

[CONTRIBUTION FROM THE IBM RESEARCH CENTER, YORKTOWN HEIGHTS, N. Y.]

Kinetics of the Photochemical Dimerization of Olefins to Cyclobutane Derivatives. I. Intramolecular Addition

BY R. SRINIVASAN

RECEIVED MAY 16, 1962

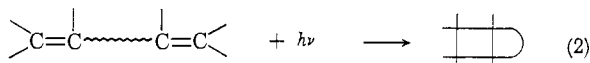
The photoisomerization reaction (2), has been studied in six 1,3-dienes and in 1,3,5-cycloheptatriene. It was observed that 1,3-pentadiene, isoprene and 2,3-dimethyl-1,3-butadiene gave rise to 3-methyl-, 1-methyl- and 1,2-dimethylcyclobutene, respectively, while 1,3-cyclooctadiene and 1,3,5-cycloheptatriene yielded the previously reported cyclobutane derivatives. The formation of 1,2-dimethylcyclobutene from 2,3-dimethyl-1,3-butadiene in the vapor phase was studied in the presence of oxygen, nitric oxide and ether. The reaction is believed to be intramolecular and to originate in the singlet state of the molecule. The quantum yields for the photoisomerization reaction in solution at 2537 Å. fell in decreasing order as: 1,3-cyclooctadiene > 2,3-dimethyl-1,3-butadiene > isoprene > 1,3-pentadiene = 1,3,5-cycloheptatriene. Under the same conditions, the formation of a cyclobutene product from 1-methoxy-1,3-butadiene and 2,4-dimethyl-1,3-pentadiene could not be detected. Rate studies on the irradiation of a mixture of *cis*- and *trans*-1,3-pentadiene in solution indicated that the *trans* compound was the sole source of 3-methylcyclobutene, and that this reaction was faster than the photoisomerization of *trans*- to *cis*-pentadiene.

Introduction

The photodimerization reaction (1) is well known

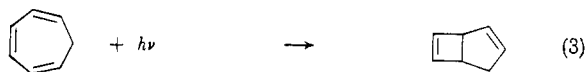


in the condensed phases^{1,2} but appears to be unknown in the vapor phase. For example, irradiation of ethylene³ or of a butene⁴ in the vapor phase has not been found to lead to cyclobutane or its derivatives. As part of an extended study of the kinetics of photodimerization reactions, it seemed desirable at first to pick the special case of 1 in which reaction occurs in a system in which both olefinic groups are located in the same molecule. In such an instance, 1 may be written as 2, which is a photoisomerization process. Since 2 is not *directly* dependent on

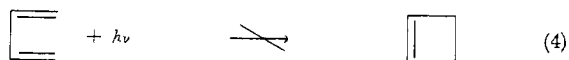


collisional processes, it is possible to compare results obtained in the condensed phase with those obtained in the vapor phase.

Only one example of 2 is known to occur in both gaseous and condensed phases. This is the photoisomerization of 1,3,5-cycloheptatriene to bicyclo[3.2.0]hepta-2,5-diene (reaction 3).^{5,6} The oc-



currence of 3 in detectable yield in the vapor phase seemed difficult to reconcile with the previously reported failure⁷ to detect the photoisomerization of 1,3-butadiene to cyclobutene in the vapor phase, although the strain involved in the formation of



bicycloheptadiene by reaction 3 should be greater than the strain in the formation of cyclobutene.

(1) A. Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1959, p. 22.

(2) A. Mustafa, *Chem. Revs.*, **51**, 1 (1952).

(3) M. C. Sauer, Jr., and I. M. Dorfman, *J. Chem. Phys.*, **35**, 497 (1961).

(4) W. F. Kieffer and J. P. Howe, *J. Am. Chem. Soc.*, **64**, 1 (1942).

(5) W. G. Dauben and R. I. Cargill, *Tetrahedron*, **12**, 186 (1961).

(6) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 3432 (1962).

(7) R. Srinivasan, *ibid.*, **82**, 5063 (1960).

