dark tube. After a period of time the tube was opened with recovery of trace amounts of $C_6N_2$.

*Diamide of acetylenedicarboxylic acid.* Dimethyl acetylenedicarboxylate (Madison Laboratories) (100 g., 0.705 mole) was added dropwise with stirring to 400 ml. ammonium hydroxide at $-10°$. After 2 hr. the precipitated diamide was filtered, washed with several portions of absolute ethanol and dried under vacuum for 2 days. There was obtained a light tan product (70 g., 89%), m.p. 190–192° (lit.[5] m.p. 290–292°). A nitrogen analysis indicated 0.5 molecule of water.

*Anal.* Calcd. for $C_4H_4N_2O_2 \cdot {}^1/_2H_2O$: N, 23.13. Found: N, 23.35.

*Dicyanoacetylene.* An intimate mixture of diamide (6 g.), fine sea sand (Calcined) (100 g.) and $P_2O_5$ (50 g.) was divided into four test tubes and connected to a glass apparatus. The system contained a Dry Ice–acetone-cooled receiver and was evacuated, refilled with dry nitrogen and then reevacuated. This procedure was carried out several times. The evacuated system of test tubes was then placed in a preheated bath at 215° whereupon distillation of $C_4N_2$ took place. After *ca.* 45 min. the cooled receiver contained 1.4 g. of fairly pure product which gave upon atmospheric distillation in a glass helices-packed column under prepurified nitrogen, pure dicyanoacetylene, m.p. 20.5–21°.[5] A discussion of the critical features of this dehydration and the system employed is found in ref. (5).

*Acknowledgment.* The author wishes to express his gratitude and deep appreciation to Dr. Aristid V. Grosse and E. A. Nodiff for their invaluable suggestions during the course of this work.

PHILADELPHIA 44, PA.

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[CONTRIBUTION FROM THE PHYSICAL RESEARCH LABORATORY AND THE SPECTROSCOPY LABORATORY, THE DOW CHEMICAL COMPANY]

# Preparation of Cyclohexanone Dimethyl Acetal[1,2]

ROBERT E. McCOY, ALVIN W. BAKER,[3] AND ROLAND S. GOHLKE

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Cyclohexanone dimethyl acetal was identified by infrared absorption and mass spectrometry among the products of reaction of salts of *aci*-nitrocyclohexane with methanol and acid, with methyl sulfate, and with ethyl sulfate when methanol was used as solvent. Direct preparation from cyclohexanone and methanol, even without addition of a catalyst, was found feasible. The ease of obtaining this compound in contrast to ketals in general is believed explainable from steric considerations. Attempts to prepare cyclohexanone diethyl acetal directly indicate an unfavorable equilibrium, but the mass spectrometer showed an appreciable conversion.

During an investigation of conversion of nitroparaffins to oximes,[4] an unexpected by-product was discovered in several reactions of *aci*-nitrocyclohexane salts.

Acidification of methanolic solutions or suspensions of *aci*-nitrocyclohexane salts produced cyclohexanone oxime in yields of 35% or less. Infrared and mass spectra of the crude reaction mixtures showed the presence of nitrocyclohexane, cyclohexanone, and a component not immediately identified, in addition to the oxime. Reaction of methyl sulfate with salts of *aci*-nitrocyclohexane gave the same products, although the yield of oxime was higher. Substitution of ethyl sulfate for methyl sulfate gave similar results if methanol was used as solvent, but in other solvents no fourth product was found. Likewise only nitrocyclohexane, cyclohexanone, and cyclohexanone oxime were observed on acidifying salts of *aci*-nitrocyclohexane in ethanol.

When a mixture of cyclohexanone and the unknown was diluted with a large volume of water, ultraviolet and mass spectra revealed no large molecule other than cyclohexanone.

