

CATALYTIC EXOTHERMIC RETROCONVERSION OF
HIGH ENERGY COMPOUNDS PRODUCED THROUGH
SOLAR ENERGY

by

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ABSTRACT

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Two systems were evaluated for their potential use in a novel photochemical solar energy storage method dubbed HELEOS (Hydrocarbon Entrapment of Light Energy of the Sun). This method consists of storing solar energy through photochemical production of high energy synthetic fuels and releasing the energy by catalytic conversion of the fuels back to the starting material.

The first system investigated was the model system consisting of the starting material norbornadiene (I), the fuel quadricyclene (II), and Wilkinson's catalyst both in polymer-bound (V) and unbound (IV) forms. This system was found to be ideally-suited for application in HELEOS, based on several criteria. First, the photoreaction of norbornadiene was found to have (i) broad band absorption in the UV-visible portion of the solar spectrum when used in conjunction with a photosensitizer known as Michler's ketone (III), and (ii) a high yield and specificity for production of quadricyclene, which was found to be optimized by reaction of norbornadiene in high concentration using benzene as the solvent. Second, quadricyclene was found to be thermally stable at ambient temperatures and quite reactive to catalytic conversion to norbornadiene; the second order rate constant for catalytic conversion was found to be $7.0 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for the unbound catalyst (IV), and $8.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$

for the polymer bound catalyst V (at 36°C). Finally, the conversion of quadricyclene to norbornadiene was found to be highly exothermic, releasing 24 kcal/mol at 25°C.

The second system studied consisted of the starting material N-methyl-2-pyridone (VI, R = CH₃), and the fuels Dewar pyridone (VII, R = CH₃) and 4 + 4 dimer (VIII, R = CH₃). Conditions were found which optimized the production of each fuel from the starting compound VI, and both photoreactions were found to display both a high specificity for production of each respective fuel and broad band absorption in the UV-vis region of the solar spectrum. However, the fuels resisted catalytic conversion to the starting compound VI using a variety of catalysts at both ambient and elevated temperatures. For this reason, it has been decided that this system is unsuitable for use in a HELEOS - type application without some structural modifications of the fuels allowing facile catalyzed retroconversions to the starting compound VI.

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INTRODUCTION

Evaluation of Present Energy Resources. Among the many problems facing the world at the present time, the energy crisis has certainly proved itself to be one of the most prevalent. While the world's supply of fossil fuels has certainly not been depleted, a shortage exists in many cases. The United States is a prime example. Estimates of our reserves show that a distinct possibility exists that within the next ten years we will be unable to produce enough crude oil to meet our liquid hydrocarbon requirements.¹ Conservation, while it is a step in the right direction, will not alleviate the necessity of developing new sources of energy to supplement and eventually replace fossil fuels. The availability of ideas for new sources of energy as well as means of exploiting them are certainly not scarce. Among the alternatives are nuclear, solar, and geothermal energy, as well as extensions of fossil fuel resources.² The practical and economical implementation of these options, however, presents a major problem.

All of the above areas of energy research should be thoroughly investigated since each offers its advantages as well as its drawbacks. Nuclear energy, for example, while being the most developed alternative source of energy, is still experiencing many problems with the breeder reactors as well as difficulties with the safe storage of nuclear materials and wastes. Consider also geothermal energy. This environmentally clean source may someday provide some energy relief in the western half

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of the United States and other such areas close to the source, but its overall energy potential is limited in that it is non-renewable and on a world scale is relatively minor.³ Hydroelectric power, an almost ideal, efficient source on the other hand is renewable, but unfortunately it is already being utilized at about 33% of its potential so that a large increase is not possible.⁴ Another source of energy is fusion. This source has great potential, but it has a major drawback in that the development of the technology necessary for its utilization may well proceed into the 21st century at the present rate.⁵

A final alternative lies in solar energy which is by far the most abundant renewable resource. Its utilization presents no major environmental hazards or effects. In fact, the Energy Research and Development Administration foresees as much as "25 percent of the nation's energy coming from solar technologies by the year 2020."⁶ However, solar energy has its problems as well. Its diffuse character requires large areas for sufficient energy yield; its intermittence requires its use in light periods; and no efficient way of storing the energy has been found as yet. The fact remains, however, that solar energy is still a relatively unexplored area as compared to nuclear energy or research on the extension of fossil fuel supplies. For this reason this resource has been chosen for study.

Solar Energy Storage. As mentioned above, before solar energy can be utilized to its full potential, a convenient method of storing the energy must be found. At present, there are two methods of storing the energy generated by solar heating. The first involves the direct heating of some object which can be thermally isolated from its surroundings.

The heat is extracted later by passing a suitable working fluid over the heated object. This method, however, requires a lot of space, and the effective period for heat storage is short.⁷ A second method of thermal storage makes use of the latent heat associated with a phase change. Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is commonly used in this connection. Heat is stored by melting the compound and recovered later by allowing it to solidify. The disadvantages of this method are that many such heat of fusion materials are expensive, corrosive, subject to supercooling and short-lived due to the thermal recyclization.⁷ Thus it appears that some other forms of storing solar energy are needed.

A somewhat unique approach to the problem to be explored in this study utilizes selected photochemical reactions to store solar energy under isothermal conditions. In essence, this method uses light-induced valence isomerization reactions of selected organic compounds to produce highly strained cyclic products which store the solar energy as potential energy in the bonds of the molecules. The energy is then released by the catalytic conversion of the product back to the original photoreactive starting material. The chemical components used in this manner are conserved by the cyclic nature of the process. The energy that can be stored and released in this method is comparable to the present methods of thermal storage. For example, photochemical production of strained benzene from normal benzene has a similar capacity per volume to that of Glauber's salt.⁸ Also, long term storage of the energy in the proposed method is possible since there is no requirement for thermal insulation. A total solar energy package employing this storage system could include the developing technologies of direct heating and photovoltaic capacities

of solar energy as well. An additional reason for exploring this conversion technique is that the simple irradiation of hydrocarbon feedstocks could increase energy output of fuels used for combustion by as much as 20-30%.⁸

Application of the Photochemical Method of Solar Energy Storage.

