dynaimic sense only because the k_4 values for the two systems are similar. Mechanistically the effect can be ascribed to the partitioning of the intermediate, already discussed, which so strongly favors the ester over the amide in the oxazoline system.

An N–O-acyl shift occurs when proteins are placed in concentrated mineral acids.[9] In anhydrous formic acid, however, formylation of the serine residues of proteins takes place with little acyl transfer.[10,11] In solutions of low water content the equilibrium constant for ethyl formate formation,[12] K_E = (ester)^2/(acid)(alc) $\simeq$ 5. Combining this constant with K_{NO} = (N)(H$^+$)/(OH$^+$), where (OH$^+$) is the concentration of O-acetylated residues, we obtain K = (ester)^2/(OH$^+$) = $K_E K_{NO}$(acid)/(H$^+$). The acidity func-

(9) D. F. Elliot, *Biochem. J.*, **50**, 542 (1951).
(10) K. Narita, *J. Am. Chem. Soc.*, **81**, 1751 (1959).
(11) L. B. Smillie and H. Neurath, *J. Biol. Chem.*, **234**, 355 (1959).
(12) R. F. Schultz, *J. Am. Chem. Soc.*, **61**, 1443 (1939).

tion[13] of anhydrous, 26 M, formic acid is 160. Substitution of these values with those of the equilibrium constants yields K $\simeq$ 10^{-6}. This equilibrium constant indicates that N–O transfer is thermodynamically favored over formylation when proteins are placed in anhydrous formic acid. The small value of K is well beyond any uncertainties introduced by unusual values of equilibrium constants as discussed above. The conclusion is that formylation rather than transfer occurs because the former reaction is favored kinetically. This conclusion is borne out by a half-life for formylation of about 4 hours[11] as compared with longer times for transfer to occur.[9] Possibly the free amino acid serine does not formylate under the same conditions because the positive charge on the molecule inhibits the acid-catalyzed esterification.

(13) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

Dependence of the *cis* Effect on Ring Size. Magnitude of the Steric Interaction of the Phenyl Rings in *cis*-1,2-Diphenylcyclopentane and Demonstration of Restricted Rotation[1]

By David Y. Curtin, Henry Gruen, Yngve Gust Hendrickson and H. E. Knipmeyer

Equilibration of *cis*- and *trans*-1,2-diphenylcyclopentane at 110° has given an equilibrium constant of 33 which is compared with data available for the stilbenes and the 1,2-dimethylethylenes, cyclopropanes and cyclopentanes. Evidence for restricted rotation of the phenyl groups of *cis*-1,2-diphenylcyclopentane (but not for the stilbenes, diphenylcyclopropanes or *trans*-1,2-diphenylcyclopentane) has been adduced from an unusually broad aromatic proton spectrum in the n.m.r., with narrowing when the sample is heated.

Some of the consequences of the steric interaction of substituents adjacent to one another in 2- (olefin-forming), 3-, 4- and 5-membered cyclic transitions states have been reviewed.[2] Even a semi-quantitative knowledge of the magnitudes of such *cis* effects has been almost entirely lacking, however. It has seemed likely that there should be significant variations of the *cis* effect with ring size in 2-, 3-, 4- and 5-membered cyclic compounds. The present investigation is concerned with the effect on the free energy of the *cis*-1,2-diphenyl interaction in *cis*-1,2-diphenylcyclopentane (*cis*-I) (relative to the *trans* isomer). A further consequence of the proximity of the two phenyl groups in this molecule is the restriction of the rotation of the phenyl rings around the single bonds joining them to the cyclopentane structure. Evidence from n.m.r. studies supporting such restricted rotation will be reported later in this paper.

**Equilibration of *cis*- and *trans*-1,2-Diphenylcyclopentane (*cis*-I).—*cis*- and *trans*-1,2-diphenylcyclo-

(1) This investigation was supported in large part by the National Science Foundation (Grants G 4467 and 14480) to whom we are indebted. The early part of this investigation is described in the Ph.D. Theses of Y. G. Hendrickson (1955) and H. E. Knipmeyer (1957) submitted to the University of Illinois [*C. A.*, **50**, 2478h (1956); **51**, 14635d (1957)].
(2) D. Y. Curtin, *Record Chem. Progr. Kresge–Hooker Sci. Lib.*, **15**, 111 (1954); D. Y. Curtin and E. Tanda, *J. Jap. Chem.*, **10**, 567 (1956); L. D. Bergel'son, *Uspekhi Khim.*, **27**, 817 (1958).

pentane had been prepared previously by Weidlich.[3] It was desired to equilibrate these two substances in order to have a direct measure of the free energy difference between the *cis* and *trans* isomer. Equilibrations were carried out at 110° using potassium in di-*n*-butylamine and also 5% palladium-on-charcoal in the presence of hydrogen to prevent dehydrogenation.[4] Equilibrium was approached from both the *cis* and *trans* side. Since preliminary experiments indicated that the equilibrium lay well toward the *trans* isomer a rather sensitive analytical method was needed and a differential infrared spectroscopic method employing differences in absorption at 690 and 750 cm.$^{-1}$ was found satisfactory. The results are summarized in Table I.

