raphy at 150° on a diisodecyl phthalate column. Only ether, carbon tetrachloride, chlorobenzene, anisole and hexachloroethane were detected (in that order). Anisole served as an internal standard, and yields of chlorobenzene and hexachloroethane were calculated after calibration of the system with known mixtures.

The products of a CO experiment were further definitely identified as follows. After removal of most of the solvent, a reaction mixture was fractionally distilled at 17 mm. pressure. Chlorobenzene was first collected and identified by boiling point and infrared spectrum. As the temperature was raised a mixture of benzoyl chloride and sublimed hexachloroethane was collected. It was rinsed into a flask with ether and gently evaporated. The liquid portion had an infrared spectrum identical with authentic benzoyl chloride artificially contaminated with ether, and reacted exothermically with aniline to give benzanilide. Continued distillation of the residue at 0.09 mm. pressure gave a liquid, b.p. 122°, which solidified on standing. Its melting point on recrystallization was 39–42° (reported for benzoic anhydride, 42°) and its infrared spectrum was identical with authentic anhydride.

Experiments in Benzaldehyde.—A 0.1 *M* solution of benzoyl peroxide was decomposed in freshly distilled benzaldehyde at 70° under nitrogen, and the reaction followed by titration of aliquots (Fig. 1). After complete reaction the excess benzaldehyde was removed at 67° and reduced pressure, the residue dissolved in ether and extracted with $NaHSO_3$ solution to remove remaining aldehyde. The dibenzoate of dihydrobenzoin which separated from the ether solution and is a known product of the reaction[16] was removed and identified by m.p. (245.4–246.0°). A known aliquot of the ether solution was next extracted with bicarbonate and anhydride determined by hydrolysis as above. Further evidence for anhydride was obtained by extracting another aliquot with bicarbonate and examinating the infrared spectrum of the residue which showed strong peaks at 5.58 and 5.80 μ. Treatment of the residue with aniline and warming briefly yielded benzanilide, identified by m.p. and mixed m.p.

Deuterated benzoyl peroxide was prepared by treating toluene with two successive portions of D_3PO_4 (from D_2O and P_2O_5) for 88 hours at 80°. The deuteriotoluene was next oxidized to deuteriobenzoic acid with neutral $KMnO_4$, converted to the acid chloride with $SOCl_2$ and treated with a cold solution of Na_2O_2 (over-all yield 32%). A small scale run of the first step indicated 95% replacement of the ring protons by n.m.r. spectra, but the actual preparation used showed only 35–40%. Kinetic runs are shown in Fig. 2, and calculation indicates that, if deuteration were random, a value of $k_H/k_D = 1.5$ should give a 25-minute increase in half-life of the peroxide which should be readily apparent (actually, deuteration was probably selective in the *o*- and *p*-positions which would considerably increase the sensitivity of the experiment). As a further check, the n.m.r. spectra of benzoic acids prepared from (a) unused deuterated peroxide and (b) peroxide remaining after 73% reaction were compared. No significant difference (±5%) in deuterium content could be detected.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Equilibration of *cis*- and *trans*-Cycloalkenes[1]

BY ARTHUR C. COPE, PHYLIS T. MOORE[2] AND WILLIAM R. MOORE

RECEIVED AUGUST 13, 1959

The *cis* and *trans* isomers of cyclononene, cyclodecene, cycloundecene and cyclododecene have been equilibrated in acetic acid solution at 79.9, 100.4 and 130.0°. The standard free energies, enthalpies and entropies of isomerization have been calculated at 100.4°. The equilibrium *cis*-olefin/*trans*-olefin ratios in acetic acid at 100.4° are cyclononene, 232; cyclodecene, 12.2; cycloundecene, 0.406; and cyclododecene, 0.517. Possible effects of the solvent on the positions of these equilibria are discussed. In the isomerization of *trans*-cyclononene, it was found that *cis*-cyclononene and cyclononyl acetate are formed at nearly equal rates; the concentration of the latter then slowly decreases as the system approaches equilibrium.

Our continuing interest in medium ring compounds has prompted a study of the equilibria between the *cis* and *trans* isomers of cyclononene, cyclodecene, cycloundecene and cyclododecene in acetic acid solution. No systematic study of these equilibria has been reported previously, although the greater stability of the *cis* relative to the *trans* isomer in the C_9- and C_{10}-rings has been recognized. Thus, *cis*-cyclononene essentially free of its *trans* isomer was obtained from *trans*-cyclononene that had been heated at 150° in the presence of β-naphthalenesulfonic acid.[3] Heating *trans*-cyclodecene in the presence of the same catalyst at 90–180° has resulted in substantial (70–80%)[4] to nearly complete[3] isomerization to *cis*-cyclodecene. Recently Allinger[5] has reported that treatment of either *cis*- or *trans*-cyclodecene with concentrated sulfuric acid at 25° gave *cis*-cyclodecene containing less than 0.5% of *trans*-cyclodecene (based on infrared analysis) and thus estimated that at equilibrium the *cis*/*trans* ratio was ≥ 200.[6]

Turner and Meador[7] have determined the heats of hydrogenation in acetic acid at 25° for *cis*- and *trans*-cyclooctene, cyclononene and cyclodecene. The enthalpies of isomerization (*trans* to *cis*) calculated for the C_8-, C_9-, and C_{10}-olefins from their hydrogenation results are −9.2, −2.9 and −3.3 kcal./mole, respectively.