The photochemical method of solar energy storage could perhaps be utilized in a system called HELEOS (Hydrocarbon Entrapment of Light Energy Of the Sun), in which a solar converter is used to produce the high-energy fuels and a reactor utilized to effect the catalyzed retroconversion to the initial reactants, accompanied by the elimination of heat.⁸ This system is depicted in Figure 1. In addition the apparatus would have a reactant inlet system, a storage vessel for the synthetic fuel, several ports for on-line sampling of the material by a gas chromatograph, a calorimeter system surrounding the reactor for heat measurements, and various other features shown in Figure 1 that are necessary for the operation of HELEOS. However, before a detailed study of such a system is possible, research must be conducted to find and evaluate the chemical compounds that show potential for use as the "fuel" portion of the HELEOS system. It is this aspect of the application of HELEOS to photochemical solar energy storage that this study will be concerned with.

Object of this Work and Outline of Study. The purpose of this work is to select and evaluate organic compounds that are capable of participating in the chemical reaction cycles necessary for utilization in HELEOS. The scientific criteria for selection of a system for photochemical solar energy storage have been listed previously.^{9,10} (1) The starting material or sensitizer must have broad band absorption in the

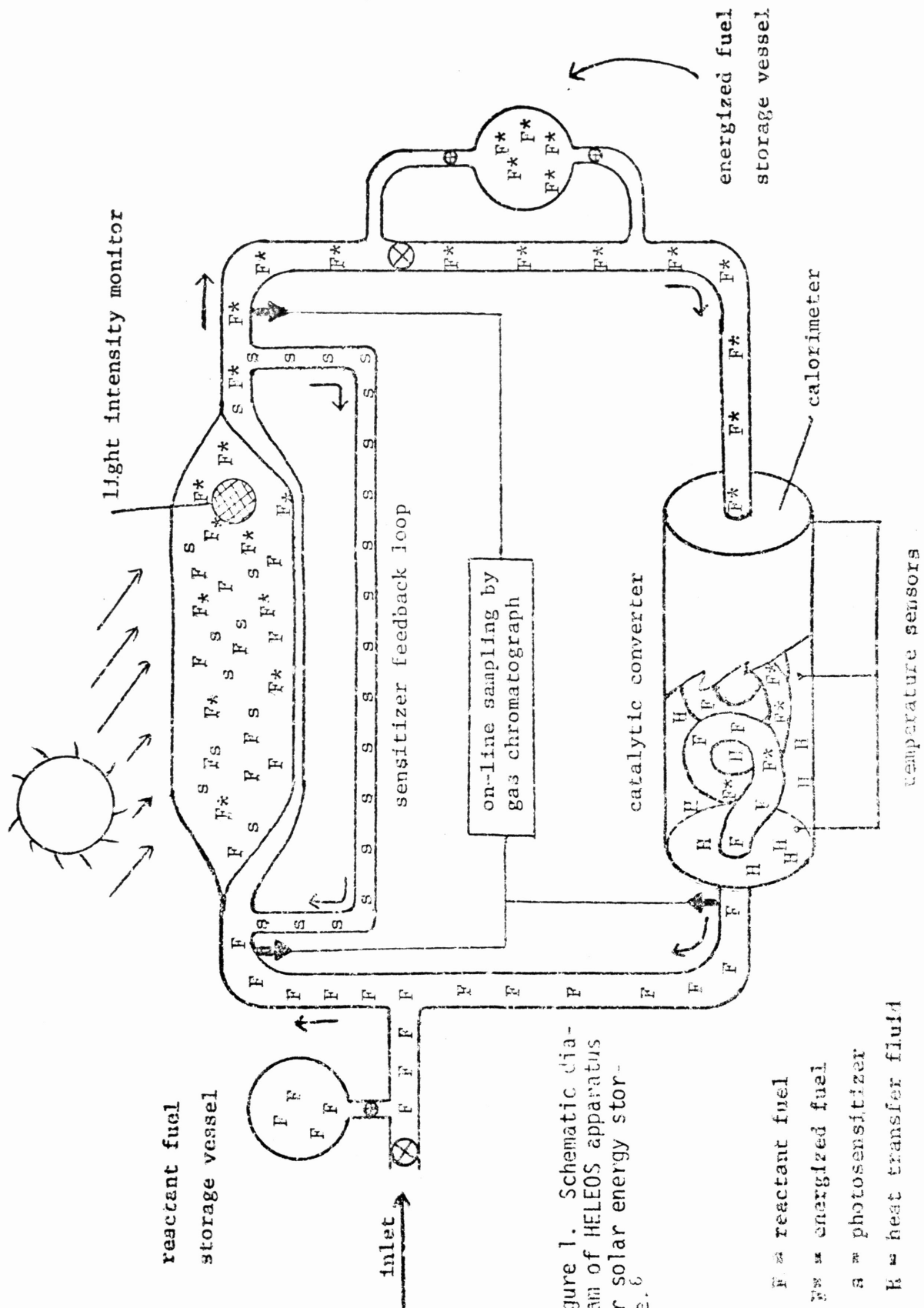


Figure 1. Schematic diagram of HELEOS apparatus for solar energy storage.

- F = reactant fuel
- F* = energized fuel
- s = photosensitizer
- K = heat transfer fluid

UV-visible portion of the solar spectrum. (2) The photolysis reaction must have a high yield and specificity for production of the high energy state. (3) The high energy product must have thermal and photolytic stability but still store a significant amount of energy. (4) There must be a specific, efficient method of releasing the energy to regenerate the starting material. The last criterion has often been neglected in evaluations of this type, but this study will put particular emphasis on it. Specifically, this criterion insures that the thermodynamic and kinetic properties of the fuel are such that one obtains optimal exothermicity of the conversion process as well as a suitable reaction rate at room temperature. All of the above criteria will serve as the basis for selection of possible systems.

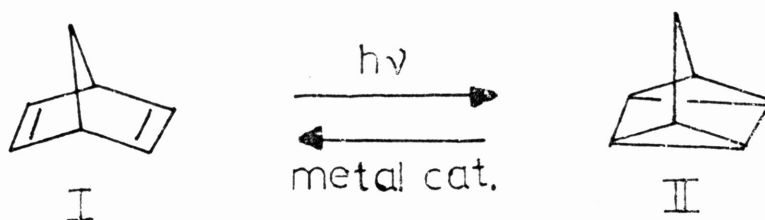
A prototype reaction cycle that illustrates the energy-storage reaction and retroconversion is shown in equation 1.



Equation 1 illustrates the absorption of light ($h\nu$) from the sun by compound A forming the high-energy compound B, and the subsequent metal catalyzed back reaction releasing heat ($-\Delta$). A and B are the compounds to be selected and evaluated for use in HELEOS.

