Gas Chromatographic Study of the Formation of Hydrogen Bond Complexes between Bicyclic Alcohols and Tris(*p-tert*-butylphenyl) Phosphate

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Abstract: A gas–liquid chromatographic (glc) method has been used to study the formation constants and strengths of intermolecular hydrogen bond complexes between a series of bicyclic alcohols and tris(*p-tert*-butylphenyl) phosphate (TBPP). The method involves the measurement of the gas–liquid partition coefficients of the bicyclic alcohols on columns of varying concentrations of TBPP in an inert solvent—dotriacontane. The formation constants of *endo*-bicyclo[2.2.1]hept-5-en-2-ol and *syn*-bicyclo[2.2.1]hepten-7-ol were found to be significantly smaller than the corresponding exo and anti isomers, indicating an intramolecular H bond between the double bond and the endo and syn hydroxyl protons. The strength of this intramolecular H bond was estimated to be 0.5 kcal/mole. Intramolecular H bonding to a cyclopropane ring was also observed in this work. The influence of steric effects on intermolecular H bonding was also detected, with methyl substitution on the C-2 carbon of the bicyclo[2.2.1]heptane ring having a greater influence than methyl substitution at the C-1 or C-7 positions. This study lends further weight to the validity of the glc method for obtaining formation constants and heats of formation of reversible complexes.

Much of the data for hydrogen bond (H bond) formation constants and strengths, for the same donor–acceptor systems reported by various authors, often differ far in excess of the stated experimental error.[1-3] Recent work has involved the refinement of methods for the accurate measurement of H bond strengths and the correlation of these values with the properties of the proton donor and acceptor. Active in this area have been Arnett, Schleyer, and Taft,[2,4,5] using infrared (ir), calorimetric, and nuclear magnetic resonance (nmr) methods, and Drago and coworkers,[6-8] using a calorimetric method. Of these techniques, the method which can give the most precise results but which is experimentally difficult is calorimetry. This technique requires the use of extremely pure reagents.

A problem of all the above mentioned techniques is that large concentrations of the proton donor or acceptor must be used in order to obtain measurable changes. Under such conditions, self-association of the proton donor or acceptor (especially in the case of alcohols) can give rise to simultaneous equilibria and thus give erroneous results. Emslie, *et al.*,[9] have demonstrated that Beer's law often is not obeyed for weak complexes where large concentrations of the base are needed. In general, the spectroscopic techniques use some form of the Benesi–Hildebrand equation[10,11] to determine formation constants. The limitations and errors in this are well known.[12,13] Consequently there is a need for new methods of determining H bond formation constants and strengths.

Gas–liquid chromatography (glc) has recently been used for the measurement of formation constants of nonionic complexes in nonaqueous media. In its most general form, the partition coefficient K_R is measured as a function of the concentration of an additive C_A in an inert solvent, the additive being capable of reversibly complexing with the solute. The formation constant of the complex can then be obtained from the slope of the linear relationship between K_R and C_A. Purnell[14a] has discussed this measurement in great detail. The first workers to apply the method were Bradford, *et al.*[14b] This method was then used in detail by Gil-Av and Herling,[15] Muhs and Weiss,[16] and Cvetanovic and coworkers[17] in the determination of the formation constants of silver–olefin complexes in ethylene glycol. Formation constants for charge-transfer complexes have been measured by Purnell and coworkers,[18,19] Eon,[20] and in a slightly different form by Langer, *et al.*[21] Of pertinent interest to the present work, the method has also been applied to H bonding complexes;[22-24] see also ref 25.

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The glc technique has some distinct advantages over the previous techniques for the measurement of H bonding formation constants: (1) the proton donor solutes need not be of high purity, (2) the method has an inherent wide temperature range capacity, (3) the method is experimentally simple, and (4) small formation constants can be precisely measured at infinite dilution of the solute. The results to date for H bonding complexes[25] and for electron donor–acceptor complexes[20] indicate satisfactory agreement between glc and other experimental methods, when self-association is not significant.

In this paper, we explore further the glc method for measuring formation constants of H bonding complexes by studying the complexation between bicyclo[2.2.1]heptanols and tris(*p-tert*-butylphenyl) phosphate (TBPP). The bicyclo[2.2.1]heptane system is ideal for such studies because of the rigidity of the molecule and because the steric and electronic environment of the alcohol can be systematically varied. The compounds thus provide a good test of the method, as well as information on such fundamental details as intramolecular H bonding. In addition, the formation constant for H bonding between phenol and TBPP has been measured to provide some comparison with literature values.

Experimental Section

A. Solutes. All of the compounds used in this work were synthesized as described in the literature unless noted otherwise. Their structures and the references to their syntheses are shown in Table I. Glc on two columns (Carbowax 6000 and tris-1,2,3-cyanoethoxypropane, each 6 ft × 0.25 in. with a 20% loading on DMCS-treated Chromosorb P) was able to detect a minimum purity level of 99%. Those compounds which showed impurities were purified by preparative glc using a 10 ft × 0.375 in. column packed with a 20% loading of Carbowax 6000 in DMCS-treated Chromosorb P. All solutes that were chromatographed in the study were pure to 99%+.

B. Chromatography. 1. Apparatus. The instrument used in this work was a Varian Aerograph Model 1520 gas chromatograph equipped with a thermal conductivity detector. Instead of the instrument's oven, accurate temperature control of the column was achieved by using a silicone oil bath equipped with two variable speed stirrers, a proportional temperature controller with a thermistor probe (Fisher Scientific), two 500-W immersion heaters, and a Variac. With this system the temperature was controlled to better than 0.1° between 105 and 135° as determined from a calibrated thermometer (Brooklyn Thermometer Co.) which could be read to ±0.05°. The bath was placed next to the gc unit, and the column outlet was connected by a heated 6-in. piece of stainless steel capillary tubing (0.02 in. i.d.) directly through the rear of the instrument into the thermal conductivity detector. The carrier gas flow was controlled by a two-stage regulator on the helium tank, followed by the needle valves of the Varian Aerograph unit. Before entering the column, the carrier gas was heated to the column temperature by means of a 10 ft coil of 0.125 in. o.d. copper tubing placed inside the bath. Two T-joint fittings were placed after this coil. To the first a mercury manometer was attached to read the column pressure drop, and to the second fitting, one arm supported a silicone rubber septum and to the other arm the column was attached for one column injection. The flow rate through the column was measured after the detector by means of a soap bubble flow meter.

