

described in the previous paper.⁹ The first-order reactions in "30%" aqueous ethanol were followed conductimetrically using the procedure described by Murr.¹³ The Λ_{∞} and S_{α} for the solution of HCl in "30%" ethanol were estimated to be 213 and 96.4, respectively.¹⁹

The β -deuterium isotope effects in the reactions of the bromides, measured titrimetrically, are estimated to be accurate to $\pm 4\%$.⁹ The solvolysis rates of the chlorides were measured conductimetrically and the derived γ -deuterium isotope effect should be accurate to $\pm 0.2\%$.²⁰

(19) T. Erdey-Gruz, E. Kugler and J. Hidvegi, *Acta Chim. Acad. Sci., Hung.*, **19**, 89 (1959).

(20) Comment added at the referee's suggestion. The absence of any appreciable "inverse" isotope effect in the solvolysis of IV is perhaps somewhat surprising in view of the small influences previously observed in several reactions and attributed to inductive interactions

between the isotopic and reaction centers.²¹ In the present example the accuracy of the rate constant determination is limited mainly by the operation of a small mass law effect⁹ which prevents the reaction from following the first-order rate law precisely. The estimated error in the isotope effect ratio is $\pm 0.2\%$. An "inductive" isotope effect of this order of magnitude for a deuterium in the γ -position would not be excessively small in comparison to the $1.5 \pm 1.0\%$ effect attributed to possible inductive interaction between a solvolysis reaction center and a β -situated deuterium.^{21b} It seems small, perhaps, when compared with some "inductive isotope effects" observed in other reactions.^{21a,d} Conclusions drawn from such comparisons are obviously very uncertain in view of the limited amount of information available and the relatively large errors in many of the observed ratios.

(21) (a) E. A. Halevi, *Tetrahedron*, **1**, 174 (1957); (b) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **82**, 2655 (1960); (c) A. J. Kresge and K. N. Rao, *Chemistry & Industry*, 53 (1961); (d) H. S. Klein and A. Streitwieser, Jr., *ibid.*, 180 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Proximity Effects. XXV. Pyrolysis of Cyclooctyl and Cyclodecyl Esters¹

BY ARTHUR C. COPE AND MARY J. YOUNGQUIST²

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The acetates, benzoates, hydrogen phthalates and S-methyl xanthates of cyclooctanol and cyclodecanol have been pyrolyzed, and the pyrolysates have been analyzed with emphasis on the detection of possible transannular products. The acetates and benzoates gave open-chained α,ω -dienes and the expected cyclic olefins; small amounts of bicyclic compounds and ring contraction products were formed along with the cyclic olefins from the hydrogen phthalates. The xanthates gave only the cyclic olefins at the temperatures used.

Previously published work³ has shown that the pyrolysis of cyclooctyl acetate yields some 1,7-octadiene and the pyrolyses of cyclodecyl acetate and cyclodecyl-S-methyl xanthate yield 1,9-decadiene along with the expected cyclic olefins. The formation of these dienes can be explained either by a direct transannular elimination or by a secondary reaction in which the cyclic olefin is further transformed to the open-chained diene. Since gas chromatography has made possible the detection and isolation of small amounts of by-products, the present work was undertaken to determine if other unusual products are formed by the pyrolysis of the acetates, benzoates, hydrogen phthalates and S-methyl xanthates of cyclooctanol and cyclodecanol.

The pyrolyses of the acetates and benzoates were carried out at 500° in a hot tube (described in the Experimental section) and the hydrogen phthalates and S-methyl xanthates were decomposed by heating them in a flask attached to a distillation column or reflux condenser. The pyrolysates were analyzed by gas chromatography and samples were isolated by the same method and identified (with one exception) by their infrared spectra. Results of the pyrolyses are summarized in Tables I and II.

In the case of the cyclooctyl esters, the acetate and benzoate were pyrolyzed at 500° to give the expected mixture of *cis*-cyclooctene, *trans*-cyclooctene and 1,7-octadiene. The yield of *cis*-cyclooctene from these two esters remained fairly

constant over a series of experiments, while the yields of the *trans*-olefin and the diene varied somewhat (see Table I). This is in accord with the work of Blomquist³ who found that the open-chained dienes also arose from pyrolysis of the *trans* isomer of the cyclic olefins and only at temperatures above 450°. Thus, slight variations in temperature or contact time of the olefin in the hot tube affect the amount of cyclic olefin that is transformed to the diene.