In this paper, the kinetics of the photochemical formation of cyclobutenes from 1,3-dienes and one triene, mostly in solution, but in one instance in the vapor phase, are reported. Particular attention has been given to the influence of substitution on the ease of ring closure.

Experimental

Apparatus.—Photolyses in the vapor phase were conducted in a quartz cell, 4.4 cm. × 3.7 cm. A conventional vacuum line was used, but stopcock grease (Apiezon N) was not excluded from contact with the reactants. The light source was a Hanovia 100 watt medium pressure mercury arc used without filters.

Photolyses in solution were conducted in a quartz test-tube 7 mm. o.d. with a ground glass stopper. In the runs in which it was necessary to degas the solution, the stopper was eliminated and the test-tube was directly attached to a vacuum line. The light source was a bank of 12 low pressure mercury lamps (General Electric G8T5, 8 watts) arranged in a circle with their long axes parallel to the quartz reaction tube. The useful radiation was the 2537 Å. line. The intensity of the radiation, as calibrated with a uranyl oxalate actinometer, was 1.46×10^{17} quanta/sec. in the volume of the solution (8.5 ml.). This value was checked just before and during the course of the experiments listed in Table I.

Materials.—The following hydrocarbons of research grade were used as obtained: isoprene, 2,3-dimethyl-1,3-butadiene, 1-methoxy-1,3-butadiene (K & K Laboratories, Jamaica, N. Y.), 1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 1,3-cyclooctadiene (Aldrich Chemical Co., Madison, Wis.), 1,3,5-cycloheptatriene (Chemical Procurement Laboratories, College Point, N. Y.). The purity of these chemicals was checked by gas chromatography and found to be at least 96%. The impurities in all cases were not found to undergo photolysis. Analytical grade ether (Mallinckrodt Chemical Co.) and spectrograde cyclohexane (Eastman Kodak Co.) were used as solvents.

Analysis.—The isomeric products that were obtained in the photolyses of isoprene,⁸ cycloheptatriene^{9,6} and cyclooctadiene⁹ were identified by the comparison of the infrared spectra with those of known compounds in the literature. Quantitative analysis for the photoisomers was carried out by measuring the area under the curve in the gas chromatogram. The instrument was calibrated with the parent hydrocarbon.

Results

Products.—Irradiation of 2,3-dimethyl-1,3-butadiene (hereafter dimethylbutadiene) in diethyl ether at 2537 Å. gave rise to a product (b.p. 68°) of formula C₆H₁₀ and hence isomeric to the starting

(8) E. Gil-Av and J. Herling, *Tetrahedron Letters*, **No. 1**, 27 (1961). The author wishes to thank Professor W. D. Walters of the University of Rochester for making available to him the spectrum of a sample prepared in this way.

(9) W. G. Dauben and R. I. Cargill, *J. Org. Chem.*, **27**, 1910 (1962).

TABLE I
QUANTUM YIELDS FOR PHOTOISOMERIZATION OF OLEFINS TO CYCLOBUTENES IN SOLUTION
2537 Å. radiation, solutions not degassed

| Reactant | Solvent | Concn., moles/ ml. × 10 ⁴ | Time, min. | Cyclobutene | | Quantum yield disappearance of reactant | Side reactions |
|----------|---------------|---|---------------|-------------|------------------|---|-------------------------------------|
| | | | | Formula | Quantum yield | | |
| | Cyclohexane | 2.03 | 237 | | 0.09 | 0.11 | Polymn. |
| | Diethyl ether | 1.86 | 258 | | .12 | .12 | None; polymn. at higher concn. |
| | Cyclohexane | 1.96 | 300 | | .03 | .04 | <i>trans</i> → <i>cis</i> ; polymn. |
| | Diethyl ether | 1.49 | 1440 | | < .001 | Not detected | <i>trans</i> → <i>cis</i> |
| | Diethyl ether | 10 | 1320 | | < .001 | Not detected | |
| | Diethyl ether | 2.17 | 253 | | .03 | 0.03 | |
| | Diethyl ether | 2.00 | 274 | | .14 | .18 | Other isomn. (?) |

^a 68.3% *trans* isomer. ^b Mostly *trans* isomer.

