC KETONES

	Compound[a]	Smallest ring size for ring containing C=O group	C=O stretching vibration, cm.$^{-1}$		CH$_2$ stretching vibrations, cm.$^{-1}$					Smallest ring involving CH$_2$ groups	Other CH stretching vibrations assignment uncertain
			% Concn. in CCl$_4$	This work	% Concn. in CCl$_4$	ν_{asymm}[b]	ν_{symm}	$\Delta\nu$[c]	$\nu_{av.}$[d]		
1	Cyclobutanone	4	0.1	1791[e]	0.1	3006m	2931m	75	2969	4	
						2976s	2895w	81	2936		
2	Cyclopentanone	5	.01	1750	.1	2970s	2921w	49	2946	5	
						2948m	2885m	63	2917		
3	Cyclohexanone	6	.1	1717	.1	2942s	2867m	75	2905	6	
4	Cycloheptanone	7	.1	1704	.1	2935s	2859m	76	2897	7	
5	Cycloöctanone	8	0.01, 0.1	1701	.01	2936m	2861w	74	2898	8	
6	Bicyclo[2:2:1]heptan-2-one (Ia)	5	0.01, 0.1	1751	.1	2969s	2882m	87	2926	5	2918w prob. *t*-CH group
7	4,7-Methanohexahydroindan-5-one (Va)	5	0.1	1750	.1	2958s	2868m	90	2913	5	2929w prob. *t*-CH group
8	1,4,5,8-Bis-endomethylene-2-decalone (VIIa)	5	.1	1748	.1	2956s	2887w	69	2922	5	3054 prob. due to unsaturated impurity
9	Nortricyclanone (IXa)	5	.1	1768 1755	.1	2951s	2877s	74	2914	5	3078w 3032w } 3-membered ring 2918w prob. *t*-CH group
10	Tetracyclo[3:2:1^{3,8}:0^{2,4}]nonan-6-one (IV)	5	.1	1751	.1	2957s	2871s	86	2914	5	3070m 3-membered ring
						2985w	2914w	71	2949		
11	Tetracyclo[3:3:1:1^{3,9}:0^{2,4}]decane-6-one (VII)	6	.1	1715	.1	2941s	2871m	70	2901	6	3069w 3008w } 3-membered ring
				1718		2982w	2910w	72	2946	Bridge 5	
12	Bicyclo[2:2:2]octan-2-one (XIa)	6	.01	1731	0.1, 0.01	2948s	2873m	75	2910	6	2915 w prob. *t*-CH group
13	Bicyclo[3:2:1]octan-2-one (XVa,b)	6	.01	1717	0.1	2944m	2870m	74	2907	6	
14	Bicyclo[3:3:1]nonan-3-one	6	.1	1717 1706	.1	2929broad	2857m	72	2893	6	2883w
15	9,10-Ethanoanthracen-9-one	6	.1	1740 1731							3078m 3048w } aromatic CH 3031m 2932w 2960m } ? 2922m
16	Bicyclo[2:2:1]heptane				.1	2955s	2871s	84	2913	6	2920m prob. *t*-CH
17	Bicyclo[2:2:1]heptadiene				.1	2940m	2871m	69	2905	Bridge 5	3072m 2993s } unsaturated CH 2987w most prob. *t*-CH

[a] Roman numerals refer to the preceding article (ref. 10) for all compounds except nos. 10 and 11. The latter are described by H. K. Hall, Jr., *J. Org. Chem.*, in press. [b] w = weak, m = medium, s = strong band intensities only relative within one compound. [c] $\Delta\nu = \nu_{asymm.} - \nu_{symm.}$ [d] $\nu_{av.} = (\nu_{asymm.} + \nu_{symm.})/2$. [e] P. von R. Schleyer, Ph.D. Thesis, Harvard, 1955, gives 1792 cm.$^{-1}$.

TABLE II

CARBONYL STRETCHING FREQUENCIES AND SUBSTITUENT BOND ANGLE AS A FUNCTION OF RING SIZE

Ring size 4	5	6	7	8
1791 (82°)^{1a}	1750 (101°)^{2}	1717 (116°)^{3}	1704 (121°)^{4}	1701 (123°)^{5}
	1751 (100°)^{6}	(1718) (115°)^{11}		
		(1715) (117°)		
	1750 (100°)^{7}	1731^{b} (109°)^{12}		
	1748 (102°)^{8}	1717 (116°)^{13}		
	(1768)^{b} (92°)^{9}	(1717) (116°)^{14}		
	(1755) (98°)	(1706) (121°)		
	1751 (100)^{10}	(1740)^{b} (105°)^{15}		
		(1731) (109°)		

[a] The superscript numbers refer to the compounds listed in Table I. [b] Frequencies are somewhat higher than expected due to bond angle deformation because of unusual structure.