Cyclooctyl hydrogen phthalate was pyrolyzed at 275–400° and yielded the complex mixture of products shown in Table I. No 1,7-octadiene was formed because of the low pyrolysis temperature. The bicyclic compounds could have been formed by direct elimination of a hydrogen atom on C₂ or C₈ rather than the usual β -hydrogen atom. Another possibility is the protonation of cyclooctene (formed during the pyrolysis) to yield a carbonium ion which then rearranged to the usual products.⁴

We thought that the 1-methylcycloheptene could have been formed by further pyrolysis of bicyclo[5.1.0]octane. Pyrolysis of bicyclo[5.1.0]octane in a hot tube at 360° left the hydrocarbon unchanged; however, when samples of the hydrocarbon were heated at 300° for three to twenty hours in a sealed tube in the presence of a small amount of *n*-butyl hydrogen phthalate (added to furnish phthalic acid at the pyrolysis temperature), the pyrolysate contained 1–2% of 1-methylcycloheptene. Thus it is likely that 1-methylcycloheptene was formed in this manner during the original ester pyrolysis.

Several similar sealed tube pyrolyses were done in an attempt to explain the formation of the

(1) Supported in part by a research grant (NSF-G5055) of the National Science Foundation. Paper XXIV, A. C. Cope, S. Moon and P. E. Peterson, *J. Am. Chem. Soc.*, **84**, 1935 (1962).

(2) National Science Foundation Predoctoral Fellow, 1957–1960; National Institutes of Health Predoctoral Fellow, 1960–1961.

(3) A. T. Blomquist and P. R. Taussig, *J. Am. Chem. Soc.*, **79**, 3505 (1957).

(4) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt and Co., New York, N. Y., 1959, p. 502.

TABLE I
 PYROLYSIS OF CYCLOOCTYL ESTERS

Ester	Run	Total olefin yield, %	1,7-Octadiene, %	<i>cis</i> -Cyclooctene, %	<i>trans</i> -Cyclooctene, %	<i>cis</i> -Bicyclo[3.3.0]octane, %	1-Methylcycloheptene, %	Bicyclo[5.1.0]octane, %	1-Ethylcyclohexene, %
Acetate	1	85	7.8	90.5	1.7
	2	87	7.6	91.0	1.4
Benzoate	1	82	11.3	88.7	<0.05
	2	82	3.6	92.6	3.5
	3	90	6.1	92.2	1.7
Hydrogen phthalate	1	72	..	92.7	0.1	2.2	4.7	0.3	<0.05
	2	80	..	94.5	.3	2.1	3.1	.05	<.05
	3	85	..	95.8	.3	2.2	1.7	.05	<.05
	4	89	..	93.8	.6	2.4	3.0	.1	.1
S-Methyl xanthate	1	80	..	100.0
	2	95	..	100.0

 TABLE II
 PYROLYSIS OF CYCLODECYL ESTERS

Ester	Run	Total olefin yield, %	1,9-Decadiene, %	<i>cis</i> -Cyclodecene, %	<i>trans</i> -Cyclodecene, %	<i>trans</i> -Decalin, %	<i>cis</i> -Decalin, % ^a	Other, % ^b
Acetate	1	40 ^c	6.1	13.2	80.7
	2	86	32.6	14.0	53.4
Benzoate	1	86	19.2	13.2	67.6
	2	84	5.6	14.6	79.8
Hydrogen phthalate	1	81	..	17.6	82.1	0.2	0.05	0.05
	2	83	..	17.6	82.1	.2	.05	.05
	3	83	..	16.5	83.2	.2	.05	.05
	4	81	..	16.9	82.8	.2	.05	.05
	5	79	..	16.4	83.1	.3	.1	.1
S-Methyl xanthate	1	.. ^d	..	17.8	82.2
	2	63 ^c	..	17.9	82.1

Identified only by retention time on gas chromatography using four different columns. ^b Unidentified. ^c Small scale experiment with some loss during distillation of the product. ^d Yield undetermined.

trace amounts of 1-ethylcyclohexene. No 1-ethylcyclohexene was found in the preceding pyrolyses of bicyclo[5.1.0]octane, nor was any formed when bicyclo[4.2.0]octane was subjected to the same conditions. (Gas chromatography on all available columns failed to separate a small amount of bicyclo[4.2.0]octane from *cis*-bicyclo[3.3.0]octane in a mixture of the two; thus a small amount of bicyclo[4.2.0]octane would not have been detected in the original ester pyrolysate. However, infrared analysis showed no evidence of bicyclo[4.2.0]octane.)

