upon standing. A recrystallized sample melted at 122–124.5°; reported for β(1-hydroxycyclohexane)propiolic acid: 125°,[6] 123–126°.[2]

Condensation of ethyl propiolate with cyclohexanone and with diethyl ketone. The following procedure was used to condense both cyclohexanone and diethyl ketone with ethyl propiolate. A solution containing 5.0 g. (0.05 mole) of ethyl propiolate and 5.0 g. (0.05 mole) of cyclohexanone was added to a suspension of 4 g. of powdered potassium hydroxide in 50 ml. of ether. The mixture was shaken frequently over a period of 1 hr. and was then poured into cold water. Neutral material was removed by ether extraction; the solution was acidified and extracted with three small portions of ether. After removing the ether from the extract, the residue was kept under a current of air until it crystallized. A 2.77-g. sample of β(1-hydroxycyclohexane)propiolic acid (m.p. 123–126° after recrystallization from benzene-alcohol) was obtained.

The same procedure was used to condense ethyl propiolate (40 g.) with diethyl ketone (35 g.). 4-Hydroxy-4-ethyl-2-hexynoic acid (III) was obtained in 22% yield, m.p. (after repeated recrystallizations from carbon tetrachloride) 79.5–80°.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.60; H, 7.57. The same product was obtained in a 19% yield when sodium hydride was substituted for the potassium hydroxide.

Amide of 4-hydroxy-4-ethyl-2-hexynoic acid. A sample of 4-hydroxy-4-ethyl-2-hexynoic acid was esterified by refluxing with absolute alcohol containing a little concd. sulfuric acid. The ester distilled at 136–139°, 14.5 mm. Upon standing for several days with a saturated ammonia solution, the ester was converted into the crystalline amide; m.p. 107.8–108.3° after recrystallization from chloroform.

Anal. Calcd. for $C_8H_{13}O_2N$: C, 61.93; H, 8.44. Found: C, 61.79; H, 8.64.

Amide of 4-hydroxy-4-ethylhexanoic acid. 4-Hydroxy-4-ethylhexynoic acid (1.35 g.) in 40 ml. of ethanol was shaken with 0.05 g. of platinum oxide under hydrogen (35 p.s.i.) until absorption of hydrogen ceased. After removal of the alcohol from the filtered solution, the lactone of 4-hydroxy-4-ethylhexanoic acid was purified by distillation, b.p., 105–110°, 12 mm. This lactone was allowed to stand with frequent shaking with a saturated solution of ammonia in water. The amide of 4-hydroxy-4-ethylhexanoic acid gradually crystallized from the solution, m.p., 120–121°, after recrystallization from chloroform.

Anal. Calcd. for $C_8H_{17}O_2N$: C, 60.36; H, 10.76. Found: C, 60.57; H, 10.71.

There was no depression in melting point when this amide was mixed with an authentic sample of the amide (prepared from the lactone of 4-hydroxy-4-ethylhexanoic acid which in turn was prepared by the method of Hepworth.[5]

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Ketal *versus* Hemiketal Formation for Cyclohexanone and Methanol

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We have found, in agreement with Lorette, Howard, and Brown,[3] that ketal formation occurs to a significant extent for cyclohexanone and methanol. Lorette *et al.* have shown also that, in general, ketal formation from ketones and alcohols occurs to a significant extent under the proper conditions. Our investigation was started because of the obvious discrepancy between the work of McCoy *et al.*,[4] who also observed ketal formation for these reactants, and of Wheeler,[5] who concluded that hemiketal formation is the predominant reaction even at mole ratios as high as 100:1 of methanol to cyclohexanone.

The approximate equilibrium constant has been determined for ketal formation from cyclohexanone and methanol at three mole ratio levels. The values of K_x were calculated from mole fractions, with the concentrations of all of the constituents having been determined by chemical analysis. The results are shown in Section I of Table I. It is thus seen that K_x is reasonably constant over a rather large mole ratio range.