2. Liquid Phases. Dotriacontane (n-$C_{32}H_{66}$), the inert phase, was purchased from Aldrich Chemical Company and used without

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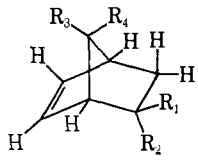
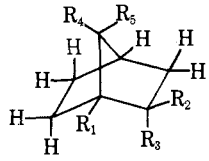
Table I.



A



B

A. Bicyclo[2.2.1]heptenols

No.	R_1	R_2	R_3	R_4	Ref
1	H	OH	H	H	*a,b*
2	OH	H	H	H	*b,c*
3	H	H	OH	H	*d,e*
4	H	H	H	OH	*f*
5	H	OCH_3	H	H	*g*
6	H	H	H	OCH_3	*h*

B. Bicyclo[2.2.1]heptanols

No.	R_1	R_2	R_3	R_4	R_5	Ref
7	H	OH	H	H	H	*i–k*
8	H	H	OH	H	H	*l,m*
9	H	H	H	H	OH	*f,n*
10	H	CH_3	OH	H	H	*o–q*
11	H	OH	CH_3	H	H	*o,q,r*
12	CH_3	OH	H	H	H	*o,q,r*
13	CH_3	H	OH	H	H	*m,q*
14	CH_3	OH	H	CH_3	CH_3	*s*
15	CH_3	H	OH	CH_3	CH_3	*s*
16	CH_3	OCH_3	H	CH_3	CH_3	*t*
17	CH_3	H	OCH_3	CH_3	CH_3	*u*
18	H	CH_3	OCH_3	H	H	*v*

C. Other Alcohols and Ethers

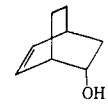
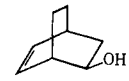
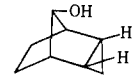
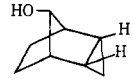
No.	Structure	Ref
19		*k*
20		*k*
21		*w*
22		*w*
23	C_6H_5OH	*s*
24	$C_6H_5OCH_3$	*s*

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Table II. Densities of Liquid Phases at Chromatographic Temperatures

Temperature, °C	Density, g/ml					
	Pure n-$C_{32}H_{66}$	Pure TBPP[a]	0.16 M TBPP in n-$C_{32}H_{66}$	0.32 M TBPP in n-$C_{32}H_{66}$	0.24 M TBPP in n-$C_{32}H_{66}$	0.08 M TBPP in n-$C_{32}H_{66}$
135.0	0.7242	0.9912	0.7609	0.7809	0.7699	0.7425
130.0	0.7271	0.9947	0.7368	0.7841	0.7731	0.7454
125.0	0.7304	0.9982	0.7671	0.7872	0.7761	0.7488
120.0	0.7335	1.0017	0.7699	0.7903	0.7792	
115.0	0.7365	1.0053	0.7730	0.7934	0.7823	0.7548
110.0	0.7395	1.0087	0.7763	0.7966	0.7854	
105.0	0.7425	1.0121	0.7791	0.7997	0.7885	0.7608

[a] TBPP = tris(*p-tert*-butyphenyl) phosphate.

further purification. Its ir spectrum indicated that no polar functional groups were present. Tris(*p-tert*-butylphenyl) phosphate (TBPP), the electron donor, was synthesized according to the procedure given by Kosolapoff.[26]

In order for the partition coefficients, K_L, to be calculated, the volume of liquid phase in the column must be known at all of the chromatographic temperatures. These volumes were measured by determining their densities by means of mercury dilatometry.[27] The data are given in Table II.

3. Preparation of Columns. All columns used in this work were 0.25 in. o.d. × 6 ft. The support was Chromosorb P, 80–100 mesh (acid washed, DMCS treated). For the series of columns of differing amounts of 0.16 M TBPP in dotriacontane, all of the coatings were made from one stock solution to avoid variation in TBPP concentration. The exact weight of coating was determined by careful weighing before and after coating and by Soxhlet extraction of a weighed portion of the coated support. The two weights were averaged (agreement better than 0.1%).

4. Chromatographic Procedure. The solutes were dissolved individually in methylene chloride and injected directly onto the column with a 10-μl Hamilton syringe. All solutes were injected as individual isomers except for isomers **19** and **20** and isomers **21** and **22** which were chromatographed as isomeric mixtures. The general procedure for the accurate measurement of retention volumes has been discussed previously by many authors.[28–30]

To check for the effect of sample size upon retention times, an F & M Model 810 gas chromatograph equipped with a flame ionization detector was used. Variation of sample size from 0.1 to 2 μl gave no change in retention time within experimental error. For the thermodynamic work, the sample sizes range from 0.2 to 1.4 μl of solution (1×10^{-3} mole/ml), which was the limit of sensitivity on the Varian instrument.

Theory

Glc Approach. The simplest and most favorable case in glc is the formation of a 1:1 complex between the volatile solute B reacting with a complexing nonvolatile additive A dissolved in an unreactive solvent S. The equilibria are

$$B(g) \overset{K_L^0}{\rightleftharpoons} B(l)$$

$$B(l) + A(l) \overset{K_f}{\rightleftharpoons} AB(l)$$

where K_L^0 is the partition coefficient of uncomplexed B between the bulk liquid S and the gas phase, and K_f is the formation constant of AB in S. The observed partition coefficient, assuming no volume change in dissolution of B and ideal behavior of A in S, is given by[14]

$$K_L = K_L^0(1 + K_f C_A) \quad (1)$$

where C_A is the additive concentration. K_L is evaluated from the fully corrected net peak maximum retention volume, V_N, through the well-known retention equation at infinite dilution:

$$V_N = K_L V_L \quad (2)$$

where V_L is the volume of stationary phase and V_N is independent of sample size.

Serious problems may arise using an inert stationary solvent whose polarity is low in comparison to the additive and the solute. A solvent which is inert to the complexation interaction may then also be a poor solvent for the solute (B). Since in glc the solvent is spread over a support, the surface area of the liquid will be large; hence, the possibility of the solute adsorbing on the liquid surface is great. In addition, solute adsorption may occur on the solid support itself. Under such conditions eq 2 is no longer valid, and methods must be used to cancel the adsorption contribution to the retention volume V_N.