After the work described in this paper had been completed, Svoboda and Sicher[8] reported that the sulfuric acid-catalyzed equilibration of the cyclododecenes at room temperature gives a *cis*/*trans* ratio of about 40/60.

Preparation of Olefins.—*cis*-Cyclononene,[9,10] *cis*-cyclodecene[4,11] and *cis*-cycloundecene[12] were pre-

---

(1) Preliminary communication, A. C. Cope, P. T. Moore and W. R. Moore, THIS JOURNAL, **81**, 3153 (1959).

(2) National Science Foundation Predoctoral Fellow, 1955–1957.

(3) A. C. Cope, D. C. McLean and N. A. Nelson, THIS JOURNAL, **77**, 1628 (1955).

(4) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *ibid.*, **74**, 3636 (1952); A. T. Blomquist and A. Goldstein, *ibid.*, **77**, 1001 (1955).

(5) N. L. Allinger, *ibid.*, **79**, 3443 (1957).

(6) Dr. P. E. Fanta has informed us that in similar experiments he has found *ca.* 1% of the *trans* isomer (analysis by gas chromatography) indicating an equilibrium *cis*/*trans* ratio of *ca.* 100.

(7) R. B. Turner and W. R. Meador, THIS JOURNAL, **79**, 4133 (1957).

(8) M. Svoboda and J. Sicher, *Chemistry & Industry*, 290 (1959).

(9) A. T. Blomquist, L. H. Liu and J. C. Bohrer, THIS JOURNAL, **74**, 3643 (1952).

(10) V. Prelog, K. Schenker and W. Kung, *Helv. Chim. Acta*, **35**, 471 (1952).

(11) V. Prelog, K. Schenker and H. H. Gunthard, *ibid.*, **35**, 1598 (1952).

(12) V. Prelog and V. Boarland, *ibid.*, **38**, 1776 (1955).

pared by partial hydrogenation of the corresponding acetylenes. *trans*-Cyclononene[9] and *trans*-cycloundecene,[12] prepared by reduction of the corresponding acetylenes with sodium in liquid ammonia, were purified by gas chromatography to remove the *cis* isomers which were formed in varying amounts in these reductions. At the present time, it is not known whether the formation of *cis*-olefins resulted from some change in the normal mechanism of reduction (*trans* addition) or whether the *trans*-olefins were isomerized in some manner.[13] *trans*-Cyclodecene was prepared by the pyrolysis of cyclodecyltrimethylammonium hydroxide.[3,4,11] However, analysis (by gas chromatography) of the hydrocarbon fraction of the pyrolysate showed that the product consisted of 98% *trans*-cyclodecene and 2% *cis*-cyclodecene. The *cis*-olefin had not been detected previously as a product of this Hofmann decomposition. Cyclododecyl acetate was pyrolyzed at 500° to give a mixture in which *trans*- and *cis*-cyclododecene were present in a ratio of 5:1. The two isomers were separated by gas chromatography.

Blomquist and Goldstein[4] obtained similar results in the pyrolysis of cyclodecyl acetate (*trans*-cyclodecene/*cis*-cyclodecene = 3.6).

Equilibration Procedures and Results.—The equilibrations of olefins were carried out in oxygen-free acetic acid employing 0.1 to 0.5 *M* *p*-toluenesulfonic acid as a catalyst. Olefin concentrations varied from about 0.2 to 0.4 *M*.[14] Under these conditions, the equilibrations proceeded with no detectable polymerization or charring. Equilibrium was approached from both sides for each *cis*–*trans* pair of isomers at three temperatures. By appropriate procedures, the olefins were separated from the solvent, and the *cis*/*trans* ratio of each sample then was determined by gas chromatography.

Table I summarizes the equilibration results. Except for the cyclononenes, at each temperature equilibrium was reached, as judged by the identity (within 1%) of the *cis*/*trans* ratios obtained starting from both *cis*- and *trans*-olefins. In the cyclononene series, equilibrium was not quite attained since the *cis*/*trans* ratios obtained from the *trans* samples were about 9% lower than the ratios obtained from the *cis* samples. However, the arguments which follow indicate that at each temperature the average of the two ratios should lie within 5% of the equilibrium ratio.

In the equilibrations of the cycloundecenes and cyclododecenes trace amounts of other products (detected by gas chromatography) were formed, but were not identified.

Under the conditions employed to reach equilibrium between the cyclodecenes, small amounts of *cis*- and *trans*-decalin[3] were formed. Decalin formation was at a maximum at 130° at which temperature the equilibrated mixtures (obtained from both *cis*- and *trans*-olefins) contained *ca.* 4% each of *cis*- and *trans*-decalin. In addition, 1 to 2% of a higher-boiling material was formed which appeared to be cyclodecyl acetate (judging from its behavior in gas chromatography).