The yields of ketal, based on chemical analysis are 28, 59, and 71% for the 2:1, 8:1, and 15:1 mole ratio mixtures, respectively. These yields are considerably less than those previously reported by McCoy *et al.*[4] but are in line with the yield (46%) obtained by Lorette *et al.*[3] for a 4:1 mole ratio.

The reaction mixtures, which had been analyzed chemically were then diluted in 1,4-dioxane and the concentrations of cyclohexanone were determined by means of the ultraviolet spectrum (carbonyl absorption). In a similar manner, the analyzed mixtures were diluted in *t*-butyl alcohol and these solutions were analyzed for cyclohexanone by means of the ultraviolet and the infrared spectra. The concentrations of the other constituents of the equilibrium were calculated on the basis of the concentrations of cyclohexanone and the stoichiometry for ketal formation. The values of K_x (mole fraction) are shown in Table I-B (ultraviolet dioxane), Table I-C (ultraviolet *t*-butyl alcohol) and Table I-D (infrared - *t* - butyl alcohol). The values of K_m (molarities) are also shown and are seen to vary by a factor of 10 to 20 as the mole ratio was changed from 15:1 to 2:1.

On the basis of these results we conclude that ketal formation is the predominant reaction whether the reaction is conducted neat or in an inert solvent and K_x is approximately 0.15 at 27° ±5. The results by spectral analysis appear to be somewhat less reliable than the results by chemical analysis

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TABLE I

EQUILIBRIUM CONSTANT, K_x, FOR KETAL FORMATION FROM METHANOL AND CYCLOHEXANONE

A. K_x for Neat Reaction Mixtures, Chemical Analysis

Initial	Reactants^a		Equilibrium Concentrations										
			Ketone		Alcohol		Ketal		Water		Total	Total	
Mole Ratio	Ketone	Alcohol	Wt. %	Moles/100 g.	Wt. %	Moles/100 g.	Wt. %	Moles/100 g.	Wt.%	Moles/100 g.	%	Moles/100 g.	K_x
2:1	98.0	64.0	43.2	0.440	28.4	0.886	24.7	0.171	3.31	0.184	99.6	1.68	0.153
8:1	98.0	256	11.1	0.113	61.8	1.93	24.0	0.166	3.06	0.170	100.0	2.38	0.160
15:1	98.0	480	4.77	0.0486	75.3	2.35	17.9	0.124	2.23	0.124	100.2	2.65	0.152

B. K_x by Ultraviolet Analysis in Dioxane^b

Initial Mole Ratio	G. Mixture in 100 Ml. Solution	Initial Molarity of Cyclohexanone	Initial Molarity of Methanol	Equilibrium Concentrations, M							
				Absorbance	Cyclo-hexanone	Methanol	Ketal	Water	Total Moles/l.	$K_m{}^c$	K_x
2:1	1.4678	0.0905	0.1810	1.010	0.0641	0.128	0.0264	0.0264	0.245	0.66	0.16
8:1	6.1797	0.1745	1.396	1.145	0.0726	1.192	0.102	0.102	1.469	0.10	0.15
15:1	14.300	0.2475	3.712	1.175	0.0745	3.366	0.173	0.173	3.786	0.036	0.13
C. K_x by Ultraviolet Analysis in t-Butyl Alcohol^d											
2:1	1.5894	0.0981	0.1962	1.07	0.068	0.134	0.0309	0.0309	0.264	0.78	0.21
8:1	6.1782	0.1744	1.395	1.10	0.070	1.19	0.103	0.103	1.46	0.11	0.16
15:1	14.275	0.2469	3.705	1.07	0.068	3.02	0.179	0.179	3.45	0.052	0.18
D. K_x by Infrared Analysis in t-Butyl Alcohol^e											
2:1	1.5894	0.0981	0.1962	0.231	0.071	0.142	0.0271	0.0271	0.267	0.51	0.14
8:1	6.1782	0.1744	1.395	0.235	0.072	1.19	0.102	0.102	1.47	0.10	0.15
15:1	14.275	0.2469	3.705	0.222	0.069	3.35	0.178	0.178	3.77	0.041	0.15

