The N.m.r. Spectra of Heterocyclic Compounds. I. The Spectra of 1,4-Dioxanes, 1,3-Dioxolanes, and 1,4;5,8-Naphthodioxane[1]

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The n.m.r. spectra of 2,3-disubstituted 1,4-dioxanes, 2-substituted 1,3-dioxolanes, and 1,4;5,8-naphthodioxane were taken and interpreted by two methods. Characteristic chemical shifts were observed for the various groups of compounds studied.

Since little information is available about n.m.r. spectra of heterocyclic compounds, a systematic study of such molecules was undertaken in our laboratory in which the n.m.r. spectra of certain substances containing at least two oxygen atoms in the skeleton is described.

Experimental

Melting points were taken on a micro hot stage and are corrected. Boiling points are uncorrected. Elemental analyses were provided by Dr. S. Nagy, Massachusetts Institute of Technology, Cambridge, Mass., and Illini Micro Lab, Urbana, Illinois. Ultraviolet spectra were recorded with a Cary Model 11 MS spectrometer, and infrared spectra with a Perkin-Elmer Model 137 spectrometer.

N.m.r. Spectra.—A Varian Associates Model 4300 n.m.r. spectrometer with a field homogeneity control unit was used to obtain the n.m.r. spectra at a frequency of 60 Mc. The magnetic field was swept at rates varying from 0.5 c.p.s./sec. to 3 c.p.s./sec. A Varian Associates variable temperature accessory, Model 4340, was used for low temperature studies.

The samples were 4–10% solutions (wt./vol.) in deuterochloroform containing tetramethylsilane as an internal reference and were contained in 4-mm. i.d. borosilicate glass tubes.

The spectra were calibrated using the side band technique. A Hewlett-Packard wide range oscillator, Model 200 CDR, together with a Hewlett-Packard electronic counter, Model 521 CR, was employed for this purpose. Peak positions were measured by interpolation and reported in τ units, where

$$\tau = 10.00 - \frac{\nu_{TMS} - \nu_{X}}{\nu_{TMS}} \times 10^6$$

trans-**2,3-Diphenyl-1,4-dioxane** (*1a*) was obtained from *trans*-2,3-dichloro-1,4-dioxane and phenyl magnesium bromide.[2] The product crystallized from ethyl acetate as colorless crystals; m.p. 46–47° (reported 43–46°), $\lambda_{max}^{isooctane}$ 253 mμ (ε 306), 259 (399), 266 (319), λ_{max}^{KBr} identical to those reported.

2,3-Diphenyl-1,4-dioxane.—The 2,3-diphenyl-1,4-dioxane was prepared from the ethylene ketal of benzoin as described by Summerbell and Berger.[2] The product crystallized from ethanol as colorless plates; m.p. 90–93° (reported 94–95°), $\lambda_{max}^{isooctane}$ 314 mμ (ε 10,450), λ_{max}^{KBr} identical to those reported.

cis-**2,3-Diphenyl-1,4-dioxane** (*2a*) was prepared as described[2] by hydrogenating 2,3-diphenyl-1,4-dioxane in the presence of Adams catalyst. The *cis*-2,3-diphenyl-1,4-dioxane was recrystallized from ethanol as colorless rods; m.p. 130.5–132.5° (reported 132.7–133.5°), $\lambda_{max}^{isooctane}$ 253 mμ (ε 307), 259 (434), 266 (361), λ_{max}^{KBr} identical to those reported.

trans-**2,3-Dichloro-1,4-dioxane** (*1b*).—Dioxane was chlorinated according to the procedure of Böeseken, *et al.*[3] The product distilled at 70–72°/10 mm. (reported b.p. 82.4°/14 mm.). Crystallization of the oil from ether–pentane gave colorless crystals, m.p. 29–30° (reported 28–30°), λ_{max} 7.83, 8.59, 9.01, 9.66, 11.08, 11.42, 13.27 μ.

cis-**2,3-Dichloro-1,4-dioxane** (*2b*) was prepared by chlorinating dioxane as previously described.[4] A pure sample crystallized from ether–pentane as colorless needles; m.p. 52–53° (reported 53°), λ_{max} 8.83, 9.02, 9.55, 9.91, 10.55, 11.15, 11.58, 11.99 μ.