TABLE I

EQUILIBRIUM *cis*/*trans* OLEFIN RATIOS

	cis/*trans* ratios[a] Temperature, °C.		
Starting olefin	79.9	100.4	130.0
cis-Cyclononene	312	242	187
trans-Cyclononene	284	222	170
Mean	298	232	178
cis-Cyclodecene	16.20	12.20	8.61
trans-Cyclodecene	16.24	12.18	8.60
Mean	16.22	12.19	8.60
cis-Cycloundecene	0.405	0.406	0.412
trans-Cycloundecene	0.400	0.406	0.410
Mean	0.402	0.406	0.411
cis-Cyclododecene	0.531	0.517	0.495
trans-Cyclododecene	0.537	0.517	0.499
Mean	0.534	0.517	0.497

[a] Each value represents the mean of two or more determinations. Values could be reproduced to within 1–3% in the cyclononene system and to within 1% in all other cases.

The cyclononene system was complicated by several factors. The relatively rapid, reversible formation of cyclononyl acetate (identified by gas chromatography and its infrared spectrum) was particularly striking. With the reaction times employed, the equilibrium *cis* olefin/acetate ratios were nearly attained (this ratio is *ca.* 3 at 100° and increases with increasing temperature). The rate of formation of the acetate is much greater from *trans*- than from *cis*-cyclononene. Starting an equilibration from *trans*-cyclononene (Fig. 1), the concentration of *trans*-olefin drops abruptly to a very low level and a mixture of *cis*-cyclononene and cyclononyl acetate (in a ratio of *ca.* 1 to 1) is produced. The concentration of cyclononyl acetate then drops slowly with time as the *cis*-cyclononene concentration slowly increases. In an equilibration starting from *cis*-cyclononene (Fig. 2), from the outset the cyclononyl acetate concentration slowly increases while the *cis*-cyclononene concentration slowly decreases.[15] In either case, it can be seen that attainment of *cis*/*trans* equilibrium is greatly slowed by the formation of cyclononyl acetate.

The conditions employed for the determination of equilibrium *cis*/*trans* ratios also led to the forma-

---

[13] The formation of *cis*-cyclononene in the reduction of cyclononyne with sodium in liquid ammonia, although not reported by earlier workers (ref. 9), has been observed in unpublished research of W. R. Moore and R. C. Bertelson. Svoboda and Sicher (ref. 7) observed similar results in the reduction of cyclododecyne.

[14] The amount of an olefin found after "quenching" an equilibration reaction is the sum of the amount of free (unprotonated) olefin present at equilibrium and the amount of olefin obtained upon irreversible deprotonation of protonated olefin species (*e.g.*, π-complexes). If significant fractions of the olefins are protonated and if the isomers differ in basicity (as is likely), the *cis*/*trans* olefin ratios found would not represent the equilibrium ratios of unprotonated olefins. Such effects of protonation were precluded in the present study since observed *cis*/*trans* ratios were essentially constant over a fivefold variation of catalyst concentration. However the very high acidities which must result in the absence of a solvent (ref. 5) such as acetic acid, which can be protonated, may well make considerations of the extent of protonation imperative, particularly in cases where one isomer predominates at equilibrium.

[15] The experiments summarized in Figs. 1 and 2 were performed at lower catalyst concentrations than ultimately were employed (Table III).

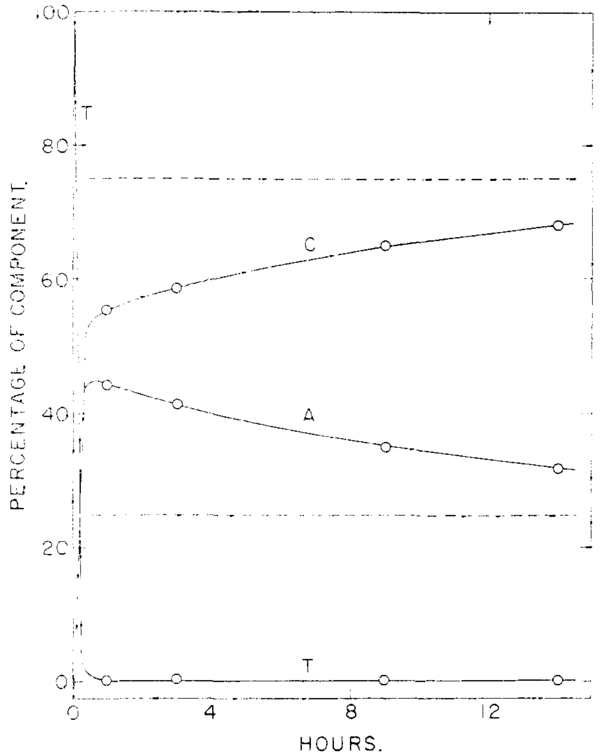


Fig. 1.—The relative concentrations of the products produced at 100.0° from *trans*-cyclononene in acetic acid containing 0.05 *M* *p*-toluenesulfonic acid; C, *cis*-cyclononene; T, *trans*-cyclononene; A, cyclononyl acetate. Dashed lines represent approximate equilibrium values.