[a] One drop of concd. hydrochloric acid was added as a catalyst and the mixtures were maintained under an atmosphere of nitrogen. [b] $\epsilon = 15.77$ at $\lambda_{max} = 287$ mμ with a 1.0 cm. cell. The solutions were balanced against dioxane as a blank. [c] This value is based on molar concentrations. [d] $\epsilon = 15.74$ at $\lambda_{max} = 284$ mμ with a 1.0 cm. cell. The solutions were balanced against t-butyl alcohol as a blank. [e] $\lambda_{max} = 5.83$ μ with a 0.079 mm. sodium chloride cell. The solutions were balanced against t-butyl alcohol as a blank.

but clearly are of the same order of magnitude. The value of K_x is 0.19 calculated from the 46% yield for a 4:1 mole ratio under the conditions used by Lorette *et al.*[3]

We have concluded also that hemiketal existence is negligible for this system. This is based upon the fact that we obtained essentially the same values of K_x for the reaction by chemical analysis and by spectral analysis. The chemical analysis for ketone cannot distinguish between ketone and hemiketal (that is aldehydes and ketones are quantitatively determined by oximation in neutral or basic alcoholic solutions). However, the determination of carbonyl absorption in either the ultraviolet or infrared regions of the spectra should not include hemiketal or hydrated carbonyl.[6] Therefore, the combination of chemical analysis of neat reaction mixtures and spectral analysis for carbonyl in inert solvents should be an excellent method to determine the extent of hemiacetal formation in the presence of acetal for those systems where both equilibria occur to significant extents. We are investigating currently the effects of structure of the carbonyl reactant on the mechanism of this reaction which leads to hemiacetal and acetal in some cases and to acetal only in other cases.

We can only conjecture the reasons as to why Wheeler failed to detect ketal formation. First and foremost it would appear that in some manner his dioxane solutions became contaminated with an appreciable amount of water after having been dried and before the measurements were made. If we assume for the purposes of calculation that the K_x value we obtained is correct, then Wheeler's solutions must have contained approximately 0.5% water (0.25M). With this assumption K_x was calculated for the concentration range he used.[7] The average value of K_x was found to be about 0.14 and was fairly constant over the range.

Calculation of the equilibrium constants for acetal formation should be made on the basis of mole fractions and not molarities. Little is known of the activity coefficients of the equilibrium constituents[6] and the reaction is of the general type,

$$A + 2B \rightleftharpoons C + D$$

for which there is a net decrease in the total number of molecules. Therefore,

$$K_x = \frac{n_C \times n_D}{n_A \times n_B^2} \times N \qquad (1)$$

where n_A = moles A, etc., N = total moles, and $K_m = K$ for molar concentrations and is volume (V) dependent.[8] It follows that

$$K_x = K_m \frac{N}{V} \qquad (2)$$

Since K_x appears to remain constant for this system and N is a variable while V is essentially a constant for the reaction conducted in a solvent, then K_m must vary inversely with N.[9] However, we must point out that we did not include the moles of solvent in our K_x calculations. In an approximate calculation of K_x including the moles of solvent for the data of Table I-B, K_x varied from about 6 to 1 to 0.4 as the mole ratio was varied from 2:1 to 8:1 to 15:1. However, the solutions were becoming much more concentrated in this same order and K_x is seen to be approaching the value for the neat reactions. Because of this and because we wanted to compare K_x for the neat reaction mixtures with those for the solvent mixtures we have not included the moles of solvent in our calculations.

To verify further that ketal formation occurred under the conditions similar to those used by Wheeler, a solution of dioxane was prepared which was 3.4M in methanol, 0.14M in cyclohexanone, and 0.1M in hydrochloric acid. After allowing several hours at room temperature for the mixture to equilibrate the acid was neutralized and the mixture was distilled. A fraction was obtained which contained 71.5% 1,1-dimethoxycyclohexane and 24.1% cyclohexanone and represented a 62% yield of the ketal.

