

**Reaction of Cumylpotassium with *t*-Nitrocumene.**—Cumylpotassium was prepared by the method of Morton<sup>22</sup> from 7.8 g. (0.20 g.-atom) of potassium sand, 24.0 g. (0.20 mole) of cumene, and 10.6 g. (0.10 mole) of 1-chloropentane in 75 ml. of heptane. *t*-Nitrocumene (16.8 g., 0.10 mole) was added with stirring to the deep red cumylpotassium solution while maintaining the temperature at  $-10$  to  $-5^\circ$  during its addition. Stirring at this temperature was continued for 1 hr. after the addition was completed. *t*-Butyl alcohol, 20 ml., was then added to destroy any excess potassium. The solution was filtered to give 16.0 g. of colorless solid which assayed for a mixture of 7.25 g. of potassium chloride and 9.20 g. of potassium nitrite, in yields of 97 and 107%, respectively. The filtrate, 79.0 g., contained  $2.6 \times 10^{-4}$  mole of di-*t*-cumylnitroxide having a nitrogen h.c.c. of 14.9 gauss. Analysis of the filtrate by v.p.c. showed the presence of bicumyl (7.6 g., 42% yield based on reacted *t*-nitrocumene),  $\alpha$ -methylstyrene (0.9 g.), cumene (13.3 g.), *t*-nitrocumene (4.0 g.), and four unidentified components (combined weight, 1.9 g.) which were not further investigated.

**Reaction of Cumylpotassium with *t*-Nitrobutane.**<sup>21a</sup>—*t*-Nitrobutane (10.2 g., 0.10 mole) was added to 0.10 mole of cumylpotassium in 75 ml. of heptane at  $-15^\circ$  over a period of 1 hr. After stirring for 0.5 hr., the reaction mixture was allowed to warm to room temperature and *t*-butyl alcohol (20 ml.) was added to destroy excess potassium. The mixture was hydrolyzed with 100 ml. of water, extracted with ether, and the extract dried over magnesium sulfate. Evaporation of the solvent *in vacuo* resulted in the loss of *t*-nitrosobutane and left a red oily residue which was analyzed by v.p.c. Among the 22 components detected, heptane (5.08 g.), *t*-nitrobutane (0.091 g.), cumene (13.8 g.), di-*t*-butylnitroxide (0.585 g.), tri-*t*-butylhydroxylamine (1.99 g.), and bicumyl (0.461 g.) were identified by their retention times relative to *o*-dichlorobenzene. The remaining components, ranging in amount from 0.030 to 0.390 g., were not further investigated.

(22) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1636 (1958).

**Reaction of *t*-Butylmagnesium Chloride with *t*-Nitrobutane.**—*t*-Nitrobutane (50.0 g., 0.485 mole), dissolved in an equal volume of ether, was added to the Grignard reagent prepared from 46.5 g. (0.5 mole) of *t*-butyl chloride and 12.2 g. (0.5 mole) of magnesium. The Grignard solution was cooled to  $-78^\circ$  prior to the addition of the nitro compound. During its addition, over the course of 1 hr., the reaction mixture turned green and a solid precipitated. The reaction mixture was stirred at  $25^\circ$  for 0.5 hr. after which it was hydrolyzed by the addition of water at  $0^\circ$ . Hydrolysis was accompanied by the evolution of isobutylene. The organic layer was separated and dried over anhydrous magnesium sulfate. Analysis by e.s.r. showed it to contain about  $10^{-2}$  mole of di-*t*-butylnitroxide. Other products, identified by v.p.c., were *t*-nitrosobutane, *t*-butyl alcohol, *t*-butyl nitrate, and tri-*t*-butylhydroxylamine.

***p,p'*-Dianisylnitroxide.**—The Grignard reagent was prepared from *p*-bromoanisole (61 g., 0.326 mole) and 8.7 g. (0.358 mole) of magnesium in 1 l. of 1:1 ether-benzene by the procedure of Reid.<sup>23</sup> It was cooled in ice and *p*-nitroanisole (42.4 g., 0.326 mole) was added over a 1-hr. period. At the end of this time 200 ml. of water was added slowly until the magnesium salts had coagulated. The organic layer was decanted from the magnesium salts and evaporatively distilled at  $30^\circ$ . The residue showed a typical nitroxide e.s.r. signal. All attempts at purification, however, failed. Small amounts of di-*p*-anisyl and di-*p*-anisylamine were shown to be present in this residue by comparison of its infrared spectrum with those of authentic samples.

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(23) J. C. Reid and H. B. Jones, *J. Biol. Chem.*, **174**, 427 (1948).

[CONTRIBUTION FROM THE U. S. ARMY BALLISTICS RESEARCH LABORATORIES, ABERDEEN PROVING GROUNDS, MD.; FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.; AND THE UNIVERSITY OF LUND, LUND, SWEDEN]

## Conformational Effects and Hydrogen Bonding in 1,4-Diols<sup>1</sup>

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Study of the influence of conformation and configuration on intramolecular hydrogen bonding in diols has been extended to 1,4-dihydroxybutane derivatives. The 3  $\mu$  infrared spectra of 57 butane-1,4-diols substituted only upon the 2- and 3-positions—acyclic, unsaturated, monocyclic, and bicyclic examples—were examined in detail. In a formal sense these 1,4-diols resemble the 1,2-diols studied earlier by similar techniques, the  $-\text{CH}_2\text{OH}$  groups of 1,4-diols replacing the  $-\text{OH}$  groups of 1,2-diols; however, the two series of compounds behave quite differently. In 1,2-diols the spectral shifts ( $\Delta\nu$ ) due to intramolecular hydrogen bonding decrease with increasing azimuthal angle between OH groups, but the reverse is true for 1,4-diols. A maximum  $\Delta\nu$  appears to be reached when the azimuthal angle between adjacent  $\text{CH}_2\text{OH}$  groups in 1,4-diols is about  $90^\circ$ . A conformational analysis of 1,4-diols with different azimuthal angles provides an explanation for this behavior; optimum hydrogen bonding interactions can be achieved only in certain geometrical arrangements. Evidence is presented that more than one major conformation permitting hydrogen bonding is present in certain of the diols. The influence of other structural variations on spectral details is discussed.

Intramolecular hydrogen bonding is particularly sensitive to changes in molecular geometry. For 1,2-diols, the most extensively studied class of compounds, the magnitude of the infrared spectral shifts ( $\Delta\nu$ ) of the fundamental OH stretching vibrational bands due to intramolecular association have been correlated with configurational and conformational factors.<sup>6-8</sup> In 1,2-

diols, the azimuthal angle,  $\phi$ , between two C—O bonds on adjacent carbon atoms is of prime importance in determining  $\Delta\nu$ <sup>3,9</sup>; values ranging from  $\Delta\nu = 0 \text{ cm.}^{-1}$  for compounds where the hydroxyl groups are too far apart to permit intramolecular interaction (e.g., *trans*-cyclopentane-1,2-diol,  $90^\circ < \phi < 120^\circ$ )<sup>6,9</sup> to  $\Delta\nu = 103 \text{ cm.}^{-1}$  (*cis*-*exo*-norbornane-2,3-diol,  $\phi = 0^\circ$ )<sup>10,11</sup> have been reported (Table II).

(9) F. V. Brutcher, Jr., and W. Bauer, Jr., *J. Am. Chem. Soc.*, **84**, 2236 (1962), propose a modified equation relating  $\Delta\nu$  and OH...O distances for 1,2-diols to replace the original Kuhn<sup>6a</sup> equation now known to be in error. This modified equation is not successful for higher diols, however, and a more general relationship is under investigation (by L. P. K.).

(10) H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954); H. Kwart and G. C. Gatos, *ibid.*, **80**, 881 (1958); H. Krieger, *Ann. Acad. Sci. Fennicae*, **AII**, No. 109 (1961). Cf. also S. J. Agyal and R. J. Young, *J. Am. Chem. Soc.*, **81**, 5467 (1959); G. Jacob and G. Ourisson, *Bull. soc. chim. France*, 734 (1958); T. Takeshita and M. Kitajima, *Bull. Chem. Soc. Japan*, **32**, 985 (1959); and E. L. Eliel and C. Pillar, *J. Am. Chem. Soc.*, **77**, 3600 (1955); **84**, 4999 (1962).

(11) Even though  $\phi \cong 0^\circ$  in *cis*-cyclobutane-1,2-diols,  $\Delta\nu \cong 65 \text{ cm.}^{-1}$  because of the greater OH...O distance caused by distortion of the C—C—C ring angles to  $90^\circ$ : R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959); E. J. Moriconi, W. F. O'Connor, L. P. Kuhn, E. A. Keneally, and F. T. Wallenberger, *J. Am. Chem. Soc.*, **81**, 6472 (1959). See Table IV.

(1) Presented at the Fourth Delaware Valley Regional Meeting, American Chemical Society, Philadelphia, Pa., Jan., 1962, Abstracts, p. 77, and at the Ninth Conference on Reaction Mechanisms, Brookhaven, N. Y., Sept., 1962.

(2) Ballistics Research Laboratories, paper V of a series on hydrogen bonding; paper IV: L. P. Kuhn and R. E. Bowman, *Spectrochim. Acta*, **17**, 650 (1961). Also see L. P. Kuhn and G. G. Kleinspehn, *J. Org. Chem.*, **28**, 721 (1963).