2,3,4,6-Tetrachloro-1,4-dioxane (*3*).—Into a solution composed of dioxane (50 ml.) and carbon tetrachloride (50 ml.) at 83° (reflux) was passed chlorine (*ca.* 6–7 mmoles/min.) for 3 hr. The reaction temperature was maintained at 83–90° during the addition. After the cooled reaction mixture was flushed with nitrogen, it was distilled *in vacuo* to remove the solvent. Distillation of the residue at 0.40–0.45 mm. gave four fractions. Dilution of the latter two fractions (b.p. 53–53.5° and 53.5–54°) with 2:1 ether–pentane and subsequent storage gave 0.83 g., m.p. 94–95° and 1.18 g., m.p. 90–94°, of crude product. Repeated recrystallization from ether–pentane gave 2,3,5,6-tetrachloro-1,4-dioxane as colorless crystals; m.p. 99–100° (reported[5] 100–101°), λ_{max}^{KBr} 7.58, 8.75, 9.99, 11.15, 11.50, 13.15, 13.48 μ.

Anal. Calcd. for $C_4H_4Cl_4O_2$: Cl, 62.78. Found: Cl, 62.95.

trans-**2,3-Diacetoxy-1,4-dioxane** (*1c*).—This compound was prepared as described.[3] The compound crystallized from ether as colorless crystals; m.p. 104–106° (reported 104–105.5°), λ_{max}^{KBr} 5.74, 7.33, 8.19, 8.58, 9.86, 10.60, 11.20 μ.

trans-**1,4;5,8-Naphthodioxane** (*4*).—This compound was isolated by fractional recrystallization (ethanol) of the reaction mixture from *trans*-2,3-dichloro-1,4-dioxane and ethylene glycol as described.[3] The product exhibited a melting point of 128–132° (reported 133–136°), λ_{max}^{KBr} 6.89, 7.45, 7.81, 8.72, 8.79, 9.14, 9.26, 9.78, 10.96, 11.47, 12.78 μ.

2,2′-Bis-1,3-dioxolane (*6*) was isolated from the above reaction in the latter crops of fractional recrystallization. The compound is not the *cis*-1,4;5,8-naphthodioxane as stated,[3] but was later shown to be 2,2′-bis-1,3-dioxolane.[6] The isolated material had a melting point of 107–112° (reported 109–112°).

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[1] This work was supported by Grant CY-4663 and A-5326 from the U. S. Public Health Service.

[2] R. K. Summerbell and D. R. Berger, *J. Am. Chem. Soc.*, **81**, 633 (1959).

(3) J. Böeseken, F. Tellegen, and P. C. Henriguez, *Rec. trav. chim.* **50**, 909 (1931).

(4) R. K. Summerbell and H. E. Lunk, *J. Am. Chem. Soc.*, **79**, 4802 (1957).

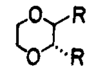
(5) This melting point is for one of four tetrachloro isomers, which do not have previously assigned structures. See R. C. Elderfield (ed.), "Heterocyclic Compounds," Vol. 6, Wiley and Sons, New York, 1957, p. 15.

(6) V. Faass and H. Hilgert, *Ber.*, **87**, 1343 (1954); O. Hassel and C. Rømming, *Acta Chem. Scand.*, **10**, 136 (1956).

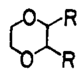
TABLE I
SUMMARY OF N.M.R. DATA FOR DIOXOLANES

	C-2,3 Protons		C-5,6 Protons		
Compound	Peaks[a]	Conformation	Peaks center[a]	No. of peaks	Ring conformation
Dioxane	...	...	6.29	1	Inverting chair
trans-Diphenyl (*1a*)	5.22	...	5.58	1	Inverting chair
cis-Diphenyl (*2a*)	4.88	Eq.	6.14	14	Rigid boat
trans-Dichloro (*1b*)	4.05	Eq.	5.95	10	Rigid chair
cis-Dichloro (*2b*)	4.30	Ax.	6.01	14	Rigid boat
Tetrachloro (*3*)	3.89	Eq.	...	1	Chair
trans-Diacetoxy (*1c*)	4.23	...	6.09	10	Rigid chair
trans-Naphtho (*4*)	5.35	Ax.	6.21	16	Rigid chair

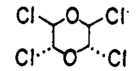
[a] Expressed in τ units.



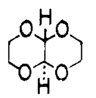
1.
a. $R=C_6H_5$
b. $R=Cl$
c. $R=CH_3CO{\cdot}O$



2.
a. $R=C_6H_5$
b. $R=Cl$



3.



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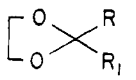
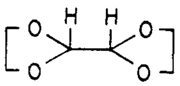


5.
a. $R=CH_3$; $R_1=C_2H_5$
b. $R=C_{11}H_{23}$; $R_1=H$



6.

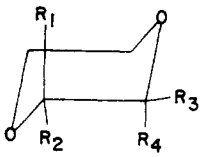


Fig. 1.—Chair form of 1,4-dioxane.

