

of TBF in the frozen portion of a two-phase system was less in the initial stages of freezing and less when the freezing was carried out slowly. It is unlikely that crystals of *p*-xylene directly incorporate any significant amount of TBF.

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Relative Stability of Cyclic Olefins. I. Equilibrium Isomerization of Monocyclic Olefins Containing Four- to Six-Membered Rings¹

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The equilibria of five groups of isomeric cyclomonoolefins having four-, five-, and six-membered rings and a one- or two-carbon side chain were measured at 25° over a sodium-alumina catalyst and at 250° over acidic alumina. Under these conditions the double bond migrates to all possible positions. Equilibrium constants, enthalpies, and free energies of isomerization were calculated. The equilibrium ratio methylenecycloalkane/1-methylcycloalkene has a minimum value for the five-membered ring compounds. The ethylenecycloalkane/1-ethylcycloalkene ratio at 25° is higher for the six- than for the five-membered ring series, but the relative order is reversed at 250°. The 1-alkylcycloalkenes are by far the most stable isomers in all series studied. Among the endocyclic isomers having a disubstituted double bond, the 3-alkyl isomer is more stable than the 4-alkyl isomer in the five-membered ring series, whereas the reverse is observed for the six-membered ring compounds. 3-Methylcyclobutene is very unstable with respect to the 1-alkyl isomer ($K^{25} \sim 8500$).

The variation with ring size of the stability of methylenecycloalkenes and 1-methylcycloalkenes has attracted considerable attention in recent years. In particular, the predictions of Brown and co-workers⁴ as to the relative stability of *exo*- and 1-*endo*cyclic olefins in the five- as compared with the six-membered ring series has led to some controversy. Turner and Garner^{5,6} determined the heats of hydrogenation of pairs of such isomers having five- and six-membered rings and hence derived the enthalpies of isomerization. Subsequently,

accurate measurements of the equilibria at 25° under acid-catalyzed conditions were carried out by Cope and co-workers.⁷

As the latter authors used a relatively mild catalyst, *i.e.*, *p*-toluenesulfonic acid in acetic acid solution, migration of the double bond was observed between the *exo* and the 1-*endo* position only. In the present work, on the other hand, equilibration was carried out by employing as catalyst sodium on alumina⁸ at room temperature and activated alumina at 250°. Under these conditions, migration of the double bond occurred to all available positions and a complete picture could thus be obtained of the relative stability of all olefinic isomers possible for a given ring size. Furthermore, measurements were extended to compounds having a four-membered ring, as well as to derivatives with a two-carbon side chain.

The cyclic olefins studied are listed in Tables I and II. The sodium-alumina catalyst did not cause any detectable side reactions at 25°, and carbon skeleton rearrangement did not exceed 1–5% on activated alumina at 250°. The data given in Tables I and II represent the average of a number of experiments, with approach to equilibrium being effected in most cases from different sides. Analysis of the equilibrated mixtures was carried out by gas-liquid chromatography (see Experimental).

The present results are in agreement with data of Cope and co-workers⁷ as far as the equilibrium constants at 25° of the 1-*endo*-*exo* pairs of isomers in the five- and six-membered ring series are concerned. Further, the values of ΔF° calculated from the equilibrium constants are close to the corresponding ΔH° values determined by Turner and co-workers^{5,6} from heats of hydrogenation. The significance of these findings has been amply discussed in the literature.^{4–7}

Since the present data were obtained by equilibrium isomerization of the olefins in the form of pure liquids (or in a saturated hydrocarbon as solvent), it is evident that the possible association of the olefins with acetic

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Table I. Equilibria between Isomeric Cyclic Olefins at 25°

