The methylene chloride solution was drained from the reaction buret and the ozonide was decomposed with dimethyl sulfide. The organic layer was concentrated to give a nearly quantitative yield of the crude dialdehyde.

Preparation of 12 (R = Ts).—To a 10-ml flask, *p*-toluenesulfonyl chloride (0.4 g, 0.0021 mol) was added and to this was added dropwise a solution of **12** (R = H) (0.1 g, 0.0005 mol) dissolved in 3 ml of dry pyridine. The mixture was cooled by means of an ice water bath. After addition was complete, the mixture was placed in the refrigerator for 18 hr. The mixture was then poured over ice water and the aqueous mixture was extracted three times with 20-ml portions of methylene chloride. The organic layers were combined and washed with 10% HCl, saturated $NaHCO_3$, and water, respectively. The extract was dried with sodium sulfate and concentrated to give 0.1 g (39%) of the ditosylate **12** (R = Ts) after one recrystallization from methylene chloride–petroleum ether (30–60°). The analytical sample was obtained after five recrystallizations: mp 147–149°; ir (KBr) 1600 (aromatic C=C), 1170 (S—O), and 956 cm^{-1} (C—O); nmr ($CDCl_3$) δ 7.60 (A_2B_2 centrosymmetric quartet, 8, J = 8 Hz, aromatic protons), 3.80 (d, 4, J = 7 Hz, $-CH_2-$OTs), 3.54 (m, 4, $-CH_2-O-CH_2-$), 2.47 (s, 6, $-CH_3$), and a pattern spread over 2.6 to 1.1 for 10 H for the ring envelope hydrogens.

Anal. Calcd for $C_{25}H_{32}O_7S_2$: C, 59.04; H, 6.34. Found: C, 58.71; H, 6.57.

Preparation of 2.—To a 10-ml flask was added lithium aluminum hydride (0.05 g, 0.0014 mol), 1 ml of dry 1,2-dimethoxyethane, and **12** (R = Ts) (0.1 g, 0.0002 mol) dissolved in 4 ml of dry 1,2-dimethoxyethane. The reaction mixture was refluxed for 20 hr and then cooled. Water was added to destroy the excess lithium aluminum hydride. The salts were filtered by suction and washed with methylene chloride. The organic material was concentrated to give 0.021 g (60%) of an oil. The analytical sample was obtained after this material had been chromatographed on alumina (activity I) and eluted with petroleum ether–benzene (1:1), then distilled: bp 70–75° (0.5 mm); nmr ($CDCl_3$) δ 3.60 (m, 4, $-CH_2-O-CH_2-$), 2.4–1.1 (m, 10, ring hydrogens), and 0.93 (d, 6, J = 6.5 Hz, $-CH_3$).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.63; H, 11.79.

Preparation of Ditosylate 9 (R = Ts).—The *p*-toluenesulfonyl chloride (10.5 g, 0.055 mol) was dissolved in 5 ml of dry pyridine and the solution was cooled in an ice bath. A solution of **9** (R = H) (5.0 g, 0.027 mol) in 25 ml of dry pyridine was added dropwise to the cold toluenesulfonyl chloride solution. After the addition was complete, the mixture was placed in the freezer for 24 hr. The reaction mixture was poured over ice water and allowed to stir for 20 min to insure the hydrolysis of any excess *p*-toluenesulfonyl chloride. The heterogeneous mixture was extracted with three 30-ml portions of methylene chloride. The organic layers were combined and washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, and water, respectively. The organic phase was dried overnight with anhydrous sodium sulfate. The organic phase was concentrated with the rotary evaporator to give 9.4 g (85%): ir (KBr) 1600 (aromatic C=C), 1180 (S—O), and 952 cm^{-1} (C—O); nmr ($CDCl_3$) δ 7.63 (centrosymmetric A_2B_2 quartet, 8, J = 8 Hz, aromatic protons), 5.87 (m, 2, H—C=C—H), 3.92 (m, 4, $-CH_2OTs$), 2.47 (s, 6, aromatic CH_3), 2.35 (m, 4, tertiary protons), and 1.45 (m, 6, $-CH_2-$ of ring). The analytical sample was obtained after four recrystallizations from ether, mp 93–94°.