2-Ethyl-2-methyl-1,3-dioxolane (*5a*).—The dioxolane was synthesized exactly as described by Dauben, *et al.*,[7] and had a boiling point of 114-116.5° (reported 116.5–117°).

2-Lauryl-1,3-dioxolane (*5b*) was prepared according to the usual ketal formation method by refluxing laurylaldehyde, ethylene glycol, benzene, and *p*-toluenesulfonic acid. The water formed during the reaction was removed by azeotropic distillation with benzene. The product distilled at 130°/4 mm., λ_{max} 6.81, 8.72, 8.89, 9.63 μ.

Anal. Calcd. for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 72.97; H, 12.24.

Results and Discussion

1,4-Dioxanes.—Results for this group of compounds can be interpreted by assuming that the molecules either exist in a preferred conformation or invert rapidly. In the latter case, on an average time basis, they can be regarded as planar. Both interpretations will be presented. Although n.m.r. spectroscopy alone does not allow a rigorous structural assignment, the available evidence from other sources seems to favor the concept of preferred conformation (see below).

Preferred Conformation Analysis.—The results of the n.m.r. spectra interpreted by this method are summarized in Table I. At room temperature the spectrum of 1,4-dioxane consists of a single peak. Models show that the molecule can exist in chair or boat conformations similar to those of cyclohexane. Inversion between extreme chair conformers can occur by passing through the boat form.

In the chair conformation the protons at carbons 2,3 and 5,6 occupy axial and equatorial orientations. As a consequence of inversion between extreme chair conformations, protons which were axial will become equatorial and vice versa. By analogy with cyclohexane systems, a chemical shift between signals for axial and equatorial protons would be expected.[8] However, in cyclohexane, because the rate of chair-chair interconversion is of the same order of magnitude as the chemical shift between axial and equatorial protons, this shift is averaged to zero,[9a] and only one peak is observed for all protons in cyclohexane. We would therefore assume that in dioxane inversion occurs at a fairly rapid rate at room temperature. In contrast to cyclohexane,[9b] when the temperature of the tested dioxane solution was lowered to −104°, the peak remained unsplit. Thus the energy barrier to inversion must be even lower than that of cyclohexane, which at that temperature shows separation of axial and equatorial peaks.

When various functional groups are substituted for the protons at carbons 2 and 3 of dioxane, both configurational and conformational isomerism are possible. For each configurational isomer, several conformations would be possible. If the ring of *cis* isomers occupies a chair conformation (Fig. 1), one substituent is axial and the other equatorial. The protons at carbons 2 and 3 are likewise oriented and are not equivalent. Hence, two peaks can be expected in the n.m.r. spectrum, that from the axial proton occurring at higher field than that from the equatorial.[8] Two boat forms of the ring are possible (Fig. 2, A and B). In form A the two oxygen atoms occupy the "bow"

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[7] H. J. Dauben, Jr., B. Löken, and H. J. Ringold, *J. Am. Chem. Soc.*, **76**, 1359 (1954).

[8] R. Lemieux, R. K. Kulling, and R. Y. Moire, *ibid.*, **80**, 2237 (1958).

[9] (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 388. (b) W. B. Moniz and S. A. Dixon, *J. Am. Chem. Soc.*, **83**, 1671 (1961).

Table II

Conformational Arrangement of Configurational Isomers of 2,3-Substituted 1,4-Dioxanes

	cis		trans	
Ring conformation	Position of protons	Conformation of protons	Position of protons	Conformation of protons
Chair form (Fig. 1)	R_2, R_4	Eq.-axial	R_2, R_3	Diequatorial
			R_1, R_4	Diaxial
Boat form A (Fig. 2)	R_2, R_4	Diaxial	R_2, R_3	Eq.-axial
	R_1, R_3	Diequatorial		
Boat form B (Fig. 2)	R_2, R_4	Eq.-axial	R_2, R_3	Diequatorial
			R_1, R_4	Diaxial

and "stern" of the boat, while in form B two carbon atoms occupy these positions. In the first form (A), the *cis* substituents may be either diaxial or diequatorial and in either case are eclipsed. The protons are thus equivalent, so that only a single peak is expected. In the second form (B) one substituent is axial and the other equatorial, as are the hydrogens. Two peaks would therefore be expected.

If the ring for the *trans* isomers is in the chair conformation (Fig. 1), the substituents may be either diaxial or diequatorial. In the first boat form (A) (Fig. 2) the *trans* substituents will be axial and equatorial, each eclipsing the proton on the adjacent carbon. These protons are not equivalent, and two peaks would result. In the second boat form (B) the *trans* substituents will be either diaxial (opposed) or diequatorial (skewed), as will be the protons. From the models it appears that conversion from one boat form to the other should occur quite readily, much more so than from one chair form to the other. However, this supposition does not take into account repulsive forces between atoms, which may serve, in some cases, to hold the ring in a preferred conformation.