(3) Princeton University. Alfred P. Sloan Research Fellow. Paper XI of a series on hydrogen bonding; paper X: A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1715 (1963).

(4) Princeton University. American Cyanamid Junior Research Fellow, 1960-1962; National Institutes of Health Fellow, 1962-1963.

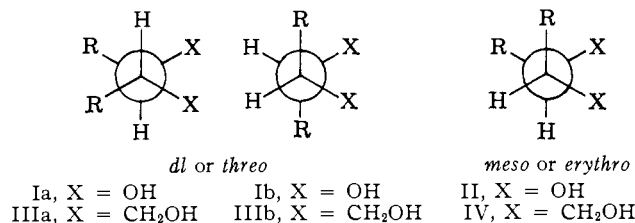
(5) University of Lund.

(6) (a) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); (b) *ibid.*, **76**, 4323 (1954); (c) *ibid.*, **80**, 5950 (1958).

(7) P. von R. Schleyer, *ibid.*, **83**, 1368 (1961), and references cited therein.

(8) For a review, see M. Tichý, *Chem. Listy*, **54**, 506 (1960).

muthal angles near  $60^\circ$  and  $\Delta\nu$  values between 30 and 50  $\text{cm.}^{-1}$ ; hence, conformational differences can be detected in nonrigid systems. In acyclic 1,2-disubstituted ethylene glycols, nonbonded repulsions result in larger  $\Delta\nu$ 's for *dl*- or *threo*- (I) than for *meso*- or *erythro*- (II) isomers (Table III).<sup>6,8,12</sup> The reverse is true for cyclohexane-1,2-diols where, probably due to a flattening of the ring from the regular geometry usually assumed,<sup>13</sup> *cis*-*ea*-diols give a larger  $\Delta\nu$  than *trans*-*ee* isomers.<sup>6,8</sup> The same is found, of course, for rings smaller than six membered; for larger rings,  $\Delta\nu_{\text{trans}}$  first becomes larger than  $\Delta\nu_{\text{cis}}$  in the cyclodecane-1,2-diols (Table IV).



A second structural effect on  $\Delta\nu$  recognized in 1,2-diols is the alteration of geometry due to substituents, particularly bulky ones (e.g., 1,1,2,2-tetra-*t*-butyl-ethylene glycol,  $\Delta\nu = 170$ , the largest observed value for 1,2-diols; Table V).<sup>6</sup> C-C-C angle distortion ("Thorpe-Ingold effect"), suggested as a possible factor, has been assessed by similar techniques in a study of 1,3-diols.<sup>7</sup>

Very few spectral measurements on 1,4-diols have been reported in the literature; less than a dozen aliphatic examples are known.<sup>6,8,14-17</sup> We here report an investigation on 2- and 3-substituted butane-1,4-diols. In a formal sense these resemble 1,2-diols with the OH groups of the latter replaced by CH<sub>2</sub>OH groups. *The spectral behavior of analogously constituted 1,2- and 1,4-diols is completely different, however; possible reasons for this discrepancy are considered in this paper.*

### Experimental Procedures and Results

**Preparation of Diols.**—The diols listed in Table I were prepared using accepted methods outlined in detail in the literature.<sup>18</sup> In general the following procedure was employed: an excess of lithium aluminum hydride was slurried in anhydrous ether, and the carboxylic acid, anhydride, or ester precursor of the desired diol in ether solution was added at such a rate as to maintain gentle reflux. After the addition was complete the reaction mixture was refluxed for 1 hr. and then decomposed either with water or with saturated sodium sulfate solution. The ether was removed and the products were distilled if liquids or recrystallized if solids. Diacids occasionally were converted to their methyl esters with diazomethane before reduction. In the case of some of the diols (listed by an asterisk in Table I) the reductions were run on such a small scale, owing to the availability of only small quantities of the precursors, that it was not feasible to purify the diols obtained. For these examples the infrared spectra were run on the crude material, it having been demonstrated in many other

(12) G. Chiurdoglu, R. De Groot, W. Masschelein, and M. H. Van Risseghem, *Bull. soc. chim. Belges*, **70**, 342 (1961).

(13) The C-C-C angles in cyclohexane are about  $111.5^\circ$  and not  $109.5^\circ$ ; V. A. Atkinson and O. Hassel, *Acta Chem. Scand.*, **13**, 1737 (1959); V. A. Atkinson, *ibid.*, **15**, 599 (1961).

(14) M. Mousseron, M. Mousseron, and M. Granier, *Bull. soc. chim. France*, 1418 (1960).

(15) (a) J. Sicher, F. Šipoš, and J. Jonaš, *Coll. Czech. Chem. Comm.*, **26**, 262 (1961); (b) A. B. Foster, A. H. Haines, and M. Stacey, *Tetrahedron*, **16**, 177 (1961).

(16) D. W. Davidson, *Can. J. Chem.*, **39**, 2139 (1961); J. Rigaudy and P. Courtot, *Tetrahedron Letters*, No. 3, 95 (1961); R. D. Stolow, *J. Am. Chem. Soc.*, **83**, 2592 (1961); P. Courtot, *Ann. chim.*, [8], 197 (1963); R. D. Stolow and M. M. Bonaventura, *J. Am. Chem. Soc.*, **85**, 3636 (1963); J. Tadanier, *J. Org. Chem.*, **28**, 1744 (1963); J. Fajkoš, J. Joska, J. Pišha, and F. Šorm, *Coll. Czech. Chem. Commun.*, **28**, 2337 (1963); J. Pišha, J. Joska, and J. Fajkoš, *ibid.*, **28**, 2611 (1963).

(17) H. Christol, M. Levy, and Y. Pietrasanto, *Bull. chim. soc. France*, 1132 (1963).

(18) N. G. Gaylord, "Reduction With Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, Chapters 8 and 9.

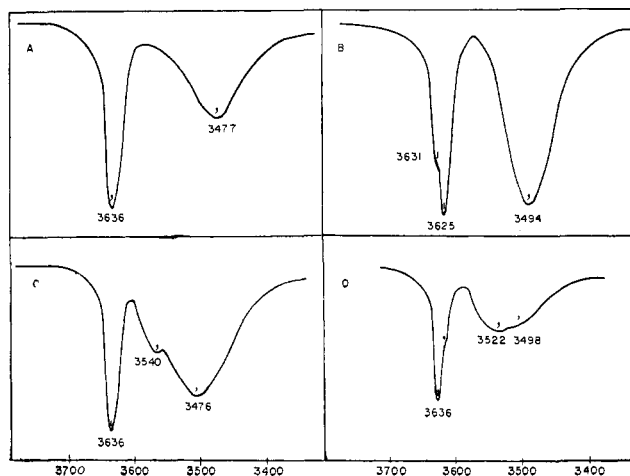


Fig. 1.—Representative hydroxyl region infrared spectra of butane-1,4-diol derivatives; concentrations all 0.005 *M* in CCl<sub>4</sub> solution, 1-cm. cells: A, butane-1,4-diol (1); B, 2-norbornene-*cis*-*endo*-5,6-dimethanol (47); C, cyclooctane-*cis*-1,2-dimethanol (42); D, cycloheptane-*cis*-1,2-dimethanol (40).

instances that small amounts of impurities had little or no effect on the position of the peaks. Where possible, the physical constants of the diols were determined and are reported in Table I; agreement with the literature was good for known compounds.

**Sources of Compounds.**—Compounds 1, 21a, 24, and 47 were commercially available and were redistilled or recrystallized before use. Compounds 4 through 20 were prepared by reduction of the appropriate carboxylic acids.<sup>19</sup> *cis*-Cyclopentane-1,2-dicarboxylic acid, furnished by Dr. N. L. Allinger,<sup>20a</sup> was used for the preparation of compounds 31 and 32. Compounds 27, 29 and 30 were supplied by Dr. A. T. Blomquist and Dr. A. G. Cook. Compounds 41 and 43 were donated by Dr. J. Sicher, as were the carboxylic acid precursors for the *cis* examples, 40 and 42.<sup>15</sup> Compound 55 was furnished by Dr. J. Meinwald; hydrogenation gave compound 54. Compounds 2, 33, 34, 37, 44, 45, 46, 50, and 51 were prepared by the catalytic hydrogenation of compounds 22, 35, 36, 38, 47, 48, 49, 52, and 53, respectively. The remaining compounds were prepared by reduction of appropriate precursors or by following literature methods.

**Infrared Spectral Procedures.**—The infrared curves were obtained in CCl<sub>4</sub> solutions by the same procedures outlined previously.<sup>6,7</sup> The 1,4-diols showed a strong tendency to associate intermolecularly and it was desirable to use very dilute solutions, 0.002 *M* or less, to avoid interference from the dimer band which comes at about the same position as the intramolecularly bonded peak. For this purpose 2-cm. matched silica cells were employed in several instances in place of the 1-cm. cells ordinarily used. The recent availability to us of a Perkin-Elmer 421 grating spectrometer equipped with scale expansion has permitted the examination of very dilute solutions in 1-cm. cells. Agreement with the earlier results has been excellent; the sharp, free peaks were reproduced with an accuracy of  $\pm 1 \text{ cm.}^{-1}$  and the broader, bonded peaks to  $\pm 2 \text{ cm.}^{-1}$ . Spectral shifts,  $\Delta\nu$ , can be reproduced within 2  $\text{cm.}^{-1}$  and intensity ratios within 10%. Data are summarized in Table I.