material. (Anal.¹⁰ Found: C, 87.80; H, 12.35. Calcd. for C₆H₁₀: C, 87.74; H, 12.26.) The infrared spectrum (pure liquid) showed a peak at 1675 cm.⁻¹ and no intense absorption from 1000 to 700 cm.⁻¹. The presence of a peak at 1375 cm.⁻¹ indicated that there was at least one methyl group in the molecule. The ultraviolet spectrum (in cyclohexane) showed end absorption: $\epsilon_{2200} = 540$, $\epsilon_{2150} = 905$, $\epsilon_{2100} = 1010$. The compound may have one tetrasubstituted olefinic group located in a ring. The n.m.r. spectrum (solvent, CCl₄; tetramethylsilane as internal standard) consisted of only two peaks, both unsplit and of relative intensities 2:3. The smaller peak which was at 7.79 τ may correspond to four identical protons located in a four-membered ring and allylic in nature. The large peak which was at 8.46 τ would then correspond to six protons from two methyl groups located on olefinic carbons. The structure 1,2-dimethylcyclobutene (I) for the new compound would fit all of these observations.^{10a}

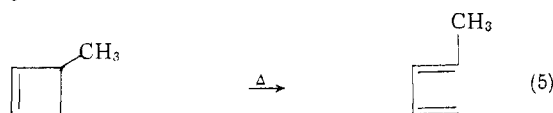


Irradiation of a mixture of *trans*- and *cis*-1,3-pentadiene in cyclohexane gave rise to a product (b.p. -9.7° at 156 mm., 29.9° at 760 mm.) of the same molecular weight (vapor density 34.7) as the starting material. The infrared spectrum of this product (in bromoform) showed a weak absorption peak at 1560 cm.⁻¹ and an intense absorption at 775 cm.⁻¹, which suggested the presence of a cyclobutene ring. An absorption at 1370 cm.⁻¹ indicated the presence of a methyl group in the mole-

(10) Microanalysis by Micro-Tech Laboratories, Skokie, Ill.

(10a) Dr. P. Leermakers has informed the author that a sample of I made in this way gave rise to acetyl acetone on ozonolysis. This reaction also supports the proposed structure.

cule. A vapor sample of the material was sealed in a Pyrex glass bulb under a vacuum and heated to 155° for 85 min. None of the parent material remained at the end of the pyrolysis. The only product that was obtained was *trans*-1,3-pentadiene. These observations suggested that the product of photolysis was 3-methylcyclobutene (II) which pyrolyzed in a manner exactly similar to cyclobutene.¹¹



The photolysis of all of the olefins reported in this study gave rise to varying amounts of high boiling or solid products. The importance of polymerization reactions was found to depend on both the concentration of the solution and the intensity of the light source. As a result, the quantum yields for cyclobutene formation which are listed in Table I are not realizable at a higher concentration of reactants.

The only compound that was studied in the vapor phase was dimethylbutadiene. The products that were obtained were 1,2-dimethylcyclobutene (I), hydrogen which amounted to a maximum of one-third of the cyclobutene, and small amounts of other hydrocarbon products.

Quantum Yields.—Quantum yields for the formation of the appropriate cyclobutene products from seven different di- and triolefins at 2537 Å. in solution are shown in Table I. The solutions were not degassed. Conversions ranged from 6 to 45%. The quantum yields are believed to be reliable to ± 0.01 .

Photolysis of 1,3-Pentadiene in Solution.—The photolysis of *cis,trans*-1,3-pentadiene in cyclohexane

(11) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958).

at 2537 Å. at room temperature is shown as a function of time in Fig. 1. All the recorded points are averages of duplicate analyses. Those points with projections are based on photolysis with degassed and sealed samples.