The average value of the results at 110° and the probable error are 2.91 ± 0.07 which corresponds to an equilibrium constant at this temperature of 33.4 ± 0.8 and a free energy difference of 2.68 ± 0.16 kcal. It is striking that measurements of the equilibrium constants[5] of the reactions of *meso*- and *dl*-hydrobenzoin with the *cis*- and *trans*-cyclic acetals (*cis*- and *trans*-II), respectively, combined with an estimated free energy difference

(3) H. A. Weidlich, *Ber.*, **71B**, 1601 (1938).
(4) N. L. Allinger and J. L. Coke, *J. Am. Chem. Soc.*, **81**, 4080 (1959).
(5) P. H. Hermans, *Z. physik. Chem.*, **113**, 337 (1924).

TABLE I

EQUILIBRATION OF *cis*- AND *trans*-1,2-DIPHENYLCYCLO-
PENTANE (*cis*- AND *trans*-I) AT 110°

Time, hr.	Equilibration method	Isomer employed	% *cis*-I at equil. detd. at 750 cm.$^{-1}$	695 cm.$^{-1}$
144	Pd/C	*trans*	2.95	3.04
144	K/dibutyl- amine	*trans*	2.85	2.98
44	Pd/C	*cis*	2.97	2.97
150	Pd/C	*cis*	2.82	2.73
		Av.	2.91 ± 0.07	
		At 150°		
30	K/dibutyl- amine	*cis*	2.54	2.98
30	Pd/C	*cis*	2.60	2.60

of 0.9 kcal. between the diastereoisomeric hydrobenzoins (the *dl*-isomer being more stable)[6] lead
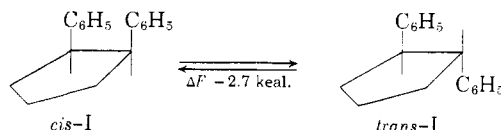
to a free energy difference between *cis*- and *trans*-II of 2.7 kcal./mole. Although the agreement is undoubtedly in part fortuitous, it is reassuring.
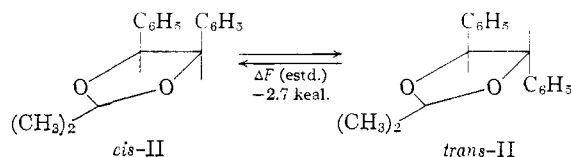
It is of interest to compare the available thermochemical data for the dimethylethylenes, dimethylcyclopropanes and dimethylcyclopentanes with those for the diphenylethylenes and the present results. The data are summarized in Table II.

Consideration of the data in Table II for the three pairs of dimethyl compounds leads to several points of interest. Calculation of the distance between the methyl carbon atoms in the series of dimethyl compounds suggests that the methyl-methyl distances in *cis*-2-butene and *cis*-dimethylcyclopropane are nearly equal. Similarly, the thermochemical data available suggest that the potential energy differences between the *cis* and *trans* isomers in the two systems are comparable.[8] As can be seen, the effect of an increase in ring size is to decrease the methyl-methyl distance. A corresponding increase in the destabilization of the *cis* isomer relative to the *trans* is suggested by the increase in the enthalpy or free energy difference from about 1 kcal. for the butenes or dimethylcyclopropanes to about 1.7 kcal. for the dimethylcyclopentanes.[9] The distances were cal-

TABLE II

EFFECT OF RING SIZE ON THE EQUILIBRIA (*cis* ⇌ *trans*)
BETWEEN *cis* AND *trans* ISOMERS AT 25°

	ΔH^0, kcal./ mole	ΔF^0, kcal./ mole	Distance between methyl carbons, Å.^{a}
1,2-Dimethylethylenes[b] (2-butenes)	−1.0	−0.69	2.92
1,2-Dimethylcyclopropanes[c]	−1.07	(−1.13)	2.90
1,2-Dimethylcyclobutanes	[e]	[e]	2.80
1,2-Dimethylcyclopentanes[b]	−1.71	−1.76	2.59
1,2-Diphenylethylenes[d] (stilbenes)	−5.7	[e]	
1,2-Diphenylcyclopropanes[g]	−3.0		
1,2-Diphenylcyclopentanes[f]	[e]	(−2.3)	

^{a} Distances calculated using the best estimates of the molecular geometry available in "Tables of Interatomic Distances and Configuration in Molecules and Ions," L. E. Sutton, Editor, The Chemical Society, London, 1958. ^{b} Values for the gaseous substances were taken from F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Penna., 1953. The calculated $\Delta H°$ is 1.24 kcal. for the butenes and 1.73 for the cyclopentanes, demonstrating that the difference is primarily a potential energy effect.[7] ^{c} M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.* (*London*), **257**, 122, (1960). The free energy was estimated from their data by extrapolation of the value reported at 380° assuming a constant value of $\Delta H = 1.07$ kcal./mole. ^{d} R. B. Williams, *J. Am. Chem. Soc.*, **64**, 1395 (1942). ^{e} No reliable value known. ^{f} Present work. The free energy difference at 25° was obtained by extrapolation from 110° using a value of 2.7 kcal./ mole for ΔH. Since the correction is small the choice of ΔH is not critical.[6a]

culated with the assumption that all of the rings are planar. In Fig. 1 are shown drawings of *cis*-2-butene and *cis*-1,2-dimethylcyclopentane. In the drawing the cyclopentane ring is puckered in such a way as to maximize the methyl-methyl distance. It is seen that even here the methyl groups are significantly nearer to each other than they are in the butene.[10]