No.	Compd.	Mole % ^a	K (1-alkyl isomer ^b / other isomer)	$\Delta F^\circ_{\text{isom}}$ (other isomer → 1-alkyl isomer), kcal./mole
I	Methylenecyclobutane ^c	15.0	5.66 ± 0.16	-1.03 ± 0.02
II	1-Methylcyclobutene ^c	85.0		
III	3-Methylcyclobutene ^c	~0.02	~8500	~-5.4
IV	Methylenecyclopentane ^d	0.09	1084 ± 54	-4.13 ± 0.03
V	1-Methylcyclopentene ^d	97.6		
VI	3-Methylcyclopentene ^d	1.65	118 ± 3.5	-2.84 ± 0.02
VII	4-Methylcyclopentene ^d	0.66	148 ± 6	-2.98 ± 0.01
VIII	Methylenecyclohexane ^e	0.46	198 ± 8	-3.15 ± 0.01
IX	1-Methylcyclohexene ^e	90.9		
X	3-Methylcyclohexene ^e	3.14	57.8 ± 2.8	-2.41 ± 0.02
XI	4-Methylcyclohexene ^e	5.45	33.4 ± 1.0	-2.09 ± 0.03
XII	Vinylcyclopentane ^f	<i>g</i>		
XIII	Ethylidenecyclopentane ^f	4.65	20.3 ± 0.7	-1.78 ± 0.02
XIV	1-Ethylcyclopentene ^f	94.2		
XV	3-Ethylcyclopentene ^f	0.91	207 ± 18	-3.16 ± 0.05
XVI	4-Ethylcyclopentene ^f	0.22	428 ± 25	-3.59 ± 0.03
XVII	Vinylcyclohexane ^h	<i>g</i>		
XVIII	Ethylidenecyclohexane ^h	9.54	8.63 ± 0.3	-1.28 ± 0.02
XIX	1-Ethylcyclohexene ^h	82.4		
XX	3-Ethylcyclohexene ^h	3.03	54.4 ± 1.2	-2.37 ± 0.01
XXI	4-Ethylcyclohexene ^h	5.02	32.8 ± 0.6	-2.07 ± 0.01

^a Mean values of concentrations obtained by approach to equilibrium from different sides, carrying out two equilibrations with each starting material. ^b The deviations were calculated from the maximal deviations from mean values of experimental equilibrium concentrations. ^c Equilibrium reached from the side of I, II, and III (III, in 2,4-dimethylpentane as solvent; see Experimental). ^d A mixture of 98% V and 2% IV was equilibrated. ^e Equilibrium reached from the side of VIII, IX, and a mixture of 30% X and 70% XI. ^f A mixture of 92% XIV and 8% XIII in cyclohexane was equilibrated. ^g The limits of detectability by gas chromatography of XII and XVII under the experimental conditions employed is estimated at 0.1%. ^h A mixture of 89% XIX and 11% XVIII in cyclohexane was equilibrated.

Table II. Equilibria between Isomeric Cyclic Olefins at 250°

No.	Compd.	Mole % ^a	K (1-alkyl isomer ^b / other isomer)	$\Delta F^\circ_{\text{isom}}$ (other isomer → 1-alkyl isomer), kcal./mole
IV	Methylenecyclopentane ^c	0.80	100 ± 4	-4.78 ± 0.04
V	1-Methylcyclopentene ^c	80.0		
VI	3-Methylcyclopentene ^c	12.9	12.4 ± 0.4	-2.61 ± 0.04
VII	4-Methylcyclopentene ^c	6.3	12.7 ± 0.5	-2.64 ± 0.04
VIII	Methylenecyclohexane ^d	1.80	34.9 ± 1.5	-3.69 ± 0.04
IX	1-Methylcyclohexene ^d	62.9		
X	3-Methylcyclohexene ^d	16.5	7.62 ± 0.3	-2.11 ± 0.04
XI	4-Methylcyclohexene ^d	18.8	6.68 ± 0.25	-1.97 ± 0.04
XII	Vinylcyclopentane ^e	~0.1	~700	~-6.8
XIII	Ethylidenecyclopentane ^e	10.9	6.53 ± 0.2	-1.95 ± 0.03
XIV	1-Ethylcyclopentene ^e	7.2		
XV	3-Ethylcyclopentene ^e	11.8	12.1 ± 0.3	-2.59 ± 0.04
XVI	4-Ethylcyclopentene ^e	6.1	11.6 ± 0.7	-2.54 ± 0.07
XVII	Vinylcyclohexane ^d	~0.1	~600	~-6.65
XVIII	Ethylidenecyclohexane ^d	8.50	7.03 ± 0.3	-2.03 ± 0.04
XIX	1-Ethylcyclohexene ^d	59.8		
XX	3-Ethylcyclohexene ^d	15.8	7.56 ± 0.3	-2.10 ± 0.04
XXI	4-Ethylcyclohexene ^d	15.9	7.52 ± 0.3	-2.09 ± 0.04