Wheeler has applied the ultraviolet method to the determination of the ring size of ketones based on the extents of hemiketal formation.[10] This method would appear to be quite valid except that it is based upon ketal formation and not hemiketal formation.

EXPERIMENTAL[11]

Purification of reagents and solvents. Commercial cyclohexanone was purified by fractional distillation at 50 mm. A series of mid-fractions was collected for which the boiling point was 73° and had n_D^{20} 1.4498 over the range. This material was 98.3% pure by chemical analysis (oximation) and no impurities could be detected by mass spectrometry.

The methanol was AAA grade and was 99.4% pure by chemical analysis (phthalation) and contained a maximum of 0.03% water (Karl Fischer reagent).

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(6) N. C. Melchior, *J. Am. Chem. Soc.*, **71**, 3651 (1949).

(7) K_x values were calculated for ketal formation based on the data for the eight runs shown in Table I of Wheeler's article[5] and assuming the dioxane was 0.25M in water. The values, from top to bottom, were 0.156, 0.160, 0.161, 0.116, 0.125, 0.136, 0.135, 0.131.

(8) S. Glasstone, *Textbook of Physical Chemistry*, 2nd ed., D. Van Nostrand Co., Inc., New York, 1956, p. 822.

(9) We are indebted to Dr. O. D. Bonner of the University of South Carolina for pointing out this relationship to us.

(10) O. H. Wheeler and J. L. Mateos, *Anal. Chem.*, **29**, 538 (1957).

(11) We wish to thank Mr. R. G. Lowther for help in conducting many of these experiments.

A sample of 1,1-dimethoxycyclohexane was prepared as described by McCoy *et al.*;[4] n_D^{20} 1.4395; purity, 99.8% (oximation).

The dioxane was purified by treatment with sodium borohydride to remove peroxides, followed by distillation which provided a material which contained negligible absorption over the range of 250 to 350 mμ. The distillate was then redistilled from lithium aluminum hydride to remove last traces of water. This solvent was not satisfactory for use in the infrared work because it showed some absorption in the carbonyl region (5.8 μ) which was not removed by either the sodium borohydride or lithium aluminum hydride treatment.

t-Butyl alcohol was purified by distillation and was found to be free of carbonyl absorption in both the infrared and ultraviolet region of the spectrum. This material contained less than 0.01% water (Karl Fischer).

Chemical analyses. The determinations of the equilibrium concentrations for the neat mixtures were made by the following methods from Siggia:[12] total carbonyl, as cyclohexanone and 1,1-dimethoxycyclohexane, by the hydroxylamine method (1 hr. reaction time in a steam bath); cyclohexanone by the hydroxylamine-pyridine method (1 hr. reaction time at 27° ±5°); methanol by the phthalic anhydride–pyridine method (5 min. reaction time in a steam bath) and water by the Karl Fischer reagent.

To check the validity of these methods, a synthetic mixture of all components including the catalyst was made having near the equilibrium concentrations for a 2:1 mole ratio mixture (set up for $K_x = 0.172$). The value of K_x based on the analyses of the mixture was 0.157 which compares very well with the values shown in Table I-A. A further check of the methods is furnished by the results shown in Table I-A. In all three cases the total analysis is essentially 100% and the moles of ketal per 100 g. of mixture is essentially equal to the moles of water per 100 g. of mixture.

The values of K_x are considered to be only approximate inasmuch as the samples were not maintained at a constant temperature. In all cases, however, room temperature was 27° ±5°.

Spectral analyses. The ultraviolet measurements were made using a Carey Model 11 spectrophotometer. The solutions were run with either dioxane or *t*-butyl alcohol, as appropriate, in the comparison cell. Solutions of cyclohexanone in dioxane ($\lambda_{\max} = 287$ mμ; $\epsilon = 15.77$) and *t*-butyl alcohol ($\lambda_{\max} = 284$ mμ, $\epsilon = 15.74$) followed Beer's law over the concentrations checked in the ultraviolet.