The infrared spectrum (discussed below), the mass spectrum (Table 1), and the facts presented above show clearly that the unexpected product is cyclohexanone dimethyl acetal. Preparation of this compound has been reported previously only by reaction of methyl orthosilicate[5] or methyl sulfite[6] with cyclohexanone. Direct preparation of cyclic ketals from 1,2- and 1,3-glycols is known,[7,8] but it is commonly stated that simple ketals can be prepared only by indirect methods.[9] This opinion is probably correct for most ketals, but the frequent occurrence of cyclohexanone dimethyl acetal in the above reactions suggests that its direct preparation is feasible. This was confirmed by mixing cyclohexanone and methanol, as described in the experimental section.

The successful direct preparation of cyclohexanone dimethyl acetal, contrasted to the usual ex-

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(1) Presented in part at the 129th meeting of the AMERICAN CHEMICAL SOCIETY, Dallas, Tex., April 1956.

(2) For specific compounds we have followed Chemical Abstracts' nomenclature, but generically we have used the more popular term "ketal" as a matter of convenience.

(3) Present address: The Dow Chemical Company, Pittsburg, Calif.

(4) R. E. McCoy and R. S. Gohlke, *J. Org. Chem.*, **22**, 286 (1957).

(5) B. Helferich and J. Hausen, *Ber.*, **57B**, 795 (1924).

(6) W. Voss, *Ann.*, **485**, 283 (1931).

(7) J. Boeseken and F. Tellegen, *Rec. trav. chim.*, **57**, 133 (1938).

(8) E. J. Salmi, *Ber.*, **71**, 1803 (1938).

(9) For example: (*a*) H. W. Post, *The Chemistry of the Aliphatic Orthoesters*, ACS Monograph 92, Reinhold Publishing Corp., New York, 1943, Chapter 3. (*b*) C. A. Mackenzie and J. H. Stocker, *J. Org. Chem.*, **20**, 1695 (1955).

TABLE I

RELATIVE MASS SPECTRUM (PRINCIPAL PEAKS) OF CYCLOHEXANONE DIMETHYL ACETAL

| $\frac{M}{e}$ | Peak Height[a] | Explanation or Comment |
|---|---|---|
| 144 | 11.2 | Molecular ion |
| 113 | 50.4 + 0.4[b] | Loss of $CH_3O$ |
| 101 | 100.00[c] | Loss of $(CH_2)_3$ and H from ring |
| 88 | 8.2 | Loss of CH from 101 |
| 81 | 23.7 | Loss of 2 $CH_3O$ + H? |
| 69 | 23.5 | Loss of C from 81? |
| 55 | 32.0 | Fragment of ring |
| 53 | 6.0 | |
| 45 | 11.9 | |
| 43 | 18.9 | |
| 42 | 13.5 | |
| 41 | 5.8 | |
| 39 | 7.3 | |
| 27 | 5.8 | |

[a] Relative to mass 101. [b] Average of three runs. [c] Actual peak height is 1/5.52 that of the parent peak of an equal weight of toluene, 1/1.85 that of the 98 peak of the same weight of cyclohexanone, or on an equimolar basis 1/1.26 that of the 98 peak of cyclohexanone. (Conversions are most readily calculated using the molar factor.)

perience with ketals, probably results from the fact that the *exo* double bond in cyclohexanone is unstable relative to tetrahedral bonding[10] for each of the six carbons. This is sufficient to place the equilibrium on the side of the ketal. Moreover, the carbonyl group of the cyclic ketone is considerably less hindered than that in most ketones, and this may contribute to the ease of reaction.

Relative to cyclohexanone, the *exo* double bond in cyclopentanone is comparatively stable. Therefore, despite the smaller steric hindrance of the carbonyl group in the latter compound[11] one would expect that the ketal of cyclopentanone would be more difficult to prepare than that of cyclohexanone. Experiments verify this prediction. Under conditions where cyclohexanone will react almost completely (excess methanol, a trace of HCl, room temp.) no reaction is observed with cyclopentanone.

Ketals of cyclohexanone with alcohols other than methanol can also be prepared directly, but the equilibria are distinctly less favorable. For example, equal volumes of cyclohexanone and ethanol with a trace of HCl catalyst gave a conversion to the ketal of only approximately 10%, (with methanol 78%). This reduction in reaction equilibrium is probably caused by an external steric hindrance which is greater in the ethyl than the methyl compound.