In the cases where the protons on carbons 2 and 3 are not equivalent, a chemical shift would be expected between peaks for such protons. Spin-coupling between these protons would be expected to lead to varying degrees of splitting of these peaks. The manner in which coupling constants vary with the dihedral angle between protons on adjacent carbon atoms was derived by Karplus.[10] Other authors[11] have shown that protons in cyclic systems also exhibit a similar variation in coupling. In cases where the protons are equivalent, no coupling would occur, and only a single, unsplit peak should be observed. Thus the spectra of the substituted dioxanes would then be expected to present evidence of preferred conformations for these compounds. The possible conformations and configurations for such isomers are summarized in Table II. The spectra of *trans*- and *cis*-2,3-diphenyl- and 2,3-dichloro-1,4-dioxanes of proved configuration[2,4] were studied and were viewed on the basis of this hypothesis.

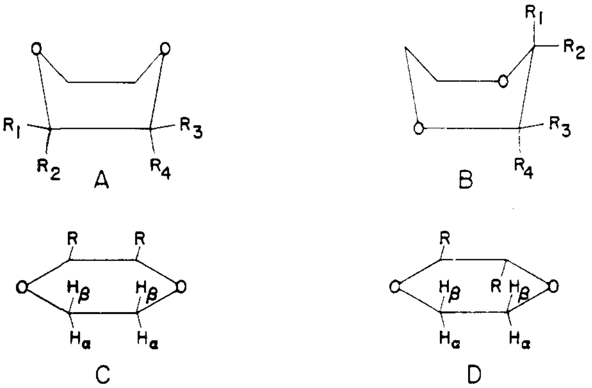

Fig. 2.—Boat forms of 1,4-dioxane.

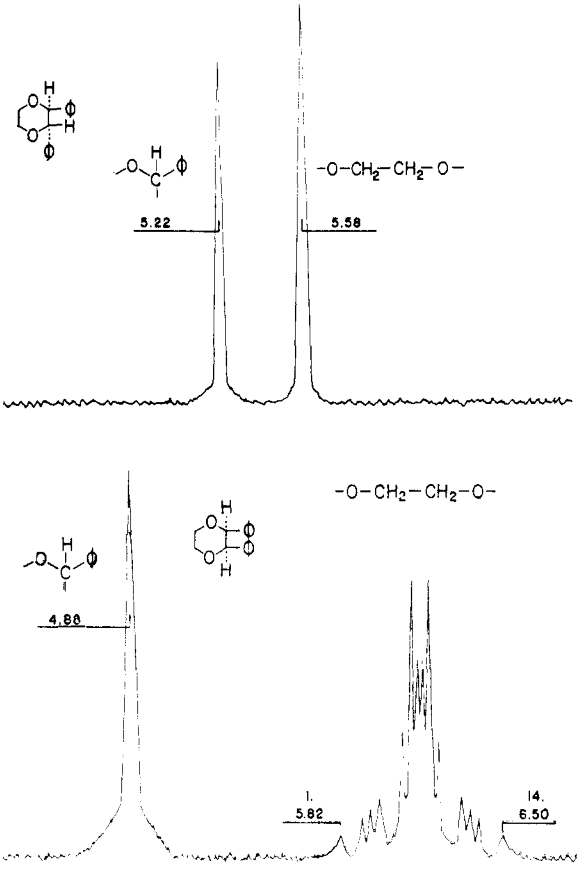

Figure 3

The spectrum of *trans*-2,3-diphenyl-1,4-dioxane (*1a*) has two lines for the dioxane-ring protons (Fig. 3A). The peak at 5.22 is assigned to the

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(10) M. Karplus, *J. Chem. Phys.*, **33**, 316 (1960).

(11) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); J. I. Musher, *J. Chem. Phys.*, **34**, 594 (1961).