Molecular models of *cis*-stilbene and 1,2-diphenylcyclopentane (see Fig. 2) indicate as in the dimethyl examples that if the destabilization of the *cis* isomers relative to the *trans* were purely steric, then the *cis* effect should be greater in the cyclopentane system than in the olefin. However, here the magnitudes of the steric effects are reversed, *cis*-stilbene being destabilized some 3 kcal. more than *cis*-1,2-diphenylcyclopentane.[11] It is

(6) This estimate is not particularly reliable, being based on values of ΔH determined from heats of combustion [E. Berner, *Arch. Math. Naturvid.*, **39**, 121 (1926); *Chem. Zentr.*, **99**, II, 2537 (1926)] with the assumption that ΔS for the equilibrium is 0.

(6a) ADDED IN PROOF.—M. P. Kozina, M. Yu. Lukina, N. D. Zubapeva, I. L. Safonova, S. M. Skuratov and B. A. Kazanskii, *Dokl. Akad. Nauk* (U.S.S.R.), **138**, 843 (1961).

(7) See L. P. Hammett, "Introduction to the Study of Physical Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1952, p. 161 ff. and L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 76 ff.

(8) It is of interest that the energy increase due to the methyl-methyl interaction in *cis*-2-butene (relative to the *trans* isomer) has been calculated to be 1.85 kcal. assuming it to be entirely steric in origin [T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948)] (see discussion by W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," Edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 58–59).

(9) A semi-empirical calculation for the 1,2-dimethylcyclopentanes has given a value of 1.7 kcal. for the difference between the energies of the *cis* and *trans* isomers [J. N. Harensnape, *Chemistry & Industry*, 1091 (1953)].

(10) It should be recognized that in comparing differences between *cis* and *trans* isomers we have been assuming that the significant difference was in the energies of the *cis* isomers; that is, the *trans* isomers have been arbitrarily set at the same energy level. A more refined treatment must take into account differences in potential energy of the *trans* isomers and also effects of restriction of rotation of the methyl groups.

(11) It would be of considerable value to have a free energy difference for the equilibration of the stilbenes. Unfortunately, although

concluded that some additional influence(s) must be operating to alter the equilibria in the diphenyl systems. Steric inhibition of resonance in *cis*-stilbene[14,15] has been suggested previously as being responsible for most of the enthalpy difference between *cis*- and *trans*-stilbene. Since steric inhibition cannot affect the diphenylcyclopentane equilibrium it adequately accounts for the difference.

Equilibration of *cis*- and *trans*-Diphenylcyclopropane.—The 1,2-diphenylcyclopropanes have long been known as a liquid mixture of diastereoisomers.[16] These could be separated by distillation under reduced pressure through a spinning-band column. The *cis* isomer so obtained was a solid, m.p. 38.5°, while the *trans* isomer was a liquid. The basis of the configurational assignments is the ultraviolet and n.m.r. spectra to be described in the next section. After this portion of the work was completed,[1] results of an independent separation and configurational assignment of the two isomers in agreement with the present work were published.[17]

Equilibration of the diphenylcyclopropanes was complicated by the presence of side reactions and, in the early part of the study, by irreproducibility of results.[18] Although the *cis* isomer at 150° in the presence of palladium-on-charcoal did give some of the *trans* isomer there was produced in addition an olefin, presumably 1,3-diphenylpropene. The *trans* isomer was found to rearrange to the olefin but none of the *cis*-cyclopropane was found. These results are not surprising in view of the report of Kazanskii and his associates that both *cis*- and *trans*-1,2-diphenylcyclopropane are hydrogenated over palladium to 1,3-diphenylpropane.[17] Other attempts at isomerization also led to partial ring opening and have thus far pre-

several sets of investigators have reported equilibrium constants for this equilibration, there appears to be no reliable value.[12] Taking a value of 39.8 × 10^{-89} g.-cm.^{2} for the moment of inertia of planar *trans*-stilbene around an axis through the center of gravity and parallel to the bonds joining the phenyl rings to the olefinic carbon atoms and a value of 14.8 × 10^{-49} g.-cm.^{2} for the moment of inertia associated with the rotation of a phenyl ring, the calculated[15] entropy associated with the rotation of each phenyl ring is 7.2 cal./deg.-mole. It seems likely, however, that the phenyl rings are largely restricted to their coplanar positions in *trans*-stilbene by the energy minimum associated with resonance in the planar conformation[14] and are restricted sterically in *cis*-stilbene to non-coplanar positions so that the effect of a difference in entropy associated with internal rotation of the phenyl groups is very much diminished.

(12) D. C. Downing and G. F. Wright, *J. Am. Chem. Soc.*, **68**, 141 (1946).

(13) G. J. Janz, "Estimation of Thermodynamic Properties," Academic Press, Inc., New York, N. Y., 958, p. 26 ff.