Perhaps the best treatment of the adsorption problem comes from the work of Purnell, Conder, and Locke[31,32] who have considered the general problem of bulk liquid partition, liquid interfacial adsorption, and solid support adsorption occurring concurrently. They have proposed that the several retention mechanisms can be treated as essentially independent if sufficient solvent is present to act as bulk liquid. On this basis, the observed partition coefficient at infinite dilution, K_R, is given by

$$K_R = \frac{V_N}{V_L} = K_L + \frac{K_I A_I}{V_L} + \frac{K_S A_S}{V_L} \quad (3)$$

where K_I and K_S are the liquid surface and solid support partition coefficients, respectively, and where A_I and A_S are the surface areas of the liquid and exposed solid support, respectively. The partition coefficient of the bulk liquid K_L can be evaluated from the intercept of plots of K_R *vs.* V_L^{-1}. Conder[33] has developed a method to derive K_L in cases where asymmetrical peaks are observed.

Equation 1 has recently been criticized[20,34] for not considering the activity coefficients of the various species in solution or the consequences of the different sizes of the additive and inert solvent. Now (1) converting from a concentration based formation constant, K_f (l./mole), to one based on mole fraction, K_X; (2) assuming that the molar volume of the mixture of addi-

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tive A and solvent S, $v_{A,S}^0$, is linear with mole fraction of additive; (3) dividing the activity coefficients into thermal and athermal contributions and assuming the simple Flory–Huggins equation[35] for the athermal portion, Eon[20] derives

$$v_{A,S}^0 K_L = v_S^0 K_L^0 \left[1 + \left(\psi + K_X \frac{\gamma_{A(A,S)}\gamma_{B(S)}}{\gamma^\infty_{AB(A,S)}}\right) X_A\right] \quad (4)$$

where v_S^0 = molar volume of solvent

$$\psi = \frac{a_{\gamma^\infty_{B(S)}}}{a^\infty_{B(A)}} - 1 = \frac{v_A^0}{v_S^0}\left[\frac{\exp(v_B^0/v_A^0)}{\exp(v_B^0/v_S^0)}\right]^{-1}$$

v_B^0 = molar volume of solute, v_A^0 = molar volume of additive, $a_{\gamma^\infty_{B(S)}}$ = athermal activity coefficient of B in S at infinite dilution, $a_{\gamma^\infty_{B(A)}}$ = athermal activity coefficient of B in A at infinite dilution, $\gamma^\infty_{B(S)}$ = total activity coefficient of B in S at infinite dilution, $\gamma^\infty_{AB(A,S)}$ = total activity coefficient of the complex AB in A,S at infinite dilution, and $\gamma_{A(A,S)}$ = activity coefficient of A in A,S at concentration X_A.

From eq 4, a plot of $v_{A,S}^0 K_L$ *vs.* X_A will give, after subtraction of ψ, K_X times the activity coefficient factor, and not directly K_X. However, if we assume $\gamma_{A(A,S)}$ is not appreciably different from γ^∞_A (probably true in the low concentrations of A used in the glc experiment), and if we define a new constant of complex formation

$$K_X^* = \frac{X_{AB}}{X_A X_B} \frac{\gamma_{AB}^*}{\gamma_A^* \gamma_B^*} \quad (5)$$

where γ^* is the activity coefficient of the given species with a reference state of infinite dilution, then eq 4 can be written as

$$v_{A,S}^0 K_L = v_S^0 K_L^0 [1 + (\psi + K_X^*) X_A] \quad (6)$$

The formation constant, K^*, as pointed out by Eon,[20] is now a thermodynamically meaningful constant; however, it must be remembered that it is based on an infinitely dilute reference state in a *given solvent*. The heat of hydrogen bond formation can be obtained from the slope of the linear plot of ln K_X^* *vs.* $1/T$, and the free energy and entropy of formation can be found in the standard manner.

It is instructive to compare the value of the formation constant obtained from eq 1, K_f, with that obtained from eq 6, K_X^*. If

$$v_{A,S}^0 = v_S^0 + (v_A^0 - v_S^0) X_A \quad (7)$$

then eq 1, 6, and 7 can be combined to give

$$K_X^* = \frac{K_f}{v_S^0} + \frac{v_A^0}{v_S^0}\left(1 - \frac{\exp(v_B^0/v_A^0)}{\exp(v_B^0/v_S^0)}\right) \quad (8)$$

Taking density data in Table II at 115°, v_S^0 = 0.612 l./mole, and v_A^0 = 0.497 l./mole, and estimating v_B^0 = 0.100 l./mole, eq 8 becomes

$$K_X^* = \frac{K_f}{0.612} - 0.034 \quad (9)$$

Equation 9 shows that the importance of the athermal correction term is a function of the value of K_f. For strong complexes, such as H bonding (see Table IV), the correction term is insignificant; however, for weak complexes, the correction can be significant. In this work, we have determined K_f from eq 1, and then converted to K_X^* with eq 8.

Pure Base Approach. Recently, a new approach based on calorimetric determination of H bonding enthalpies has been developed.[2,36] The heat of solution, $\Delta\bar{H}_S$, of the solute (proton donor) is composed of two terms, the excess enthalpy of solution, $\Delta\bar{H}_E$, and the heat of vaporization, ΔH_V. The $\Delta\bar{H}_E$ term is composed of all the solute–solvent interactions, one of which is H bonding. The pure base approach involves the cancellation of all energy terms other than H bonding. For this purpose a model compound, the methyl ether of the corresponding alcohol, is chosen. Specifically, the method involves the measurement of $\Delta\bar{H}_S$ of the alcohol and its methyl ether in both the pure base B and an inert solvent S which acts as a reference solvent so that the ΔH_V values cancel. The heat of formation of the H bonding $\Delta H°$ is then given by

$$\Delta H° = [(\Delta\bar{H}_S)_{ROH} - (\Delta\bar{H}_S)_{ROMe}]_B - [(\Delta\bar{H}_S)_{ROH} - (\Delta\bar{H}_S)_{ROMe}]_S \quad (10)$$

The results of the calorimetric measurements were found to agree well with the values determined by other techniques.[2]

We decided to test this approach by the glc method using methyl ethers of the bicyclo[2.2.1]heptanols. It is to be noted that for $\Delta H°$ to reflect true H bonding enthalpies three assumptions must be made: (1) the alcohol is 100% complexed with B, (2) no extra solvation terms arise upon complexation; (3) the methyl ether model completely cancels all interaction contributions to $\Delta\bar{H}_E$ except H bonding. For bases which give no solvent enhancement upon complexation,[37] the $\Delta H°$ values have precisions of the order of ±0.1 kcal/mole by the calorimetric method.[2] However, since this method has no theoretical justification and owing to the fact that it has failed in certain circumstances, the $\Delta H°$ values should be treated with caution.