^a Mean value of concentrations obtained by approach to equilibrium from different sides. ^b The deviations were calculated from the maximal deviations from mean values of experimental concentrations. ^c Equilibrium reached from the side of IV, V, and a mixture of 60% VI and 40% VII. ^d Equilibrium reached from each pure component. ^e Equilibrium reached from XIII, XIV, XII containing 14% XIII, and a mixture of 58% XV and 42% XVI.

acid^{5,7} does not essentially affect the ΔF° values.⁹ Furthermore, the equilibrium in the gas phase can be estimated by taking into account the vapor pressures¹⁰

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of the components and assuming ideal behavior. Whereas IV and V have practically the same vapor pressure, methylenecyclohexane (VIII) is estimated to

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Table III. Enthalpies and Free Energies of Isomerization of Alkyl Cycloalkenes Containing a Disubstituted Double Bond^a

No.	Compd.	25°		250°		$\Delta H^\circ_{\text{isom}},^b$ kcal./mole
		K (3-endo/ 4-endo)	$\Delta F^\circ_{\text{isom}}$ (4-endo \rightarrow 3-endo), kcal./mole	K (3-endo/ 4-endo)	$\Delta F^\circ_{\text{isom}}$ (4-endo \rightarrow 3-endo), kcal./mole	
VI	3-Methylcyclopentene	1.25	-0.13	1.02	-0.02	-0.28
VII	4-Methylcyclopentene					
X	3-Methylcyclohexene	0.58	+0.32	0.88	+0.13	+0.57
XI	4-Methylcyclohexene					
XV	3-Ethylcyclopentene	2.07	-0.43	0.97	+0.03	-1.0
XVI	4-Ethylcyclopentene					
XX	3-Ethylcyclohexene	0.61	+0.28	1.0	0.0	+0.65
XXI	4-Ethylcyclohexene					

^a Calculated from mean equilibrium concentrations; see Tables I and II. ^b Calculated using the equation $\Delta F^\circ = \Delta H^\circ - T\Delta S$.

be more volatile than 1-methylcyclohexene (IX) by $p^{25}_{\text{VIII}}/p^{25}_{\text{IX}} = 48/39 = 1.23$. This consideration shows that the higher relative stability of the *exo* isomer in the six-membered series, as compared with the five-membered ring series, should be larger in the gas phase than in the liquid phase (see Table I).

Differences in solvation may, however, be sufficiently important to affect markedly the entropies. Cope and co-workers⁷ have calculated ΔS°_{25} values for the isomerization IV \rightarrow V and VIII \rightarrow IX, using enthalpy values determined by Turner. The relatively high value of 2.8 cal./mole deg. thus found for VIII \rightarrow IX (as compared with 0.9 cal./mole deg. for IV \rightarrow V) appeared to contradict the conclusions drawn from the inspection of models of VIII and IX as to lesser conformational restriction in methylenecyclohexane (VIII), and has therefore been ascribed partially to differences in degree of solvation. This explanation is supported by the present free-energy data. An estimation of ΔS° for the reactions IV \rightarrow V and VIII \rightarrow IX in the gas phase using the data for 250 and 25° (corrected for the difference in vapor pressures, as mentioned above) shows, indeed, much less difference for the two equilibria, namely, 2.9 and 3.1 cal./mole deg., respectively.