(14) F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958).

(15) See G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, 1955, pp. 132, 157 ff., 196 ff. See also M. J. S. Dewar and H. W. Schmeising, *Tetrahedron*, **11**, 96 (1960) and references therein cited for a somewhat different point of view on the importance of resonance.

(16) N. Kizhner', *Zhur. Russ. Fiz.-Khim. Obshch.*, **47**, 1104 (1915); S. G. Beech, J. H. Turnbull and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

(17) (a) B. A. Kazanskii, M. Yu, Lukina, I. L. Safonova, V. T. Aleksanyan and Kh. E. Sterin, *Izvest. Akad. Nauk (S.S.S.R.), Otdel Khim. Nauk*, **10**, 1280 (1958); (b) V. T. Aleksanyan, Kh. E. Sterin, M. Yu. Lukina, I. L. Safonova and B. A. Kazanskii, *Optika i Spektroskopia*, **7**, 178 (1959); (c) B. A. Kazanskii, M. Yu. Lukina, I. L. Safonova, *Doklady Akad. Nauk (S.S.S.R.)*, **130**, 322 (1960).

(18) See the Ph.D. Thesis of H.K.E.[1] for a discussion of early results.

vented the determination of a satisfactory equilibrium constant.

Use of N.m.r. to Study Restricted Rotation of the Phenyl Rings in 1,2-Diphenyl Compounds.— In the course of an examination of the effect of *cis–trans* isomerism on the n.m.r. spectra, a number of 1,2-diphenyl compounds[19,20] were examined. In the case of *cis*- and *trans*-diphenylcyclopropane, *trans*-1,2-diphenylcyclopentane and *trans*-3,4-diphenylcyclopentanone the phenyl protons gave rise to a narrow absorption (the band widths at half height in each case were 4 c.p.s. or less measured at 60 Mc.). When the two phenyl groups were attached to adjacent carbon atoms of a five-membered ring and were *cis* to one another, however, as was the case in *cis*-1,2-diphenylcyclopentane and *cis*-3,4-diphenylcyclopentanone, the phenyl proton spectra were complex multiplets with the outer peaks separated by 25 and 31 c.p.s., respectively (60 Mc.). Two alternative explanations immediately suggest themselves. The first is that in these two *cis* isomers the *ortho*-protons are for some reason chemically shifted from the *meta*- or *para*-protons. The second possibility is that the energy barrier to rotation is high enough in the case of these two *cis* isomers to lock each of the phenyl rings (in terms of the n.m.r. time scale) in a plane perpendicular to the plane of the five-membered ring. In such a model it would be reasonable that the frequencies of the *ortho*- and *meta*-protons on the inward side of the phenyl ring should be shifted from those of the outward protons. These alternatives were submitted to an experimental test. If the second explanation is correct, thermal acceleration of rotation of the phenyl rings to a point such that the average lifetimes of the two conformations are short relative to the reciprocal of the difference in absorption frequency between the inside and outside phenyl protons should lead to coalescence of the aromatic peaks.[21] It was found that when *cis*-1,2-diphenylcyclopentane in carbon tetrachloride solution was heated above 100° the lines of the phenyl proton spectrum began to coalesce and that at a temperature of 182° the half-width had shrunk to 5 c.p.s. The change was reversible since the sample, on cooling, gave a spectrum identical with that obtained initially. Similar behavior was observed in the spectra of the pure liquid hydrocarbon. The aromatic proton spectra are shown in Fig. 3. The five-proton system is too complicated to permit the calculation of a rotation rate of energy of activation of phenyl rotation. If a guess of 13 c.p.s. is made for the chemical shift between the inside and outside *ortho*-hydrogen atoms a rate constant for rotation very much less than 80 sec.$^{-1}$ would lead to an n.m.r. spectrum of a molecule in which the phenyl rotation is "frozen out."[21] This corresponds to a free energy of activation for rotation of greater than 15 kcal. The aromatic proton

(19) D. Y. Curtin, H. Gruen and B. A. Shoulders, *Chemistry & Industry*, 1205 (1958).

(20) See also L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 119 ff.

(21) See 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. 221 ff.

absorption of *cis*-3,4-diphenylcyclopentanone also appeared to be contracting when the sample was heated but more slowly than was the case with the diphenylcyclopentane.