Results and Discussion

A. Contribution of Adsorption. Since aliphatic C_3–C_5 alcohols have been shown by Cadogan and Purnell[22] to adsorb on the surface of squalane and didecyl sebacate in squalane, the bicyclic alcohols might be expected to adsorb as well. In order to determine valid formation constants, the adsorption contribution to retention must be determined. This was achieved by measuring the partition coefficients of the solutes with columns of 25 and 10% by weight loadings of pure dotriacontane and with columns of 25, 20, and 10% by weight loadings of a 0.16 *M* solution of TBPP in dotriacontane.

Table III shows the partition coefficients at 120° of the bicyclic compounds and phenol on the pure dotriacontane columns. Except for phenol **23**, the partition coefficients are seen to be reproducible within experimental error (1%). Consequently, the adsorption contribution to the partition coefficient is negligible for the bicyclic alcohols. This conclusion is reasonable for three reasons: (1) the bicyclics have more carbon

(35) E. A. Guggenheim, "Mixtures," Oxford University Press, Oxford, 1954.

(36) E. M. Arnett, T. S. S. R. Murty, R. v. R. Schleyer, and L. Joris, *J. Amer. Chem. Soc.*, **89**, 5955 (1967).

(37) T. D. Epley, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1968; University Microfilms, No. 69-1339.

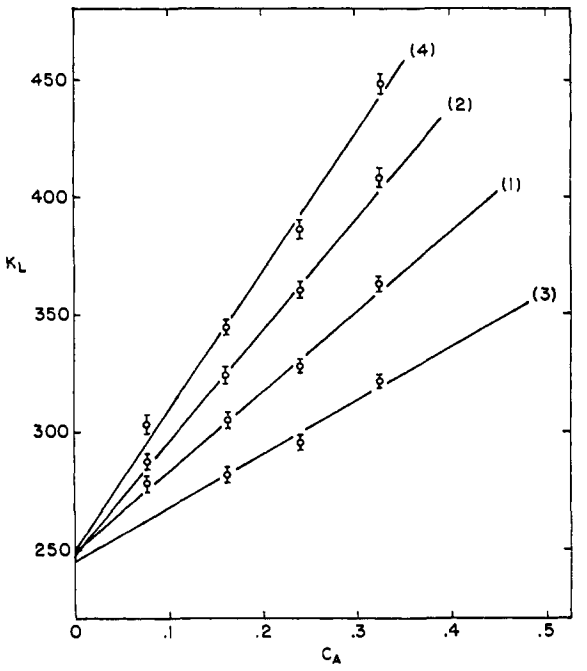

Figure 1. Plots of K_L against C_A at 105°: (1) *endo*-bicyclo[2.2.1]-hept-5-en-2-ol; (2) *exo*-bicyclo[2.2.1]hept-5-en-2-ol; (3) *syn*-bicyclo[2.2.1]hept-2-en-7-ol; (4) *anti*-bicyclo[2.2.1]hept-2-en-7-ol.

atoms, hence the solutes should be more soluble in the nonpolar solvent than the C_3–C_5 alcohols; (2) the hydroxyl group on the bicyclic alcohols is sterically hindered; and (3) a higher temperature is used in this work (105–130°) relative to the work of Purnell and Cadogan (50–70°).

Table III. Partition Coefficients K_R on Columns of Different Volumes of Pure Dotriacontane at 120°

Compound number	K_R	
	Column A[a]	Column B[b]
1	163	164
2	160	162
3	164	166
4	162	164
7	216	217
8	226	225
9	232	234
10	269	270
11	271	273
12	260	262
13	260	261
15	835	831
14	810	800
19	408	407
20	408	407
21	583	584
22	583	584
23	145	151

[a] Column A – V_L = 5.35 ml (20% loading). [b] Column B – V_L = 2.57 ml (10% loading).

The activity coefficients of *exo*- and *endo*-bicyclo-[2.2.1]hept-5-en-2-ol in dotriacontane were determined from their specific retention volumes and their vapor pressures (exo = 106.2 mm, endo = 123.7 mm) at 115° and are 1.84 and 1.69, respectively. The activity coefficients of the C_3–C_5 alcohols in squalane have been measured and a comparison of their values which range from 3 to 8 at 50° with the above indicates that the bicyclic alcohols are much more soluble in alkane solvents. Martire[38] postulated that adsorption at the gas–liquid interface is important for polar solutes on nonpolar liquids only when the activity coefficient is greater than 4 or 5. This agrees with our results.

Similarly, the results for 0.16 *M* phosphate in dotriacontane indicate no adsorption contribution for the bicyclic alcohols, except phenol, which shows a small but definite increase in partition coefficient with a decrease in per cent loading of liquid phase. However, for phenol, the values of $K_R - K_L$, which is a measure of the contribution of surface terms, were found to be equal on dotriacontane and the 0.16 *M* TBPP columns of the same per cent loading. More simply, this means that the percentage of retention due to adsorption at the gas–liquid interface is the same for a given surface area independent of C_A. Cadogan and Purnell[22] found similar results for didecyl sebacate–squalane systems. In addition, the value of $K_R - K_L$ was found to be independent of temperature between 115 and 130°. Thus, for phenol the adsorption contribution to K_R at other TBPP concentrations was calculated from the values of $K_R - K_L$ of the 0.16 *M* TBPP columns.