Vapor Phase Photolysis of Dimethylbutadiene.—

Yields of 1,2-dimethylcyclobutene in the photolysis of dimethylbutadiene in the vapor phase at room temperature are given in Table II. Conversions

TABLE II

PHOTOISOMERIZATION OF 2,3-DIMETHYL-1,3-BUTADIENE TO 1,2-DIMETHYLCYCLOBUTENE IN THE VAPOR PHASE

Medium pressure mercury arc, no filters, room temp., t is 120 min. except a , all vol. 54.7 ml.

| Press. of dimethylbutadiene, mm. | Gas added or filter | Gas press., mm. | Formation of dimethylcyclobutene, $\mu\text{moles/min.} \times 10^4$ |
|----------------------------------|---------------------|-----------------|--|
| 3.9 | ... | ... | 4.6 |
| 4.8 | ... | ... | 4.6 |
| 3.8 | Oxygen | 127.4 | 3.5 |
| 5.0 | NO | 36.9 | 4.0 |
| 4.8 | Diethyl ether | 56.0 | 6.8 |
| 4.4 | Diethyl ether | 96.5 | 7.3 |
| 3.6 | Diethyl ether | 136.9 | 7.1 |
| 3.8 | Diethyl ether | 220.9 | 7.1 |
| 4.4 ^a | Corex ^b | ... | ~0 |

^a $t = 1037$ min. ^b Corning clear glass filter which transmits 60% at 3000 Å., 16% at 2800 Å. and 0.1% at 2500 Å.

ranged from 3 to 5%. The uncertainty in the yields is 16%. Since the light source was polychromatic, the quantum yield was not determined. But the rate of formation of the product can be compared with the rate of photolysis of 1,3-butadiene with the same source in a similar system. The rate of disappearance of 1,3-butadiene was 10 to 100 times faster than the photochemical production of dimethylcyclobutene. In the experiment in which oxygen was present, some evidence for the photochemical oxidation of the diene was obtained.

Discussion

Vapor Phase Studies.—The formation of dimethylcyclobutene from the photolysis of dimethylbutadiene



constitutes the second example of reaction 2 that has been observed in the vapor phase. As in the case of cycloheptatriene (reaction 3), the process is found to be resistant to quenching by large excesses of oxygen and nitric oxide. This may be construed as evidence against the participation of long-lived free radical intermediates in 6, and more generally in 2. It may also be considered to favor the idea that 6 occurs in the singlet state of dimethylbutadiene. The quantum yield for the process can be estimated to be small—not more than 0.05—if a quantum yield of unity is assumed for the disappearance of 1,3-butadiene by unimolecular processes in its photolysis at low pressure.

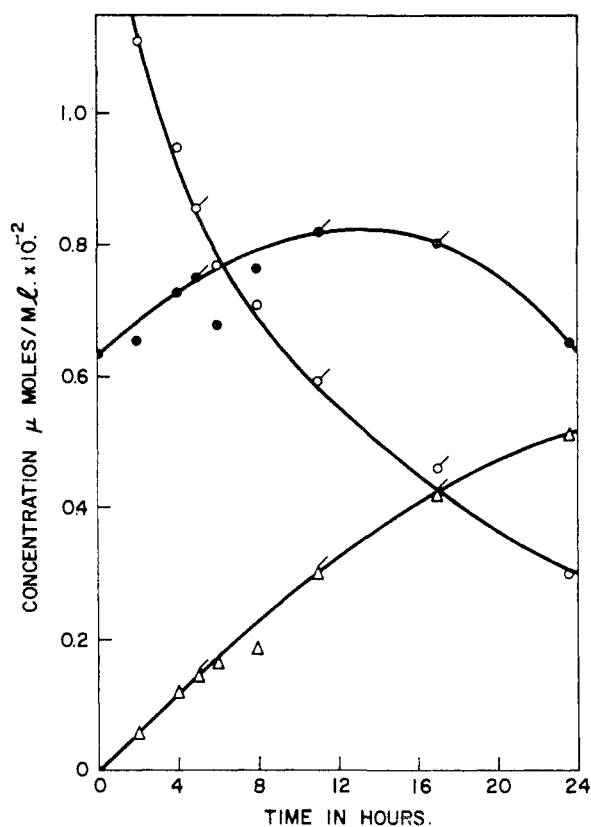


Fig. 1.—Photoisomerization of a mixture of *trans*- and *cis*-1,3-pentadiene in solution; solvent cyclohexane, 2537 Å. radiation, room temperature: Δ , 3-methylcyclobutene; O , *trans*-1,3-pentadiene; \bullet , *cis*-1,3-pentadiene. Points with projections denote degassed solutions. Concentration of *trans*-pentadiene at $t = 0$ was $1.35 \times 10^2 \mu\text{moles/ml}$.