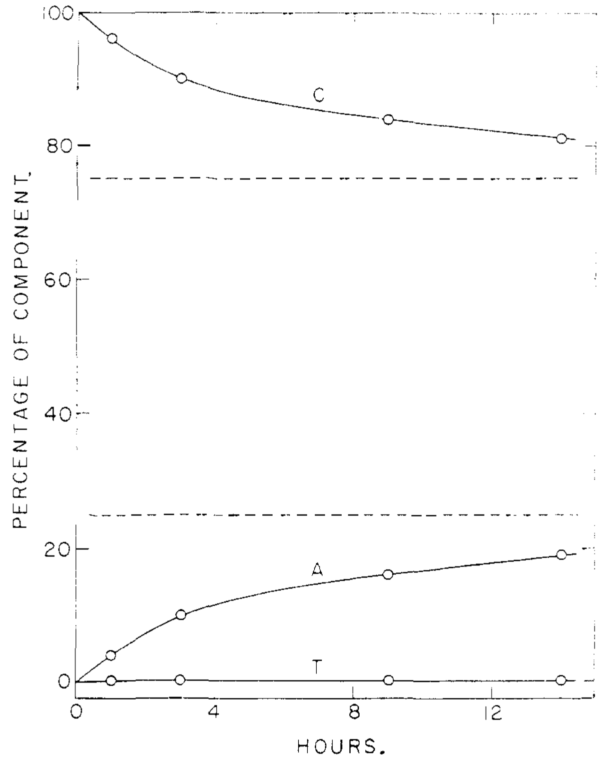


Fig. 2.—The relative concentrations of the products produced at 100.0° from *cis*-cyclononene in acetic acid containing 0.05 *M* *p*-toluenesulfonic acid: C, *cis*-cyclononene; T, *trans*-cyclononene; A, cyclononyl acetate. Dashed lines represent approximate equilibrium values.

tion of appreciable quantities (10–25% of the total composition of the equilibrium mixtures) of several other C_9-hydrocarbons (so assigned from their behavior in gas chromatography). These "abnormal" hydrocarbons appeared before the cyclononenes as four main peaks on a gas chromatogram (the liquid phase was a silicone oil) in the following relative amounts listed in order of increasing retention time: 3% of a mixture of two or three components, 7% of a component with a retention time identical to that of *trans*-hydrindane, 40% of an unidentified component, and 50% of a component with a retention time identical to that of *cis*-hydrindane.[16] Prolonged heating of the cyclononenes or cyclononyl acetate led to exceedingly complex mixtures, containing very small amounts of the cyclononenes. In these samples, several components (possibly isomers of cyclononyl acetate, judging from their retention times in gas chromatography employing a silicone oil as the liquid phase) were found to have increased considerably from the amounts present (1–2%) in the samples employed in the equilibrations. The "abnormal" product believed to be *cis*-hydrindane was found to have increased considerably at the expense of other C_9-hydrocarbons and was the major C_9-hydrocarbon present in these mixtures.

From preliminary kinetic data, it is possible to estimate that the rate of isomerization of *trans*-cyclononene to *cis*-cyclononene is much greater (at least 25–50 times) than the rate of formation of "abnormal" products from the *trans*-olefin and that the rate of isomerization of the *cis*-olefin to the *trans* isomer is substantially greater (at least 3–15 times) than the rate of formation of abnormal products from the *cis*-olefin. These results, coupled with the fact that the *cis*/*trans* ratios obtained approaching equilibrium from either side appeared to be converging, indicate that the formation of "abnormal" products did not prevent the determination of the equilibrium *cis*/*trans* ratios. The convergence alone is a sufficient criterion for approach to equilibrium if all of the reactions proceed through a common intermediate.

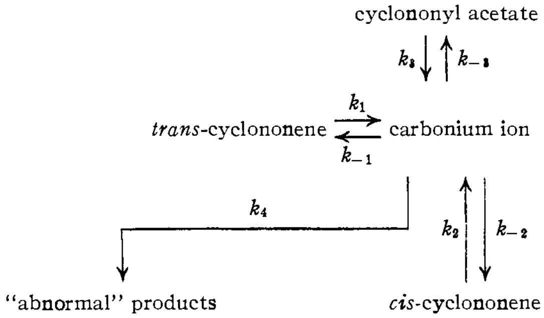
Assuming a common intermediate, a comparatively simple mechanism can account for the observations in the cyclononene system. The isomerization of either olefin probably involves rapid reversible protonation of the olefin to form a π-complex followed by rearrangement of the π-complex to a carbonium ion in the rate-determining step.[17] The carbonium ion would be expected to react as outlined below in the following competing ways (the *k*'s, for brevity, include equilibria involving π-complexes): (a) by loss of a proton to give the *cis*- or *trans*-olefin, (b) by addition of acetic acid and subsequent loss of a proton to give the

---

[16] Very nearly the same ratios were obtained from either olefin, a result not surprising, since the *trans*-olefin very rapidly falls to a low concentration with simultaneous formation of a relatively high concentration of *cis*-olefin. Shorter heating periods showed that these products were formed more rapidly from the *trans* isomer.

[17] R. W. Taft, Jr., THIS JOURNAL, **74**, 5372 (1952), and following papers; H. Kwart and L. B. Weisfeld, *ibid.*, **80**, 4671 (1958).

acetate, and (c) by formation of "abnormal" products, *e.g.*, by loss of a transannular proton with attendant bridging to form bicyclic products.[3]



The rapid formation of approximately equal amounts of *cis*-olefin and acetate from the *trans*-olefin means that $k_{-2} \simeq k_{-3}$ and the subsequent increase in the concentration of *cis*-olefin at the expense of the acetate shows that $k_3 > k_2$. The much greater reactivity of the *trans*-olefin relative to the *cis*-olefin, $k_1 >> k_2$, is a reflection of the higher free energy level of the former (see Table II). Inasmuch as the rate of isomerization of *trans to cis*-olefin was found to be much higher than the rate of formation of "abnormal" products (from either olefin), it follows that $k_{-2} >> k_4$. Thus, at any time a relatively small fraction of the carbonium ions would lead to "abnormal" products, a condition which means that the irreversible formation of these products would not greatly affect the rate of attainment of *cis–trans* equilibrium.