B. Formation Constants of the Hydrogen Bond Complexes. The H bond formation constants K_X^* were determined from a least-squares analysis of the straight line plots of the partition coefficient K_L *vs.* the concentration of TBPP, C_A, and applying eq 9. No deviation from linear behavior was found for any of the solutes; linear correlation coefficients were all in excess of 0.995. Figure 1 illustrates typical plots of K_L against C_A at 105° for several bicyclic alcohols. In Table IV are listed the derived H bond formation constants K_X^*, the standard deviation $S_{K_X}^*$, the partition coefficient of the uncomplexed solute determined by the intercept of the plot of K_L *vs.* $C_A - K_L^0$, and the partition coefficient of the solute in the pure dotriacontane column, K_R. The formation constants have a reproducibility of ±0.05. The excellent agreement between K_L^0 and K_R together with the linearity of these plots offers confirmation of eq 1 and, hence, 1:1 complex formation.

The corresponding methyl ethers of some of the alcohols were subjected to the same experimental treatment as the alcohols. Although the methyl ethers are expected to interact with TBPP, and thus are expected to be sensitive to changes in C_A, this dependence should be small. The results in Table IVD show that the K_X^* values are indeed small except for anisole **24** and the unsaturated ethers **5** and **6**. Nuclear magentic resonance evidence exists for the formation of weak complexes between bicyclo[2.2.1]heptenes and benzene.[39] Therefore, the unsaturated ether results probably reflect this interaction. Evidence from the K_X^* values discussed below also reflects complexation interactions other than H bonding. However, the saturated ethers **16** and **17** show K_X^* values, within experimental error, of zero. Therefore, the saturated bicyclic alcohols show H bonded K_X^* values, whereas the unsaturated analogs will show complexation due to H bonding

(38) D. E. Martire, *Anal. Chem.*, 38, 244 (1966).
(39) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 86, 1171 (1964).

Table IV. Values of 1:1 H Bonded Complexes K_X* (mole fraction), Standard Deviation S_{K_X}, Intercept of K_L *vs.* C_A plots, K_L^0, and K_R (on pure n-$C_{32}H_{66}$) at 115°

Compound number	K_X*	S_{K_X}*	K_L^0	K_R
	A. Bicyclo[2.2.1]heptenols			
1	2.04	0.07	188	191
2	2.84	0.08	187	189
3	1.16	0.07	193	194
4	3.53	0.09	185	188
	B. Bicyclo[2.2.1]heptanols			
7	2.37	0.07	255	255
8	2.47	0.03	259	260
9	2.70	0.04	267	268
10	1.72	0.01	309	308
11	1.83	0.01	310	310
12	1.93	0.01	309	310
13	2.16	0.03	308	310
14	2.21	0.02	952	954
15	2.39	0.02	987	990
	C. Other Alcohols			
19	1.99	0.06	475	488
20	2.78	0.06	476	480
21	2.35	0.02	672	682
22	3.33	0.05	676	682
23	21.4	0.8	145	152
	D. Methyl Ethers			
5	0.52		217	
6	0.37		189	
16	0.03		830	
17	0		869	
18	0.24		433	
24	0.90		207	

and a further contribution from the carbon–carbon double bond.

In the next several sections we shall discuss the results of Table IV in detail.

1. Bicyclo[2.2.1]hept-5-en-ols (1–4). DePuy and Story[40] in 1959 separated compounds **1** and **2** and their saturated analogs **7** and **8** by gas chromatography. In the saturated series, the endo isomer **8** eluted after the exo isomer, whereas in the unsaturated series the order was reversed. They attributed this reversal in elution to the formation of an intramolecular H bond between the hydroxyl group in the endo position and the unsaturated center. The ability of the carbon–carbon double bond to act as a base in intramolecular H bonding is, of course, well documented in the literature.[41–45]

For the compounds in Table IVA, *endo*-bicyclo[2.2.1]hept-5-en-2-ol (**1**) and *syn*-bicyclo[2.2.1]hepten-7-ol (**3**) are capable of forming an intramolecular H bond to their π system, whereas the corresponding exo isomer **2** and anti isomer **4** are incapable of such an interaction. Thus, isomers **1** and **3** should show a smaller degree of intermolecular H bonding with TBPP than the corresponding **2** and **4**.

Table IVA reflects this trend (*i.e.*, $K_{X,1}^* < K_{X,2}^*$; $K_{X,3}^* < K_{X,4}^*$. It is interesting to note that isomer **3** has a significantly smaller K_X* value than **1**, which may indicate that **3** forms a stronger intramolecular H bond. The infrared frequency shift data[42] for these compounds agree with this result. The infrared spectra taken in dilute carbon tetrachloride solution showed two bands which are assigned to the free hydroxyl stretching and the intramolecular H bond hydroxyl stretching absorptions. The frequency shift $\Delta\nu$, which is an indication of the strength of the H bond,[3,6,7] is larger for isomer **3**.

Ouellette and coworkers,[46] using nuclear magnetic resonance, studied the association of isomers **3** and **4**, as well as a number of others in this work. Their measurements, as ours, for compounds **3** and **4** reflect a strong intramolecular H bond in isomer **3**. Unfortunately, they reported no values for isomers **1** and **2**.

For isomers **2** and **4**, the significant difference in the formation constants can be explained most easily by steric effects. Molecular models show that approach of the phosphate from above the ring is much less hindered for the C-7 hydroxyl group than the exo or endo C-2 hydroxyl group.

In summary, the results in Table IVA are in agreement with the literature, and therefore suggest the validity of the glc approach.

2. Bicyclo[2.2.1]heptanols (7–9). Table IVB shows that the K_X* values for *exo*- and *endo*-2-bicycloheptanols **7** and **8**, respectively, are essentially the same within experimental error (±0.05). This indicates that the steric environments of the hydroxyls for H bonding are similar for the two isomers. This is borne out in the rate constants of hydrolysis of the corresponding acid phthalates.[47] Both compounds show the same rates of hydrolysis, indicating that steric effects are similar for the exo and endo isomers. In addition the dipole moments[48] of isomers **7** and **8** have been measured in benzene solution: 1.63 D and 1.66 D, respectively. The equivalence of the dipole moments further shows that small differences are to be expected between these isomers in H bonding. Therefore, these isomers separate for the most part on the basis of size difference. However, 7-bicycloheptanol (**9**) shows a larger K_X* which is in keeping with the trend that the C-7 position is sterically more accessible than the C-2 position.