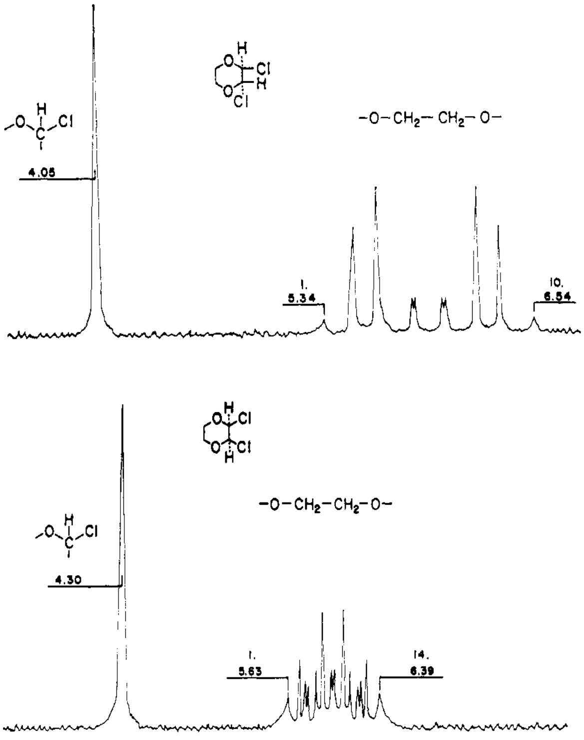

Figure 4

protons at carbons 2 and 3 of the dioxane ring and the 5.58 peak to the remaining protons at carbons 5 and 6. The intensities of the signals agree with this assignment. The finding of only one unsplit peak for the protons at carbons 5 and 6 indicates that the molecule is inverting rapidly, and hence the 5.22 peak represents the average position between axial and equatorial extremes.

The *cis*-2,3-diphenyl-1,4-dioxane (*2a*) (Fig. 3B), on the other hand, shows a series of fourteen peaks centered at 6.14 for the protons at carbons 5 and 6, revealing a rigid conformation. A single, unsplit peak at 4.88 is observed for the protons at carbons 2 and 3. If the molecule existed in either a chair conformation (Fig. 1) or "B" boat conformation (Fig. 2), one of the protons would be axial and the other equatorial. Because the molecule is assumed to be rigid, two peaks would then be observed for these protons. If the molecule were to exist in the "A" boat conformation (Fig. 2), both protons would be either diaxial or diequatorial and would give rise to only one peak, as indeed was the case. The peak observed for these protons lies further downfield than the corresponding peak for the *trans* compound (*1a*), which was assigned to lie midway between axial and equatorial positions.[8] Equatorial protons give signals at lower fields than axial protons,[8] suggesting that the protons at carbons 2 and 3 for the *cis*-diphenyl compound (*2a*) occupy diequatorial positions, with the phenyl groups being diaxial. Should this be the case, the spin-coupling between adjacent diequatorial protons would be approximately zero. The supposition that the molecule exists in a boat rather than a chair conformation does not alter the relative positions between the peaks of axial and equatorial protons. The peaks for axial and equatorial protons in bornyl acetate and isobornyl acetate (boat conformations) have the same relationship in the spectrum as do those for axial and equatorial protons in molecules which are held in rigid chair conformations (*e.g.*, steroids).[12]

Both *trans*- and *cis*-2,3-dichloro-1,4-dioxane (*1b* and *2b*) (Fig. 4, A and B) show splitting of the peak assigned to the protons at carbons 5 and 6, indicating a rigid conformation for both molecules. The peak at 4.05 for the protons at carbons 2 and 3 of the *trans* molecule is unsplit. If the molecule were to exist in the "A" boat conformation (Fig. 2), these protons would be axial and equatorial, and hence two peaks would be expected. Thus, either a chair conformation (Fig. 1) or the "B" boat conformation (Fig. 2) is preferred for the *trans*-dichloro molecule.

The *cis*-dichloro compound (*2b*) (Fig. 4,B) also gives a single, unsplit peak at 4.30 for the protons at carbons 2 and 3; therefore the protons are equivalent. The peak appears at higher field than that of the *trans* compound (*1b*), and thus the protons must be diaxial, suggesting that the *cis* compound (*2b*) exists as the "A" boat conformer with the chlorines diequatorial and eclipsed. The *trans* compound (*1b*), on the other hand, has the protons in the diequatorial conformation with the chlorines diaxial. The repulsive forces of the chlorines tend to favor the chair conformation over the "B" boat, in agreement with the results of dielectric measurements.[13]

The spectrum of 2,3,5,6-tetrachloro-1,4-dioxane[3] shows only a single unsplit peak for all the protons. This peak occurs at lower field (3.89) than the peaks for either the *cis*- or *trans*-dichloro compounds. Therefore the protons apparently are equatorial and equivalent, indicating a chair form for the molecule.

The spectrum of *trans*-2,3-diacetoxy-1,4-dioxane (*1c*) shows a series of ten peaks for the protons at carbons 5 and 6. Hence the molecule is in a rigid conformation. Only a single peak is seen for the protons at carbons 2 and 3, revealing the equivalence of these protons. Because the *cis* compound cannot be prepared,[2,3] it is not possible to state whether the acetoxy groups are diaxial or diequatorial. By analogy with the chloro compounds, they are probably diaxial.