Positions of Phenyl Ring and α-Protons.—In a preliminary communication[19] the positions of the phenyl ring protons and α-protons were described and the use of these positions to assign configuration discussed. More recently the difference in chemical shift of the α-protons of *cis*- and *trans*-stilbene has been confirmed by independent measurements[22] and shown to agree with a value calculated on the basis of a ring current effect. The value of $\delta_{trans} - \delta_{cis}$ of 0.5 p.p.m. is in substantial agreement with the value of 0.6 p.p.m. obtained from a calculation based on the nuclear shielding values of Johnson and Bovey.[23] Since our data[19] concerning the positions of the α-protons have more recently been discussed in a review[20] of n.m.r. spectroscopy, further discussion at this point seems unwarranted. The present work does provide information which permits additional analysis of the proton spectra of *cis*-1,2-diphenylcyclopentane and *cis*-3,4-diphenylcyclopentanone, however. The *cis*-diphenylcyclopentanone spectrum is completely separated into two broad peaks with centers (in deuterochloroform) at about 3.0 and 3.3τ and with relative areas of 3 to 2, respectively. A similar resolution of the aromatic proton spectrum of *cis*-1,2-diphenylcyclopentane into two peaks which overlap slightly gives relative areas of 3 to 2 with band centers at 3.1 and 3.3τ. These values may be compared with the absorption positions of 2.8 and 3.0τ for the *trans*-diphenylcyclopentanone and the *trans*-diphenylcyclopentane, respectively. Since the absorption positions of the aromatic protons of the *trans* isomers represent the effect of an average of the magnetic field at the "inside" and "outside" positions, these data suggest that the ring current effect of one ring on another *cis* to it (using the *trans* isomer as the reference point in each case) leads to a shift of 0.2–0.4 toward higher field. More complete estimates of the chemical shifts involved here should take into account anisotropy effects of the carbon–carbon and carbon–hydrogen bonds of the cyclopentane ring and the carbonyl group when it is present. It is doubtful therefore that further approximate calculations are profitable with the methods now available.

The failure of the *cis*-diphenylcyclopropane to show the broadening in the n.m.r. spectrum of the aromatic protons could mean that there is a negligible chemical shift between the "inside" and "outside" protons of a molecule in which phenyl rotation is restricted. On the other hand, it seems more likely that the increase in phenyl–phenyl distance brought about by the change from a five-membered (3.5 Å. between phenyl ring centers) to a three-membered ring (4.1 Å.) has lowered the potential barrier to rotation of the phenyl rings so that they appear to rotate freely in terms of the n.m.r. time scale. It is hoped that these possibilities may be distinguished by low-tempera-

ture n.m.r. studies. The n.m.r. method appears to hold great promise both for assigning configurations and as a tool for measuring potential barriers to rotation which can be correlated with intramolecular distances in molecules of this kind.[24]

Although the n.m.r. spectrum of *cis*-stilbene showed the usual narrow aromatic absorption with a half-width of less than 3 c.p.s., the spectrum of *trans*-stilbene was of interest because it showed a broad complex aromatic spectrum the distance between the outer peaks being 20 c.p.s. at 60 Mc. It can be seen that such broadening could again be explained if *trans*-stilbene were planar with a sufficiently large energy barrier to rotation, the magnetic environment of the "inside" protons being different from that of the "outside." This would require, however, a rotation barrier considerably higher than would seem reasonable from previous estimates.[18] It was found when the spectrum was examined at temperatures from 25 to 157° that there was very little change. For example, the distance between two prominant peaks changed from 15 c.p.s. at 25° to 13 c.p.s. at 157°. It seems likely that rotation is rapid, in this case, on the n.m.r. time scale and that the small change in the spectrum is from some other cause such as, for example, a slight redistribution of phenyl rings from the more populated planar to the less populated non-planar energy levels.[25]

Use of Other Spectral Methods to Differentiate between *cis*- and *trans*-1,2-Diphenylcycloalkanes.—Ultraviolet spectra have been employed for some time to assign configurations to *cis*- and *trans*-1,2-disubstituted imines[26] and ethylene oxides[27] in which the substituents are conjugated through the 3-membered ring. Employing the principle[26,27] that the *trans* isomer should have the more intense absorption maximum at longer wave lengths, it was possible to assign configurations to the 1,2-diphenylcyclopropanes in ethanol since one isomer (the *trans*) has λ_{max} 230 mμ, ε 17,020, while the isomer assigned the *cis* configuration had a shoulder at about 220 mμ but no maximum at higher wave lengths. The stilbene oxides employed as model compounds showed similar differences (in ethanol), the *trans* isomer having a maximum at 238 but the *cis* with only a shoulder at 218 mμ. These configurational assignments agree with those of Aleksanyan, Sterin, Lukina, Safonova and Kazanskii[17b] who have employed the observation that the integrated intensities of the Raman lines at approximately 1603 and 1230 are very much greater in

(22) Reference 21, p. 366.

(23) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958). We are very much indebted to Dr. G. V. D. Tiers for a copy of the table of nuclear shielding values referred to in this paper.

(24) For the use of high resolution n.m.r. in assigning configurations to compounds with substituted five-membered rings containing heteroatoms see J. B. Hyne, *J. Am. Chem. Soc.*, **81**, 6058 (1959), and W. S. Brey, Jr., and W. M. Jones, *J. Org. Chem.*, **26**, 1912 (1961).

(25) As a check on the reasonableness of this interpretation it may be noted that an estimate of the average ring-current effect of one of the phenyl rings on the *ortho*- and *meta*-protons of the other ring of *trans*-stilbene, assuming rapid rotational equilibration of the phenyl rings between the two planar forms, gave a difference in shielding ($\sigma_{ortho} - \sigma_{meta}$) of 0.12 p.p.m. or 7 c.p.s. at 60 Mc. The estimate was made using the table of nuclear shielding values of C. R. Johnson and F. A. Bovey[18] together with interatomic distances measured with Dreiding stereomodels.

(26) See N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952).