**Spectral Features and Complications.**—Ideally, the high resolution 3  $\mu$  spectra of 1,4-diols substituted only on the 2- and 3-positions should consist of two peaks. The higher frequency "free" peak would be sharp and a broad lower frequency band would be expected due to intramolecular OH...O hydrogen bonding. Many of the compounds examined here, such as butane-1,4-diol itself (Fig. 1A), exhibited this uncomplicated behavior. Besides the band positions, the separation between them ( $\Delta\nu$ , in  $\text{cm.}^{-1}$ ) is of interest since it is usually considered to be related to the enthalpy of the hydrogen bond and to the OH...O distance,<sup>9</sup> provided that the compounds are of the same general type.<sup>20b</sup> These data are included in Table I.

In a 1,4-diol a certain fraction of molecules will be intramolecularly hydrogen bonded, but only one of the two OH groups will be acting as a proton donor; the other will be "free." The rest of the molecules will not be internally associated; both OH groups will be "free." The free peak intensity comprises both types of systems and will be relatively insensitive to the degree of intramolecular hydrogen bonding taking place. The bonded peak will be due only to internal association and should serve as a

(19) L. Ebersson, *Acta Chem. Scand.*, **13**, 40 (1959).

(20) (a) N. L. Allinger and V. B. Zalkow, *J. Am. Chem. Soc.*, **83**, 1144 (1961); (b) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

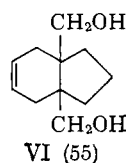
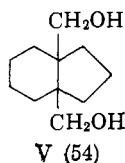
TABLE I  
 PHYSICAL AND SPECTROSCOPIC PROPERTIES OF 1,4-DIOLS

No.	Compound	Con- figura- tion	M.p. or b.p. (mm.), °C.	$n_D^{20}$	Lit. ref.	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	$\nu_{\text{free}}$	$\nu_{\text{bonded}}$	$\Delta\nu$	Free/ bonded intensity ratio <sup>a</sup>
Acyclic 1,4-diols											
1	Butane-		133.5 (16)	1.4460	21			3638 <sup>b</sup> (3634) <sup>s</sup> (3640) <sup>16</sup>	3477 (3478) <sup>s</sup> (3484) <sup>16</sup>	159 (156) <sup>s</sup> (156) <sup>16</sup>	2.6  (2.6) <sup>16</sup>
2	2-Methylbutane-		94-95 (0.5)	1.4488	22			3638 <sup>c</sup>	3477 3546sh	159 90	1.5 5.0
3	2,2-Dimethylbutane-		*		23			3636 <sup>c</sup>	3477 3534sh	159 102	1.8 3.0
4	2,3-Dimethylbutane-	<i>dl</i>	124-126 (8)	1.4528	24			3635	3482 <sup>c</sup>	153	2.5
5		<i>meso</i>	125-127 (8)	1.4521	24	60.98 61.22	11.94 12.16	3633	3466	167	1.1
6	2,3-Diethylbutane-	<i>dl</i>	130-132 (8)	1.4548		65.71 66.01	12.41 12.58	3632 <sup>d</sup>	3473	159	1.0
7		<i>meso</i>	130-132 (8)	1.4537		65.71 65.2	12.41 12.6	3632	3466	166	0.8
8	2,3-Diisopropylbutane-	<i>dl</i>	89-91			68.91 69.04	12.73 12.09	3626	3476 <sup>d</sup>	150(160) <sup>e</sup>	0.7
9		<i>meso</i>	42-43			68.91 68.8	12.73 12.6	3632	3463	169	1.3
10	2,3-Di- <i>i</i> -butylbutane-	<i>dl</i>	175-178			71.29 71.28	12.87 13.00	3629	3515	114(121) <sup>e</sup>	1.7
11		<i>meso</i>	109-110			71.29 71.21	12.87 13.10	3631	3476	155	1.1
12	2,3-Dineopentylbutane-	<i>dl</i>	96-98	m.m.p.		72.98 72.66	13.13 12.84	3627	3476	151(160) <sup>e</sup>	1.9
13		<i>meso</i>	96-98	65-90		72.98 74.20	13.13 13.06	3627	3463	164(173) <sup>e</sup>	0.9
14	2,3-Dicyclohexylbutane-	<i>dl</i>	84-86			75.53 75.3	11.89 11.9	3623	3472	151(164) <sup>e</sup>	0.7
15		<i>meso</i>	125-126			75.53 74.4	11.89 11.8	3627	3460	167(176) <sup>e</sup>	1.3
16	2,2,3,3-Tetramethylbutane-		217-219		25			3630	3458	172	
17	2,2,3,3-Tetraethylbutane-		92-93			71.29 71.40	12.87 13.10	3632	3436 3509	196 123	0.9
18	2,2,3,3-Bisdimethylene- butane-		78-79			65.57 67.4	9.93 9.97	3620 (3610) <sup>f</sup>	3476	144(160) <sup>g</sup>	0.9
19	2,2,3,3-Bistrimethylene- butane-		60-61, then solidifies remelts at 75-76			70.54 70.71	10.66 10.5	3633 <sup>d</sup>	3481	152	1.0
20	2,2,3,3-Bistetramethylene- butane-		92-93			72.68 72.6	11.18 11.2	3633	3535 <sup>w</sup> 3468	78 165	0.9
Unsaturated acyclic diols											
21	2-Butene-	<i>cis</i>	99-100 (0.7)	1.4779	26			3628sh <sup>b,g</sup> 3622	3498	130	5.5
21a		<i>trans</i>	97 (0.2)		27			3635sh <sup>g</sup> 3626	..	0	...
22	2-Methyl-2-butene-	<i>cis</i>	100-101 (0.5)	1.4686	28			3628sh <sup>b,g</sup> 3623	3480	148	2.1
23	2,3-Dimethyl-2-butene-	<i>cis</i>	90-91 (0.1)		29			3631sh <sup>b,g</sup> 3621	3540	91	4.1
24	2,3-Dibromo-2-butene-	<i>trans</i>	114.8-116.0		30			3623 <sup>b,g</sup> 3615	3606 <sup>j</sup>	0 (17) <sup>j</sup>	...
24a	2-Butyne-		43-45		31			..	3610 <sup>o</sup>	0	...
Monocyclic diols											
25	3,3-Dimethylcyclopropane-	<i>cis</i>	123-124 (8)	1.4700		64.62 63.53	10.77 10.75	3619 <sup>f</sup>	3512	107(124) <sup>g</sup>	1.1
26	1,2-dimethanol	<i>trans</i>	123-124 (8)	1.4701		64.62 63.60	10.77 10.80	3625	None	0	...
27	Cyclobutane-1,2-dimethanol	<i>cis</i> <sup>h</sup>						3634	3507	127	1.2
28		<i>trans</i>	103-104 (0.5)	1.4728		62.04 61.79	10.41 10.38	3635	3498	137	1.2
29	3,4-Diphenylcyclobutane- <i>cis</i> -1,2-dimethanol <sup>h</sup>				32			3628	3509	119(127) <sup>g</sup>	...
30	3-Cyclobutene-1,2- dimethanol	<i>cis</i> <sup>h</sup>						3623	3498	125(138) <sup>g</sup>	...
31	Cyclopentane-1,2-dimethanol	<i>cis</i>	*		18			3632	3501	131	1.2
32		<i>trans</i>	*		18			3634	3475	159	1.0
33	Cyclohexane-1,2-dimethanol	<i>cis</i>	42-43		6, 33			3634	3533sh	101	2.5
34		<i>trans</i>	51-52		6, 33			3635	3502 3534sh	132 <sup>k</sup> 101	2.2 3.3
35	4-Cyclohexene-1,2- dimethanol	<i>cis</i>	141-143 (1.7)	1.5080	34			3638 <sup>d</sup>	3491 3551	144 <sup>l</sup> 87	2.1 3.8
36		<i>trans</i>	113-115 (0.25)	1.5063	35			3636 <sup>d</sup>	3472 3534	166 <sup>m</sup> 102	1.4 2.1
37	4-Methylcyclohexane- <i>cis</i> -1,2- dimethanol	*						3636 <sup>d</sup>	3517 3496	119 <sup>m</sup> 140 <sup>l</sup>	2.1 3.6
38	4-Methyl-4-cyclohexene-1,2- dimethanol	<i>cis</i>	142-144 (0.7)	1.4967	36			3636 <sup>d</sup>	3496 3536	159 <sup>m</sup> 100	1.6 2.2
39		<i>trans</i>	134-136 (0.7)	1.5021		69.19 69.26	10.32 10.45	3636 <sup>d</sup>	3511 3522	125 <sup>n</sup> 114	2.2 1.9
40	Cycloheptane 1,2-dimethanol	<i>cis</i>	*					3636	3498	114	1.9
41		<i>trans</i> <sup>i</sup>						3642	3484	158	2.8
42	Cyclooctane-1,2-dimethanol	<i>cis</i>	*					3636	3476	160	1.8
43		<i>trans</i> <sup>i</sup>						3640	3540sh 3480	96 160	2.5
Bicyclic diols											
44	Norbornane-2,3-dimethanol	<i>endo-cis</i>	61.6-62.6		37, 38			3623 <sup>o</sup>	3498	125(138) <sup>g</sup>	1.0
45		<i>exo-cis</i>	*		37			3623 <sup>o</sup>	3487	136(149) <sup>g</sup>	1.0
46		<i>trans</i>	119-120 (0.3)	1.5065	37	69.13 69.02	10.33 10.42	3635 <sup>d</sup>	3496	139	1.4
47	2-Norbornene-5,6- dimethanol	<i>endo-cis</i>	84.4-85.6		37, 38			3625 <sup>c</sup>	3494	131(142) <sup>g</sup>	1.1
48		<i>exo-cis</i>	126-128 (0.3)	1.5203	37	70.10 69.69	9.15 9.33	3623 <sup>c</sup>	3487	136(149) <sup>g</sup>	1.0
49		<i>trans</i>	149-150 (1)	1.5123	37	70.10 69.55	9.15 9.36	3636 <sup>d</sup>	3503	133	1.7
50	Bicyclo[2.2.2]octane-2,3- dimethanol	<i>cis</i>	89.4-90.2		38	70.55 70.61	10.65 10.60	3623	3490	133(146) <sup>g</sup>	0.9
51		<i>trans</i>	76.3-77.0			70.55 70.71	10.65 10.94	3636 <sup>d</sup>	3477	159	1.6