When considering the various endocyclic isomers, it is seen that the 1-alkylcycloalkenes which have a trisubstituted double bond are by far the most stable isomers at 25° ($K(1\text{-endo}/\text{other } \text{endo}) = 33.4$ to ~ 8500). At 250°, however, the 1-*endo* isomer is less predominant and the equilibrium constants decrease by a factor of 5–10 (compare Tables I and II). In Table III ΔF° and ΔH° values for the isomerization of endocyclic olefins containing a disubstituted double bond are listed. Where necessary (all compounds of this group except VII and XVI), the presence of an asymmetric center has been taken into account by calculating the equilibrium constants with respect to one of the enantiomers only. The disubstituted isomers differ very little from each other in structure, and, accordingly, the free energies of isomerization and the enthalpies are small. However, whereas in the five-membered ring series the 3-isomer is somewhat more stable than the 4-methyl isomer, the reverse is true for the six-membered ring derivatives. It should also be noted that at 250° the ΔF° values approach zero in all but one case (XI \rightarrow X). Increase of the side chain from one to two carbon atoms increases the stability, at 25°, of the

3-isomer in the five-membered ring series but does not affect materially the relative equilibrium concentration of the corresponding cyclohexenes. Differences in nonbonded interaction which contribute to the relative stabilities are discussed in part II.¹¹

The enthalpy data of Turner⁵ for the isomerization at 25° of ethylidenecyclopentane (XIII \rightarrow XIV) (-1.3 kcal./mole) and of ethylidenecyclohexane (XVIII \rightarrow XIX) (-1.2 kcal./mole) differ little. The relative value of the *exo/endo* ratio for these two pairs of compounds should thus be sensitive to the magnitude of the $T\Delta S$ term.⁷ These conclusions, drawn from data obtained in acetic acid solution, are confirmed by the present results. In fact, as the temperature is increased from 25 to 250°, the *exo* compound in the five-membered ring series becomes somewhat more stable ($K_{\text{XIV/XIII}} = 6.5$) than the corresponding isomer in the six-membered ring series ($K_{\text{XIX/XVIII}} = 7.4$). Thus the introduction of a methyl group at the double bond in IV and VIII not only increases considerably the equilibrium concentrations of the *exo* isomers but also reverses the relative order of the *exo/endo* equilibrium ratio in the two series at 250°.

In the four-membered ring series, 3-methylcyclobutene (III) is unexpectedly very unstable with respect to 1-methylcyclobutene (I) ($K_{\text{I/II}} \sim 8500$; $\Delta F^\circ \sim -5.4$ kcal./mole). An interpretation of the relative stabilities of the 1-methyl and 3-methyl isomers will be given in part II of this series.¹¹

The vinylcycloalkanes XII and XVII could not be detected in the equilibrium mixtures at 25° under the gas chromatographic conditions used (Table I), and were present to an extent of only $\sim 0.1\%$ at 250°. The relative instability of these olefins can be understood by the difference in the number of alkyl groups attached to the double bond, the vinyl compounds being the only isomers which carry not more than one alkyl substituent at the double bond. A similar effect of substitution is found in corresponding alkenes, such as 3-methyl-1-butene and 3-methyl-1-pentene.¹²

According to calculations of Rossini and co-workers,¹² the mole fraction of these vinylic derivatives at equilibrium (298°K.) amount to 0.002 and 0.0004, respec-

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tively, as against 0.867 for 2-methyl-2-butene and 0.273 for the sum of *cis*- and *trans*-3-methyl-2-pentene.

Experimental

Materials. *Experiments at 25°.* Methylene cyclobutane (I) was prepared by the reaction of pentaerythrityl tetrabromide with zinc powder.¹³ Fractional distillation of the product with a Piros-Glover spinning-band column yielded I of 99% purity. The impurity (1%) was spiro-pentane, which is not affected by the isomerization procedure. 1-Methylcyclobutene (II) of 99% purity was obtained by fractional distillation of the equilibrium mixture of I and II.¹⁴ The impurity (1%) consisted of I. 3-Methylcyclobutene (III) of 97% purity was synthesized by thermal decomposition of N,N-dimethyl-3-methylcyclobutylamine oxide.¹⁵

The 1-alkylcycloalkenes (V, IX, XIV, and XIX) were prepared by acid-catalyzed dehydration of the corresponding alcohols. The products contained the following amounts of *exo* isomers: 1-methylcyclopentene (V), 2% of IV; 1-ethylcyclopentene (XIV), 8% of XIII; and 1-ethylcyclohexene (XIX), 11% of XVIII. These mixtures were used as such for isomerization. 1-Methylcyclohexene (IX, 99%) was obtained by fractional distillation of the dehydration product.^{16a} Methylene cyclohexane (VIII, 99%) was prepared by thermal decomposition of hexahydrobenzyl acetate at 500°.^{16a,17}

The mixture of 3- and 4-methylcyclohexene (70% X and 30% XI) was a commercial product (Phillips Petroleum Co.).