Anal. Calcd for $C_{25}H_{30}O_6S_2$: C, 61.20; H, 6.16. Found: C, 61.59; H, 6.35.

Preparation of 13.—To a 100-ml three-neck round-bottom flask was added 1.0 g (0.024 mol; 58.6% mineral oil dispersion) of sodium hydride. This was washed with four 10-ml portions of dry 1,2-dimethoxyethane. After washing, 15 ml of dry 1,2-dimethoxyethane was added and the system placed under nitrogen. To this mixture diethylmalonate (3.8 g, 0.024 mol) was added. After the hydrogen evolution had ceased, **9** (R = Ts) (3.6 g, 0.0074 mol) dissolved in 30 ml of dry 1,2-dimethoxyethane was added dropwise. After the addition was complete, the mixture was refluxed for 72 hr with stirring. The reaction mixture was allowed to cool and most of the salt was filtered by suction. The residue was washed with two 30-ml portions of hot 1,2-dimethoxyethane. The organic phase was concentrated with the rotary evaporator. To this residue, 20 ml of water was added and the mixture extracted with four 20-ml portions of methylene chloride. The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated. The residue was distilled to give 0.78 g (33%): bp 135–140° (0.5 mm); nmr (CCl_4) δ 4.07 and 4.16 (2 q, 4, J = 7 Hz, $-O-CH_2-$), 1.18 and 1.22 (2 t, 6, J = 7 Hz, $-CH_3$), 6.12 (m, 2, H—C=C—H), and 2.4–1.5 (several peaks, 14). The analytical sample was obtained after a portion of this material had been chromatographed on an alumina column (activity III). The *gem* diester was eluted from the column with an ether–benzene mixture (1:9). The material was then redistilled, bp 135–140° (0.5 mm).

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.83; H, 8.72.

Registry No.—**2**, 25090-89-5; **7**, 25090-90-8; **9** (R = H), 25090-91-9; **9**, (R = Ts), 25090-92-0; *cis*-**10**, 25090-93-1; **12** (R = Ts), 25090-94-2; **13**, 25090-95-3.

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Conformational Analysis. LXVII. The Effect of Solvent on the Conformational Energy of the Carbethoxy Group[1,2]

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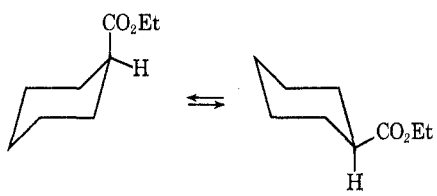
In recent years, conformational equilibria of the type



have been the subject to many investigations.[4] These investigations have resulted in the determination of numerous $-\Delta G°$ values (termed "conformational energies,"[5] "G values,"[5] or "A values"[6]) for a large variety of substituents.[7] These values are often thought of as constants related to the steric "size" of the particular substituent, and in a recently compiled table of conformational energies,[7] only two substituents (hydroxyl and amino) were listed as having more than one "best value." In these two cases, it is well known that hy-

(1) Paper LXVI: N. L. Allinger, I. Lillien, C. L. Neumann, H. Sugiyama, and N. A. Pamphilis, *J. Org. Chem.*, **35**, 1255 (1970).

(2) This Research was supported by Grants GP 6763 and GP 15263 from the National Science Foundation and is abstracted from a Ph.D. dissertation presented to Wayne State University by R. A. F., June 1968.

(3) (a) Catholic University; (b) University of Georgia.

(4) Comprehensive reviews include (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (b) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1965; (c) M. Hanack, "Conformational Theory," Academic Press, New York, N. Y., 1965; (d) J. McKenna, "Conformational Analysis of Organic Compounds," The Royal Institute of Chemistry Lecture Series, No. 1, London, 1966.