TABLE I (Continued)

No.	Compound	Con- figura- tion	M.p. or b.p. (mm.), °C.	Lit. ref.	Carbon, %		Hydrogen, %		$\nu_{\text{free}}$	$\nu_{\text{bonded}}$	$\Delta\nu$	Free/ bonded intensity ratio <sup>a</sup>
					Calcd.	Found	Calcd.	Found				
52	2-Bicyclo[2.2.2]octene-5,6-	<i>endo-cis</i>	103.0-103.8	38	71.39	71.76	9.59	9.70	3623 <sup>c</sup>	3485	138(151) <sup>e</sup>	1.0
53	dimethanol	<i>trans</i>	72.5-73.0		71.39	71.80	9.59	9.70	3638 <sup>d</sup>	3488	150	1.7
54	Compound V	<i>cis</i>	*						3639	3505	134	1.6
55	Compound VI	<i>cis</i> <sup>o</sup>							3635	3480	155	1.1
										3602 <sup>w</sup>	33 <sup>p</sup>	

\* This compound prepared in insufficient quantity for characterization; see text. <sup>a</sup> Extinction coefficient (peak height) free peak/bonded peak. <sup>b</sup> 2-cm. cells used for these determinations. <sup>c</sup> Peak unsymmetrical on the high frequency side. <sup>d</sup> Peak unsymmetrical on the low frequency side. <sup>e</sup>  $\Delta\nu$  calculated from an assumed free peak position of 3636  $\text{cm}^{-1}$  (see text). <sup>f</sup> Band probably due to intramolecular hydrogen bonding to the cyclopropane ring.<sup>7,33</sup> <sup>g</sup> Allylic or propargylic alcohol hydrogen bonding<sup>8,39,40</sup>;  $\Delta\nu$  computed from high frequency shoulder. <sup>h</sup> Pure samples supplied by Dr. A. T. Blomquist and Dr. A. G. Cook, Cornell University. <sup>i</sup> Pure samples supplied by Dr. J. Sicher, Czechoslovak Academy of Science, Prague. The infrared spectra of compounds 40-43 were identical with similar curves by Dr. Sicher. <sup>j</sup> Hydrogen bonding to bromine.<sup>8</sup> <sup>k</sup> Previously reported<sup>6</sup> to have  $\Delta\nu = 137 \text{ cm}^{-1}$ ; also  $\Delta\nu = 140 \text{ cm}^{-1}$  has been reported for another compound of this type.<sup>14</sup> <sup>l</sup> Previously reported<sup>6</sup> to have  $\Delta\nu = 152 \text{ cm}^{-1}$ . <sup>m</sup>  $\Delta\nu = 171-176 \text{ cm}^{-1}$  has been reported for three compounds of this type.<sup>14</sup> <sup>n</sup>  $\Delta\nu = 127 \text{ cm}^{-1}$  has been reported for two compounds of this type.<sup>14</sup> <sup>o</sup> Pure sample supplied by Dr. J. Meinwald, Cornell University. <sup>p</sup> Hydrogen bonding to the double bond.<sup>8,39,40</sup>



much more sensitive indicator of the extent to which this is occurring. The inate intensity of an OH . . . O peak is greater than that of the free peak,<sup>20b</sup> so often both are of comparable height (Fig. 1). Ideally, areas under each of these bands should be compared, but it is easier to measure their relative extinction coefficients. Such free/bonded intensity ratios (Table I) should be related to the proportions of molecules engaged in intramolecular hydrogen bonding, for a given type of system. This assumption, a convenient one, is based on the supposition that the extinction coefficients of both free and bonded peaks remain more or less constant from one 1,4-diol to another. This assumption does not appear unreasonable to us. Primary alcohols are known to have similar free peak extinction coefficients.<sup>41</sup> Since the  $\Delta\nu$ 's of the 1,4-diols examined are roughly comparable, it is possible that their extinction coefficients are also similar, but this is less amenable to direct test. Obviously, if a diol had no bonded peak, it is not intramolecularly hydrogen bonded. We feel that the distinct difference in free/bonded intensity ratios displayed by examples A and B in Fig. 1 indicate a significant difference in the extents of intramolecular association between the two compounds.

Not all the 1,4-diols examined displayed an ideal two-peak

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 (22) A. F. Shepard and J. R. Johnson, *ibid.*, **54**, 4385 (1932); B. Wojcik and H. Adkins, *ibid.*, **55**, 4939 (1933).  
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 (30) A. Valette, *Ann. chim.*, [12] **3**, 663 (1948).  
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 (38) S. F. Birch, N. J. Hunter, and D. T. McAllan, *J. Org. Chem.*, **21**, 970 (1956); M. A. P. Bowe, R. G. T. Miller, J. B. Rose, and D. G. M. Wood, *J. Chem. Soc.*, 1545 (1960); J. Pirsch, *Monatsh. Chem.*, **88**, 578 (1957).  
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 (41) See the references cited in footnote 17 of ref. 7.

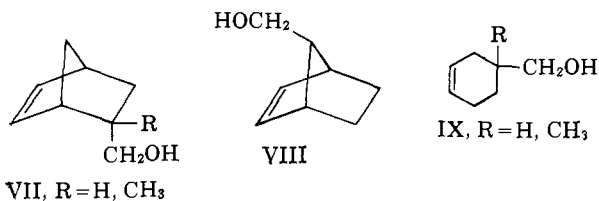
spectrum. Complications consisted in the appearance of additional bands and in the abnormal positions of some of the peaks. The bonded peaks, although quite broad, were often quite symmetrical (Fig. 1A and B). In other compounds an asymmetry or a distinct second band was present at somewhat lower frequencies (Fig. 1C). The intensity of this additional bonded band occasionally was comparable to that of the main peak (Fig. 1D). This complication appeared in saturated and unsaturated compounds alike; the magnitudes of  $\Delta\nu$  observed were too large for OH . . .  $\pi$  hydrogen bonding.<sup>8</sup> We attribute this feature to the presence of alternative competitive conformations for OH . . . O hydrogen bonding (*vide supra*); it was most prominent in the spectra of compounds 2, 3, 17, 19, 33-36, 38, 40 (Fig. 1D), and 42 (Fig. 1C).

Primary alcohols usually absorb in the range 3632-3643  $\text{cm}^{-1}$ , but the band shapes are not simple. A shoulder or asymmetry at about 13  $\text{cm}^{-1}$  lower frequencies, often present, has been attributed to conformational inhomogeneity.<sup>41</sup> All of the 2-substituted 1,3-diols examined earlier displayed these features,<sup>7</sup> but the spectra of the 1,4-diols reported here were more complicated. While many of the compounds studied gave free peaks which fell into the range quoted above (see Fig. 1A, 1C, and 1D), a number absorbed at frequencies significantly lower. These exceptions fall into three categories: (1) those with bulky substituents (8, 10, 12-15, and possibly 29); (2) *cis*-bicyclic diols (44, 45, 47—see Fig. 1B, 48, 50, and 52; the *trans* counterparts 46, 49, 51, and 53 were normal); (3) compounds with other available proton-accepting sites such as cyclopropane rings<sup>7,39</sup> (18, 25, and 26), double or triple bonds (21-24a, 30, and 55),<sup>8,39,40</sup> and bromine atoms (24).<sup>8</sup> Compounds in the first two categories often had shoulders on the high frequency side of the free peaks suggesting that the conformational equilibria favored the form with the lower frequency—a reasonable explanation in view of the crowded environment of the  $\text{CH}_2\text{OH}$  groups of these compounds. Variations in "free" peak positions of the third category, those with additional proton-accepting sites, are easy to understand in terms of previous experience.<sup>7,8,39,40</sup> The observed higher frequency peak is not "free" at all; rather it is bonded to the alternative, weaker site. A detailed analysis of such spectra has been included in Table I.

Noteworthy is the frequent nonobservance of OH . . .  $\pi$  hydrogen bonding in molecules which appear from models to be ideally constituted for such interactions. Such compounds include 35, 36, 38, 39, 47, 49, 52, and 53. Compound 30 displayed a pronounced "free" peak complication, but the magnitude of the shift, if present, was too small for an OH . . .  $\pi$  hydrogen bond. Interestingly, only compound 55 (VI) displayed an OH . . .  $\pi$  peak, even though closely analogous compounds 35 and 38 did not. Evidently the five-membered ring in 55 (VI) alters the molecular geometry in favor of such interactions. We have noted the nonobservance of OH . . .  $\pi$  hydrogen bonding in apparently favorable cases many times in monohydroxy olefins; examples pertinent to the present study include VII-IX.<sup>42</sup> These molecules prefer conformations in which the OH groups are not in proximity to the olefinic  $\pi$ -electrons. Such observations

(42) Unpublished observations, Princeton University.

emphasize the obvious, that negative evidence (such as the non-observance of hydrogen bonding) cannot be used with certainty to support a positive conclusion (such as an assignment of configuration).