Cyclooctyl-S-methyl xanthate was pyrolyzed at 135–290° and the resulting olefin was distilled from the reaction mixture as it formed. Analysis by gas chromatography showed only one hydrocarbon, *cis*-cyclooctene. No *trans*-cyclooctene was found (less than 0.05% could have been detected).

Cyclodecyl acetate and cyclodecyl benzoate were pyrolyzed at 500° with results analogous to those obtained in the C₈-series. Again, the yields of the *cis*-olefin remained constant over the series of experiments, while the yields of *trans*-olefin and diene varied (more variation was observed in the C₁₀- than in the C₈-series). The *trans*-olefin was the major product in all of the cyclodecyl ester pyrolyses.

The pyrolysis of cyclodecyl hydrogen phthalate at 275–400° gave only very small amounts of transannular products; in this case, *cis*- and *trans*-

decalin. The *trans*-decalin was isolated by gas chromatography and identified by its infrared spectrum, while *cis*-decalin was identified by gas chromatography. The formation of the decalins can be explained by mechanisms similar to those postulated for the formation of bicyclic hydrocarbons from cyclooctyl hydrogen phthalate.

Cyclodecyl-S-methyl xanthate was pyrolyzed at 150–220° and yielded only *cis*- and *trans*-cyclodecene, the latter being the major product.

Experimental⁵

Cyclooctyl Acetate.⁶—Reaction overnight at room temperature of 7.71 g. of cyclooctanol and 14 ml. of acetic anhydride in 20 ml. of pyridine yielded 10.0 g. (98%) of cyclooctyl acetate, b.p. 52–54° (0.6 mm.), *n*_D²⁰ 1.4581 (lit.⁶ b.p. 95–96° at 11 mm., *n*_D²⁰ 1.4593). Other acetates and benzoates described below were prepared by the same method.

Cyclodecyl Acetate.—A mixture of 5.02 g. of cyclodecanol and 7 ml. of acetic anhydride in 20 ml. of pyridine yielded 5.8 g. (92%) of cyclodecyl acetate, b.p. 68–71° (0.4 mm.), *n*_D²⁰ 1.4672 (lit.⁶ b.p. 120–121° at 11 mm., *n*_D²⁰ 1.4682; b.p. 90–95° at 2.5 mm., *n*_D²⁰ 1.46897).

(5) Melting points are corrected and boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer recording spectrophotometer, model 21, using a sodium chloride cell. Methods used for gas chromatography were those described by A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1647 (1959), footnote 24, with the stationary phases specified below. We are indebted to Dr. S. M. Nagy for microanalyses and to Mrs. N. Alvord for spectral determinations.

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

Cyclooctyl Benzoate.—Cyclooctanol (7.71 g.) and 6.4 ml. of benzoyl chloride in 40 ml. of pyridine yielded 1.44 g. of recovered cyclooctanol and 9.75 g. (86%) of cyclooctyl benzoate, b.p. 127–128° (0.5 mm.), n_D^{25} 1.5250.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.35; H, 8.72.

An excess of cyclooctanol was used to prevent the formation of benzoic anhydride, which occurred in a similar preparation using benzoyl chloride in excess.

Cyclodecyl Benzoate.—Cyclodecanol (7.09 g.) and 6 ml. of benzoyl chloride in 30 ml. of pyridine yielded 1.07 g. of recovered cyclodecanol and 6.98 g. (72%) of cyclodecyl benzoate, b.p. 140.0–141.5° (0.38 mm.), n_D^{25} 1.5250.

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.36; H, 9.19.

Cyclooctyl Hydrogen Phthalate.—Cyclooctanol (15.6 g.) and 18.1 g. of phthalic anhydride were heated at 110° overnight and gave 28.2 g. (84%) of cyclooctyl hydrogen phthalate, m.p. 134.0–134.5° (recrystallized from benzene).

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.39; H, 7.31.

Cyclodecyl Hydrogen Phthalate.—Cyclodecanol (19.6 g.) and 18.6 g. of phthalic anhydride were treated as above and gave 31.9 g. (84%) of cyclodecyl hydrogen phthalate, m.p. 122–123° (recrystallized from chloroform and 30–60° petroleum ether).

Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 71.30; H, 7.87.