(27) See C. L. Stevens, R. J. Church and V. J. Traynelis, *ibid.*, **19**, 522 (1954); N. H. Cromwell and R. A. Setterquist, *J. Am. Chem. Soc.*, **76**, 5752 (1954).

the *trans*-diphenylethylene than in the *cis* in assigning the configuration.

The electronic spectra of *cis*- and *trans*-diphenylcyclopentane have been examined by Cram, Allinger and Steinberg[28] in the course of a study of the steric consequences of bringing two benzene rings face to face. Their results showed that the phenyl groups attached to a cyclopentane ring and *cis* to one another are too far apart to have a significant effect on the spectrum.[29]

Experimental[30]

cis-3,4-Diphenylcyclopentanone, m.p. 108–109°, was prepared from dimethyl *meso-β,β'*-diphenyladipate by condensation with sodium dispersion in benzene with a catalytic amount of methanol, essentially the method of Weidlich,[3] in 30% yield.

A more satisfactory synthesis was one involving reduction of anhydroacetonebenzil and reoxidation of the resulting alcohol with chromic acid, essentially the method of Burton and Shoppee.[31] Recrystallization from 95% ethanol gave a product, m.p. 107.3–107.9°. The n.m.r. spectrum (5% solution in deuteriochloroform with tetramethylsilane as an internal standard at 60 Mc.) showed the aromatic protons separated into two complex bands centered at 3.00 and 3.32τ with relative areas measured with a polar planimeter of 3.02 to 1.98 (averages of several measurements).

trans-1,2-Diphenylcyclopentanone, m.p. 179–180° (lit.[3] m.p. 177°), was prepared by isomerization of the *cis* isomer over palladium-on-charcoal at 150° for 13 hr. employing essentially the procedure described for the preparation of *trans*-1,2-diphenylcyclopentane below. It was purified by recrystallization from methanol.

cis-1,2-Diphenylcyclopentane was prepared by reduction of the diphenylcyclopentanone with zinc amalgam and concentrated hydrochloric acid,[3] then purified by chromatography on activated alumina (elution with 10% ether in hexane, 20% ether in hexane and 50% ether in hexane). It could be obtained in a yield of 50% with a m.p. of 46–46.5° (lit.[3] m.p. 47°).

trans-1,2-Diphenylcyclopentane was prepared by isomerization of the *cis* isomer (0.72 g, 0.032 mole) by treatment with 0.60 g. of 5% palladium-on-charcoal in an atmosphere of hydrogen (sealed glass tube) at 150° for 48 hr. The crude product after extraction with purified *n*-hexane under a nitrogen atmosphere amounted to 0.70 g. of white solid, m.p. 62–65°, which was purified by chromatography on activated alumina and then on activated ferric oxide.[32] Recrystallization from methanol gave *trans*-1,2-diphenylcyclopentane, m.p. 66–66.5° (lit.[3] 65°).

Analysis of Mixtures of *cis*- and *trans*-1,2-Diphenylcyclopentane.—Preliminary attempts at analysis were made by examining the infrared spectra of known mixtures of the two isomers containing from 1 to 5% of the *cis* component utilizing the fact that the *cis* isomer absorbs at 749 and 770 cm.⁻¹ while the *trans* isomer has a single (stronger) absorption at 755 cm.⁻¹. It was found that the method was incapable of detecting less than about 3% of the *cis* isomer, however. For this reason a differential method[33] was employed as follows. To 20% stock solutions of *trans*-1,2-diphenylcyclopentane in carbon disulfide were added

amounts of a 20% stock solution necessary to prepare standard solutions of mixtures containing from 0.5% to 3.5% of the *cis* isomer. A 20% standard reference solution of the *trans* isomer was placed in the reference beam of a Perkin-Elmer model 21 spectrophotometer and the solution of known composition in the sample beam. The spectrum was then traced on an expanded scale between 900 and 650 cm.⁻¹. The solutions were then reversed and the spectra retraced. Areas enclosed by the two curves (maxima at 745 and 695 cm.⁻¹) were measured with a polar planimeter and a calibration curve prepared by plotting the values of areas against known concentrations of the standard solution. The same procedure with the equilibration mixtures gave areas which allowed the % of *cis* isomer to be read directly from the calibration curve.

Isomerization of the 1,2-Diphenylcyclopentanes. (a) Palladium-on-Charcoal.[4]—In a typical experiment 0.0793 g. of the *trans* isomer and 0.10 g. of 5% palladium-on-charcoal were introduced into a Pyrex tube which, after replacement of the air by nitrogen and hydrogen, was sealed and heated at 110° for 144 hr. Extraction with hexane under nitrogen gave, after removal of the solvent, 0.0718 g. (90.7%) of white solid which was found by the differential method described above to contain 2.99% of the *cis* isomer. An ultraviolet spectrum of the product showed not more than 0.2% conjugated olefin as indicated by the absence of absorption at 280 mμ and the magnitude of absorption at 237 mμ employing β-methylstyrene as a model.