*Identification of compound from spectra.* Cyclohexanone dimethyl acetal was first detected (but not identified) by means of the $\frac{m}{e}$ 101 peak in the mass spectra of the reaction mixtures. After determining that both this compound and cyclohexanone oxime[4] contribute to the $\frac{m}{e}$ 113 peak, the main features of the spectrum (Table 1) were obtained. The presence of the parent peak and the 113 peak, representing the loss of one methoxyl group, provide strong evidence that the compound is correctly identified. The 101 peak is less easily explained but is probably due to a fragment which retains both methoxyl groups while a portion of the ring has been lost. A similar fragment $\left(\frac{m}{e}\ 129\right)$ is observed in the mass spectrum of cyclohexanone diethyl acetal, and unpublished data show that the same type of fragment is obtained from the bicyclic ketals formed from cyclohexanone and glycols.

In the infrared spectrum, two strong, typical ether bonds occur at 9.06 μ and 9.48 μ. These bands have approximately equal absorption coefficients and may correspond respectively to the antisymmetric and symmetric carbon-oxygen stretching frequencies. A third band occurring at 11.81 μ appears to be characteristic of acetals in general and is confirmation that the structure is correctly assigned.

The methoxyl groups are detected by an increased absorption at 3.5 μ (C—H stretching) and by a band at 7.4 μ ($CH_3$—O methyl deformation). Neither carbonyl nor C═C groups are present. Cyclohexyl structure is preserved as indicated by a typical, weak band at 3.7 μ. The remaining bands do not provide *a priori* evidence of structure and are not discussed.

## EXPERIMENTAL

Distilled cyclohexanone and methanol were used in the direct preparation of the acetal. The catalyst, when used, was generally methanolic HCl.

The reaction of cyclohexanone and methanol is comparatively rapid in the absence of an inhibitor, particularly at 100°. Thus, the mass spectra, obtained from a mass spectrometer having a heated inlet system at 100°,[12] of catalyzed and uncatalyzed mixtures are essentially the same regardless of the time between mixing and introduction to the heated inlet. At room temperature infrared spectra of samples show that equilibrium is approached within a very few hours without a catalyst. The reaction is accelerated by a trace of soluble acid or by insoluble acids such as the hydrogen form of an ion exchange resin. Reaction under catalyzed conditions occurs with liberation of appreciable amounts of heat. By adding a small amount of base or cyclohexanone oxime after a selected reaction time, the mass spectrometer could be used to determine the conversions at room temperature. With such inhibitors, no measurable reaction occurs at 100° for several hours or at room temperature for several days. At 25° a stoichiometric mixture (2:1 mol. ratio) of methanol and cyclohexanone gives a conversion to the ketal of more than 50%. The conversion can be increased easily by using an excess of methanol or a drying agent. Concentrated sulfuric acid, however, gives considerable bimolecular dehydration to a product identified as 2-(1-cyclohexenyl)-cyclohexanone.[13] At 100° equilibrium is somewhat less

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[10] H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

[11] A .W. Baker, *J. Phys. Chem.*, **60**, 1660 (1956).

[12] V. J. Caldecourt, ASTM Committee E-14 Conference on Mass Spectrometry, New Orleans, May 1954.

[13] *Cf.* J. Reese, *Ber.*, **75A**, 384 (1942).

favorable to the ketal. Equal volumes of cyclohexanone and methanol give only a 28% conversion. From equal volumes at 25°, about 78% conversion was obtained. The conversion could be increased to 92% from a mixture of 23.1% by weight cyclohexanone, or to more than 95% from a mixture of 12.1% cyclohexanone.

By distillation, a sample of the ketal was obtained which had only a trace of ketone. It had a boiling point of 73.0° at 50 mm. and a refractive index $n_D^{25}$, of 1.4372. This compares reasonably well with the value $n_D^{17.5}$ of 1.4416 for a sample prepared from methyl orthosilicate.[5]

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MIDLAND, MICH.