Pyrolysis of Esters. (a) **Acetates and Benzoates.**—A 50 × 12-cm. Pyrex tube with a side-arm 6 cm. from the top was packed over a length of 18 cm. with glass helices (top of packing ca. 10 cm. from the top of the tube). The top of the tube was closed with a No-Air rubber stopper and the bottom of the tube was connected to a series of two traps cooled in Dry Ice-acetone. The side arm was connected to a bubbler tube which was connected to a nitrogen source. A micro-combustion furnace was used to heat the tube (over the packed area) and the temperature was measured by means of a thermocouple wire taped to the tube inside the furnace. The furnace was heated to 500 ± 10° while the system was flushed with a rapid stream of nitrogen. When temperature equilibrium was reached, the nitrogen flow rate was reduced to ca. 6 ml. per min., the traps were cooled, and the sample was injected through the No-Air stopper with a hypodermic syringe. Samples were added at a rate of 1–2 g. per hr.; the sample size ranged from 1.0–4.5 g. After all the sample was added, the tube was cooled to room temperature and flushed with ether. The combined material from both traps was dissolved in ether; the ether solution was washed with 10% aqueous sodium hydroxide, then with water, and dried. The solvent was removed through a semi-micro column and the olefin was distilled through the same column.

(b) **Hydrogen Phthalates and S-Methyl Xanthates.**—A distilling flask attached to a distillation column or reflux condenser was charged with the ester to be pyrolyzed. The flask was immersed in a Woods metal-bath and the temperature was raised slowly until decomposition began. The hydrogen phthalates began to decompose at ca. 230–250° and the final pot temperature was never over 450°. The S-methyl xanthates decomposed at 135–220°. In the case of the cyclooctyl esters, the olefins were distilled from the reaction mixture at atmospheric pressure, but the cyclodecyl pyrolysates were extracted from the residues with pentane and distilled under reduced pressure.

Identification of Products.—The olefin mixtures were analyzed by gas chromatography using one or more of the following stationary phases at the temperatures indicated: 35% of a saturated solution of silver nitrate in tetraethylene glycol (30–98°), 30% 1,2,3-tri-(β-cyanoethoxy)-propane (40–135°), 20% 4-methyl-4-nitropimelonnitrile (35–70°) and 20% Dow-Corning Silicone oil No. 550 (90–135°). Samples of the products were collected by gas chromatography and infrared spectra were obtained and compared with those of authentic samples. Before collecting *trans*-cyclooctene by gas chromatography it was separated from *cis*-cyclooctene by silver nitrate extraction.⁸

(7) A. T. Blomquist and A. Goldstein, *J. Am. Chem. Soc.*, **77**, 1001 (1955).

Authentic samples used for comparison purposes were prepared as follows:

1,7-Octadiene.—Pyrolysis of 1,8-octanediol diacetate⁹ at 500° in the hot tube gave 24% of a mixture which consisted of 5% of 1,7-octadiene and 95% of 7-octen-1-yl acetate. The remainder of the product was unchanged diacetate. The 7-octen-1-yl acetate was analyzed (for physical properties see below).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.77; H, 10.64.

Pyrolysis of 7-octen-1-yl acetate at 500° gave a mixture of 60% 1,7-octadiene and 40% unchanged acetate. The recovered 1,8-octanediol diacetate (6.7 g.) from the first pyrolysis was pyrolyzed at 565–575° and yielded 0.99 g. (31%) of 1,7-octadiene, b.p. 57.0–57.5° (92 mm.), n_D^{25} 1.4209 (lit.¹⁰ b.p. 116°, n_D^{25} 1.4215), and 1.06 g. (21%) of 7-octen-1-yl acetate, b.p. 102–104° (18 mm.), n_D^{25} 1.4284. Gas chromatography using a 1,2,3-tri-(β-cyanoethoxy)-propane column at 120° showed the 1,7-octadiene to be >99.9% pure and the infrared spectrum was identical to the spectra of samples obtained from the cyclooctyl ester pyrolyses.

1,9-Decadiene was prepared by pyrolysis of 1,10-decanediol diacetate in a hot tube at 600°. The diene, n_D^{25} 1.4305 (lit.¹¹ n_D^{25} 1.4302), was isolated by gas chromatography using a silver nitrate-tetraethylene glycol column at 76°. Its infrared spectrum was identical to the spectra of samples obtained from the cyclodecyl ester pyrolyses.