(5) E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, **4**, 761 (1965).

(6) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).

(7) J. A. Hirsch in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1967.

drogen bonding with the solvent can cause large increases in conformational energies.[8] Other solvent effects, however, have for the most part been ignored.

Although no definite evidence has been offered to support the idea, it would be very surprising if hydrogen bonding did not affect the conformational energies of groups other than amino and hydroxyl.[9] It would also be surprising if solvent effects other than hydrogen bonding were not important. In spite of this, a close look through the literature reveals that only very limited studies of solvent effects on conformation have been made.[8-10] In the present work, it was shown that not only can hydrogen bonding substantially change the conformational energy of the carbethoxy (CO_2Et) group, but even in cases where hydrogen bonding is not possible, solvent can have an appreciable effect.

In checking the various reported G values for the ester groups,[11] an interesting observation was made. Eliel and Gianni's[11c] value of 1.1 kcal/mol for CO_2Et, obtained by what seemed to be the best method,[12] was lower than all but one[8b] of the others, including those for the carbomethoxy group. This is particularly surprising considering the reported values range from 1.05 to 1.7 kcal/mol. Examination of the conditions of these determinations revealed one unique characteristic of the Eliel and Gianni work. Their value was obtained using carbon tetrachloride as a solvent, while all other values were determined using either ethanol or methanol as a solvent. This was our first clue that hydrogen bonding might increase the G value of the ester group. With this in mind, a systematic study of the effect of solvent on the conformational energy of the carbethoxy group was undertaken.

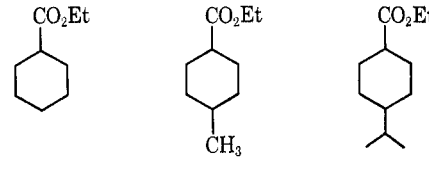
Method.—Of the various methods that have been used to determine conformational equilibria, the nmr method[5,13] seemed to be the most straightforward. In particular, the method of Eliel[12] seemed to lend itself very well to the systems of interest and has been used for this purpose previously.[11c] This method involves the determination of the time-averaged chemical shift (ν) of the proton α to the functional group which with the chemical shift of the axial and equatorial protons (ν_a and ν_e) yields the equilibrium constant K (eq 1).[14]

$$K = (\nu_a - \nu)/(\nu - \nu_e) \quad (1)$$

Determination of ν_a and ν_e could be made from the spectra of the conformationally biased *cis*- and *trans*-4-*t*-butylcyclohexyl derivatives, respectively. This method, however, has been the subject of recent controversy.[15] The criticism has been made[15] that the 4-*t*-butyl group has an effect on the chemical shift of the α hydrogen. This effect might arise from either the magnetic anisotropy of the *t*-butyl group or the ring distortion forced by this group. Molecular mechanics calculations have indicated that the latter is probably negligible.[16]

Whatever the *t*-butyl effect may be due to, one should be able to reduce this effect by making measurements on hydrogens further from it than the α hydrogen, if such hydrogens are available in which the chemical shift differs between the axial and equatorial conformations. In the case of the carbethoxy function, the methylene hydrogens of the ethyl group satisfy these requirements. It was found that this difference is about 3 Hz at 60 MHz in carbon tetrachloride. While this is quite small, very careful measurements utilizing the sideband calibration technique[17] would be expected to yield meaningful results. That this is indeed the case is evidenced by the very low standard deviations obtained in repeated measurements by this method (Table I), and by the excellent agreement between determinations in similar but different solvents.