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[CONTRIBUTION FROM THE APPLIED SCIENCE DEPARTMENT, UNIVERSITY OF CINCINNATI]

# Selenium-catalyzed Isomerization of *cis*-Stilbene

J. D. FITZPATRICK[1] AND MILTON ORCHIN

*Received March 4, 1957*

The isomerization of *cis* to *trans*-stilbene can be achieved by elemental selenium at 200–210°. The reaction is homogeneous and depends upon the formation and decomposition of a *pi* complex between selenium and the stilbene. The reaction is pseudo first order wih respect to *cis*-stilbene. The catalyst dependence appears to involve the concentration of selenium to the one-third power and suggests that, as in the case of the oleic-elaidic acid transformation, a dissociation of $Se_6$ to $3Se_2$ is involved.

In previous work in this laboratory[2] it was shown that the selenium-catalyzed interconversion of oleic (*cis*) and elaidic (*trans*) acids is a homogeneous reaction, the first step of which consists of the formation of a *pi* complex between the unsaturated fatty acid and selenium. The reversible formation and decomposition of the complex results in the isomerization. It was further shown that most other olefinic substrates complex reversibly with selenium at 200°. If the substrate contains a hydrogen atom on the carbon alpha to the double bond, the catalytic activity of the selenium slowly disappears, presumably by irreversible rearrangement of the *pi* complex to a new species (*sigma* complex) in which it is assumed that a carbon-selenium *sigma* bond is formed. In the present work, the isomerization of *cis*-stilbene was investigated not only because this is a classical substrate for *cis-trans* studies but also because the lack of an *alpha* hydrogen atom would preclude formation of the postulated sigma complex.

## EXPERIMENTAL

*Apparatus.* The isomerization studies were performed in a short test tube fitted with a stirrer, a side-arm inlet for inert gas and a small bore, angled side arm for the insertion of a sampling tube. The test tube was placed in a salt bath heated by a mantle. Temperature control was maintained at ± 1° in the temperature range 190–210° by means of a Thermocap relay. Samples for analysis were removed by inserting an open-end, melting-point capillary tube through the side arm, allowing the liquid to fill the capillary to the desired level, and then withdrawing the tube and sample.

*Materials. cis*-Stilbene purchased from the Aldrich Chemical Co. was used as received since the ultraviolet spectrum showed it to be of good quality. Selenium powder, reagent grade, was purchased from the Fisher Scientific Co. and was used as received.

*Analytical Procedure.* The ultraviolet spectra of *cis* and *trans*-stilbene show significant differences[3] and a quantitative method based on ultraviolet absorption spectroscopy was therefore applied. After consideration of several possible methods of selecting and treating the data, the graphical absorbance ratio method[4] was employed. In this method a graph is used, which has as one coordinate, the ratio of observed absorbances at two wave lengths, one of which is an "isoabsorptive" point (the wave length at which both isomers have the same absorptivity). The other coordinate is the relative composition of the mixture and hence runs from 0 to 100% of one of the isomers. This method does not require a prior knowledge of the total concentration of the two components, a fact which is of advantage in the present work where very small liquid samples are involved. The method does however place great weight on the accurate selection of the isoabsorptive wave length. Because the graph is a straight line, the accuracy can be improved by drawing the best straight line through intermediate points of known composition as well as the intercepts. Fig. 1 shows an experimental plot of the ratio of the absorbance at the indicated wave length over the absorbance at the isoabsorptive point (λ 266 mμ) *vs.* the percent of *trans*-stilbene in the mixture. The best straight line was drawn through the points and the composition determined from these best values.

The determinations were made by removing samples from the reaction vessel by means of the capillary tube. The filled capillary was dropped into a volumetric flask without weighing and broken up by means of a glass rod. The flask was filled to the mark with spectral grade cyclohexane. Aliquots of this solution were taken for further dilution until absorbance readings were of a suitable magnitude. Readings

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(1) Present address, Emery Industries Inc., Cincinnati 2, Ohio.

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(4) R. C. Hirt, F. T. King, and R. G. Schmitt, *Anal. Chem.*, **26**, 1270 (1954).