Bicyclo[5.1.0]octane.—The method of Simmons and Smith¹² with the modification of Shank and Shecter¹³ was used to prepare this compound. Methylene iodide (2.68 g.), 0.08 g. of iodine, 8.20 g. of zinc-copper couple and 19.2 g. of cycloheptene gave a mixture of the desired hydrocarbon and cycloheptene. Distillation of the product through a 46-cm. spinning band column at atmospheric pressure gave 8 fractions (total weight 12.44 g., 61% material balance). The purest of these fractions, b.p. 141°, n_D^{25} 1.4612, contained 99% of bicyclo[5.1.0]octane. The total yield of bicyclo[5.1.0]octane was 37% (calculated from gas chromatograms of the 8 fractions). An analytical sample was isolated by gas chromatography using a 4-methyl-4-nitropimelonnitrile column at 46°.

Anal. Calcd. for C_8H_{14} : C, 87.19; H, 12.81. Found: C, 87.16; H, 12.87.

1-Ethylcyclohexene.—Crude 1-ethylcyclohexanol prepared from 17.0 g. of cyclohexanone and ethylmagnesium bromide was dehydrated by heating with iodine and yielded 8.1 g. (44% yield from cyclohexanone) of 1-ethylcyclohexene, b.p. 136.0–137.5° (lit.¹⁴ b.p. 136.2°). A sample purified by gas chromatography using a silver nitrate-tetraethylene glycol column at 76° had n_D^{25} 1.4553 (lit.¹⁴ n_D^{25} 1.4583) and its infrared spectrum was identical to the spectrum of 1-ethylcyclohexene obtained from the pyrolysis of cyclooctyl hydrogen phthalate.

n-Butyl hydrogen phthalate was prepared as described.¹⁵ The crude product was recrystallized twice from benzene and 30–60° petroleum ether and obtained as white crystals, m.p. 72.5–73.5° (lit.¹⁵ m.p. 73.1–73.5°).

Pyrolysis of Bicyclo[5.1.0]octane. (a) **Hot Tube.**—Bicyclo[5.1.0]octane (0.446 g.) was dropped through the usual pyrolysis tube at 360° over an 8-min. period. Analysis of the pyrolysate by gas chromatography using a 4-methyl-4-nitropimelonnitrile column at 44° showed no change from the starting material.

(b) **Sealed Tube.**—Bicyclo[5.1.0]octane (0.20 g.) and 0.04 g. of *n*-butyl hydrogen phthalate were heated in a sealed tube at 300° for 3 hr. Analysis of the pyrolysate by gas chromatography using a silver nitrate-tetraethylene glycol column at 49° and a 4-methyl-4-nitropimelonnitrile

(8) A. C. Cope, R. A. Pike and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

(9) M. S. Kharasch, F. S. Arimoto and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951).

(10) J. L. Everett and G. A. R. Kon, *J. Chem. Soc.*, 3131 (1950).

(11) C. S. Marvel and W. E. Garrison, Jr., *J. Am. Chem. Soc.*, **81**, 4740 (1959).

(12) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(13) R. S. Shank and H. Shecter, *J. Org. Chem.*, **24**, 1825 (1959).

(14) F. K. Signaigo and P. L. Cramer, *J. Am. Chem. Soc.*, **55**, 3330 (1933).

(15) J. F. Goggans, Jr., and J. E. Copenhaver, *ibid.*, **61**, 2909 (1939).

column at 37° showed it to be a mixture of 1.2% of 1-methylcycloheptene and 98.8% of bicyclo[5.1.0]octane. A second experiment was done under identical conditions except it was run for 20 hr. Analysis showed the pyrolysate to contain 94.9% of bicyclo[5.1.0]octane, 2.3% of 1-methylcycloheptene and 2.8% of an unidentified material (not 1-ethylcyclohexene, cycloheptane or ethylidene-cyclohexane).

Pyrolysis of Bicyclo[4.2.0]octane.—A 50-mg. sample of bicyclo[4.2.0]octane and a small amount of *n*-butyl hydro-

gen phthalate were heated in a sealed tube at 280° for 17 hr. Gas chromatograms of the product using the columns mentioned in the preceding experiment showed no 1-ethylcyclohexene. A blank was run at the same time by heating in another tube a sample of *n*-butyl hydrogen phthalate. The contents of the tube were analyzed by gas chromatography using the same columns, and a few small peaks appeared with retention times similar to the unknown material obtained from the above sealed tube pyrolysis of bicyclo[5.1.0]octane.