TABLE I



	I	II	III
Solvent	G value	G value	G value
Isooctane	1.07 ± 0.04 1.04 ± 0.04[a]	1.11 ± 0.03	1.18 ± 0.03
CCl_4	1.05 ± 0.02	1.08 ± 0.04	1.24 ± 0.03
Acetone	1.08 ± 0.02	1.25 ± 0.04	1.27 ± 0.06
Acetonitrile	0.93 ± 0.03 0.92 ± 0.03[a]	1.14 ± 0.04	1.26 ± 0.06
$CHCl_3$	1.20 ± 0.01 $1.18 + 0.03$[b]	1.29 ± 0.03 $1.31 + 0.02$[b]	1.42 ± 0.03 $1.37 + 0.04$[b]
HOAc	1.27 ± 0.04		1.28 ± 0.04

[a] Repeats at the same concentration. [b] Repeats at lower concentration.

To check the validity of this method, a determination was made in carbon tetrachloride to compare with the earlier G value of 1.1 kcal/mol obtained by Eliel and Gianni[11c] in this solvent using the α-hydrogen chemical

(8) (a) E. L. Eliel, E. W. Della, and T. H. Williams, *Tetrahedron Lett.*, 831 (1963); (b) E. L. Eliel and S. H. Shroeter, *J. Amer. Chem. Soc.*, **87**, 5031 (1965); (c) J. Sicher, J. Jonas, and M. Tichy, *Tetrahedron Lett.*, 825 (1963).

(9) Some evidence has been presented for an increase in the G values of the halogens in hydrogen bonding solvents, but this evidence is far from definitive: E. L. Eliel and R. J. L. Martin, *J. Amer. Chem. Soc.*, **90**, 689 (1968).

(10) (a) G. Chiurdoglu and W. Masschelein, *Bull. Soc. Chim. Belg.*, **69**, 154 (1960); (b) F. A. L. Anet, *J. Amer. Chem. Soc.*, **84**, 1053 (1962); (c) J. Reisse, J. C. Celotti, and G. Chiurdoglu, *Tetrahedron Lett.*, 397 (1965); (d) J. C. Celotti, J. Reisse, and G. Chiurdoglu, *ibid.*, 2249 (1966); (e) E. L. Eliel and R. J. L. Martin, *J. Amer. Chem. Soc.*, **90**, 689 (1968).

(11) (a) N. L. Allinger and R. J. Curby, *J. Org. Chem.*, **26**, 933 (1961); (b) E. L. Eliel, H. Haubenstock, and R. V. Acharya, *J. Amer. Chem. Soc.*, **83**, 2351 (1961); (c) E. L. Eliel and M. H. Gianni, *Tetrahedron Lett.*, 97 (1962); (d) G. J. Fonken and S. Shiengthong, *J. Org. Chem.*, **28**, 3435 (1963); (e) B. J. Armitage, G. W. Kenner, and M. J. T. Robinson, *Tetrahedron*, **20**, 744 (1964); (f) R. J. Ouellette, *J. Amer. Chem. Soc.*, **86**, 3089 (1964); (g) R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **31**, 587 (1966); (h) N. L. Allinger and L. A. Freiberg, *ibid.*, **31**, 894 (1966); (i) M. Tichy, F. Sipos, and J. Sicher, *Collect. Czech. Chem. Commun.*, **31**, 2889 (1966); (j) E. L. Eliel and M. C. Reese, *J. Amer. Chem. Soc.*, **90**, 1560 (1968).

(12) This method compares the nmr chemical shift of the hydrogen α to the substituent with that of the analogous hydrogen in the *cis* and *trans* 4-*t*-butyl derivatives which are used as models for the pure equatorial and axial conformations: E. L. Eliel, *Chem. Ind. (London)*, 568 (1959).

(13) Reviews of the use of nmr in conformational analysis include: (a) H. Feltkamp and N. L. Franklin, *Angew. Chem., Int. Ed. Engl.*, **4**, 774 (1965); (b) *Justus Liebigs Ann. Chem.*, **683**, 55 (1964); (c) ref 1b, pp 152–156.