TABLE III

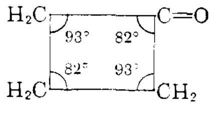
AVERAGE OF SYMMETRIC AND ANTISYMMETRIC CH_2 STRETCHING VIBRATIONS AS A FUNCTION OF RING SIZE

Ring size 4	5	6	7	8
(2969)^{a} (82°)^{1}	(2946)^{c} (90°)^{2}	2905 (104°)^{3}	2897 (106°)^{4}	2898 (106°)^{5}
(2936)^{b} (93°)	(2917)^{c} (100°)			
	2926 (97°)^{6}	2901 (105°)^{11}		
	2913 (101°)^{7}	2910 (102°)^{12}		
	2922 (98°)^{8}	2907 (103°)^{13}		
	2914 (101°)^{9}	2893 (108°)^{14}		
	(2914) (101°)^{10}	2913 (101°)^{16}		
	(2949)^{d} (89°)			
	2946^{d} (90°)^{11}			
	2905^{e} (104°)^{17}			

[a] CH_2 group opposite C=O group. [b] CH_2 groups adjacent to C=O group. [c] Cannot be assigned to specific CH_2 groups in the ring. [d] Bridge CH_2 group. [e] Bridge CH_2 group.

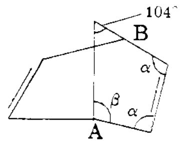
straight line for such a correlation was determined by two points. We have chosen chloro- and bromocyclopropane[5] as one point ($\nu_{av.} \sim 3035$ cm.$^{-1}$, bond angle = 60°) and an open chain CH_2 group as a second one ($\nu_{av.} = 2890$ cm.$^{-1}$, bond angle = 109°). The bond angles listed in Table III (in parentheses after the frequency values) were calculated from a linear relation determined by these two points. Some results will now be discussed in terms of the geometrical structure of the compounds.

Cyclobutanone has two different kinds of CH_2 groups corresponding to substituent bond angles of 82 and 93°, respectively. Since the bond angle at the carbonyl group is 82° (Table II) the molecule must have the following shape which corresponds



to a slightly puckered ring. Cyclopentanone has also different kinds of CH_2 groups (bond angles 90° and 100°), but by this work alone they cannot be identified with specific groups in the ring.

It is interesting to note that the bridge CH_2 substituent bond angle can vary over a wide range among different structures. For compounds 6, 7, 8, 9, 12, 13 and 16 (Table I) it must be similar to the other bond angles (about 100°) since no additional absorption bands at higher frequencies are observed. For 10 and 11 it is only about 90° due to the unusual structures while for the bridge in bicycloheptadiene (17) the angle is 104°. This high value can be explained by the fact that atoms A and B are relatively far apart



since the bond angle α at the double bond prefers to be 120° rather than 109°. This causes the angle β to be relatively small and the tertiary CH stretching frequency at 2987 cm.$^{-1}$ is about 70 cm.$^{-1}$ higher than in compounds 6, 9, 12 and 16 (Table I).

TABLE IV

C–H BENDING VIBRATIONS

Concentration 0.1% in carbon tetrachloride.

	Cyclic monomer	Size of smallest ring	Frequencies, cm.$^{-1}$
1	Pyrrolidone	5	1467, 1449
2	2-Piperidone	6	1466, 1447
3	Caprolactam	7	1471, 1457, 1444, 1437
4	Caprylolactam	9	1475, 1457, 1453
5	6-Azabicyclo[3:2:1]octan-7-one	5	1467, 1461, 1444, 1429
6	2-Azabicyclo[2:2:2]octan-3-one	6	1481, 1457, 1449
7	γ-Butyrolactone	5	1460, 1424
8	δ-Valerolactone	6	1461, 1444, 1433
9	ξ-Caprolactone	7	1456, 1446, 1435
10	6-Oxabicyclo[3:2:1]octan-7-one	5	1467, 1457, 1446
11	2-Oxabicyclo[2:2:2]octan-3-one	6	1471, 1456, 1448, 1439

C–H Bending Frequencies.—Recently Chiurdoglu, de Proost and Tursch[9] showed the existence of a correlation between the C–H bending frequencies and the degree of transannular hydrogen crowding in a series of cycloalkanes and cycloalkyl halides.

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[9] G. Chiurdoglu, R. de Proost and B. Tursch, *Bull. soc. chim. Belges*, **67**, 1958 (1958).

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

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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]

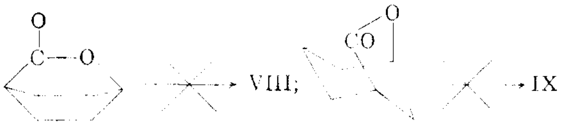
Dehydration of 3- and 4-hydroxycyclohexanemethanols gave other products than the desired 6-oxabicyclo[3:2:1]octane (IX) and 2-oxabicyclo-[2:2:2]octane (VIII), respectively.

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).