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Conformational Analysis in Symmetrically Substituted Cyclohexanones. The Alkyl Ketone Effects¹

BY BRUCE RICKBORN

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The *cis-trans* equilibria and thermodynamic parameters of a series of 2,6-dialkylcyclohexanones have been evaluated and used as a measure of the 2-alkyl ketone effect. Though the effect is negligible for a methyl group, a smaller difference in conformational preference is found for ethyl, isopropyl and *t*-butyl substituents than that expected in the corresponding hydrocarbons. The magnitude of the 3-alkyl ketone effect for a methyl group was obtained from the menthone-isomenthone equilibrium. The conversion of a methylene group to carbonyl does not lower appreciably the energy of a 3-axial methyl substituent.

The conformational effects associated with an alkyl group substituted α or β in a cyclohexanone have been discussed by Klyne,² and by Robins and Walker.³ Klyne, using earlier data of Johnston and Read,⁴ calculated a value of 1.0 kcal./mole for the energy of interaction of an equatorial methyl group with an adjacent carbonyl group. Robins and Walker, following a suggestion made by Dreiding,⁵ estimated that loss of one of the 1,3-methyl-hydrogen interactions would cause the energy of a 3-axial methyl group in a cyclohexanone to be half that found in the corresponding hydrocarbon.

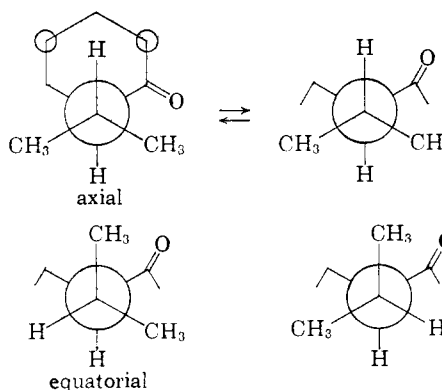
Allinger and Blatter⁶ have recently obtained a direct measurement of the 2-alkyl ketone effect by examining the equilibria in a series of 2-alkyl-4-*t*-butylcyclohexanones. This work indicated that the effect was small, if present at all, for a methyl group,⁷ but became appreciable for larger substituents.

In the present study the *cis-trans* isomerization of symmetrically substituted cyclohexanones has been used to obtain the magnitude of the 2-alkyl ketone effect. The equilibria and thermodynamic parameters for a series of 2,6-dialkylcyclohexanones have been evaluated. The results are shown in Table I.

The *cis* isomer in each case is essentially "frozen," as the alternate chair form has a 1,3-diaxial alkyl-alkyl interaction; even in the dimethyl compound, this conformation should make a negligible contribution.⁸ The two chair conformations of the *trans* isomer are equivalent because of molecular symmetry.

Since the equilibrium in question involves the isomerization of a racemic mixture to a *meso* compound, the magnitude of the 2-alkyl ketone effect is obtained by correcting the observed free energy for the extraneous entropy of mixing of the DL-pair (-1.4 e.u.). This value should also be reflected in the experimentally determined entropy. The data in Table I indicate that this is the case for the methyl and ethyl substituted compounds; the experimental entropy terms for the isopropyl and *t*-butyl ketones, however, deviate considerably from that expected for a chair-chair interconversion.⁹

The slight positive ΔS associated with the *trans-cis* isomerization of 2,6-diisopropylcyclohexanone is presumably caused by the entropy of internal rotation of the isopropyl groups. Consideration of the staggered rotamers of equatorial and axial 2-isopropylcyclohexanone suggests that such a conversion would involve a positive entropy change



(1) Presented at the 141st Meeting of the American Chemical Society, Washington, D. C., March 26, 1962.

(2) W. Klyne, *Experientia*, **12**, 119 (1956).

(3) P. A. Robins and J. Walker, *Chemistry & Industry*, 772 (1955).

(4) R. G. Johnston and J. Read, *J. Chem. Soc.*, 1138 (1935).

(5) A. S. Dreiding, *Chemistry & Industry*, 1419 (1954).

(6) N. L. Allinger and H. M. Blatter, *J. Am. Chem. Soc.*, **83**, 944 (1961).

(7) A similar conclusion was drawn from the position of equilibrium for cholestan-6-one: N. L. Allinger, M. A. DaRooge, and R. B. Herman, *J. Org. Chem.*, **26**, 8626 (1961).

(8) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **83**, 2145 (1961).

(9) N. L. Allinger and L. A. Freiberg, *J. Am. Chem. Soc.*, **82**, 2393 (1960).

(10) The author is indebted to Professor N. L. Allinger for disclosure of this *A*-value for the isopropyl group prior to publication.