(b) Potassium and Dibutylamine.—A solution of 0.1035 g. of *trans*-1,2-diphenylcyclopentane in 0.6 ml. of freshly distilled di-*n*-butylamine was placed in a Pyrex tube and 0.3 g. of potassium metal was added. After replacement of the air by nitrogen as before the tube was sealed and heated at 110° for 144 hr. A light orange color developed after 18 hr. but disappeared rapidly when the tube was opened. Extraction with ether and removal of the solvent as before yielded 0.0944 g. (91%) of the hydrocarbon mixture shown by analysis as before to contain 2.92% of the *cis* isomer. The ultraviolet spectrum indicated a maximum olefin content of 0.4% estimated by comparison of the absorption at 280 and 237 mμ employing β-methylstyrene[34] as a model.

cis- and *trans*-Diphenylcyclopropane were separated from the liquid mixture prepared by the method of Kizhner'[16] by distillation through a 4-ft. spinning-band column. From 95 g. of benzalacetophenone was obtained 28 g. of the *cis* isomer, b.p. 126.5–129° (3.8 mm.), n^{20}D 1.5892, and 33 g. of the *trans*, b.p. 144–145.3° (3.8 mm.), n^{20}D 1.5995. The *cis* isomer solidified and on recrystallization from ethanol–water had m.p. 38.0–38.5° (lit.[17] m.p. 36.7°). The *trans* isomer when redistilled gave four fractions each of which had the refractive index reported above. It was not crystallized (lit.[17] m.p. 15.3°).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.7; H, 7.3. Found (*cis* isomer): C, 92.9; H, 7.3. Found (*trans* isomer): C, 92.9; H, 7.3.

Sensitivity to Air Oxidation of the Diphenylcyclopropanes, -pentanes and -pentanones.—On exposure to the atmosphere at 25° the solid *cis*-1,2-diphenylcyclopentane was observed to soften within 2–3 days and then to change to a yellow oil after 4–5 days. The infrared absorption of an oxidized sample showed strong absorption at 1690 cm.⁻¹ with a shoulder at 1730 cm.⁻¹ and other significant changes. Absorption at 775 cm.⁻¹, characteristic of the starting hydrocarbon had disappeared. At 5° under the same conditions essentially no oxidation had occurred and a solution in methanol showed no decomposition at 25°. *cis*-1,2-Diphenylcyclopropane as well as the *trans*-diphenylcyclopropane, -cyclopentane and -cyclopentanone showed no oxidation under comparable conditions.

N.m.r. spectra were at first measured with a Varian Associates V-4300-C high resolution spectrometer with a 12″ electromagnet system equipped with a VK-3606 flux stabilizer operating at 40 Mc. Audiofrequency side bands generated with a Hewlett–Packard 200-CD oscillator, together with an external methylene chloride standard were used to determine positions of absorption maxima. Later spectra were determined on the same instrument modified to operate at 60 Mc. with positions of maxima determined with the use of tetramethylsilane as an internal standard. Less care was taken with these latter spectra to make fre-

(28) D. J. Cram, N. L. Allinger and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954).

(29) Our spectra show reproducible differences in fine structure which might be useful for identification but are in substantial agreement with those reported.[28]

(30) All melting points are corrected. Microanalyses were carried out by the microanalytical laboratory of the University of Illinois under the supervision of Mr. Josef Nemeth. Infrared spectra were obtained with a Perkin–Elmer model 21 spectrophotometer; n.m.r. spectra were obtained by Mr. Ben Shoulders and Mr. O. Norton; ultraviolet spectra were obtained with a Cary model 11 and a Cary model 14M spectrophotometer. We are indebted to Miss Geraldine Meerman for assistance with some of the spectra.

Ultraviolet and infrared spectra are available in the Ph.D. Theses referred to in ref. 1 and available from Univ. Microfilms, Ann Arbor, Mich.

(31) H. Burton and C. W. Shoppee, *J. Chem. Soc.*, 567 (1939).

(32) O. Glemser and G. Rieck, *Angew. Chem.*, **69**, 91 (1957).

(33) D. Z. Robinson, *Anal. Chem.*, **24**, 619 (1952).

(34) R. Y. Mixer, R. F. Heck, S. Winstein and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953).

quency measurements with a high degree of accuracy. Chemical shifts between the *cis* and *trans* isomer calculated from measurements on the pure compounds agreed well with the same shifts measured with spectra of 50–50 mixtures of the same compounds.

The high temperature spectra were measured with the Varian model V-4340 variable temperature probe and the model V-4331-THR Dewar insert. Solutions of *cis*-1,2-diphenylcyclopentane in carbon tetrachloride (30% by volume) in 2.5 mm. i.d. Pyrex tubes were degassed and then sealed under prepurified nitrogen and inserted in 5-mm. tubes. Tetramethylsilane (0.3–3% by volume) was used as an internal standard. Spectra of the pure liquid *cis*-diphenylcyclopentane were also examined at higher temperatures and gave results similar to those obtained with the solutions. *cis*-3,4-Diphenylcyclopentanone was examined in carbon tetrachloride (11% by volume) and care was taken to protect it from light. The temperature was maintained by a flow of hot air and the insert temperature was calibrated for a range of settings from 25–185° using a dummy sample tube containing a thermocouple— the temperature of the insert jacket being monitored by means of a copper–constantan thermocouple located in it. The temperatures are considered reliable to about ±1°. As a check on chemical stability and reproducibility of the spectra, the spectra at 25° were re-run after the samples had been examined at 152 and 182°. Although a slight yellowish discoloration was noticed with the carbon tetrachloride solution after heating, the spectra obtained before and after heating were