Discussion

The *cis/trans* ratios determined experimentally (Table I) represent apparent equilibrium constants, K', for the reaction

$$trans\text{-cycloalkene} \rightleftarrows cis\text{-cycloalkene}$$

$$\frac{\gamma_{cis}\,(cis\text{-cycloalkene})}{\gamma_{trans}\,(trans\text{-cycloalkene})} = K = \frac{\gamma_{cis}}{\gamma_{trans}} \times K'$$

To obtain thermodynamic equilibrium constants, K, the ratios of activity coefficients, $\gamma_{cis}/\gamma_{trans}$, must be known.[18] The activity coefficients of non-polar molecules in acetic acid would be expected to be very close to unity over the olefin concentration range employed in this study (molarity ≤ 0.4, mole fraction ≤ 0.025). In particular, for such closely related substances as the *cis* and *trans* isomers of olefins, it seems reasonable to assume that the ratios of activity coefficients would be one, and thus $K = K'$.

For each cycloalkene, the logarithm of the equilibrium constant was found to vary linearly with the reciprocal of the absolute temperature over the temperature range studied, 80–130°. From the slopes of these van't Hoff plots the standard enthalpies of isomerization (ΔH^0) have been determined. The standard free energies of isomerization (ΔF^0) and standard entropies of isomerization (ΔS^0) have been evaluated at 100.4° (373.6°K.) and are presented with the enthalpies of isomerization in Table II.

The enthalpies of isomerization obtained in this study are in good agreement with the values for the cyclononenes (−2.9 kcal./mole) and the cyclodecenes (−3.3 kcal./mole) determined by Turner and Meador[7] from heats of hydrogenation in acetic acid at 25°.

The values in Tables I and II reveal several interesting points. The thermodynamic stability[19] of *trans*-cycloundecene is greater than that of its *cis* isomer in acetic acid. Clearly the eleven-membered ring marks the turning point in the relative stability of the cyclic *cis* and *trans* isomers (at least in acetic acid solution). However, the stability order results almost wholly from the entropy change. Similarly, *trans*-cyclododecene is more stable than its *cis* isomer. In this case the stability order is based entirely upon the entropy change, since *cis*-cyclododecene has a *lower* enthalpy than *trans*-cyclododecene.

TABLE II

THE STANDARD FREE ENERGIES, ENTHALPIES AND ENTROPIES OF ISOMERIZATION OF *trans*-CYCLOALKENES TO *cis*-CYCLOALKENES IN ACETIC ACID AT 373.6°K.

Cycloalkene	ΔF^0, kcal./mole	ΔH^0, kcal./mole	ΔS^0, cal./mole °K.
Cyclononene	−4.04	−2.9	3.0
Cyclodecene	−1.86	−3.6	−4.7
Cycloundecene	0.67	0.12	−1.5
Cyclododecene	0.49	−0.41	−2.4

In the nine- and ten-membered ring olefins, the expected greater thermodynamic stability of the *cis* relative to the *trans* isomers is shown by the data in Tables I and II. However, the greater decrease in enthalpy in the isomerization of *trans*- to *cis*-cyclodecene ($\Delta H^0 = -3.6$ kcal./mole) compared to the change observed for the isomerization of *trans*- to *cis*-cyclononene ($\Delta H^0 = -2.9$ kcal./mole) seems surprising to us, particularly in view of the corresponding entropy changes. The sign and possibly the magnitude of the entropy of isomerization of *trans*- to *cis*-cyclononene ($\Delta S^0 = 3.0$ cal./mole °K.) were not unexpected since examination of molecular models indicates that the *trans* isomer is more highly restricted conformationally than the *cis* isomer. However, to a lesser extent, models indicate the same trend in relative rigidity in the cyclodecene series, but the isomerization of the *trans* to the *cis* isomer results in a substantial decrease in entropy ($\Delta S^0 = -4.7$ cal./mole °K.). These enthalpy and entropy changes must result from differences in medium-ring strain possibly combined with solvation effects.

It should be re-emphasized that the data in Tables I and II refer to acetic acid solution and not the gas phase. The trends indicated in this study may also be found in the gas phase, but in some respects it appears probable that the solution data may differ somewhat from gas phase values. Unfortunately there are few data in the literature pertinent

---

(18) For this study, the standard states of the olefins clearly must refer to acetic acid solution and thus are taken as the conventional one molar solutions with activity coefficients of one. The activity coefficients are defined as unity at infinite dilution.