The *trans*-1,4;5,8-naphthodioxane (*4*) spectrum (Fig. 5) shows a series of sixteen peaks for the protons at carbons 2, 3, 6, and 7. Thus the molecule exists in a rigid conformation. In a *trans* ring junction of two chairs the protons at

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(12) Unpublished observations.

(13) C. Altona, C. Romers, and E. Havinga, *Tetrahedron Letters*, **10**, 16 (1959).

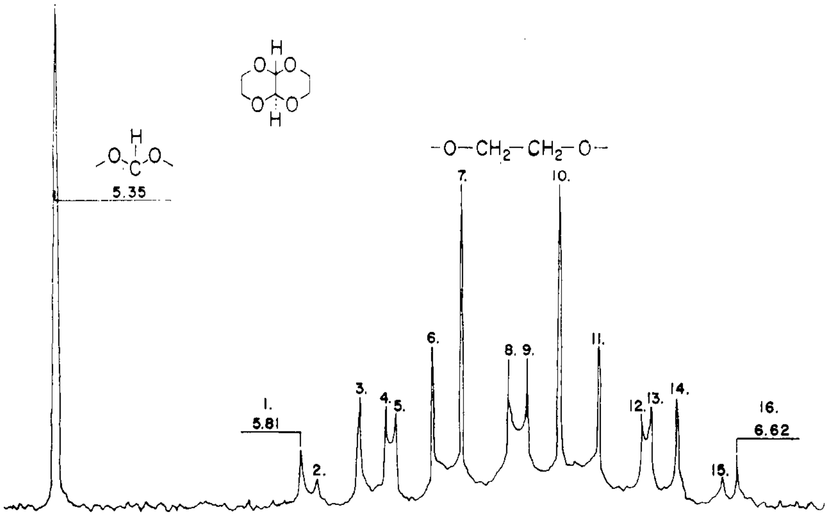

Figure 5

carbons 9 and 10 must be diaxial. A single, unsplit peak is seen at 5.35 for these protons; therefore the protons at the ring junctures are equivalent. The dihedral angle between these protons, which should give a coupling constant of about 9 c.p.s. is approximately 180°. Because of the symmetry of the molecule, these protons are completely equivalent, and thus no splitting is observed.[12]

Rapid Inversion Analysis.—The spectra obtained at room temperature for *trans*- (Fig. 3A) and *cis*- (Fig. 3B) 2,3-diphenyl-1,4-dioxane and *trans*- (Fig. 4A) and *cis*- (Fig. 4B) 2,3-dichloro-1,4-dioxanes might be interpreted as A_2B_2 spectra arising from nonequivalence of the protons at carbons 5 and 6. A non-equivalence would result from these protons being *cis* or *trans* to the substituents at carbons 2 and 3.

The lack of splitting of the peak for the protons at carbons 2 and 3 could indicate rapid ring inversion at room temperature. An average of all shifts due to axial-equatorial non-equivalence would then occur. The *cis* or *trans* non-equivalence would not be affected by inversion, so that chemical shifts between these two species of protons would remain, whatever the frequency of inversion. If the inversion rate is rapid enough, the molecule may be treated as planar for n.m.r. purposes. Using the designations "α" and "β," in the sense of steroid nomenclature, we then have for the *cis* and *trans* isomers the indicated distribution for protons (Fig. 2, C and D).

If the molecules invert rapidly at room temperature, the shift between axial and equatorial protons will average out. However, the shift between protons *cis* or *trans* to the substituent would still be present, but this shift would be unaffected by inversion. At *some* temperature the inversion must slow down sufficiently to reintroduce shifts between axial and equatorial protons, resulting in more complex spectra.

To test this possibility the spectra were run over a range of temperature. In addition to room temperature spectra were recorded as follows: *trans*-dichlorodioxane (*1b*) (55°, −9°, −14.5°, −30°, −36°, −42°), *cis*-dichlorodioxane (2b) (55°, −14°), *trans*-diphenyldioxane (*1a*) (55°, −20°, −28°, −41°), and *cis*-diphenyldioxane (*2a*) (55°, −19°). In no case was any apparent difference in the spectra obtained. Since the temperature at which inversion slows down is not known, it is possible that it is lower than the temperatures employed. Raising the temperature should not affect the spectrum if the molecules are already inverting. The absence of changes in the spectra due to temperature variations *does not* allow a choice between the two alternative interpretations presented on the basis of n.m.r. alone. This is because it is not known *a priori* to what portion of the energy scale the temperatures investigated correspond. Had there been differences, a distinction could have been made about the nature of the nonequivalence causing splitting of the peaks. In contrast, *conclusive evidence* has been provided by dipole measurements[13] that *trans*-2,3-dibromo- and *trans*-2,3-dichloro-1,4-dioxanes exist in a rigid conformation in which the rings are in a chair form and the substituents are diaxial. Thus it seems reasonable to assume that other substituted dioxanes will also adopt a preferred conformation. Should this assumption be the case, the dioxanes will exist in the forms indicated in Table I.