The larger K_X* value for **9**, relative to norborneol (**8**) and isonorborneol (**7**), agrees with the limiting slope nmr data obtained by Ouellette, *et al.*[46] However, a larger limiting slope was found for **7** than **8**, suggesting that the exo isomer should have the larger formation constant for dimerization. This result should not be disturbing since the steric requirements of the alcohol acting as an electron donor are vastly different from those of the phosphate. Molecular models indicate that the oxygen atom that is one atom removed from the bicycloheptane ring is much more hindered than the oxygen of P=O. In the latter case the aromatic groups are bent away from the site of interaction. It may well be that relative steric accessibility (exo *vs.* endo) of the oxygen from the hydroxyl group is such

(40) C. H. DePuy and P. R. Story, *Tetrahedron Lett.*, 20 (1959).
(41) R. West, *J. Amer. Chem. Soc.*, 81, 1614 (1959).
(42) (a) L. Joris, P. v. R. Schleyer, R. Gleiter, *ibid.*, 90, 327 (1968); (b) P. v. R. Schleyer, D. A. Trifan, and R. Bacskai, *ibid.*, 80, 6691 (1958).
(43) L. P. Kuhn and R. E. Bowman, *Spectrochim. Acta, Part A*, 23, 189 (1967).
(44) M. Oki and H. Iwamura, *Bull. Chem. Soc. Jap.*, 32, 1135 (1959).
(45) C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *J. Phys. Chem.*, 60, 1311 (1956).
(46) (a) R. J. Ouellette, K. Liptak, and G. E. Booth, *J. Org. Chem.*, 32, 2394 (1967); (b) R. J. Ouellette, K. Liptak, and G. E. Booth, *J. Amer. Chem. Soc.*, 87, 3436 (1965).
(47) S. Beckmann and S. Hohenheim, *Bull. Soc. Chim. Fr.*, 1319 (1960).
(48) P. Hirsjarvi and H. Krieger, *Suomen Kemistilehti B*, 37, 140 (1964); *Chem. Abstr.*, 62, 2321*a* (1965).

that the exo isomer has the larger formation constant. This discussion points out that in terms of H bonding, the measurement of the formation constants for dimer complex is not as valid as the measurement of complexation constants at very low concentrations using a separate electron-donating species. In the former case secondary effects dealing only remotely with the ability of the hydroxyl proton to be involved in H bonding can influence the complexation constant. However, a better measure of H bonding for both methods is the enthalpy of complex formation. Values for these and other compounds will be given in a later section.

Comparison of *exo*-2-bicycloheptenol (**1**) with *exo*-2-bicycloheptanol (**7**) and *anti*-7-bicylcoheptenol (**4**) with 7-bicycloheptanol (**9**) indicates that in both cases the bicycloheptenols have the larger K_X* value. Since the steric environment of the hydroxyl group in each pair of isomers is the same, steric effects cannot be used to explain the difference in formation constants. Recalling that the corresponding methyl ethers of isomers **1** and **4** showed an indication of weak complexation with the phosphate (see Table IVD) and that bicyclo[2.2.1]-heptenes are known to form complexes with benzene[39] the enhancement in the K_X* values for alcohols **1** and **4** is probably caused by non-hydrogen-bonded interaction between the solute and TBPP.

3. Methylbicyclo[2.2.1]heptanols (10–15). Substitution of a methyl group on the carbon bearing the hydroxyl group greatly reduces the formation constant for H bonding. Table IV shows that *endo*-2-methyl-*exo*-2-bicycloheptanol (**11**) has a much lower formation constant then *exo*-2-bicycloheptanol (**7**). The same trend occurs for the *exo*-methyl isomer **10** as compared to *endo*-2-bicycloheptanol (**8**). As with the 2-bicycloheptanols **7** and **8**, the formation constants of isomers **10** and **11** indicate that the difference between the exo and endo position in H bonding is small even in the presence of a methyl group at C-2.

The steric effect of a methyl group in the 1 position upon the hydroxyl group in the 2 position would be expected to be a function of the dihedral angle between the methyl and hydroxyl groups. Since the dihedral angle is less with the hydroxyl in the exo position, the formation constant of 1-methyl-*exo*-2-bicycloheptanol (**12**) is expected to be less than that of 1-methyl-*endo*-2-bicycloheptanol (**13**). The formation constants are 1.93 and 2.16, respectively. Clearly, the methyl group at C-1 hinders the exo 2 position better than the endo 2 position. The same trend is indicated by the rates of hydrolysis of the corresponding acid phthalates.[47]

Comparison of methyl substitution at C-1 relative to C-2 in bicycloheptanol indicates that substitution at C-2 is more effective in inhibiting H bonding. However, nmr data for association of these alcohols indicates that the exo alcohol **12** is more associated than the endo isomer **13**. We have already discussed a possible reason for this difference in the previous section.

4. Trimethylbicyclo[2.2.1]heptanols (14–15). It is expected that substitution of a methyl group at C-7 syn to the hydroxyl group at C-2 would reduce K_X*, as was found with methyl substitution at C-1. Steric hindrance in this case is expected to be largest with the hydroxyl group in the exo position at C-2. Furthermore, with a methyl group at both C-7 and C-1, the formation constant is expected to be lower than that of compound **12** which has a methyl group at C-1.

However, Table IVB indicates that 1,7,7-trimethyl-*exo*-2-bicycloheptanol (**14**) has a higher formation constant than 1-methyl-*exo*-2-bicycloheptanol (**12**), the formation constants being 2.21 and 1.93, respectively. In addition, compound **14** has only a slightly smaller formation constant than the unsubstituted *exo*-2-bicycloheptanol (**7**). A similar trend is found with the corresponding endo isomers. The formation constants of 1,7,7-trimethyl-*endo*-2-bicycloheptanol (**15**), 1-methyl-*endo*-2-bicycloheptanol (**13**), and *endo*-2-bicycloheptanol (**8**) are 2.39, 2.16, and 2.47, respectively. Here again the formation constant is significantly smaller for the monomethyl-substituted compound **12**.

These results may be tied up with the solvent effects of the dotriacontane. Thus in the case of the trimethyl-substituted bicyclic alcohols, the complex may be better solvated than for those alcohols with a smaller methyl substitution. It is not surprising that the formation constants might be a function of the solvent. A truer picture of H bonding is, of course, given by the heat of complex formation. These values will be discussed in a later section.