The variability in "free" peak position presents a problem in interpretation of results. If spectral shifts are measured from the observed free peaks (apparent  $\Delta\nu$ ), an error may be introduced when  $\Delta\nu$  comparisons are made with uncomplicated molecules. Two solutions to this problem, neither completely free from objection, are possible: (1)  $\Delta\nu$  measurements in the complicated cases can be made from an assumed free peak position, such as 3636 cm.<sup>-1</sup>. There is ample precedent for this approach in the literature<sup>41</sup>; such "corrected"  $\Delta\nu$  values are included in Table I. (2) Comparisons can be made in bonded peak positions directly, obviating the necessity of assuming free peak positions. Free and bonded peak variations also complicate interpretation of intensity ratios. We will compare such ratios only in a very crude and general way, so that this will not be a serious problem.

### Discussion

**Comparison of 1,2- and 1,4-Diols.**—Interpretation of complex data is facilitated by isolation of individual factors responsible for observed effects. In the present instance, analysis of the hydrogen bonding behavior of 1,4-diols can be patterned after the analysis of analogously constituted 1,2-diols for which a sizable literature exists.<sup>6,8-12</sup> In ordinary 1,2-diols the OH groups are not arranged for optimum interaction because of the small size of the hydrogen-bonded ring involved. Spectral shifts ( $\Delta\nu$ ) usually observed, 30–50 cm.<sup>-1</sup>, are considerably lower than the maximum possible for aliphatic diol hydrogen bonding, 160–200 cm.<sup>-1</sup>. Any alteration of molecular geometry of 1,2-diols which brings the OH groups closer together results in an increase of  $\Delta\nu$ ; significant alterations are a decrease of the azimuthal angle between vicinal OH groups and a decrease in  $\theta$  angle (defined in Table VI) due usually to distortions caused by bulky substituents ("Thorpe-Ingold effect").

For 1,4-diols the situation is quite different. The size of the hydrogen-bonded ring is much larger and the interaction between OH groups in ordinary 1,4-diols approaches the optimum ( $\Delta\nu$  for 1,4-butanediol itself is 159 cm.<sup>-1</sup>). Furthermore, the addition of two more carbon atoms to the ring introduces much greater conformational flexibility, since rotations around three C–C bonds and not just one as in 1,2-diols are possible. To minimize complications we have examined here 1,4-diols substituted only upon the 2- and 3-positions; the resulting compounds facilitate comparisons with 1,2-diols, the OH groups of which have been replaced by CH<sub>2</sub>OH substituents. We state again for emphasis: despite their formal similarity, intramolecular hydrogen bonding of such 1,2- and 1,4-diols responds entirely differently to analogous alterations of molecular structure.

The azimuthal angles between vicinal substituents can be fixed or restricted to a narrow range when attached to a ring, especially a rigid one. Table II demonstrates the different response of 1,2- and 1,4-diols to changes in azimuthal angles. Spectral shifts for 1,2-diols decrease monotonously with increase in  $\phi$ ,<sup>9</sup> but little regular behavior is noted for 1,4-diols, although  $\Delta\nu$  goes through a maximum between azimuthal angles of 60 and 120°. When  $\phi = 180^\circ$  even the hydroxyl groups of 1,4-diols are too far apart to interact, but the lack of a series of suitable molecules with fixed  $\phi$  angles between 120 and 180° precludes determination of the angle at which interaction just ceases.

TABLE II

Compound	Con-figuration	X–C–C–X azimuthal angle	1,2-Diols	1,4-Diols
			(X = OH) <sup>a</sup> $\Delta\nu$ (OH...O), cm. <sup>-1</sup>	(X = CH <sub>2</sub> OH) <sup>b</sup> $\Delta\nu$ (OH...O), cm. <sup>-1</sup>
	<i>cis</i>	0°	91–103 <sup>10</sup>	133 ± 3.5 <sup>c</sup>
	<i>cis</i>	>0	61	131
	<i>cis</i>	<60	38	136 ± 4 <sup>d</sup>
	<i>trans</i>	>60	33	144
	<i>trans</i>	<120	0	159
	<i>trans</i>	120	..	155 ± 4 <sup>e</sup>
		125	0 <sup>10</sup>	136 ± 3 <sup>f</sup>
	<i>trans</i>	180	..	0
	<i>trans</i>	180	..	0

<sup>a</sup> Data from ref. 6 unless otherwise indicated. <sup>b</sup> Data from Table I. <sup>c</sup> Average of six compounds, 44, 45, 47, 48, 50, and 52, apparent  $\Delta\nu$ ; average corrected  $\Delta\nu = 146$  cm.<sup>-1</sup>; see text. <sup>d</sup> Average of two compounds, 33 and 37. <sup>e</sup> Average of 51 and 53. <sup>f</sup> Average of 46 and 49.

Comparison of data for stereoisomeric 2,3-disubstituted 1,4-butanediols with data for the corresponding disubstituted 1,2-diols reveals a further discrepancy (Tables III and IV). That isomer which has the larger

TABLE III

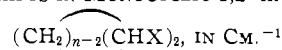
SPECTRAL SHIFTS OF *meso*- AND DL-1,2- AND 1,4-DIOLS, RCHX–XCHR, IN CM.<sup>-1</sup>

Substituent R =	1,2-Diols (X = OH) <sup>a</sup>		1,4-Diols (X = CH <sub>2</sub> OH) <sup>b</sup>	
	$\Delta\nu$ , <i>meso</i>	$\Delta\nu$ , <i>dl</i>	$\Delta\nu$ , <i>meso</i>	$\Delta\nu$ , <i>dl</i>
H	..	32	..	159
CH <sub>3</sub>	42	49	167	153
C <sub>2</sub> H <sub>5</sub>	..	..	166	159
<i>n</i> -C <sub>3</sub> H <sub>11</sub>	43	53	..	..
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	55 w	81	169	150
Cyclohexyl	..	..	167	151
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	0	94	155	114
neo-C <sub>5</sub> H <sub>11</sub>	..	..	164	151

<sup>a</sup> Data from ref. 6. <sup>b</sup> Data from Table I.

TABLE IV

SPECTRAL SHIFTS IN MONOCYCLIC 1,2- AND 1,4-DIOLS,



Ring size <i>n</i> =	1,2-Diols (X = OH) <sup>a</sup>		1,4-Diols (X = CH <sub>2</sub> OH) <sup>b</sup>	
	$\Delta\nu$ , <i>cis</i>	$\Delta\nu$ , <i>trans</i>	$\Delta\nu$ , <i>cis</i>	$\Delta\nu$ , <i>trans</i>
3	..	..	107 <sup>c</sup>	0
4	65 <sup>11</sup>	0 <sup>11</sup>	127	137
5	61	0	131	159
6	38	33	132, 101	144, 101
7	44	37	138, 114	158
8	51	43	160, 96	160
9	49	45	..	..
10	44	45	..	..
12	38	51	..	..

<sup>a</sup> Data, unless indicated, from ref. 6. <sup>b</sup> Data from Table I. <sup>c</sup> Apparent  $\Delta\nu$ ; corrected  $\Delta\nu = 127$  cm.<sup>-1</sup>; see text.

$\Delta\nu$  in the 1,4-series has the smaller  $\Delta\nu$  in the 1,2-series. For acyclic compounds (Table III) the *meso*-1,4-diols give larger spectral shifts than their *racemic* isomers, but just the opposite is true for 1,2-diols. Monocyclic compounds (Table IV) behave similarly;  $\Delta\nu$ 's are larger

for *trans*- than for *cis*-cycloalkane-1,2-dimethanols (1,4-diols), but again the reverse is true for 1,2-dihydrocycloalkanes. The data of Tables III and IV confirm conclusions concerning the effects of azimuthal angles deduced from Table II. Newman projections of the *racemic* and *meso* isomers (I-IV) illustrate the argument. Repulsions between R and R or R and X groups in the *racemic* isomers I and III produce a decrease from  $60^\circ$  in azimuthal angle between X substituents in either of the two bonding conformations, a or b. As a result,  $\Delta\nu$  for 1,2-diols is increased, but  $\Delta\nu$  is decreased for 1,4-diols. R-R and R-X repulsions in *meso* isomers have the opposite effect: an increase from  $60^\circ$  in azimuthal angle between X substituents, an increase in  $\Delta\nu$  for 1,4-diols but a decrease in  $\Delta\nu$  for 1,2-diols. Cyclic isomers (Table IV) can be analyzed similarly. Until the ring size becomes quite large, *cis* substituents have smaller azimuthal angles than do *trans* groups,<sup>6,9,13</sup> as illustrated by the behavior of 1,2-diols (Table IV). For most cases *trans*-1,4-diols in the monocyclic series give larger  $\Delta\nu$ 's than do *cis*-1,4-diols; a significant exception is the *trans*-cyclopropane derivative 26 which does not exhibit intramolecular OH...O hydrogen bonding. Reasons for this are discussed below.