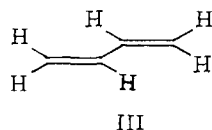
Of particular interest is the effect observed on the addition of an inert gas. Since diethyl ether does not absorb any of the radiation that is useful in the photolysis of dimethylbutadiene, its presence can serve only one purpose, *viz.*, to equilibrate vibrational energy among the molecules present. As the pressure of ether is increased, the rate of formation of dimethylcyclobutene and hence its quantum yield increases by a factor of 1.5. But a further increase in ether pressure causes the rate to level off sharply. This behavior is entirely similar to that observed in the case of 1,3,5-cycloheptatriene in reaction 3.⁶ The explanation is probably the same in both instances, *i.e.*, an increase in pressure serves to stabilize the cyclobutene that is formed photochemically, by the removal of the excess vibrational energy that it possesses. Since the energy of the photon corresponds to about 110 kcal./mole and reaction 6 is believed to be endothermic by about 15 kcal./mole or less, about 90 or more kcal./mole of energy may be expected to be present in the cyclobutene molecule at the instant of its formation. In line with this reasoning it can be pointed out that for both dimethylbutadiene and 1,3,5-cycloheptatriene⁶ the quantum yield for cyclobutene formation at 2600 Å. increases on going from the vapor phase to solution.

An alternative explanation for the role of the inert gas which is based on the loss of vibrational

energy in the excited state of the diene by deactivating collisions with the surrounding molecules cannot be discarded on the basis of the data given here. But one serious objection to this explanation which has already been offered in the case of 1,3,5-cycloheptatriene⁶ is that the radiative lifetime of the singlet excited state which can be calculated from the absorption spectrum is of the order of 10^{-8} to 10^{-9} sec. for both compounds. In the pressure range used in this study, the number of deactivating collisions in the lifetime of the excited state may be too small to cause significant pressure effects.

Effect of Structure on Quantum Yield.—The results in Table I show the effect of structure on the quantum efficiency of reaction 2. All five of the linear 1,3-dienes that are listed absorb in the same general region of the ultraviolet spectrum, the long wave length limit in each case falling close to 2500 Å. Cyclooctadiene and 1,3,5-cycloheptatriene absorb at longer wave lengths, but the intensity of the absorption, which is high ($\log \epsilon_{\max} > 3$), is of the same order as for the linear dienes.

The two cases in which the formation of a cyclobutene was not detected are compounds in which the end carbon of the 1,3-diene chromophore is substituted with one bulky group, methoxy or with two smaller groups, namely methyls. Quantum yields in the remaining five cases fall in the order cyclooctadiene > dimethylbutadiene > isoprene > pentadiene = cycloheptatriene. It was not possible to monitor the disappearance of the reactant with the same accuracy as the formation of the cyclobutenes. Within this limitation the values which are listed for the quantum yields for cyclobutene formation and the disappearance of the reactant appear to be the same. It follows that the gradation observed in the yield of cyclobutenes is real. It is reasonable to assume that the configuration with the minimum energy for 1,3-butadiene is III which would not be favorable

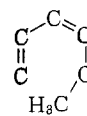


for ring closure. The lifetimes of the excited singlet states of the di- and triolefins considered here are too short to permit many rearrangements in the configuration in the excited state. It seems likely that only the small fraction of molecules that are in nearly the right arrangement at the moment of absorption of a photon can participate in 2. Substituents on the chromophore which cause the molecule to twist to configurations that are favorable for ring closure have the largest quantum yield for cyclobutene formation. 1,3-Cyclooctadiene in which the two double bonds must be nearly overlapping and which leads to a bicyclic product of no greater strain than cyclobutene itself has the largest quantum yield of the compounds in Table I. The presence of two methyl groups in the 2- and 3-positions in a linear



1,3-diene should also favor arrangements of the molecule which are more disposed toward ring closure than an unsubstituted 1,3-diene. This effect may explain the relatively high quantum yield of 0.12 for reaction 6, and a lower value for the isomerization of isoprene, which has only one methyl substituent.