(19) It is understood that in the discussion here and elsewhere in this paper, the term "thermodynamic stability" refers to the free energy of isomerization when each olefin is in its standard state. A positive free energy change in the isomerization of a *trans*- to a *cis*-olefin under these conditions defines the *trans*-olefin as "thermodynamically more stable" than the *cis* isomer.

to this point. Turner and co-workers[20,21] found that heats of hydrogenation in acetic acid solution at 25° were *ca.* 0.5 to 1.7 kcal./mole more positive (*i.e.*, less exothermic) than the gas phase values (at 82°) determined by Kistiakowsky and his collaborators.[22] This result indicates that olefins interact with acetic acid to a greater extent than do the related saturated compounds, a fact which is not surprising in view of the greater polarizability of the olefins. In the single case where enthalpies of isomerization for simple olefins have been compared by hydrogenation in the gas phase and in solution, 2,4,4-trimethyl-2-pentene → 2,4,4-trimethyl-1-pentene, the values were nearly identical: −1.2 kcal./mole (gas phase)[22] and −1.3 kcal./mole (acetic acid, 25°).[21] Unfortunately it is not possible to say whether this behavior is to be anticipated in general, or whether the case cited is exceptional. Turner and co-workers[21] have found (from heats of hydrogenation) that the enthalpy of isomerization of 4-methyl-*trans*-2-pentene to 4-methyl-*cis*-2-pentene is 0.9 kcal./mole (in acetic acid at 25°), a value very close to that found for the gas phase (82°) isomerization of *trans*-2-butene to *cis*-2-butene, $\Delta H^0 = +1.0$ kcal./mole.[23,24]

Recently Allinger[5,25] has measured the dipole moments of the cyclooctenes and the cyclodecenes in *n*-heptane solution: *cis*-cyclooöctene, 0.4 D.; *trans*-cyclooöctene, 0.8 D.; *cis*-cyclodecene, 0.4 D.; and *trans*-cyclodecene, 0.0–0.1 D. Since the values determined for these *cis* isomers are "normal," it may be expected that all of the *cis*-olefins examined in the present study have small dipole moments and that the *trans*-C_{10}-, C_{11}- and C_{12}-olefins should have dipole moments nearly or exactly equal to zero. Since the *cis* isomers in these systems are the more polar they would be expected to be more highly solvated in acetic acid than the *trans* isomers. Thus at least part of the negative entropy change for *trans* to *cis* isomerization in the C_{10}-, C_{11}- and C_{12}-olefins could be due to greater restriction of solvent molecules by the *cis* isomers (and possibly greater loss of conformational degrees of freedom in the *cis* isomers than in the *trans* isomers). It would also be expected that greater solvation of the *cis*-olefins would tend to decrease slightly the enthalpies of the *cis*-olefins relative to the *trans* isomers (*i.e.*, tend to make *trans* to *cis* isomerization more exothermic). Interpolation of Allinger's results to the C_9 system indicates that *cis*- and *trans*-cyclononene should have nearly equal dipole moments, suggesting that both isomers should be solvated to approximately the same extent. (That is, in this system the effect of the solvent on the entropy and enthalpy of isomerization might be negligible.) The considerations above imply that unless the conformation of (at least) one of the cyclononenes or cyclodecenes is such that solvation is greatly enhanced (*e.g.*, *cis*-cyclodecene) or greatly inhibited (*e.g.*, *trans*-cyclodecene), it appears that solvent effects alone are not sufficiently large to account for the apparent anomalies in the entropies and enthalpies of isomerization found in these systems.

Finally, it should be noted that in the twelve-membered ring solvent effects apparently are not paramount in determining the position of equilibrium, since the equilibrium constant (*cis/trans*) in acetic acid at 25° is 0.59 (calculated from data at higher temperatures) and the value reported by Svoboda and Sicher[8] in the absence of solvent is 0.67 (apparently ±0.08).

Experimental[26]

Cycloalkynes.—Cyclononyne,[9,10] cyclodecyne,[4,11] and cycloundecyne[12] were prepared in 42, 66 and 5% yields, respectively, by mercuric oxide oxidation[11] of the corresponding dihydrazones. The first two yields are based on recrystallized dihydrazone; the last yield is based on diketone. The low yield of cycloundecyne was probably due to incomplete formation of the dihydrazone from the diketone and hydrazine in methanol at room temperature. (Prelog and Boarland[12] obtained this acetylene in 14% yield from the diketone.)

Cycloalkenes.—All of the olefins employed in this study were analyzed by appropriate gas chromatographic procedures and where necessary they were purified by gas chromatography. The identity of each of the olefins was confirmed by its infrared spectrum.

cis-Cyclononene,[9,10] *cis*-cyclodecene[4,11] and *cis*-cycloundecene[12] were prepared by partial hydrogenation (room temperature, atmospheric pressure) of the corresponding acetylenes over 10% palladium-on-Norit in methanol containing pyridine (2 ml. of pyridine per gram of palladium-on-Norit). The product from hydrogenation of cycloundecyne was found to be 93% *cis*- and 7% *trans*-cycloundecene. The pure *cis* isomer was isolated by gas chromatography. The infrared spectrum of this material showed strong absorption at 697 cm.$^{-1}$ (characteristic of *cis*-olefins) and no absorption in the vicinity of 980 cm.$^{-1}$ (characteristic of *trans*-olefins).

trans-Cyclononene[9] and *trans*-cycloundecene[12] were prepared by reduction of the corresponding acetylenes with sodium in refluxing liquid ammonia (which had been purified by distillation from sodium). In both cases, the products were shown by gas chromatography to contain the *cis* isomers in addition to the expected *trans*-olefins. For example, from cyclononyne, a product consisting of 71% *trans*-, 19% *cis*-cyclononene, and 10% cyclononyne was obtained (the composition varied with the preparation). The cycloundecenes were obtained in a ratio of *trans/cis* = 53/47. The pure *trans* isomers were isolated by gas chromatography. *trans*-Cycloundecene shows strong absorption in the infrared at 978 cm.$^{-1}$ and no absorption in the vicinity of 697 cm.$^{-1}$.