(14) H. S. Gutowski and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(15) (a) E. L. Eliel and R. J. L. Martin, *J. Amer. Chem. Soc.*, **90**, 682 (1968); (b) F. R. Jensen and B. H. Beck, *ibid.*, **90**, 3251 (1968); (c) F. R. Jensen, C. H. Bushweller, and B. H. Beck, *ibid.*, **91**, 344 (1969).

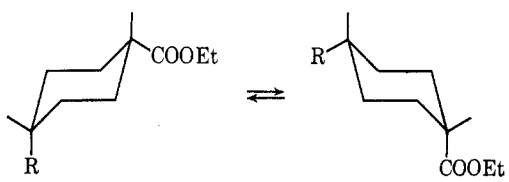
(16) (a) N. L. Allinger, M. A. Miller, F. A. Van-Catledge, and J. A. Hirsch, *ibid.*, **89**, 4345 (1967); (b) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, **90**, 1199 (1968).

(17) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 74.

shift method. The value obtained, 1.05 ± 0.02 kcal/mol, is in very close agreement. This indicates the validity of both methods and suggests the effect of the *t*-butyl in both cases is negligible to within experimental error. This conclusion is also supported by the observation that the signal for the methoxy protons in 1,1-dimethoxycyclohexane appears exactly halfway between the two signals for the methoxy protons in 4-*t*-butyl-1,1-dimethoxycyclohexane.[10e]

Discussion

Table I contains the values obtained for the conformational energy of the carbethoxy group in different solvents, and from different compounds using the "methylene chemical shift method." In the case of the *cis*-4-methyl- and *cis*-4-isopropyl-substituted compounds, correction for the *G* value of the alkyl substituents was made, based on the usual assumption that the *G* values of the substituents are additive. Since the measurements were carried out on the *cis* isomers, the actual equilibrium studied in the substituted cases was



and the *difference* in the *G* values was in fact determined. The *G* value for the methyl group is fairly well known and is 1.70 kcal/mol.[7] The corresponding value for the isopropyl group is less well known and was taken to be 2.15 kcal/mol.[7]

The data obtained for the *cis*-4-methylcarbethoxycyclohexane in isooctane and in carbon tetrachloride are in almost exact agreement with the data for the unsubstituted compound in the same solvents. This is strong support for the reported 1.70 kcal/mol value for the methyl group. On the other hand, the data for the *cis*-4-isopropyl-substituted compound are slightly higher than those for either the unsubstituted or the *cis*-4-methyl compound. This indicates that the 2.15-kcal/mol value for the isopropyl group is a little high. A value of 2.05 would give much better agreement. The greater variation between the values for the unsubstituted and the substituted compounds in other solvents could be due to some unusual solvation effects, since all of these solvents would be expected to interact with the ester group much more specifically than can either isooctane or carbon tetrachloride.

In this investigation three types of solvents were used: nonpolar solvents incapable of forming hydrogen bonds (carbon tetrachloride and isooctane), polar solvents incapable of forming hydrogen bonds to the carbethoxyl (acetone and acetonitrile), and hydrogen bonding solvents (chloroform and acetic acid). It was hoped that within any of these pairs, similar effects would be noticed. As already noted, this was certainly true for the nonpolar solvents.

It is interesting to note the effects of chloroform and acetic acid. Both of these solvents are certainly capable of hydrogen bonding to the ester group. If analogy is drawn with the amine group and the hydroxyl group, both of which are known to be strongly affected by hydrogen bonding solvents,[8] it would be expected that hydrogen bonding would increase the conformational energy of the ester group. The data in Table I show that this in indeed the case. If previous determinations of the *G* value of the ester group[11] (all in alcohol solvent, also capable of forming hydrogen bonds) are considered, the average value of about 1.2 kcal/mol fits very nicely into Table I. This effect of hydrogen bonding might be rationalized using either entropy or enthalpy effects.[11i] However, the fact that acetic acid (presumably capable of forming stronger hydrogen bonds) only increases the conformational energy by about the same amount as chloroform (relatively weak hydrogen bonds) would lead one to think that entropy effects are probably the more important in these cases.