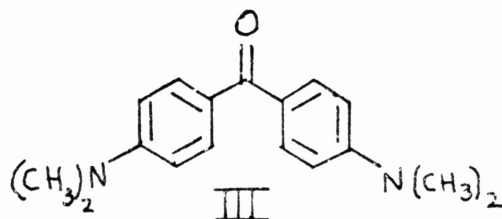
A detailed investigation of the literature has revealed that several organic systems can potentially undergo the reversible chemical processes denoted in equation 1. Of these, two have been chosen for evaluation in this study. The first is what appears to be an ideal reaction

system for use in HELEOS. It consists of the bicyclic hydrocarbon norbornadiene (I) and its valence isomer quadricyclene (II), representing compounds A and B, respectively, in equation 1. Much is known about this



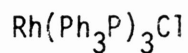
system, and for this reason it has been chosen as the model system for study. Some features of this system which make it attractive in this application are (1) the conversion of II to I possesses a large negative enthalpy (-22 kcal/mol)¹¹; (2) the uncatalyzed reaction of II to I has a small rate constant at ambient temperatures ($k_{300^\circ\text{K}} = 5.3 \times 10^{-13} \text{ sec}^{-1}$)¹¹, and (3) the catalyzed reaction of II to I has a large rate constant ($k_{300^\circ\text{K}} = 1.0 \text{ sec}^{-1}$ using $\text{Rh}_2(\text{NOR})_2\text{Cl}_2$).¹³ The only criterion that this system does not meet of those listed earlier is the first. Specifically, norbornadiene lacks broad band absorption in the UV-visible portion of the solar spectrum. However, combined studies indicate that the excited state conversion of norbornadiene to quadricyclene can be triplet photosensitized using a variety of aryl ketone photosensitizers.¹² These triplet photosensitizers absorb light in the UV-visible portion of the solar spectrum to populate their triplet excited states and participate in an energy transfer process with norbornadiene to generate the excited state of norbornadiene which is involved in the react-

ion of norbornadiene to quadricyclene. The aryl ketone chosen for this study is Michler's ketone, bis-4-N,N-dimethylaminobenzophenone (III),



since this photosensitizer has a unit intersystem crossing efficiency¹⁴, a long triplet lifetime ($\tau = 21\mu\text{sec}$) in solution,¹⁴ a favorable quantum yield for reaction with norbornadiene,^{12,15} and good absorption both in the UV portion of the solar spectrum ($\epsilon = 2.8 \times 10^4$ at 366 nm) and in the visible portion (up to 450 nm).¹⁴

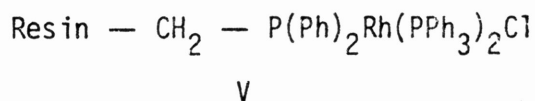
Another vital part of this model system in addition to the fuel and the photosensitizer is the catalyst. The catalyst chosen for this system is a homogeneous transition metal catalyst known as Wilkinson's catalyst, tris-(triphenylphosphine)chlororhodium (I), IV. This catalyst was chosen for two reasons. First, it contains the transition metal Rh(I),



IV

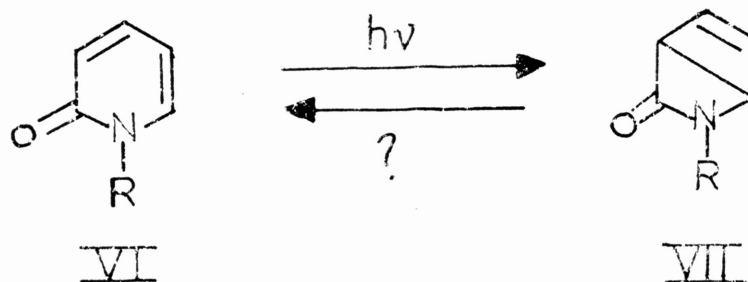
complexes of which have been shown to catalyze the conversion of II to I.^{13,16} Second, this catalyst has also been successfully chemically bound to an insoluble polymer support, thereby providing an easy method of separating the catalyst from the rest of the HELEOS system.¹⁷ This allows the controlled mixing of catalyst and fuel at that part in the

system where heat release is desired. However, the effect of using polymer-bound Wilkinson's catalyst (V) on the rate of reaction of II to I has not been determined. As a result, both the polymer and non-polymer bound catalysts will be investigated to determine their effect upon the rate of reaction of quadricyclene to norbornadiene. Also, since this model sys-



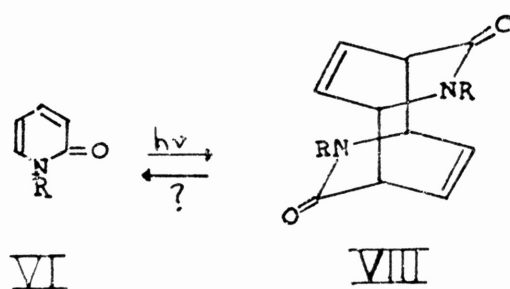
tem has been investigated before in much detail, it will serve as a check on the experimental methods and instrumentation to be employed in more exploratory phases of this study.

The second system chosen for investigation is one that is relatively unexplored compared to the model system. It involves the photoelectrocyclization reactions of N-substituted 2-pyridones (VI) to Dewar pyridones (VII), representing A and B, respectively, in equation 1. Studies



have shown that this system should be capable of undergoing the types of reactions shown in equation 1.^{18,19} It has an advantage over the compounds used in the model system in that N-substituted pyridones absorb light in the 300-400 nm wavelength region (e.g., R = CH=C(CH₃)₂, λ_{max} 309 nm

($\epsilon = 5.8 \times 10^3$); $R = \text{CH}=\text{CH}_2$ ($\lambda_{\text{max}} = 339 \text{ nm}$ ($\epsilon = 1.3 \times 10^4$)),⁸ thereby eliminating the need for a photosensitizer. The only criterion that this system doesn't satisfy is the second (requiring a high specificity of the reaction $A \rightleftharpoons B$ for production of B). Compounds VI, when irradiated in benzene solutions, are known to form, in addition to Dewar-pyridones (VII), minor amounts of 4 + 4 dimeric products with structure VIII.²⁰



This should not pose any real problem, however, since the 4 + 4 dimers (VIII) should also be capable of undergoing metal catalyzed retroconversion to the starting 2-pyridones, and their yield can be minimized through the use of dilute solutions of VI.