Cyclodecyldimethylamine, prepared by methods described previously,[3] was found to be free of impurities as shown by gas–liquid chromatography on two columns (the liquid phases were Dow–Corning Silicone oil 550 and tetrahydroxyethylethylenediamine). By treatment with methyl iodide, this amine was converted to cyclodecyltrimethylammonium iodide, m.p. 272.2–272.6° (dec., the capillary was introduced into an oil-bath at 260° with a temperature increase of 1.6°/min.), which was converted to the quaternary base. The base was pyrolyzed as described previously.[3] The product was found by gas chromatography to be 98% *trans*- and 2% *cis*-cyclodecene. No "abnormal" products were detected.

Cyclododecanone, m.p. 59.5–61.5°, was reduced with sodium borohydride in methanol to cyclododecanol, m.p. 77–82° (lit.[27] m.p. 80°), in 82% yield. This alcohol was

---

[20] R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

[21] R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *ibid.*, **80**, 1430 (1958).

[22] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, *ibid.*, **59**, 831 (1937).

[23] G. B. Kistiakowsky, J. R. Ruhoff, W. A. Smith and W. E. Vaughan, *ibid.*, **58**, 137 (1936).

[24] For the latter reaction in the gas phase at 25°, $\Delta F^0 = 0.69$ kcal./mole, $\Delta H^0 = 1.00$ kcal./mole and $\Delta S^0 = 1.0$ cal./mole °K.; "Selected Values of Thermodynamic Properties of Hydrocarbons and Related Compounds," A. P. I. Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

[25] N. L. Allinger, THIS JOURNAL, **80**, 1963 (1958).

[26] Melting points are corrected and boiling points are uncorrected. The infrared spectra were determined on a Perkin–Elmer model 21 recording spectrophotometer fitted with sodium chloride optics.

[27] M. Kobelt, P. Barman, V. Prelog and L. Ruzicka, *Helv. Chim. Acta*, **32**, 256 (1949).

heated with acetic anhydride in pyridine to give cyclododecyl acetate, b.p. 80–85° (0.07–0.10 mm.), n^{25}D 1.4682, in 70% yield (plus 17% of the acetate containing a small amount of a higher boiling component as shown by gas chromatography). The acetate was pyrolyzed under nitrogen by adding it dropwise (*ca.* 0.5 ml./min.) to a column packed with glass helices heated at 500°. The hydrocarbon fraction of pyrolysate (94%), b.p. 112.5–115.0° (17 mm.), n^{25}D 1.4825, was shown by gas chromatography to consist of the cyclododecenes[28] in a *trans/cis* ratio of 5 to 1 along with small amounts of other components which were not identified. Pure *cis*-cyclododecene, n^{25}D 1.4844 (lit.[28] n^{20}D 1.4863), and *trans*-cyclododecene, n^{25}D 1.4818 (lit.[8] n^{20}D 1.4850), were isolated by gas chromatography. The infrared spectrum of the *trans*-olefin shows strong absorption at 978 cm.$^{-1}$ whereas the *cis* isomer shows only very weak absorption at 975 cm.$^{-1}$. The latter has a strong absorption (doublet) at 693–702 cm.$^{-1}$ whereas the *trans* isomer has only a medium weak band at 700 cm.$^{-1}$.

Equilibration of Olefins.—The olefin to be equilibrated was measured with a microsyringe (0.020–0.050-ml. samples) into a sample tube containing 1.0 ml. of a stock solution of *p*-toluenesulfonic acid in glacial acetic acid. Because the rate at which *cis–trans* equilibrium was approached varied considerably with ring size, the concentration of *p*-toluenesulfonic acid in acetic acid was varied to permit equilibrium to be established in a reasonable period of time. That variation of catalyst concentration did not appreciably affect the equilibrium values obtained was demonstrated by experiments with samples of the cyclododecenes in which the same equilibrium value (within 1%) was obtained (at 130.0°) using two different catalyst concentrations (0.11 and 0.53 *M*). Preliminary experiments in the equilibration of the cyclononenes indicated that a fivefold change in catalyst concentration (0.05 to 0.26 *M*) did not produce more than a 10% change in the equilibrium *cis/trans* ratios. (The ratios may have been consistently 10% lower at the lower acid concentation.) In Table III the concentration of the catalyst in acetic acid and the heating times employed (not necessarily the minimum time sufficient to establish equilibrium) are given for each ring system.