1,3-Dioxolanes.—A summary of the results is compiled in Table III. The sharpness of the peaks observed for the ring protons of the dioxolane derivatives studied was unexpected, as illustrated by the spectrum for 2-methyl-2-ethyl-1,3-

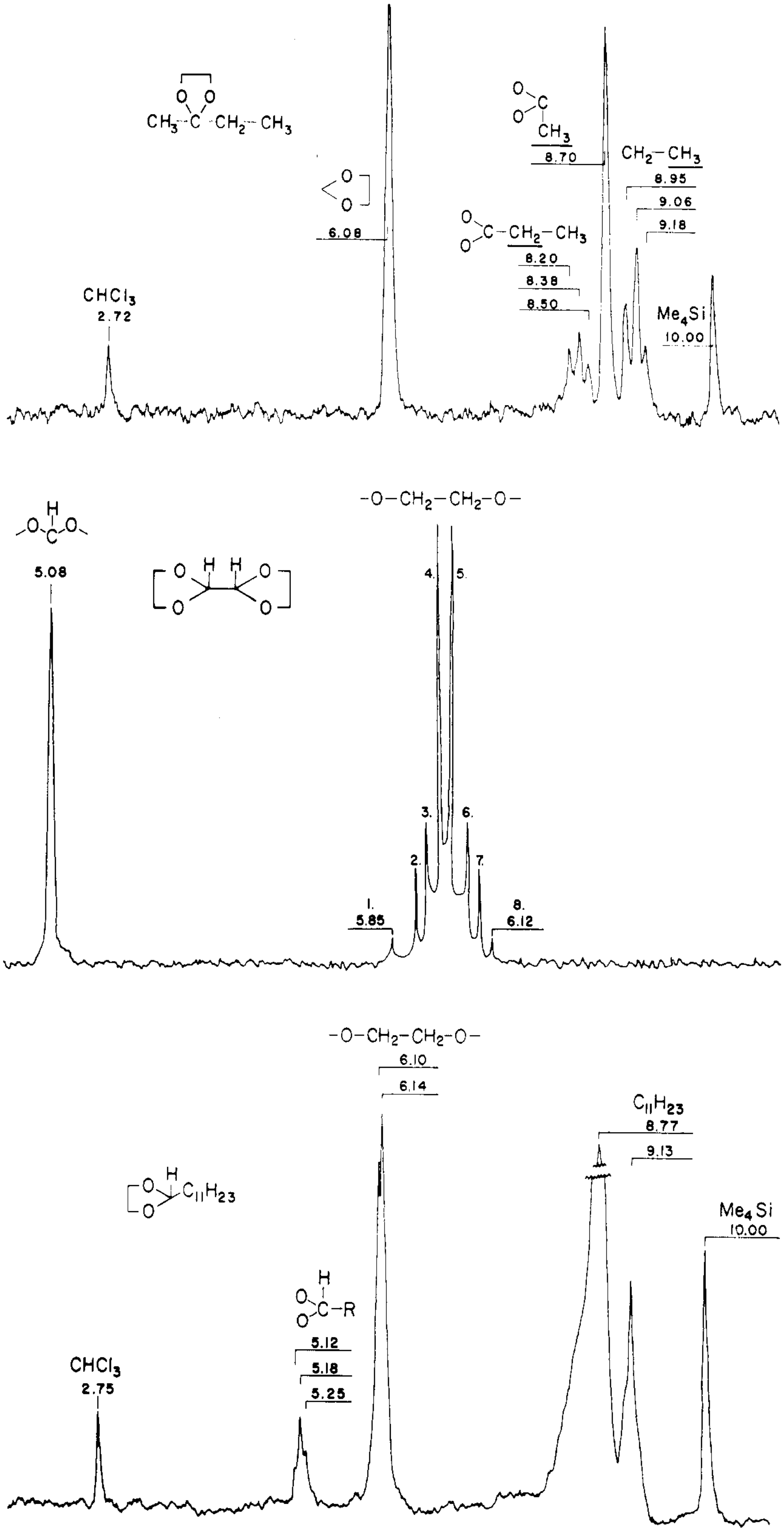

Figure 6

dioxolane (*5a*) (Fig. 6A). Dioxolane moieties attached to steroidal nuclei have also been shown to give sharp, unsplit peaks.[14,15]

Dioxolane itself is a symmetrical molecule. However, because of the substitution of various functional groups at carbon 2, the four protons at