The effect of aprotic polar solvents is not nearly as clear-cut. About the only statement that can safely be made is that the more polar the solvent, the larger the discrepancy between values obtained with I and those obtained with II and III. Our interpretation of this fact is as follows. When the ester group is in the axial position, a *cis*-alkyl substituent is equatorial. The latter position offers more opportunity for an interaction with the solvent, but a polar substituent will interact more favorably with a polar solvent. The effect of an equatorial methyl, since it disrupts the solvent–solvent interactions, is unfavorable, which therefore causes this conformation to be less favorable than in a nonpolar solvent. This in turn causes an apparent increase in the *G* value of the ester group, if the *G* value of the alkyl group is assumed to be constant. When the ester group is in the axial position, the *cis*-alkyl substituents are in the equatorial position and thus, presumably, interacting more with the solvent. If this is an unfavorable interaction, then the energy of this isomer will increase, causing an apparent increase in the *G* value of the ester group, as is observed. It is not too presumptive to expect the interaction of the alkyl group to be stronger with the more polar solvents than with the nonpolar ones.

These ideas can alternatively be expressed in terms of the "internal pressure" of the solvent.[18] This internal pressure effect is a result of the intermolecular attractive forces among molecules of the solvent, and it requires an increase in the energy of the system if a cavity is created in the solvent.[19] Such a cavity can be created by dissolving a molecule in the solvent, and the larger the solute molecule, the more energy required. (This, of course, assumes the solute molecules to have attractive interactions with the solvent which are less than the attractive interactions of the solvent molecules for one another.) Thus, if two conformations of the molecule are possible, this internal pressure effect ought to shift the equilibrium towards the smaller conformation.

In the case of substituted cyclohexanes, it is reasonable to think that the axial conformation will be smaller than the equatorial. This is known to be true in many cases, and is the basis of the "conformational

(18) J. H. Hildebrand, "International Critical Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 19.

(19) H. Russ, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.*, **32**, 119 (1960).

rule,"[20] and is typified by the experimental fact that *cis*-1,4-dimethylcyclohexane (axial–equatorial) has a higher density than *trans*-1,4-dimethylcyclohexane (equatorial–equatorial),[21] for example. The internal pressure of a solvent, therefore, would be expected to shift the equilibrium between the axial and equatorial conformations of substituted cyclohexanes toward the axial conformation. This is exactly what is observed in the great majority of cases where conformational free energies have been determined in both the gas phase and in solution.[7]

It is thus to be expected that the more polar the solvent, the higher the internal pressure, and therefore the larger the shift in equilibrium towards the axial isomer. This is certainly consistent with the value of 0.93 ± 0.03 kcal/mol determined for the unsubstituted carboethoxycyclohexane in acetonitrile. Unfortunately the data for this compound in the less polar acetone do not reveal this effect.

In conclusion, it can be said that there is definite evidence for an increase in the conformational energy of the carbethoxy group when hydrogen bonding to the solvent is possible. While an explanation of the effect of polar solvents is more complicated, there is no doubt that this effect is quite significant. Perhaps the most important point to be made is that the conformational energy of a group is not a constant but is quite dependent on solvent, as is evidenced by the variation of about 0.5 kcal/mol observed in this limited study.

Experimental Section

Spectra.—All nmr spectra for this work were run on a Varian A-60 spectrometer using two Hewlett-Packard wide-range oscillators, Model 200 CDR, for the side-band calibration. The frequency of the osillation was determined using a Hewlett-Packard electronic counter, Model 523 CR. This frequency was counted as the reciprocal to gain more accuracy, and the reading taken was the average of three ten-period averages displayed. The spectra were all run at a sweep time of 250 sec with a sweep width of 50 Hz, filter bandwidth of 4 Hz, and a radiofrequency field of 0.01 mG. In order to minimize machine error (nonlinear sweep, magnetic field shift, etc.), at least four spectra were run, each at different offset settings, and then each peak position was measured twice. In order to minimize other sources of error, several precautions were taken. All samples for a particular determination were made up to equal mole per cent concentration. This concentration was picked so as to make as dilute a solution as possible and still get a useful nmr signal. In one solvent (chloroform), determinations were made at two concentrations and the results indicated that the measurements were insensitive to concentration in the range used.