TABLE III

CATALYST SOLUTIONS AND HEATING PERIODS

Ring system	Catalyst concn., molarity	Heating period, hr. Temperature, °C. 130.0	100.4	79.9
Cyclononenes	0.26	2.0	16	87
Cyclodecenes	.11	35	880	880
Cycloundecenes	.11	285	790	1100
Cyclododecenes	.53	215	770	1320

Prior to being sealed (under reduced pressure), the sample tubes and their contents were degassed (to a large extent) by alternately freezing and thawing the contents under reduced pressure (0.05 mm.) three times. The glass ampoules containing the olefins to be equilibrated were heated for measured periods of time in oil-baths maintained at constant temperature (within ±0.1°). Upon removal from the oil-bath, each ampoule was immersed in a Dry Ice–acetone-bath. After an ampoule had been opened, *ca.* 0.5 ml. of 10% sodium hydroxide solution and 0.5 ml. of pentane were added to the frozen mixture. After thawing, the contents of the ampoule were transferred to a 10-ml. graduated cylinder fitted with a ground-glass stopper. The ampoule was rinsed thoroughly with *ca.* 2.5 ml. of pentane and the rinsings were added to the graduated cylinder. About 2 ml. of 10% sodium hydroxide solution was added followed by sufficient water to bring the aqueous layer to a volume of *ca.* 7 ml. After thorough shaking, the aqueous layer was removed with a hypodermic syringe and the pentane layer was washed with 6 ml. of 2% sodium hydroxide solution, followed by two 6-ml. portions of water. The pentane layer was concentrated by careful distillation with a bath temperature of *ca.* 55°, conditions under which the pure *cis*- and *trans*-olefins were not isomerized nor lost by volatilization. After most of the pentane had been distilled, the clear white residual oil was analyzed by gas chromatography on a suitable column.

Analysis by gas chromatography (silicone oil column) of the mixtures obtained from equilibrations of *cis*- and *trans*-cyclononene samples showed the presence of relatively large amounts of cyclononyl acetate and appreciable quantities of several hydrocarbons which were eluted more rapidly than the cyclononenes (*cis*- and *trans*-cyclononene had virtually identical retention times on this column). In addition, many components (present in trace to minor amounts) were detected which had retention times greater than that of the cyclononenes but less than that of cyclononyl acetate. Several of these materials interferred seriously with the determination of *cis/trans* ratios by analysis on the silver nitrate–4-methyl-4-nitropimelonitrile column. Hence after a preliminary analysis on the silicone column, an equilibration mixture was passed through the silicone column in a single pass and the cyclononene fraction was trapped quantitatively. Then the cyclononene fraction, as a pentane solution, was analyzed on the silver nitrate–4-methyl-4-nitropimelonitrile column. Control experiments with standard mixtures of the cyclononenes (with *cis/trans* ratios of *ca.* 100) showed that these procedures did not change the *cis/trans* ratio. Since the amount of *trans*-cyclononene present was small, in most of the work, a Liston–Becker model 14 d.c. breaker amplifier was used as a preamplifier for the Leeds and Northrup, model S speedomax type G 0–10 mv. recording potentiometer which was employed in the gas chromatograph. The preamplification procedures were similar to those described by Dal Nogare and co-workers,[29] with a ten- or twenty-fold net amplification used for the *trans* peak.

Each equilibrium mixture was analyzed at least twice and each *cis/trans* ratio listed in Table I is the average of the values thus obtained. The peak areas used in calculating these ratios were measured with a planimeter. The *cis/trans* ratios could be reproduced with a mean deviation of *ca.* 1% except in the case of the cyclononenes where the reproducibility was *ca.* 1–3%. Analysis of standard mixtures indicated that the precision was a good measure of the analytical accuracy.

Gas Chromatographic Procedures.[30]—All column liquids were supported on dust-free 50–100 mesh C-22 firebrick (Johns–Manville). Helium was employed as the carrier gas at inlet pressures of 7–28 p.s.i.g. with resultant flow rates of 50–100 ml./min. measured at room temperature and atmospheric pressure. Thermal conductivity cells (employing thermistors) were used as detectors and were operated at column temperatures. The column dimensions, percentage by weight and composition of the liquid phase, and operating temperatures were: cyclononenes: preliminary separation, 180 × 0.5 cm.; 20% Dow-Corning silicone oil No. 550; 196°; analysis, 100 × 0.4 cm.; 28% of a solution of 4-methyl-4-nitropimelonitrile (84%), tetraethylene glycol (8.4%) and silver nitrate (7.6%); 88°.

Cyclodecenes: 100 × 0.4 cm.; 35% of a solution of silver nitrate (39%) in tetraethylene glycol (61%); 95°.

Cycloundecenes: 300 × 0.4 cm.; 17% tetraethylene glycol; 100°.

Cyclododecenes: Two columns were used, 180 × 0.5 cm.; 35% of a solution of silver nitrate (39%) in tetraethylene glycol (61%); 100°. The column employed for the cycloundecenes also was employed at 110°. The same column packings were employed in somewhat larger columns (240 × 0.8 cm.) for preparative separations.

CAMBRIDGE, 39, MASS.

---

[28] V Prelog and M. Speck, *Helv. Chim. Acta*, **38**. 1786 (1955).

[29] C. E. Bennett, S. Dal Nogare, L. W. Safranski and C. D. Lewis, *Anal. Chem.*, **30**, 898 (1958).

[30] The gas chromatographic behavior of a number of the olefins included in this paper will be discussed in a future paper by W.R.M.