Qualitative comparisons of these compounds with analogous compounds in the literature provided the bases upon which this system was chosen. For example, it is expected that this system will undergo smooth and rapid transition metal catalyzed ring opening to VI on the basis of similar reactions with substituted Dewar-benzenes.²¹ Also, the retroconversion reaction (VII \rightarrow VI) is expected to have a large negative enthalpy associated with it (~ 52 - 62 kcal/mole), since the same type of reaction has been observed for the conversion of bicyclo [2.2.0]-hexane to 1, 3-cyclohexadiene, as well as for the conversion of hexamethyl-Dewar-benzene

to hexamethylbenzene, both of which have negative enthalpies in this range.^{22,23} Finally, studies conducted by Furrer¹⁸ and Deselms¹⁹ allow one to predict that this system should have a reasonably high quantum yield for production of VII and have thermal stability at ambient temperatures.

The compound chosen for initial evaluation is the N-methyl derivative of compound VI (R=CH₃). The same conditions will be used for evaluation of this system as in the model system, except that a variety of catalysts will be used to effect the retroconversion reactions VII→VI and VIII→VI in addition to Wilkinson's catalyst. These include various acidic compounds such as p-toluenesulfonic acid, trifluoroacetic acid and sulfuric acid, as well as transition metal catalysts such as palladium (II) chloride, silver (I) nitrate, copper (II) sulfate and norbornadienerhodium (I) chloride (IX). The goal here



IX

again is to examine the efficiency of the reactions depicted in equation 1 starting with compound VI (R=CH₃), and compare the results with those obtained for the model system. It is hoped that through this approach, the techniques can be developed which will allow for future analysis of other potential systems, and that conclusions can be drawn as to which system of the two being considered would be better suited for application in HELEOS.

EXPERIMENTAL

General. NMR spectra were recorded on a Varian T-60 spectrometer with tetramethylsilane as the internal standard, and ultraviolet spectra were measured using a Beckman Acta-III spectrophotometer (in 1-cm matched quartz cells). Gas chromatographic analyses were made using a Carle Model 311 chromatograph with flame ionization detector, while the purifications were made using a Varian Series 2700 thermal conductivity gas chromatograph. Melting points were run using a MEL-TEMP apparatus and are uncorrected. Photolyses were carried out using a Hanovia 500-W medium pressure mercury arc, in conjunction with standard photochemical apparatus described elsewhere.²⁴ A Parr Model 1451 solution calorimeter was used along with an Omniscribe Model A5213-4 strip chart recorder to evaluate the thermodynamics of various reactions studied.

Materials. Norbornadiene (I) was obtained in 99% purity from Aldrich Chemical Co. Michler's ketone (III) was also obtained from Aldrich Chemical Company and used without further purification. Unbound Wilkinson's catalyst (IV) was obtained from Alfa Products, Inc. and polymer bound Wilkinson's catalyst (V) (2% cross-linked on styrene) was purchased from Strem Chemicals Incorporated. Both of these were used without further purification. All solvents used (carbon tetrachloride, benzene, chloroform, acetonitrile, isopropanol, diethyl ether, methanol, and ethanol) were obtained from Fisher Scientific Company in analytical reagent-grade form, and were used without further purification. The nmr solvents (CDCl_3 and TMS) were obtained from Aldrich Chemical Co. in nmr reagent grade quality. The remaining chemicals that were used in this

study, such as palladium (II) chloride, silver (I) nitrate, *p*-toluenesulfonic acid, trifluoroacetic acid, copper (II) sulfate and sulfuric acid, as well as the compounds used in the syntheses to be described, were all obtained from the suppliers mentioned previously.

Quadricyclene (II). The synthesis of quadricyclene follows the general procedure outlined earlier by Sonntag and Srinivasan²⁴ except for two minor modifications. The solvent used was isopentane, and the quadricyclene was purified by fractional distillation at atmospheric pressure collecting the fraction boiling at 105-110°C. Use of the modified Sonntag and Srinivasan procedure gave a yield of about 50 g of quadricyclene starting with 100 g of norbornadiene. The identification and purity of quadricyclene were obtained by g.c. and nmr analysis.²⁵ Quadricyclene obtained in this way was shown to be 88% pure and contaminated with 12% norbornadiene.

1-methyl-2-pyridone (VI, R=CH₃).²⁶ A solution containing 2-pyridone (25.00g, 0.26 mol), methyl iodide (32.8 ml, 0.50 mol), anhydrous potassium carbonate (109.00 gm, 0.79 mol) and 400 ml of anhydrous benzene was refluxed for 24 hr under N₂. After cooling to room temperature the solution was concentrated in vacuo and distilled (b.p. 115°C/7 mm) giving 11.9 g of a colorless liquid (43% yield). This was shown to be the desired compound VII by nmr analysis.²⁶

Dewar-Pyridone (VII, R=CH₃) and 4 + 4-Dimer (VIII, R=CH₃). The photolysis of compound VI was carried out under conditions similar to those used for the preparation of quadricyclene, with certain exceptions noted.²⁴ The solvent used was methanol, and its concentration was var-

ied so as to maximize the yield of the Dewar pyridone (VII) versus the 4 + 4 dimer (VIII). Maximization of the yield of VII was obtained when a 0.02 M methanolic solution of VI was irradiated, while a 6.55 M solution of VI was used for maximization of VIII. The first photolysis yielded 0.92 g (23%) of VII starting with 4.0 g of VI after purification of the reaction mixture by concentration in vacuo and molecular distillation using a Kugelrohr apparatus (b.p. 26°C/0.10 mm). The identification of VII obtained as a colorless liquid was made on the basis of its nmr spectrum.²⁶ The second photolysis yielded 0.91g (32%) of a white crystalline solid, mp 207-209°C (lit.²⁷, 221.5-222°C), which was identified as VIII on the basis of the nmr spectrum.²⁷

Norbornadienerhodium (I) Chloride (IX). The homogeneous catalyst IX was prepared using the method of Wilkinson.²⁸ The yellow deposit obtained was recrystallized from hot chloroform-light petroleum to give pure IX (52.0%), decomp. 232°C (lit.²⁸, decomp. 240°C)

Quantitative Evaluation of the Norbornadiene Photoreaction. The effects of solvent, concentration of photosensitizer III, concentration of starting material I, and time of irradiation on the yield of the norbornadiene photoreaction were studied. Irradiations of norbornadiene were conducted simultaneously utilizing a sixteen compartment Merry-Go-Round apparatus. G.c. analyses were employed to determine percent yields of quadricyclene and UV analyses for monitoring changes in photosensitizer concentration. All solutions were degassed and irradiated in pyrex tubes (210 x 10 x 10 mm) using the same light source referenced earlier for the synthesis of quadricyclene.²⁴ Gas chromatographic analyses of

the photolysates were carried out at zero time, two hour, and six hour (final time) irradiation intervals using a 5% OV-101 5' x 1/8" column at 60°C, while UV spectra were taken of each sample at zero and final irradiation time only. Concentration of photosensitizer was determined using Beer's Law plots, and percent yields of photoproducts were calculated from integrated g.c. peak areas.