Experiments at 250°. All compounds were fractionally distilled before use and were of 98–99% purity, except where otherwise stated. The 1-alkylcycloalkenes were prepared as above and V and IX were purified to 99.5%. Ethylenecyclopentane (XIII,^{18b} 97%) was also obtained from the dehydration product of the corresponding tertiary alcohols. The following compounds were prepared by pyrolysis of acetates: methylenecyclopentane (IV, 91%^{18b}); methylenecyclohexane (VIII), see above; vinylcyclohexane (XVII)^{16c,18a}; ethylenecyclohexane (XVIII, 95%^{16c,18a}); vinylcyclopentane (XII, containing 14% XIII^{18a}); 4-methyl- (VII)^{16b} and 4-ethylcyclopentene (XVI),^{18b} containing each about 60% of the corresponding 3-alkyl isomer (from 3-alkylcyclopentyl acetates); and the 4-methyl- (XI)^{16a} and 4-ethylcyclohexene (XXI).^{18c} 3-Methyl- (VI) and 3-ethylcyclopentene (XV),^{18b} and

3-methyl- (X)^{16a} and 3-ethylcyclohexene (XX)^{18c} were synthesized by condensation of the appropriate alkyl magnesium bromides and 3-bromocyclohexenes.¹⁹

Isomerization Procedure. *Experiments at 25°.* The catalyst preparation,^{8,14} as well as the isomerization procedure,^{1,8} is described elsewhere. The equilibrations were carried out using as starting materials the pure or enriched compounds. No solvent was employed except where specifically mentioned (see Table I, footnotes). A check of the equilibrium of the four-membered ring derivatives by approach from III was carried out at 5° to reduce losses by evaporation of the compound, which was available in small amounts only. The difference of 20° as compared with the standard temperature does not practically affect the equilibrium concentrations.

Constant composition of the equilibrated mixture was reached in 5 hr. or less for the four-membered ring isomer and in 24 hr. for compounds IV–XI. However, in the case of the ethylcyclopentenenes and ethylcyclohexenes the equilibration time was 72 hr.

Experiments at 250°. Alumina, grade Alcoa F-10, mesh size 8–10, was used as catalyst. The equilibration experiments were carried out in a vertically mounted furnace of 60-cm. length, having an isothermal zone of about 40 cm. The reactor consisted of a coiled Pyrex tube, 120-cm. long and 10-mm. wide, packed with the above catalyst. Prior to each experiment the reactor was flushed with dry nitrogen and the temperature was adjusted and stabilized for a period of 2 hr. The nitrogen flow was then reduced to a minimum and the starting material was introduced dropwise (8–10 drops/min.) with the aid of a constant-rate dropping funnel. Starting material (10–20 ml.) was employed in most of the experiments. The product was collected in a receiver cooled with Dry Ice–acetone and, after withdrawal of a small sample for gas chromatographic analysis, it was recycled through the reactor until constant composition was reached. Equilibration required from 15 to 20 runs. A fresh batch of catalyst was used for each series of runs. The total recovery (after flushing the reactor with nitrogen) was 85–90%.

Analytical. Quantitative analysis of the equilibrium mixtures was carried out by gas chromatography, using silver nitrate–ethylene glycol as the stationary phase.¹⁶ For concentrations lower than 3% the peak areas were corrected by applying factors determined with a series of synthetic blends containing 0.1–3.0% of the examined components.

Separation of XX from XXI, though possible by the above procedure, is better carried out with a capillary column of 150 ft. in length and 0.01 in. i.d., coated with squalane and using a flame ionization detector. The data for XVII to XXI in Table I were obtained by the latter technique, operating at room temperature.

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