5. Bicyclo[2.2.2]oct-5-en-2-ols (19–20). *endo*-2-Bicyclooctenol (**19**), as *endo*-2-bicycloheptenol (**1**), is capable of forming an intramolecular H bond. The formation constants are 1.99 and 2.04, respectively, indicating that both have the same propensity to intramolecular H bond to their π system. In carbon disulfide, the infrared spectrum[49] of **19** shows two bands, a high-frequency band associated with free hydroxyl stretching and a lower frequency band attributed to the intramolecular H bond. The intramolecular H bond is further evidenced by the fact that the exo isomer **20** has a much higher K_X* value than the corresponding endo isomer **19**.

6. Tricyclo[3.2.1.0^{2,4}]octanols (21–22). Infrared evidence[42a] exists for the formation of H bond between a proton donor and a cyclopropyl group. It is believed that the edge and not the plane of the cyclopropane ring is the site of interaction. In the infrared, isomer **21** shows two hydroxyl bands whereas isomer **22** shows only one.

The formation constant glc data also indicate that the cyclopropyl group is functioning as a proton acceptor in the syn isomer **21**, as its formation constant is significantly lower than the corresponding anti isomer **22**. Since the cyclopropyl group is in the endo position, the steric environment of the hydroxyl group of **21** should be the same as that of 7-bicycloheptanol (**9**) and the K_X* value of **21** is less than that of **9**. Therefore, steric arguments cannot be used to explain the lower value of the syn isomer.

The relative ability of the cyclopropyl group in comparison to a carbon–carbon double bond to act as a proton acceptor in intramolecular H bonding in this series can be seen from a comparison of the syn isomer **21** with *syn*-7-norborneol (**3**). The respective formation constants are 2.35 and 1.16. These data indicate a greater extent of intramolecular H bonding in the case

(49) L. Goering, R. W. Greiner, and M. F. Sloan, *J. Amer. Chem. Soc.*, **83**, 1391 (1961).

in which the carbon–carbon double bond is the proton acceptor.

Finally in Table IV, it is seen that the K_X* value for phenol **23** is roughly a factor of 10 larger than for the bicyclic alcohols. This is a strong indication of H bonding, especially when anisole **24** has a K_X* value which is only 5% that for phenol. In the next section the heat of H bonding determined by glc will be compared to that obtained by ir.

C. Thermodynamic Data for the Hydrogen Bonded Complexes. Aksnes and Gramstad[50,51] using ir have made a detailed study of H bonding between phenol and a large series of phosphoryl compounds of varying phosphoryl group polarity. They found that within the series of phosphoryl compounds, $-\Delta H°$ varied from approximately 5 to 8 kcal, and $-\Delta S°$ varied from 6 to 11 eu. Although they made no measurements with aromatic substituted phosphates, they did determine equilibrium constants for trimethyl phosphate and triethyl phosphate at 20° and 50°. The values for $-\Delta H°$ and $-\Delta S°$ calculated from their data together with our value for phenol complexing with TBPP at 115° are shown below.

Base	$-\Delta H°$, kcal/mole	$-\Delta S°$, eu.
Trimethyl phosphate	5.4	8.0
Triethyl phosphate	6.8	11.5
Tris(*p-tert*-butylphenyl) phosphate	5.7 ± 0.6	9.6 ± 1.5

These data provide strong support that we are indeed measuring the formation of true 1:1 H bond complexes by the glc approach. This is the case for the saturated bicyclic alcohols; however, as noted above, the unsaturated isomers have two contributions to K_X*—strong H bond complexation and weak bicycloheptene–aromatic ring complexation. Since the latter complex is much weaker, the enthalpies of complex formation will reflect almost entirely the strength of the H bond for the unsaturated alcohols, and, of course, entirely for the saturated alcohols.

Good linearity of the plots of ln K_X* *vs.* $1/T$ was found in the temperature range of 105–130°. From the $\Delta H°$ values and K_X*, it was possible to obtain $\Delta G°$ and $\Delta S°$. Table V shows the thermodynamic data for 1:1 complexes of H bond formation. Note that $\Delta H°$ for phenol is 1–2 kcal/mole larger than for the bicyclic alcohols, as expected.[52]

In the bicyclic series, the enthalpies range from approximately 3 to 4 kcal/mole. Even though the range is small, there are some definite trends within the series that are beyond experimental error. One trend that has been noted many times by other authors[18,22,51] is the proportionality of $\Delta H°$ to $\Delta S°$. Thus, the stronger complexes tend to have larger entro y requirements. Aksnes and Gramstad[51] have interpreted this relationship in terms of an increase in polarity of the complex relative to the reactants. The increased polarity causes a greater orientation of solvent molecules around the complex, thus contributing to a negative entropy of reaction. In agreement, Sutton and coworkers[53] have found an apparent additional dipole moment of 0.8 D in the O–H···N bond in the complex of phenol and trimethylamine.

Table V. Thermodynamic Data for 1:1 H Bonding between Bicyclic Alcohols and Tris(*p-tert*-butylphenyl) Phosphate at 115°

Compound number	$-\Delta H°$, kcal mole^{-1}	$-\Delta G°$, kcal mole^{-1}	$-\Delta S°$, cal mole^{-1} deg^{-1}
1	3.0	0.55	6.3
2	3.5	0.80	6.9
3	3.0	0.11	7.4
4	3.6	0.97	6.8
7	3.5	0.66	7.3
8	3.6	0.69	7.5
9	3.7	0.76	7.6
10	2.7	0.42	5.9
11	2.6	0.46	5.5
12	3.3 (±0.5)	0.50	7.2 (±1)
13	3.5 (±0.5)	0.59	7.5 (±1)
14	3.1	0.61	6.4
15	3.3	0.67	6.8
19	2.7 (?)	0.53	5.6
22	4.6 (?)	0.92	9.5
23	5.7 (±0.6)	2.3 (±0.3)	8.6 (±1.5)
Average standard deviation (unless otherwise noted)	±0.2	±0.03	±0.6

In Table V, the smaller $\Delta H°$ values of isomers **1** and **3** relative to the corresponding isomers **2** and **4** appear to result from the formation of the intramolecular O–H···π bond. The two isomers **2** and **4**, which can form no intramolecular H bond, have enthalpies which are 0.5 kcal/mole larger. Furthermore, the fact that $\Delta H_2° = \Delta H_7°$ and $\Delta H_4° = \Delta H_9°$ indicates that complexation between the unsaturated centers on the bicycloheptenol isomers **2** and **4** and the benzene ring of the phosphate must be negligible. Therefore, $\Delta H_2° - \Delta H_1°$ and $\Delta H_4° - \Delta H_3°$ should be a good estimate of the enthalpy of formation of the intramolecular O–H···π bond. The values obtained, 0.5 and 0.6 kcal/mole, respectively, are the same within experimental error (±0.2 kcal/mole).