Exothermicity of the Catalyzed Quadricyclene to Norbornadiene Reaction. The thermodynamics of the catalyzed retroconversion process were determined using solution calorimetry. After calibration of the calorimeter using standard procedures²⁹, thermograms were obtained for the reaction of 0.12 M quadricyclene and 0.006 M unbound Wilkinson's catalyst in chloroform solution. From this the enthalpy of reaction was calculated using standard methods of analysis.²⁹ The effects of (1) solution of the formed norbornadiene; (2) solution of the catalyst, and (3) reaction between catalyst and norbornadiene formed were determined also by obtaining thermograms for each of these processes.

Kinetics for the Catalyzed Quadricyclene to Norbornadiene Reaction. Quantitative kinetic measurements were made using nmr analysis of solutions of quadricyclene and Wilkinson's catalyst in CDCl_3 at varying time intervals. The rate of disappearance of quadricyclene was followed by integration of the multiplet at 1.4 ppm relative to TMS. The determination of the rate constant was attempted for both polymer-bound (V) and unbound (IV) Wilkinson's catalyst.

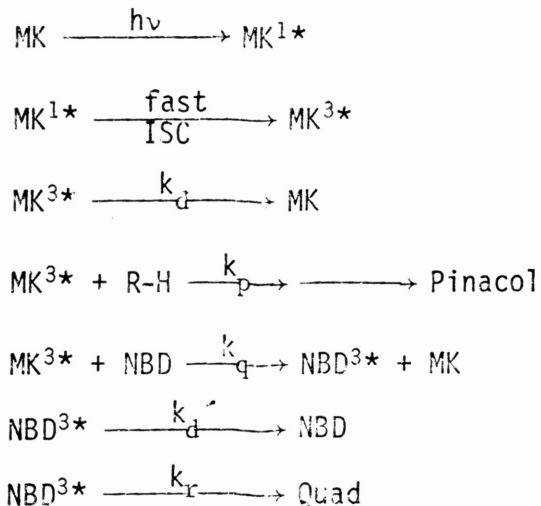
Exploration of the Dewar Pyridone (VII, $\text{R}=\text{CH}_3$) and 4 + 4 Dimer (VIII, $\text{R}=\text{CH}_3$) to N-methyl-2-Pyridone (VI, $\text{R}=\text{CH}_3$) Conversion. The invest-

igation of the thermodynamics and kinetics of the catalyzed retroconversion process was undertaken in a manner similar to that for the model system, with two exceptions noted. First, the retroconversion reaction forming VI was studied using unbound Wilkinson's catalyst only. A variety of other catalysts were also tried as mentioned earlier. Second, the kinetics of these reactions were also studied at temperatures above ambient. Solutions of VII or VIII, catalyst, solvent, and TMS (nmr internal standard) were heated at 100°C in a thermoregulated ($\pm 2^\circ\text{C}$) oil bath and examined periodically. NMR analysis for the disappearance of VII or VIII (singlet at 2.9 ppm relative to TMS) vs. TMS provided evidence of conversion.

RESULTS AND DISCUSSION

Quantitative Evaluation of the Norbornadiene Photoreaction. The photochemical conversion of norbornadiene (NBD) to quadricyclene (Quad) sensitized by Michler's ketone (MK) was investigated under a variety of conditions in which reaction solvent, reactant concentration and photosensitizer concentration were varied. The results of these experiments are summarized in Table I. The effects of these variables on several important observables, including the efficiency of quadricyclene production given as moles of quadricyclene produced per irradiation time and the efficiency of decomposition of the photosensitizer, were noted.

The observations made are consistent with the following abbreviated scheme.



The quantum yield for quadricyclene formation, ϕ_{prod} , is given by

$$\phi_{\text{prod}} = \frac{k_r k_q [\text{NBD}]}{(k_d' + k_r) (k_q [\text{NBD}] + k_d + k_p [\text{R-H}])} \quad (2)$$

A plot of ϕ_{prod}^{-1} versus $[\text{NBD}]^{-1}$ is linear with a slope given by

TABLE I: Experimental Conditions and Results^a

Initial [MND] ^b	Solvent ^c	Initial [MK] ^{b,d}	Final [MK] ^{b,e}	Final % Dec. [MK] ^{e,f}	Final Quad. Yield ^{e,g}	Rel. Quad. Yield ^h
0.197	ISP	0.018	0.013	28	122	1
0.197	ACN	0.018	0.017	6	521	4
0.197	BZ	0.018	0.010	44	942	8
0.197	ACN	0.055	0.034	38	402	3
0.197	BZ	0.055	0.028	49	902	7
0.197	BZ	0.097	0.083	14	868	7
0.197	ISP	0.009	0.005	44	304	2
0.197	ACN	0.009	0.007	22	416	3
0.197	BZ	0.009	0.004	56	926	8
0.098	ISP	0.009	0.006	33	202	2
0.098	ACN	0.009	0.004	56	314	3
0.098	BZ	0.009	0.003	67	478	4
0.393	ISP	0.009	0.006	33	385	3
0.393	ACN	0.009	0.008	11	778	6
0.393	BZ	0.009	0.004	56	1897	16
9.84	N	0.022	0.018	18	6593	54

^a Evaluated error on concentration and product yield values is 5%.

^b Concentrations expressed in moles per liter (M).