TABLE V  
SUBSTITUENT EFFECTS AND SPECTRAL SHIFTS IN 1,2- AND 1,4-DIOLS, X-C-C-X, IN CM.<sup>-1</sup>

Substituents				1,2-Diols (X = OH) <sup>a</sup>		
R	R'	R''	R'''	$\Delta\nu$	$\Delta\nu$	Free/bonded
H	H	H	H	32	159	2.6
CH <sub>3</sub>	H	H	H	...	159, 90	1.5, 5.0
CH <sub>3</sub>	CH <sub>3</sub>	H	H	...	159, 102	1.8, 3.0
CH <sub>3</sub>	H	CH <sub>3</sub>	H	49	153	2.5
CH <sub>3</sub>	H	CH <sub>3</sub>	H	42	167	1.1
(CH <sub>2</sub> ) <sub>2</sub>		(CH <sub>2</sub> ) <sub>2</sub>		...	144 <sup>c</sup>	0.9
(CH <sub>2</sub> ) <sub>3</sub>		(CH <sub>2</sub> ) <sub>3</sub>		...	152, 78	1.0
(CH <sub>2</sub> ) <sub>4</sub>		(CH <sub>2</sub> ) <sub>4</sub>		40	165	0.9
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	46	172	
C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	62	196, 123	0.9
<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr	96	...	...
<i>t</i> -Bu	<i>t</i> -Bu	<i>t</i> -Bu	<i>t</i> -Bu	170	...	...

<sup>a</sup> Data from ref. 6, unless indicated. <sup>b</sup> Data from Table I; free/bonded intensity ratios shown in the last column. <sup>c</sup> Apparent  $\Delta\nu$ ; magnitude decreased about 16 cm.<sup>-1</sup> by interaction with the cyclopropane rings; see text.

The second major angular variation possible in these systems is the  $\theta$  angle (defined in Table VI). Bulky substituents on the central atoms in X-C-C-X systems force the X groups (OH's for 1,2-diols, CH<sub>2</sub>OH's for 1,4-diols) closer together, presumably by decreasing the  $\theta$  angles (Thorpe-Ingold effect)<sup>6,7</sup> or by steric crowding. Here a similar result is observed for both 1,2- and 1,4-diols;  $\Delta\nu$  increases with increasing bulk of the substituents (Table V). In fact 2,2,3,3-tetraethylbutane-1,4-diol (17) has the largest  $\Delta\nu$  (196 cm.<sup>-1</sup>) yet reported for an aliphatic diol; similarly, 1,1,2,2-tetra-*t*-butylethane-1,2-diol ( $\Delta\nu = 170$  cm.<sup>-1</sup>) is by far the largest for vicinal diols.<sup>6</sup> The  $\theta$  angle can be increased by incorporation into a small, strained ring system. Isolation of this effect is possible if comparisons are made between compounds with fixed azimuthal angles ( $0^\circ$ , Table VI). Again, both 1,2- and 1,4-diols behave similarly;  $\Delta\nu$  decreases with increasing  $\theta$  angle, but the effect appears to be much more pronounced for 1,2-diols, as expected. Evidently the combination of  $\phi$  angle and  $\theta$  angle effects results in the nonobservance of OH...O hydrogen bonding in the *trans*-cyclopropane-1,2-di-

TABLE VI  
VARIATION OF THE  $\theta$  ANGLE AND SPECTRAL SHIFTS, 1,2- AND 1,4-DIOLS

Definition of $\theta$			Angle between RCX plane and C-C bond	
Compound				
$\theta$	150°	135°	129°	125°
<i>cis</i> -1,2-Diol, X = OH, $\Delta\nu$ , cm. <sup>-1</sup>	...	65 <sup>11</sup>	91-103 <sup>10</sup>	90
<i>cis</i> -1,4-Diols, X = CH <sub>2</sub> OH, $\Delta\nu$ , cm. <sup>-1</sup> (apparent) <sup>a</sup>	107	126 <sup>b</sup>	132 <sup>c</sup>	136 <sup>d</sup>
$\nu$ bonded, cm. <sup>-1</sup>	3512	3505 <sup>b</sup>	3493 <sup>c</sup>	3488 <sup>d</sup>

<sup>a</sup> Not corrected for free peak displacements (see text); compare with bonded peak positions. <sup>b</sup> Average of three compounds, 27, 29, and 30. <sup>c</sup> Average of 44, 45, 47, and 48. <sup>d</sup> Average of 50 and 52.

methanol derivative (26), commented on above. Calculations indicate the azimuthal angle to be about  $146.5^\circ$  in *trans*-1,2-cyclopropane derivatives<sup>43</sup> and the  $\theta$  angles are also unusually large; the resulting OH...O distance in 26 is too great for interaction to occur.

**Analysis of Hydrogen Bonding Conformations.**—To ascertain whether any correlation between molecular geometry and  $\Delta\nu$  could be determined, a study was made of the various conformations of the butane-1,4-diol systems using Cenco-Peterson and Dreiding-Büchi molecular models. The goal was to determine the effect of changes in the azimuthal angle at C<sub>2</sub>-C<sub>3</sub> upon certain key internuclear distances and angles. Because of the enormous complexities of this system, several reasonable simplifying assumptions were made. The azimuthal angles at C<sub>1</sub>-C<sub>2</sub> and at C<sub>3</sub>-C<sub>4</sub> which are not restricted by covalent bonding requirements were kept fixed at  $60^\circ$ , since this is the approximate position of minimum rotational energy. With the azimuthal angles of the C<sub>1</sub>-C<sub>2</sub> and C<sub>3</sub>-C<sub>4</sub> bonds fixed at  $60^\circ$ , there are still three minimum energy conformations around each C-C bond; the OH groups and the rest of the chain can either be in a *skew* or *trans* relationship. Only if both OH groups are *skew* is intramolecular hydrogen bonding possible, but two families of hydrogen bonding conformations result. We designate these families *syn* and *anti*.

With these molecular restrictions operative, various azimuthal angles at C<sub>2</sub>-C<sub>3</sub> were chosen and kept fixed while the models were adjusted to give the smallest O-H...O distances. Measurements of the O-H...O and C-O...H angles and the H...O and O...O distances were made; a summary of values is presented in Table VII and four important conformations are illustrated in Fig. 2. Rotations around the C-O bonds were not restricted; the barrier to such rotations is only about 1 kcal./mole, much less than could be gained by optimum hydrogen bond formation. The hydroxyl groups of the *anti* family were in each case symmetrically disposed and only one distinct conformation resulted for each value of the C<sub>2</sub>-C<sub>3</sub> azimuthal angle. Two of these conformations are illustrated in Fig. 2, for azimuthal angles  $0^\circ$  and  $90^\circ$ . Such was not the case for the *syn* family where, except for  $0^\circ$  azimuthal angle, two different conformations were present for each azimuthal angle. These two conformations arise from the spatial

TABLE VII  
 HYDROGEN BOND PARAMETERS FOR VARIOUS CONFORMATIONS OF BUTANE-1,4-DIOL<sup>a</sup>

C <sub>2</sub> -C <sub>3</sub> azimuthal angle	<i>anti</i> Conformational family			<i>syn</i> Conformational family				
	O...O dist., <sup>b</sup> Å.	O-H...O angle	H...O-C angle	O...O <sup>b</sup> I and II, Å.	OH...O I	OH...O II	H...OC I	H...OC II
0°	2.8	120°	70°	1.6	180°	180°	110°	110°
30	2.2	150	90	2.2	175	150	90	130
60	1.6	180	110	2.8	170	130	70	110
90	2.2	180	110	3.7	160	75	50	90
120	2.8	170	105	4.6				
150	3.7	160	90	5.1				
180	4.6	145	75	5.3				

<sup>a</sup> Calculated by the procedure described in the text; values for permissible hydrogen bonding conformations italicized. <sup>b</sup> The H...O distances can easily be estimated from the known O-H bond length (0.96 Å.), the O...O distances, and the O-H...O angles, listed above.

nonequivalence of the two hydroxyl groups. The geometry of the interaction C<sub>1</sub>-O-H...O-C<sub>4</sub> was not the same as that for C<sub>1</sub>-O...H-O-C<sub>4</sub>, as illustrated for the two *syn* 60° azimuthal angle conformations in Fig. 2. In these two cases the O...O distances are the same, but the O-H...O and C-O...H angles vary appreciably (Table VII).

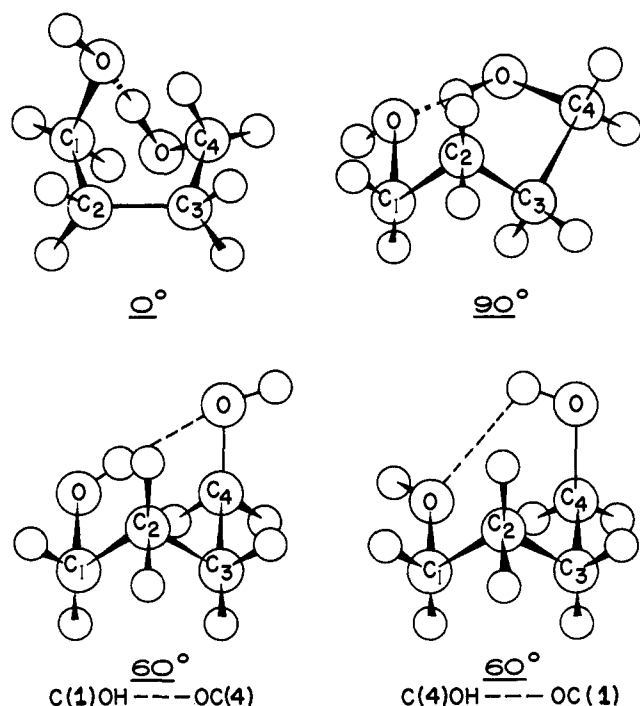


Fig. 2.—Conformation of butane-1,4-diol with different dihedral angles at C<sub>2</sub>-C<sub>3</sub>.