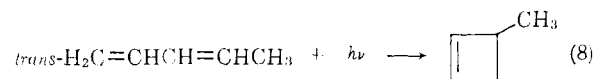
In 2,4-dimethyl-1,3-pentadiene the favorable effect of a methyl group in the 2-position is offset by the presence of two methyl groups of carbon four which should hinder the closure of the ring. The case of 1-methoxy-1,3-butadiene appears to be exceptional. Certainly in the *cis* configuration



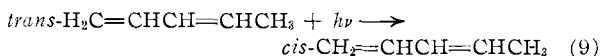
(IV) the bulky methoxy group will hinder the formation of a cyclobutene ring, but it is not clear why the compound in its *trans* configuration does not form methoxycyclobutene with as much efficiency as *trans*-1,3-pentadiene.

In 1,3,5-cycloheptatriene, the favorable effect due to the location of the two double bonds in a ring as in 1,3-cyclooctadiene is probably nullified by the necessity to form a bicyclic product of a strained nature. As a result, the quantum yield for 3 is small.

Photoisomerization of 1,3-Pentadiene.—At 2537 Å. the absorption coefficient of *trans*-pentadiene is 39.48 while that of *cis* is 8.42.¹² In the mixture of *cis*- and *trans*-pentadiene that was irradiated, although the *trans* compound constituted 68%, it absorbed 91% of the incident light. The curves in Fig. 1 show that: (i) initially *cis*-pentadiene increased while *trans*-pentadiene decreased so that methylcyclobutene may originate from the latter only.



The following reaction may also occur concurrently.



(ii) There is a fall in the rate of production of methylcyclobutene with time. The fraction of the total number of photons absorbed (which is constant) which go to excite the *trans* compound can be calculated from the formula¹³

$$I_{trans} = I\epsilon_{trans} C_{trans} / \Sigma \epsilon C$$

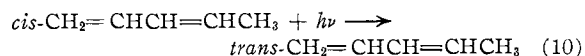
where the symbols I , ϵ and C refer to the intensity, extinction coefficient and concentration, respectively. This fraction falls off with time in exactly the same way as the rate of formation of methylcyclobutene, which confirms the conclusion reached in (i) that the *trans* compound is the sole source of methylcyclobutene.

(12) American Petroleum Institute Research Project 44, Serial Nos. 47 and 49.

(13) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 152.

(iii) A portion of the reactants disappears to give material other than C_5H_8 isomers at a rate which is nearly independent of time. Evidently both *cis* and *trans* isomers participate in this reaction which presumably gives high boiling material.

(iv) Beyond the maximum in the concentration of *cis*-pentadiene, the reaction



may account for the decrease in the *cis* isomer.

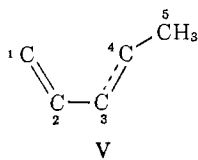
These results give more direct evidence for the statement made in an earlier section that the general reaction² is probably rapid when compared to the rates of rotation around the carbon-carbon bonds in the molecule. Reaction 8 may be pic-

tured as proceeding through an excited state (V) which is probably the same as the state which leads to the *cis* isomer through rotation around the bond between C_3 and C_4 . The latter operation has no energy barrier in the excited state up to an angle of $\pi/2$ ¹⁴ and its rate may be comparable to the rate of rotation around the bond between C_2 and C_3 . Since the rate of reaction 8 is observed to be faster than reaction 9, it follows that the former is favored by a suitable configuration in the ground state in the molecules which undergo the process.¹⁵

Acknowledgment.—The author wishes to thank Dr. Harold L. Friedman for his advice and encouragement during the course of this work. He is grateful to Drs. J. Kumamoto and J. C. Powers for many helpful discussions.