^c Abbreviations stand for: ISP = isopropanol

ACN = acetonitrile

TABLE I (cont)

BZ = benzene

N = neat (no solvent used)

- d Initial analysis conducted at zero time by absorbance measurements of the $\lambda_{\text{max}} = 350$ nm in the u.v. spectrum of Michler's ketone [III].
- e Final analysis conducted after 6 hours irradiation of the samples.
- f Percent decrease calculated as $[(\text{[III]})_i - (\text{[III]})_f] / (\text{[III]})_i \times 100$, where i = initial, f = final.
- g Yields expressed in mmol.
- h Yields given relative to sample with final quadricyclene yield = 122 mmol.

$$\frac{(k_d + k_r)(k_d + k_p[R-H])}{k_r k_q} \quad \text{and an intercept given by } \frac{k_d + k_r}{k_r} .$$

Using the data given in Table I, Figure 2 was plotted showing the reciprocal of the relative quantum yields for quadricyclene formation $(\phi_{rel})^{-1}$ as a function of the reciprocal of the initial norbornadiene concentration for each solvent. For any given concentration of norbornadiene, it can readily be seen that the largest ϕ_{rel} value was obtained using benzene, while the smallest was obtained for isopropanol. This shows that the relative quantum yield for quadricyclene formation is solvent-dependent. Thus, in terms of maximum quadricyclene production per unit irradiation time, benzene has been shown to be a better solvent for the photoreaction than acetonitrile, while acetonitrile is a better solvent than isopropanol.

Also, the reciprocal of the relative quantum yields for quadricyclene formation show a linear dependence on the reciprocal of the initial concentration of norbornadiene, as predicted by equation 2. This implies that maximization of the relative quantum yield for quadricyclene formation occurs when the concentration of norbornadiene is at a maximum.

Another interesting feature of the photosensitized reaction of norbornadiene forming quadricyclene concerns the effect that photosensitizer concentration has on the relative quantum yields for formation of quadricyclene. While photosensitizer concentration does not directly affect the ϕ_{prod} given in equation 2, it does affect the relative quantum yield ϕ_{rel} . The extent of this effect is shown in Figure 3 by a plot of the relative quantum yields for production of quadricyclene (ϕ_{rel}) as a function of initial concentration of photosensitizer (III) (using the data given in Table I) for two solvents (insufficient data for isopropanol). The plot

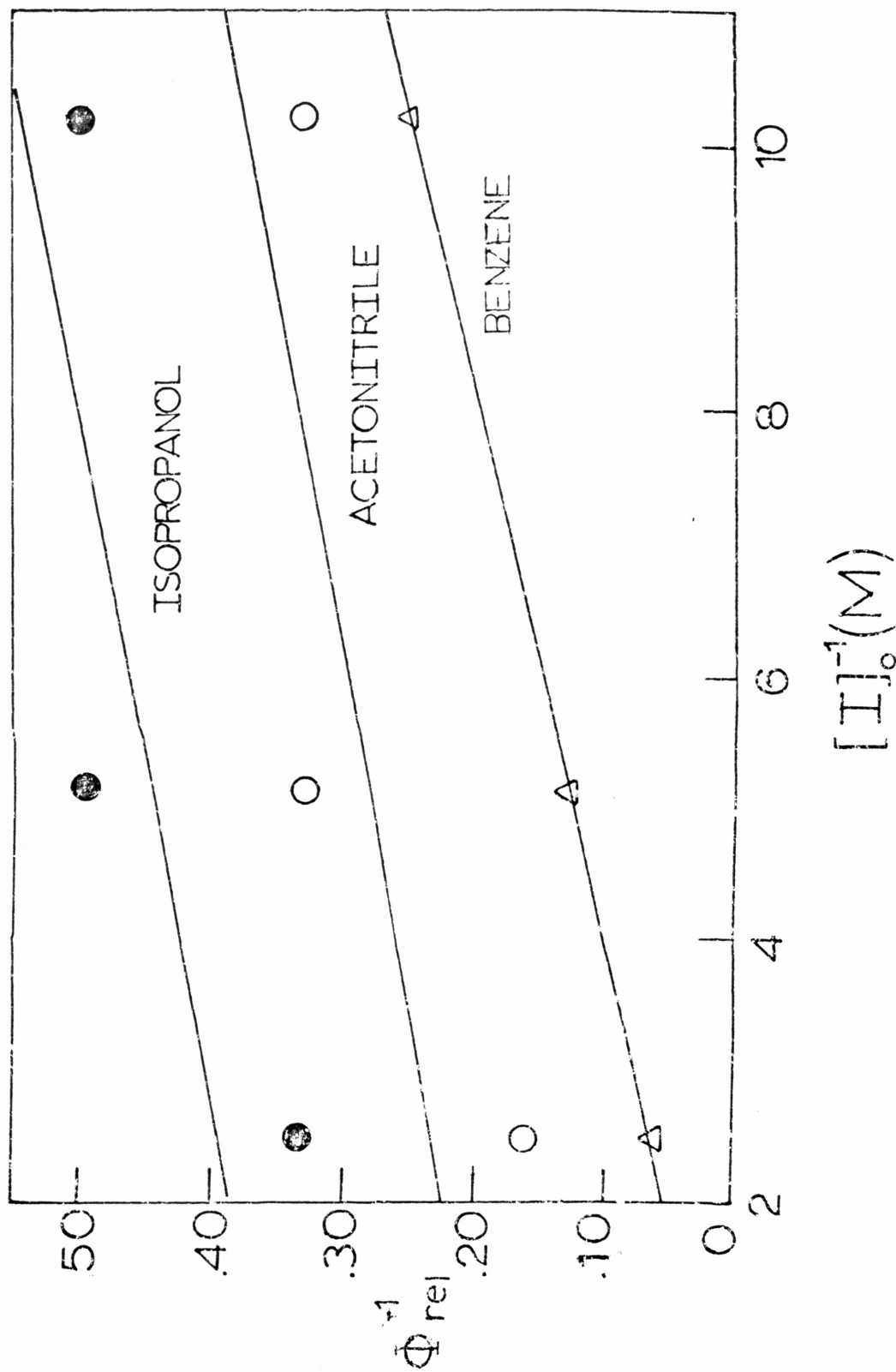


Fig. 2. A plot of the reciprocal of the relative quantum yields for production of quadricyclene (ϕ_{rel})⁻¹ vs. the reciprocal of the initial concentration of norbornadiene $[I]_0^{-1}$, for $[Michler's\ ketone]_0 = .609M$.