Let us now consider how the geometry of the butane-1,4-diols might be expected to influence the strength of the hydrogen bond and, hence,  $\Delta\nu$ . From the extensive work on 1,2- and 1,3-diols,<sup>6-11</sup> it is clear that  $\Delta\nu$  increases as the H...O (and the related O...O) distances decrease. In butane-1,4-diol the O...O distance varies with the C<sub>2</sub>-C<sub>3</sub> azimuthal angle in a roughly sinusoidal manner. The *syn* and *anti* conformational families give identical curves with the minima displaced 60° from one another (Table VII). At this minimum distance (O...O = 1.6 Å. and O...H = 0.6 Å.) the repulsion between nonbonded atoms is very large and it is highly unlikely that these conformations exist. The O...O distance in ice is 2.76 Å. and O...O distances down to about 2.4 Å. have been found in strongly hydrogen-bonded crystals.<sup>20b</sup> It is safe to assume that this distance is a lower limit for diol hydrogen bonding, but for purposes of analysis of Table VII a distance of 2.1 or 2.2 Å. as the minimum permitting hydrogen bonding was chosen, since the actual molecules have a degree of

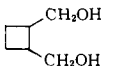
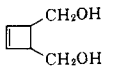
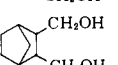
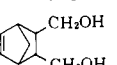
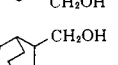
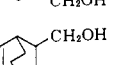
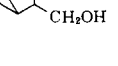
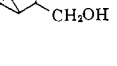
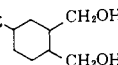
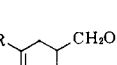
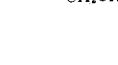
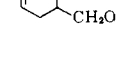
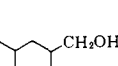
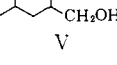
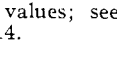
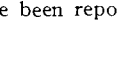
flexibility not duplicated by the models. At the other extreme, if the hydroxyl groups are too far apart, interaction between them is not possible. A reasonable O...O distance limit, 3.4 Å.,<sup>6,41</sup> fixes the maximum C<sub>2</sub>-C<sub>3</sub> azimuthal angle for the observation of intramolecular hydrogen bonding in 1,4-diols at about 140°, consonant with our experimental observations. The restriction in O...O distances, from 2.1 to 3.4 Å., limits severely the number of conformations for which hydrogen bonding is possible in 1,4-diols, but at least one permissible conformation is available for all C<sub>2</sub>-C<sub>3</sub> azimuthal angles from 0 to 140° (Table VII and Fig. 2). For some values of the azimuthal angle, namely from about 30 to 80°, more than one conformation permitting hydrogen bonding is possible. It has been mentioned above that a number of compounds examined gave more than one bonded peak, a spectral complication attributed to the presence of more than one bonding conformation. It is noteworthy that this complication is restricted to those compounds which, in view of their molecular structure, would be expected to have C<sub>2</sub>-C<sub>3</sub> azimuthal angles near 60°. In no case where azimuthal angles were fixed at 0 or 120° was more than one bonded peak observed, in accord with expectations based on Table VII.

The influence of the O-H...O and the C-O...H angles on  $\Delta\nu$  has not been established. The hydrogen bond consists of an attractive force between hydrogen and oxygen and a repulsive force between the two oxygens.<sup>44</sup> In the absence of the hydrogen bond the sum of the van der Waals radii of hydrogen and oxygen is 2.6 Å. and of two oxygens, 3.4 Å. As these distances decrease, repulsive forces set in. In hydrogen-bonded systems these distances are considerably less, indicating that two oxygen atoms can approach each other more closely when a hydrogen atom is located between them than they can in the absence of hydrogen. This shielding effect of the hydrogen should be most effective when the O-H...O angle is 180° since at this angle the H...O distance is at a minimum and the O...O distance at a maximum. Indeed, in crystals most hydrogen bonds are linear.<sup>20b</sup> The important feature of the oxygen atom of a diol which endows it with proton-accepting ability is its unshared pairs of electrons. Since the orbitals of these electrons make angles of about 110° with the C-O bond, the most favorable C-O...H angle should be 110°. Support for this hypothesis is found in the zig-zag geometry of the HF polymer.<sup>41</sup> These arguments are purely qualitative. We do not know at present how sensitive the hydrogen bond is to deviations of these angles from the optimum values of 180° (O-H...O) and 110° (C-O...H), but the effect could be quite significant for large deviations.

We can now interpret the results of Tables II-IV.

(44) C. A. Coulson, *Research*, **10**, 149 (1957); reprinted in D. Hadzi, Ed., "Hydrogen Bonding," Pergamon Press, New York, N. Y., 1959, p. 339 ff.

TABLE VIII  
 EFFECT OF DOUBLE BOND INTRODUCTION ON SPECTRAL SHIFTS IN CYCLIC 1,4-DIOLS

Saturated compound	$\Delta\nu$ , cm. <sup>-1</sup>	Unsaturated compound	$\Delta\nu$ , cm. <sup>-1</sup>		
 <i>cis</i>	127	 <i>cis</i>	125 <sup>a</sup>		
 <i>trans</i>	137	 <i>endo-cis</i>	131 <sup>a</sup>		
 <i>endo-cis</i>	125 <sup>a</sup>	 <i>exo-cis</i>	136 <sup>a</sup>		
 <i>exo-cis</i>	136 <sup>a</sup>	 <i>trans</i>	133		
 <i>trans</i>	139	 <i>cis</i>	138 <sup>a</sup>		
 <i>cis</i>	133 <sup>a</sup>	 <i>trans</i>	150		
 <i>trans</i>	159				
 <i>cis</i>	$\left\{ \begin{array}{l} R = H \\ \text{cis} \\ \text{trans} \\ R = CH_3 \\ \text{cis} \end{array} \right.$	132, 101	$\left\{ \begin{array}{l} R = H \\ \text{cis} \\ \text{trans} \\ R = CH_3 \\ \text{cis} \\ \text{trans} \end{array} \right.$	166, 87	
<i>trans</i>		144, 101		119, 102	
<i>cis</i>	140	<i>cis</i>	159 <sup>b</sup>	<i>trans</i>	125, 100 <sup>b</sup>
 <i>cis</i>	140 <sup>b,c</sup>	 <i>cis</i>	171 <sup>b,c</sup>		
V <i>cis</i>	134	VI <i>cis</i>	155		

<sup>a</sup> Apparent  $\Delta\nu$  values; see text. <sup>b</sup> Spectral shifts for similar compounds have been reported<sup>14</sup>; for other examples see ref. 17a. <sup>c</sup> Data from ref. 14.

Examination of Table VII shows that there is only one value of the C<sub>2</sub>-C<sub>3</sub> azimuthal angle, 90°, in which all three parameters are optimum; the O...O distance is 2.2 Å., the O-H...O angle is 180°, and the C-O...H angle is 110°; Fig. 2. The largest  $\Delta\nu$  should be observed in compounds having a 90° azimuthal angle, in agreement with the experimental results of Table II. When the azimuthal angle increases above 90°, the O...O distance increases and the O-H...O and C-O...H angles decrease somewhat from their optimum value;  $\Delta\nu$  should decrease also, reaching 0 cm.<sup>-1</sup> at about azimuthal angle 140°. As the azimuthal angle decreases below 90°, the O...O distance in the *anti* conformation becomes too short, and the molecule is forced to adopt the less favorable *syn* conformation, and  $\Delta\nu$  decreases. Below 90°, there is no single conformation free from some nonoptimum parameter, and the spectral shifts are hard to predict, except that they will be below the maximum. Experimentally from Tables II-IV it is observed that  $\Delta\nu$  increases as the C<sub>2</sub>-C<sub>3</sub> azimuthal angle increases from about 45° toward 90°.

We do not mean to imply that the calculated distances and angles shown in Table VII are actual distances and angles to be found in the molecules themselves, for actual molecules possess a certain flexibility with respect to rotation and bond angle deformation not well duplicated in the models. The calculations are illustrative and provide a means for explaining some of the unusual features of 1,4-diol hydrogen bonding: the difference in response to changes of central bond azimuthal angle exhibited by 1,2- and 1,4-diols; the maximum in  $\Delta\nu$  observed near a C<sub>2</sub>-C<sub>3</sub> azimuthal angle of 90°; and the appearance of more than one bonded peak in certain 1,4-diols. We have ignored nonbonded repulsions, which become serious even in unencumbered molecules when the C<sub>2</sub>-C<sub>3</sub> azimuthal angle becomes less than 60°. In such cases, the hydrogen atoms attached to C<sub>1</sub> and C<sub>4</sub> and, respectively, the hydroxyl oxygen atoms attached to C<sub>4</sub> and C<sub>1</sub> approach within their van der Waals radius sums (Fig. 2). The resulting repulsive force will undoubtedly increase the O...O distance from that shown in Table VII, will further weaken the hydrogen bond, and will decrease  $\Delta\nu$ . Substituents can also act in the opposite manner (Table V). The effect of alkyl groups in 2,2,3,3-tetra-substituted butane-1,4-diols (16 and 17) will be to de-

crease the C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> and C<sub>2</sub>-C<sub>3</sub>-C<sub>4</sub> angles.<sup>6,7</sup> The C<sub>2</sub>-C<sub>3</sub> azimuthal angles will probably remain near 60° in these compounds, but the "gem-dialkyl effect" will force the hydroxyl groups closer together, and  $\Delta\nu$  increases. The results of Table VI illustrate the opposite effect.