Oki and Iwamura,[54] using an ir, determined the O–H···π intramolecular bond enthalpy in 1,1-dimethyl-2-phenylethanol to be 0.54 ± 0.13 kcal/mole between 25 and 65°, in close agreement with our value. However, it is important to note that at the chromatographic temperature, RT amounts to 0.7–0.8 kcal/mole, which is greater than the enthalpy of formation of the intramolecular H bond for isomers **1** and **3**. Therefore, in order for this bond to form at these temperatures, the entropy of formation ($\Delta S°$) must be very small. The errors in $\Delta S°$ are too large to give a value for the entropy of formation of the O–H···π bond in isomers **1** and **3**. However, it is expected to be small because the hydroxyl groups of these two alcohols are held close to the carbon–carbon bonds by the rigidity of the bicyclic system.

For the bicycloheptanols, **7**, **8**, and **9**, the $\Delta H°$ values are within experimental error the same. Isomers **10** and **11**, which have a methyl group substituted on the same carbon as the hydroxyl groups, show a marked decrease in $\Delta H°$ as compared to isomers **7** and **8**. This same trend was followed by the K_X* values. On the

(50) G. Aksnes, *Acta Chem. Scand.*, 14, 1475 (1960).
(51) G. Aksnes and T. Gramstad, *ibid.*, 14, 1485 (1960).
(52) R. S. Drago, N. O'Bryan, and G. C. Bogel, *J. Amer. Chem. Soc.*, 92, 3924 (1970).
(53) J. R. Hulett, J. A. Pegg, and L. E. Sutton, *J. Chem. Soc. A*, 48 (1967).
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other hand, comparison of $\Delta H°$ for isomers **7** and **8** with isomers **12** and **13** reveals that methyl substitution at C-1 produces no reduction in H bond energy. Even for isomers **14** and **15**, the $\Delta H°$ values are equivalent within experimental error. The equivalency of $\Delta H°$ for compounds **7** and **14** indicates that the methyl group at C-7 syn to the hydroxyl at exo C-2 exercises no major steric effect upon the H bond strength.

The thermodynamic results for compounds **19** and **22** are not to be trusted since severe peak overlap occurred above 120°; consequently, the K_X* values are not to be trusted above this temperature, as well. (The K_X* values in Table IV are at 115° for these compounds.)

D. Pure Base Approach. In this method, the heats of solution of the alcohol and its corresponding ether were measured in the pure phosphate and the pure dotriacontane columns. The H bond enthalpy, $\Delta H°$, was then calculated by eq 10.

The values of $\Delta H°$ calculated by the pure base approach were found to be consistently lower (*ca.* 1–1.5 kcal/mole) than the values derived from the previous glc method. The low values undoubtedly result from lack of achievement of 100% complexation of the alcohol with TBPP. There are two reasons which would account for this: (1) the chromatographic temperatures are too high and (2) the pure phosphate is so highly associated that the few phosphoryl groups are available for H bonding. This, it appears that the pure base method cannot be used as a gas–liquid chromatographic technique for measuring H bond enthalpies at the temperatures used in this work.

Conclusion

Glc has been shown to be a worthwhile method for studying H bond complexes. The advantages of the method are: (1) measurements are made at infinite dilution of the solute so that self-association is not a problem; (2) purification is not required; and (3) the method is simple and rapid. As pointed out in the paper the disadvantages are: (1) secondary solvent effects can arise and (2) the precision in $\Delta H°$ is less than in calorimetry (however, comparable to other methods for determining $\Delta H°$). This study along with other recent ones[20] indicates that glc can become a standard method for studying reversible complexes.

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Mechanisms of Elimination Reactions. XVIII. The Effect of Base, Solvent, and Structure on Product Ratios in E2 Reactions of Some Sulfonium Salts[1]

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Abstract: The effect of changing from an *n*- to a *sec*- to a *tert*-butoxide–butyl alcohol medium on the products of the E2 reaction of 2- and 3-pentyldimethylsulfonium bromide was studied. For the 2-pentyl salt, the proportion of 1-pentene, the Hofmann rule olefin, increases from *n*- to *sec*-butoxide–butyl alcohol but decreases from *sec*- to *tert*-butoxide–butyl alcohol. The trans:cis ratio goes down at first, then sharply up, during the same changes. For the 3-pentyl salt, the trans:cis ratio shows the same behavior. The behavior on the change from *n*- to *sec*-butoxide–butyl alcohol is attributed to the change in the strength and bulk of the base. The reversal of this trend on the change from *sec*- to *tert*-butoxide–butyl alcohol was unexpected. A change of mechanism, perhaps to an α',β syn elimination, may be responsible. The reactions of 4-methyl-2-pentyl- and 2-methyl-3-pentyldimethylsulfonium bromide with *n*- and *sec*-butoxide–butyl alcohol were also studied. In both cases, there was an increase in the proportion of the Hofmann rule olefin accompanied by an increase in the trans:cis ratio. This pattern was previously observed with quaternary ammonium salts, and suggests the incursion of syn elimination at the *sec*-butoxide–butyl alcohol stage with these more highly branched reactants.

In E2 reactions, the change to stronger bases is expected to increase the reactant-like nature of the transition state (*i.e.*, decrease the double bond character).[4] This change can be effected by increasing the branching of an alkoxide base which, in addition, would also increase any steric interactions.[5] Both factors would favor formation of a less alkylated (Hofmann rule) olefin.

For a purely anti elimination, any change in reaction conditions that results in a transition state with less double bond character, such as an increase in base strength, should increase the proportion of the thermodynamically less stable cis olefin at the expense of the trans olefin. Increasing the steric requirements of the

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