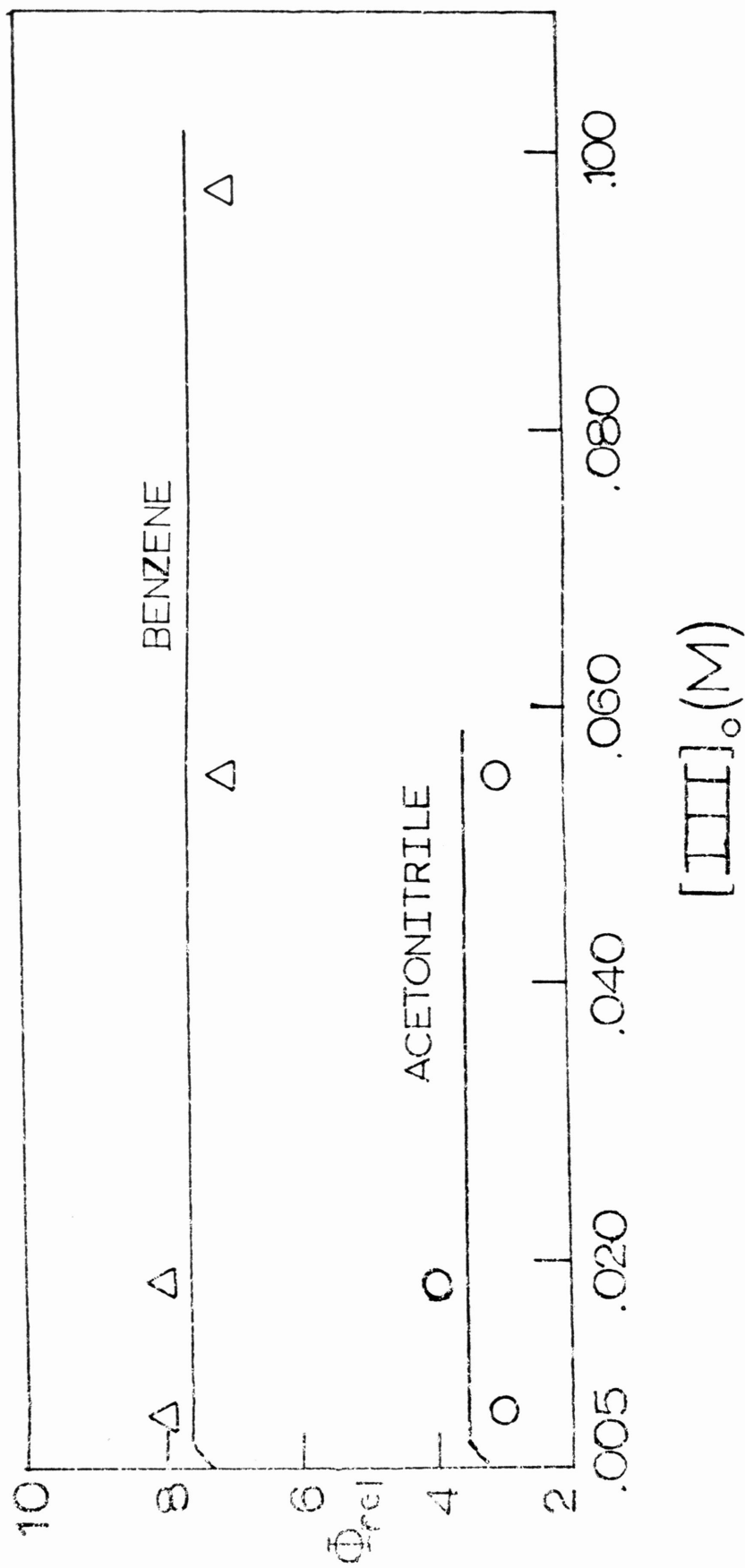


Fig. 3. A plot of the relative quantum yields for production of quadricyclene (ϕ_{rel}) vs. initial concentration of Michler's ketone $[III]_0$, for $[norbornadiene]_0 = .197M$.

shows a leveling off of the ϕ_{rel} as the initial concentration of Michler's ketone increases. This indicates that as the initial concentration of sensitizer becomes large, the absorbance of Michler's ketone in solution with norbornadiene reaches a maximum value beyond which no further absorption of light by the sensitizer occurs, thereby causing the relative quantum yield for formation of quadricyclene to level off. Thus, although Beer's Law predicts a linear increase in absorbance with concentration of chromophore, a limit is reached when all of the incident light is being absorbed by the chromophore. Determining this limit for the particular conditions used would thus prevent using unnecessarily excessive amounts of sensitizer for the reaction.

From the reaction scheme given earlier, another quantity can also be derived. This quantity is the quantum yield for disappearance of Michler's ketone (ϕ_{dis}), given as

$$\phi_{dis} = \frac{k_p[R-H]}{k_p[R-H] + k_d + k_q[NBD]} \quad (3)$$

A plot of ϕ_{dis}^{-1} versus $[NBD]$ is linear with slope $(k_p[R-H])^{-1}$ and intercept $\frac{k_d + k_q[R-H]}{k_p[R-H]}$.

Using the data given in Table I, a plot is shown in Figure 4 of the reciprocal of the quantum yields for disappearance of Michler's ketone (ϕ_{dis}^{-1}) as a function of the initial concentration of norbornadiene for each solvent used. The graph reveals an interesting trend. For a given initial concentration of norbornadiene ($>0.180M$), isopropanol has a larger value of ϕ_{dis} than does acetonitrile. This provides evidence for a photoreductive-type mechanism in the photoreaction of Michler's ketone involving the following steps (illustrated using isopropanol).