**Changes of Geometry and Spectra by Introduction of Double Bonds.**—The cyclobutane ring of cyclobutane-*cis*-1,2-dimethanol (27) is nearly planar; consequently introduction of a double bond into the 3-position (30) alters the geometry but slightly, and  $\Delta\nu$  of both compounds are similar (Table VIII). The same result pertains for the rigid or nearly rigid bicyclic compounds 44-53; the presence or absence of a double bond has very little effect on  $\Delta\nu$  for analogous compounds. The situation is quite different for cyclohexane derivatives, as summarized in Table VIII. For the saturated cyclohexane-1,2-dimethanols, the central azimuthal angle of the butane-1,4-diol system is larger for the *trans* than for the *cis* isomer, and  $\Delta\nu_{cis}$  is smaller than  $\Delta\nu_{trans}$ . The introduction of a double bond to form 4-cyclohexene-1,2-dimethanol derivatives produces a reversal in the relative magnitude of  $\Delta\nu$  for *cis* and *trans* isomers, for a large number of available compounds. The *cis*  $\Delta\nu$  is now larger than  $\Delta\nu_{trans}$ ; the change in  $\Delta\nu$  upon introduction of the double bond is quite large for both isomers, and in opposite directions. These results are readily understandable when we consider the effect of the double bond upon the geometry of the cyclohexane ring. According to Corey and Sneen,<sup>45</sup> the double bond in the 4-position produces a rotation around the C<sub>1</sub>-C<sub>2</sub> bond such that the axial bond at each of these carbons is displaced toward the center of the ring and the equatorial bonds are displaced toward each other and the plane of the ring. The result is to decrease the azimuthal angle between *trans* (diequatorial) substituents and to increase the azimuthal angle between *cis* (equatorial axial) substituents. The spectral shift inversions (Table VIII) are a consequence of this change in geometry.

The *cis*-2-butene-1,4-diols (21, 22, and 23) fall into a separate class. The two symmetrically substituted

(45) E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **77**, 2505 (1955). Confirmation of these calculations may be found in the behavior of hydrogen bonding in 4-cyclohexene-1,2-diols where  $\Delta\nu_{cis}$  is smaller than  $\Delta\nu_{trans}$  (compare Tables II and IV); M. E. Ali and L. N. Owen, *J. Chem. Soc.*, 1066 (1958).



examples, *cis*-2-butene-1,4-diol itself (21) and its 2,3-dimethyl derivative (23) both have low  $\Delta\nu$ 's (130, and 90  $\text{cm}^{-1}$ , respectively) and very weak bonded peaks (free/bonded intensity ratios 5.5 and 4.1). The unsymmetrical character of 2-methyl-*cis*-2-butene-1,4-diol (22) evidently is propitious for hydrogen bonding, since both  $\Delta\nu$  (148  $\text{cm}^{-1}$ ) and the free/bonded intensity ratio (2.1) are improved.

**Free/Bonded Intensity Ratios**—When a proton donor and a proton acceptor group are placed at different ends of a hydrocarbon chain, ring formation through intramolecular association is opposed by the natural tendency of the chain to adopt a linear, zig-zag conformation. With  $\alpha,\omega$ -diols proton donor and acceptor groups are both moderately strong; the hydrogen bond between them is sufficiently energetic to ensure that association persists to a large measure even in 1,4-diols, but intramolecular hydrogen bonding falls off drastically in 1,5-diols. Although strictly not directly comparable, the free/bonded intensity ratios of terminal diols give a convincing indication of this: Ethylene glycol = 1.3, propane-1,3-diol = 2.0,<sup>7</sup> butane-1,4-diol (1) = 2.6, and pentane-1,5-diol = *ca.* 40.<sup>1</sup>

Any conformational effect which would facilitate ring formation should increase the percentage of molecules engaged in intramolecular hydrogen bonding and decrease the free/bonded intensity ratio. Ordinarily nonbonded skew butane type repulsions would tend to favor the adoption of a *trans* conformation for the butane-1,4-diol chain; this nonbonding conformation competes with hydrogen bond ring formation. If the hydroxymethylene groups of a 1,4-diol are attached to a ring, the nonbonding conformation is not possible; considerably reduced free/bonded intensity ratios are observed for almost all monocyclic and bicyclic diols (Table I). Molecules with more than one bonded peak (such as 33–36, 39, 40, and 41) display higher ratios for

each, but both peak areas should be added together to make a more valid comparison. Alkyl groups also generally reduce the free/bonded intensity ratios. A single substituent, such as methyl (2), permits the butane chain to adopt an orientation favoring hydrogen bonding without increase in nonbonded repulsions; the  $C_4$ -carbon can as easily be *trans* to the methyl group at  $C_2$  as *trans* to the  $C_1$  carbon. The “*gem*-dialkyl effect”—the heightened tendency toward ring formation of alkyl chains bearing alkyl substituents, especially when geminal—has its chief origin in such steric influences.<sup>7</sup> The trend is best illustrated here by comparing planimeter peak area ratios,  $A_f/A_b$ , for the series: butane-1,4-diol (1), 1.0; 2-methylbutane-1,4-diol (2), 0.6; and 2,2-dimethylbutane-1,4-diol (3), 0.35. In most of the other more complicated molecules, substituents also favor intramolecular hydrogen bonding. Compound 4 appears to be anomalous in this respect. We make no claim to understanding the fine details of substituent effects. Perhaps the pronounced nonbonded interactions in these molecules, many of them quite crowded, vitiate simple analysis.

One further influence of substituents is noteworthy; they seem to favor the adoption of more than one conformation and two peaks often appear in the spectra. This influence is seen most clearly in the series 1, 2, 3, but we do not have an entirely satisfying explanation.

Extensions of this work to 1,5- and 1,6-diols have been completed, and the results will appear shortly.<sup>1</sup> Further illustrations of the effects described above are even more dramatically exemplified in longer chain molecules.

**Acknowledgments.**—We wish to thank Dr. J. Meinwald, Dr. A. G. Cook, Dr. A. T. Blomquist, Dr. J. Sicher, and Dr. N. L. Allinger for supplying compounds used in this research. Partial support of this project by a grant from the National Science Foundation to P. R. S. is acknowledged with appreciation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

## Azo Compounds.<sup>1</sup> Five-Membered Cyclic Azo Compounds. Their Stereospecific Decomposition

By C. G. OVERBERGER AND JEAN-PIERRE ANSELME<sup>2</sup>

RECEIVED AUGUST 20, 1963

Two cyclic five-membered azo compounds, 3,5-diphenyl-1-pyrazoline and 3,5-bis-(*p*-chlorophenyl)-1-pyrazoline, have been prepared. Their stereospecific decomposition to the corresponding *trans*-1,2-diarylcyclopropanes is reported and the mechanism of the decomposition is discussed.

### Introduction

Five-membered ring azo compounds (1-pyrazolines), having an  $\alpha$ -hydrogen and capable of rearranging to a conjugated system, usually isomerize to the more stable 2-pyrazolines.<sup>3</sup> However, as a part of our general studies of cyclic azo compounds, we decided to synthesize 3,5-diphenyl-1-pyrazoline (I, Ar =  $C_6H_5$ ) and study its chemistry. There were no previous authenticated reports of stable 1-pyrazolines of this type. The mechanism of the decomposition of both 1- and 2-py-

razolines has been the subject of a controversy which is still not settled at present. It was hoped that the decomposition of 3,5-diphenyl-1-pyrazoline would shed some light on the problem.

### Results and Discussion

One of the most general methods for the synthesis of 1-pyrazolines consists in the addition of an olefin to a diazoalkane. The reaction of styrene with phenyldiazomethane resulted in the formation of a white crystalline solid which melted with decomposition. The infrared spectrum had no absorption indicating the presence of  $-N-H$  and had a sharp peak of moderate intensity at 1548  $\text{cm}^{-1}$ , assigned to the azo linkage. The product from the thermal decomposition was pure *trans*-1,2-diphenylcyclopropane. The structure of the pyrazoline was confirmed by its isomerization to 3,5-diphenyl-2-pyrazoline (III, Ar =  $C_6H_5$ ) isolated as its *N*-acetyl derivative (IV, Ar =  $C_6H_5$ ). It was identical

(1) (a) This is the 43rd in a series of papers concerned with the preparation and the decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger, J.-P. Anselme, and J. R. Hall, *J. Am. Chem. Soc.*, **85**, 2752 (1963). (b) For a preliminary report of this work, see C. G. Overberger and J.-P. Anselme, *ibid.*, **84**, 869 (1962).

(2) This paper comprises a portion of a dissertation submitted by Jean-Pierre Anselme in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) T. L. Jacobs in R. Elderfield, "Heterocyclic Compounds," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 72.