Preparation of Samples.—All samples were made up to a standard mole per cent concentration. The concentrations follow: carbon tetrachloride, 0.8 mmol/g; chloroform, 0.8 and 0.5 mmol/g; acetonitrile, acetone, isooctane, and acetic acid, 10 mmol/g. All samples had a standard amount of TMS measured by volume (20 μl).

The samples were then vacuum degassed using the standard method of freeze–vacuum–thaw cycles, freezing with liquid nitrogen.

Preparation of Compounds.—All compounds were synthesized as reported.[8d] The separation of the *cis* and *trans* isomers was by gas chromatography using a 6 ft × 3/8 in. glass column packed with 22% E-20,000 on Chromsorb W. The column temperature ranged from 105° for the 4-methyl derivative to 135° for the 4-*t*-butyl derivative. All compounds gave infrared spectra identical with those obtained before and the nmr spectra were all consistent with the structure assigned.

(20) N. L. Allinger, M. Nakazaki, and V. Zalkow, *J. Amer. Chem. Soc.*, **81**, 4074 (1959).

(21) C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 40th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1958–1959.

Purification of Solvents.—All solvents were obtained as reagent grade and then (with the exception of acetic acid which was used as is) dried over sodium sulfate overnight. The solvent was then decanted and distilled through a Vigreux column under nitrogen. All refractive indices checked within experimental error with those reported.[21]

Calculation of Data.—Since the determinations were made using the methylene hydrogens of the ester, any of four peak positions could have been used. Owing to some second-order broadening, all four peak positions were not equally well defined. In all cases the lowest field peak seemed to be the most distinctive, and it was this peak that was used in the reported data. Use of any of the other three peaks gave essentially the same results. Using the chemical shifts of the *cis*- and *trans*-4-*t*-butylcarbethoxycyclohexanes as the standard, the unknown equilibrium constants were calculated using eq 1.

The eight values obtained for each compound in each solvent were then used to calculate eight free energy differences using eq 2. These eight values were then used to calculate the mean free energy and the standard deviations by the standard method.

$$-\Delta G^\circ = RT \ln K \qquad (2)$$

Registry No.—I, 3289-28-9; *cis*-II, 25244-23-9; *cis*-III, 25244-24-0.

Dehalogenation of Vicinal Dibromoalkanes with Triethyl Phosphite[1]

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In the most common example of the Michaelis–Arbuzov reaction,[2] a phosphonate ester is formed from an alkyl halide and a trialkyl phosphite (eq 1). When

$$RX + P(OR')_3 \longrightarrow RP(O)(OR')_2 + R'X \qquad (1)$$

1,2-dibromoethane is the alkyl halide, the reaction is normal, *i.e.*, the major products are the phosphonate esters **1** and **2** (eq 2).[3–6] However, for vicinal dihalides

$$BrCH_2CH_2Br + P(OEt)_3 \longrightarrow \underset{\mathbf{1}}{BrCH_2CH_2P(O)(OEt)_2} + \underset{\mathbf{2}}{(EtO)_2P(O)CH_2CH_2P(O)(OEt)_2} + EtBr \qquad (2)$$

with electron-withdrawing groups adjacent to both halogen atoms, dehalogenation is the principal reaction (eq 3). A number of electronegative substituents (G

$$G-\underset{X}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-G' + P(OR)_3 \longrightarrow G-\overset{|}{C}=\overset{|}{C}-G' + (RO)_2P(O)X + RX \qquad (3)$$

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