(14) J. R. Platt, "Encyclopaedia of Physics," Vol. 37, part 11, Springer-Verlag, Berlin, 1961, p. 204.

(15) The inference may be drawn that excited molecules with the right configuration for ring closure may react at a much faster rate to give methylcyclobutene compared to the rate of isomerization to *cis*-pentadiene. The observed 10% difference in rate between 8 and 9 may be caused by the averaging of the rate of the former over molecules in all configurations.



[CONTRIBUTION No. 224 FROM THE RESEARCH CENTER, UNITED STATES RUBBER COMPANY, WAYNE, NEW JERSEY]

The Use of Rhodium Salts as Catalysts for the Polymerization of Butadiene¹

By ROBERT E. RINEHART, HOMER P. SMITH, HARRY S. WITT AND HENDRIK ROMEYN, JR.

RECEIVED MAY 18, 1962

The study of stereoregulating polymerization effects of inorganic salts in polar solvents revealed that certain rhodium salts catalyze polymerization of butadiene to the *trans*-1,4 structure in high steric purity. The rhodium salts behave simultaneously as efficient inhibitors for the free-radical emulsion polymerization. Rhodium salts also catalyze the isomerization of *cis*- and *trans*-polybutadiene toward an equilibrium structural composition.

Crystalline *trans*-polybutadiene is usually prepared by a Ziegler-Natta catalyst system.² Such catalysts are, of course, completely destroyed by traces of water or air. In contrast, solutions of rhodium salts in water catalyze the stereospecific polymerization of butadiene to the all *trans*-1,4 configuration.^{3,4} An emulsifier may be present, but it is not necessary for polymerization, if the proper rhodium salt is selected.

In water, sodium dodecylbenzenesulfonate increases the rate with rhodium nitrate from 0.1 g./hr. to 0.4, while with rhodium chloride it increases from 0 to 2.4. A non-ionic emulsifier shows a slight rate increase for the nitrate, but is inactive with the chloride. Thus, rhodium nitrate is the more efficient catalyst in water with no emulsifier. Rhodium chloride is the more efficient catalyst in water with certain anionic emulsifiers.

(1) Presented in part at the 141st National Meeting of the American Chemical Society, Washington, March 28, 1962, and at the New York-New Jersey Regional Meeting, January 22, 1962.

(2) N. O. Gaylord and H. F. Mark, "Linear and Stereoregular Addition Polymers," Interscience Publishers, New York, N. Y., 1959, p. 368.

(3) R. E. Rinehart, H. P. Smith, H. S. Witt and H. Romeyn, Jr., *J. Am. Chem. Soc.*, **83**, 4864 (1961).

(4) After this paper had been submitted for publication, a communication⁵ appeared which reported observations parallel to our first report³ on the stereoregulating effects of $RhCl_3$ in butadiene polymerization.

(5) A. J. Canale, W. A. Hewett, T. M. Shryne and A. E. Youngman, *Chemistry & Industry*, 1054 (1962).

Rhodium nitrate catalyzes the polymerization of butadiene in alcohol to the all *trans* polymer. Rhodium chloride, with or without sodium dodecylbenzene sulfonate, is ineffective in alcohol for the formation of high polymer. Analysis by gas chromatography has shown, however, that butadiene disappears at a faster rate for rhodium chloride in alcohol than for the nitrate. The reaction product from rhodium chloride is a complex mixture of hydrocarbons. More than twenty steam-volatile components, including butene-1 and butene-2 have been separated.

Rate of Polymerization.—The rate of formation of polymer under an emulsion condition using $RhCl_3$ as the catalyst is shown in Fig. 1. The rate shows no evidence of an induction period. At high conversions, there is usually a considerable amount of precipitated polymer. It might be expected that some catalyst would be removed from reaction along with the precipitated polymer, leading to a corresponding rate decrease. Despite this, the determined rates are quite linear, even at high conversion. It is then empirically correct to assume linear conversion with time.

The dependence of rate on catalyst concentration was determined for the polymerization of butadiene by rhodium nitrate in aqueous solution, with and without an emulsifier (Fig. 2). In each case, there was a leveling off of the rate when the