TABLE III
α- AND AROMATIC PROTON RESONANCE OF *cis* AND *trans* ISOMERS IN CARBON TETRACHLORIDE SOLUTION (τ-VALUES)

Compound	Aromatic protons (Phenyl positions)			α-Protons (Benzylic positions)		
	trans	*cis*	*c − t*	*trans*	*cis*	*c − t*
1,2-Diphenylcyclo- propanes	2.87[a]	3.04[a]	0.17	7.87[a]	7.55[a]	−0.32
1,2-Diphenylcyclo- pentanes	2.99[a]	3.19[a]	.20	7.07[a]	6.67[a]	− .40
	3.01[b]	3.22[b]	.21	7.00[b]	6.68[b]	− .32
3,4-Diphenylcyclo- pentanones	2.83[c]	3.10[c]	.27	6.52[c]	6.17[c]	− .35
Stilbenes	2.62[a]	2.79[a]	.17	2.97[a]	3.47[a]	− .50
Azobenzenes	2.52[a]	3.09[a]	.57			

[a] Calculated from value obtained from extrapolation of infinite dilution in carbon tetrachloride at 40 Mc. in p.p.m. relative to water by the addition of 5.22 p.p.m.[35] [b] Value in carbon tetrachloride measured from tetramethylsilane as an internal standard at 60 Mc. [c] Value of 5% solution in deuteriochloroform using tetramethylsilane as an internal standard.

essentially-superimposible and no new peaks were evident in any sample. Positions of n.m.r. maxima are presented in Table III.

(35) Value suggested by G. V. D. Tiers in his "Tables of τ-Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Co. Report, 1958.

Transmission of Electrical Effects through Homoallylic Systems. V. The Nature of the Bonding in Ions Derived from Cyclopropylcarbinyl and Cyclobutyl Derivatives[1a]

BY RICHARD A. SNEEN, KENNETH M. LEWANDOWSKI,[1b] ISSAM A. I. TAHA[1b] AND BILLY RAY SMITH[1b]

RECEIVED JULY 12, 1961

Synthesis of the crystalline β-naphthalenesulfonate esters of cyclopropylcarbinol, of *cis*- and *trans*-2-phenylcyclopropylcarbinol and of cyclobutanol is reported. The rates of solvolysis of the three cyclopropylcarbinyl esters were determined in 90 volume per cent. aqueous dioxane at 25°. The unsubstituted ester proved to be intermediate in reactivity (k_{rel} = 1.00) between the slower *cis*- (0.62) and the faster *trans*-2-phenylcyclopropylcarbinyl β-naphthalenesulfonate (2.19). This insensitivity to phenyl substitution is interpreted as evidence that, whatever the nature of the intermediate derived on solvolysis of cyclopropylcarbinyl systems, little positive charge is dispersed to the methylene carbon atoms of the cyclopropyl ring. Kinetic salt effects on solvolysis of cyclopropylcarbinyl β-naphthalenesulfonate were carried out with results confirming Roberts' suggestion[2,22] that such reactions are accompanied by internal return. Finally, the trifluoroacetate esters of *cis*- and *trans*-2-phenylcyclopropylcarbinol have been prepared and their rates of solvolysis in 60 volume per cent. aqueous dioxane have been measured.

In spite of the general interest which was aroused by the original solvolytic studies[2-4] on cyclopropylcarbinyl and cyclobutyl derivatives, the nature of the bonding in the intermediate ions and, indeed, even the number of such intermediates involved in these ionization reactions has not yet been unequivocally established. The facts which must be accounted for are these: both cyclopropylcarbinyl and cyclobutyl derivatives react at rates abnormally fast when compared with appropriate model compounds. Further, both cyclopropylcarbinyl and cyclobutyl derivatives give rise to essentially the same distribution of solvolysis products, consisting of derivatives containing the cyclopropylcarbinyl, the cyclobutyl and the allylcarbinyl nuclei.

These facts were early interpreted in terms of a single so-called tricyclobutonium ion (I),[3,5] an intermediate assumed common to both ring structures. Such a structure would presumably account not only for the observed product distributions but also, if it is stabilized with respect to more classical ions, the enhanced rates of reaction.

More recently Roberts and co-workers[6] have shown that the highly symmetric tricyclobutonium ion cannot, at least simply, explain the results of C-14 experiments in the closely-related reaction, the decomposition of cyclopropylcarbinyl diazonium ion. Thus, although each of the three methylene carbons of the product cyclobutanol contained C-14, equilibration was not complete. These results led Roberts to propose a somewhat less

(1) (a) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September 13, 1960, Abstracts of Papers, p. 34-P. (b) Abstracted from theses submitted by K. M. L., I. A. I. T. and B. R. S. in partial fulfillment of the requirements for the degree of Master of Science.

(2) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(3) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

(4) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

(5) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 3542 (1951).

(6) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).