The infrared measurements were made using a Perkin-Elmer Model 21 spectrophotometer. The samples were run in a 0.079 mm. sodium chloride cell and *t*-butyl alcohol was used as a blank. Because these solutions did not follow Beer's law, a curve was constructed for $\log \frac{I_0}{I}$ *versus* the concentration of cyclohexanone in *t*-butyl alcohol. The values used (for $\lambda_{\max} = 5.83$ μ) were: $\log \frac{I_0}{I} = 0.071, 0.136, 0.230, 0.332$ for corresponding values of molarity of 0.0205, 0.0407, 0.0710, 0.104.

The solutions which were analyzed spectrally were made from the neat reaction mixtures of Table I-A with the appropriate solvent. The concentrations used are shown in Tables I-B, I-C, and I-D. The solutions were analyzed for cyclohexanone content and rechecked after about an hour—no variations were noted.

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Cyanocarbon Chemistry. XVI.[1] 1,1,2,2-Tetracyanocyclopropane

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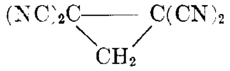
In the course of studies in the field of cyanocarbon chemistry, we have developed four independent syntheses of 1,1,2,2-tetracyanocyclopropane (I). Whereas 3-alkyl- and 3,3-dialkyl-1,1,2,2-tetracyanocyclopropanes have been prepared by earlier workers,[2,3] synthesis of the simplest member of the series has not been reported previously.

1,1,3,3-Tetracyanopropane[4] was brominated by *N*-bromosuccinimide in acetonitrile to give an 89–93% yield of an unstable dibromo derivative, probably 1,3-dibromo-1,1,3,3-tetracyanopropane (II). Addition of a solution of this compound in acetone to aqueous potassium iodide gave a 78% yield of the cyclopropane I. A smaller yield (28%) of I was obtained by reaction of an ethyl acetate solution of the dibromo compound with aqueous potassium cyanide. Proof of the structure of I is based on elemental analysis, molecular weight measurements, and infrared and proton-magnetic resonance spectral analyses.



I

$BrC(CN)_2CH_2C(CN)_2Br$

II

Addition of ethereal diazomethane to a solution of tetracyanoethylene[5] in tetrahydrofuran was accompanied by a vigorous evolution of nitrogen and precipitation of I, isolated in 38% yield after recrystallization. It is of interest that treatment of ethyl diazoacetate with tetracyanoethylene gave neither a cyclopropane nor a pyrazoline. Instead there was obtained an unstable compound, $C_{10}H_6N_6O_2$, that spectral evidence indicated may have been a 4-ethoxycarbonyl-5-tricyanovinyl-1,2,3-tri-

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(1) Paper XV, C. L. Dickenson, *J. Am. Chem. Soc.*, in press.

(2) S. Wideqvist (*Arkiv Kemi, Mineral. Geol.*, **B20**, No. **4**, 8 pp. (1945); *Chem. Abstr.*, **41**, 1621 (1947) reports the preparation of 3-alkyl- and 3,3-dialkyl-1,1,2,2-tetracyanocyclopropanes by the reaction of bromomalononitrile and potassium iodide with aldehydes or ketones. The method was unsuccessful when applied to the synthesis of I from formaldehyde. Cf. also S. Wideqvist, *Arkiv Kemi, Mineral. Geol.*, **14B**, No. **37**, 13 pp. (1941); *Chem. Abstr.*, **36**, 79 (1942).

(3) R. P. Mariella and A. J. Roth, III [*J. Org. Chem.*, **22**, 1130 (1957)] report the syntheses of 3-allyl-1,1,2,2-tetracyanocyclopropanes by the action of bromine on alkylidene bis(malononitriles).

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