TABLE III
SUMMARY OF N.M.R. DATA FOR DIOXOLANES

Compound	C-2-Proton peak[a]	C-4,5-Protons peaks[a]
Dioxolane	5.43[b]	6.43[b]
2-Ethyl-2-methyl (*5a*)	. . .	6.08
2,2′-Bis (*6*)	5.08	6.03
2-Lauryl (*5b*)	5.18	6.10, 6.14

[a] Expressed in τ units. [b] Converted from values given in "A Catalog of the Nuclear Magnetic Resonance Spectra of Hydrogen in Hydrocarbons and Their Derivatives," Humble Oil and Refining Co., Baytown, Texas, 1959.

carbons 4 and 5 are not equivalent in the compounds used for this study. Inspection of models indicates that the ring is fairly rigid and that free rotation about the carbon-carbon or carbon-oxygen bonds is severely restricted. Consequently, conformational inversion of the type found in dioxane would not be expected to cause a zero average of the chemical shift. For this reason splitting of the peak for the ring protons was expected to occur, but in most cases was not observed.

The ring protons of 2,2′-bis-1,3-dioxolane (*5b*) (Fig. 6B) gave a series of eight peaks for the protons on carbons 4 and 5. On cooling the solution to -60°, these peaks began to merge. No splitting was observed for the single downfield peak which was assigned to the protons on carbons 2 and 2′. If there is no accidental superposition of the bands, then the two rings are either eclipsed or rapidly rotating about the 2-2′ carbon-carbon bond.

The appearance of two bands for the protons at C-4 and C-5 of 2-lauryl-1,3-dioxolane (5b) (Fig. 6c), separated by 2.5 c.p.s., arises from the above mentioned non-equivalence of the ring protons, since two of the protons are *cis* to the lauryl group and two are *trans*. A somewhat similar situation should exist for the 2-methyl-2-ethyl-1,3-dioxolane, but here only an unsplit peak was observed for the protons at carbons 4 and 5.

Comparison of Spectra for Five- and Six-Membered Rings.—It is seen by a comparison of the spectra for dioxanes and dioxolanes that the chemical shift of the peaks for protons on carbons bearing two oxygen atoms is characteristic of the size of the ring. In the dioxolane derivative, this peak lies at lower field (*ca.* 5.1) than does the corresponding peak for the dioxane derivative (*ca.* 5.3).

The nature of the signals arising from the —O—CH_2—CH_2—O— portion of the ring is also characteristic of the size of the ring. Unless the molecule is inverting rapidly, the signal for the six-membered rings is split into a number of peaks, and the entire multiplet generally extends over a relatively wide portion of the spectrum. The signal for the analogous protons in five-membered rings is generally much narrower and often unsplit, especially when attached to steroids.

(14) J. Kalvoda, G. Anner, D. Arigoni, K. Heusler, H. Immer, O. Jeger, M. Lj. Mihailovic, K. Schaffner, and A. Wettstein, *Helv. Chim. Acta*, **44**, 186 (1961); R. F. Zürcher and J. Kalvoda, *ibid.*, **44**, 198 (1961).

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Addition Reactions with Methylenecyclodecane[1a,b]

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Addition reactions with methylenecyclodecane which presumably proceed by way of intermediates with substantial carbonium ion character lead to products which appear to have been formed by proton loss after the initial addition step. Methylenecyclodecane reacts with hydrogen bromide in acetic acid solution to give mainly 1-methylcyclodecene along with some 1-bromo-1-methylcyclodecane; with hypochlorous acid solution to give 1-(chloromethyl)cyclodecene and no chlorohydrin; with 2,4-dinitrobenzenesulfenyl chloride to give an unsaturated, chlorine-free sulfide; and with peroxybenzoic acid to give cyclodecanecarboxaldehyde instead of epoxide. However with hypobromous acid, which can form a bridged-ion intermediate, methylenecyclodecane reacts to give a high yield of a true addition product, a bromohydrin with abnormal orientation. The 1-bromocyclodecylmethanol undergoes rearrangement to 1-(bromomethyl)cyclodecene upon distillation.

Investigations in a number of laboratories have established that alicyclic compounds with medium-sized rings (eight to twelve members in the ring) exhibit features that set them apart from compounds with other ring sizes.[2] For example, chemical equilibria and relative rates of reaction involving numerous alicyclic compounds often show minima or maxima in the medium-ring range. Organic chemists have long rationalized these differences by assuming unusual nonclassical strains in the medium-ring compounds, and very recently

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(2) For a summary of some of the evidence for a medium-ring effect, see V. Prelog, *J. Chem. Soc.*, 420 (1950).