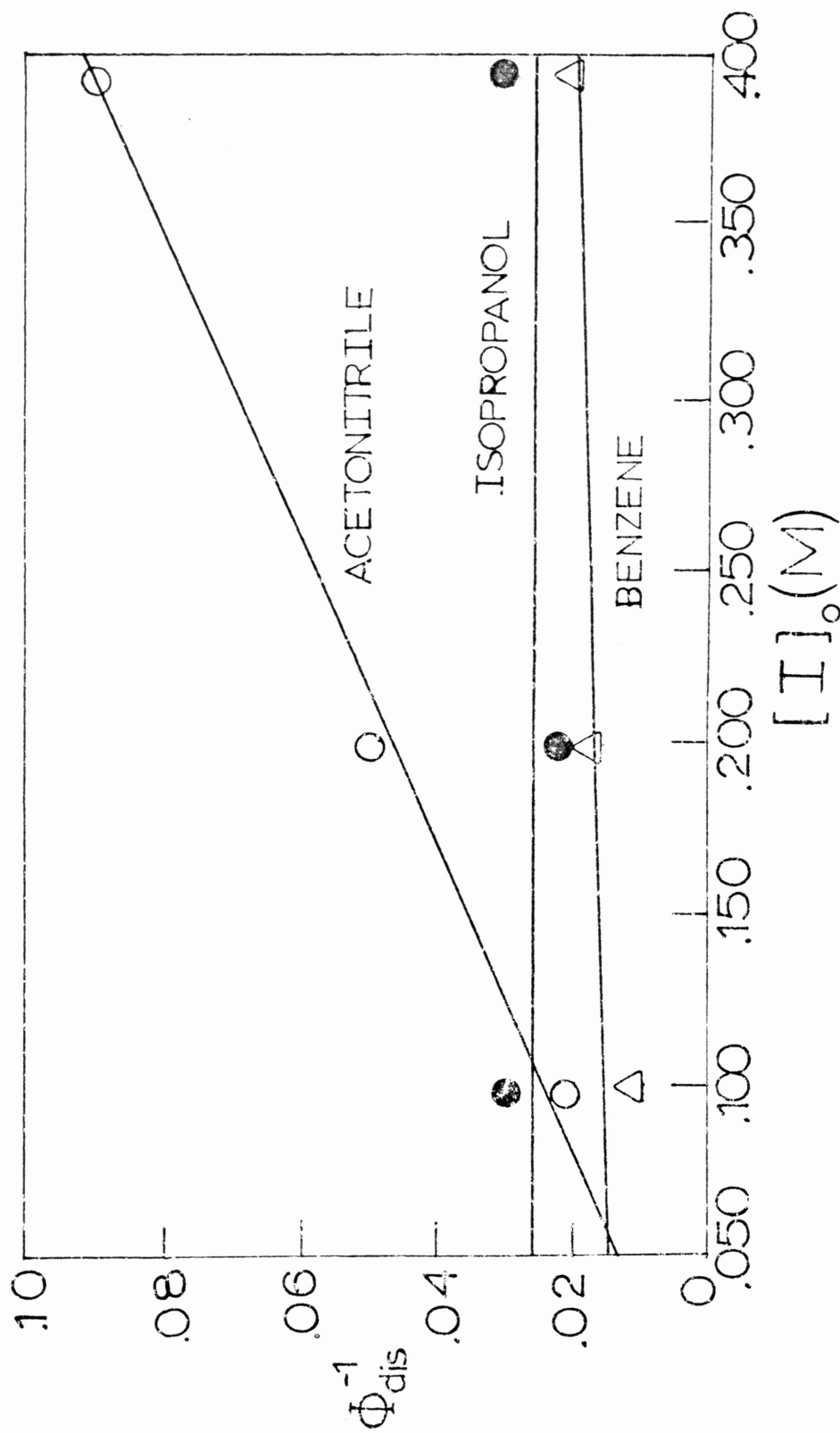
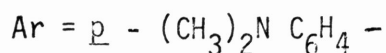
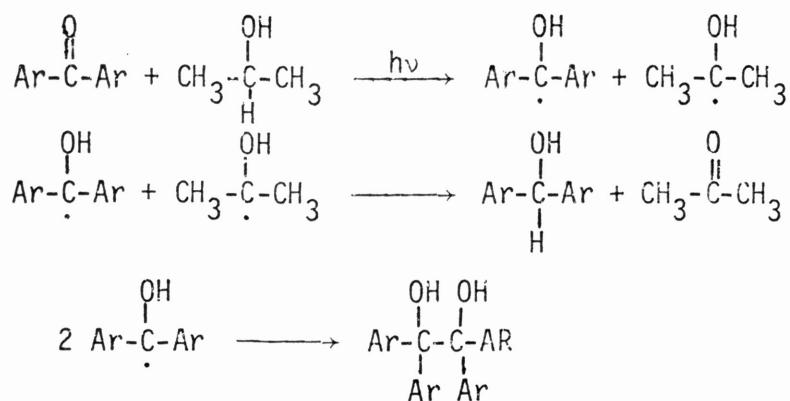


Fig. 4. A plot of the reciprocal of the quantum yields for disappearance of Michler's ketone (III) [Φ_{dis}^{-1}] vs. the initial concentration of norbornadiene $[I]_0$, for $[III]_0 = .009M$.



The dimethylcarbinol radical formed in the first step by hydrogen atom abstraction from isopropanol is more stable than the corresponding radical formed by hydrogen atom abstraction from acetonitrile. Thus, the k_p for the isopropanol reaction is larger than that for the acetonitrile reaction resulting in the larger ϕ_{dis} noted for isopropanol.

Figure 4 also show a linear dependence between ϕ_{dis}^{-1} and the initial concentration of norbornadiene, as predicted by equation 3. This implies that norbornadiene is effectively quenching the excited triplet states of Michler's ketone (which are the reactive species undergoing photoreduction). This quenching process involving triplet energy transfer effectively deactivates the photoreductive conversion described above, resulting in lower ϕ_{dis} values at large concentrations of norbornadiene.

In summary, the above data are fully consistent with a triplet photosensitization scheme in which triplet-excited norbornadiene, produced by energy transfer from Michler's ketone, undergoes internal cycloaddi-

tion to produce quadricyclene. Irradiation of benzene solutions utilizing high concentrations of norbornadiene maximizes the relative quantum yield for formation of quadricyclene (ϕ_{rel}) and minimizes the quantum yield for disappearance of Michler's ketone (ϕ_{dis}). Also, it has been shown that for a given solvent and concentration of norbornadiene, a critical concentration of Michler's ketone exists at which all of the incident light is absorbed, thus preventing a further increase in the relative quantum yield for production of quadricyclene (ϕ_{rel}). With this information, the forward photoreaction forming quadricyclene has been fully characterized for this system.

Exothermicity of the Catalyzed Quadricyclene to Norbornadiene Reaction. The reaction of quadricyclene with the unbound Wilkinson's catalyst (IV) was carried out in a solution calorimeter. The thermograms obtained were analyzed to derive the enthalpy, ΔH_R , of the reaction. As mentioned earlier, the values of ΔH_R obtained in this manner are uncorrected for such effects as the heat of solution of the catalyst and the formed norbornadiene, as well as the heat of reaction of catalyst with norbornadiene. The magnitudes of each of these effects were determined as described previously and subtracted from the uncorrected ΔH_R values to obtain a final corrected enthalpy value, ΔH_R (corr), for the catalyzed reaction of II \rightarrow I. The results are shown in Table II. A comparison of these results with literature values is shown in Table III. As can be seen the enthalpy values obtained compare quite favorably with those found in the literature, indicating that the instrumentation and techniques employed are sound. The error associated with these measure-

TABLE II

Enthalpy of Isomerization of Quadricyclene to Norbornadiene at 25°C^{a,b,c}

Trial #	$-\Delta H_R$ (tot)	$-\Delta H_R$ (sol'n I)	$-\Delta H_R$ (sol'n IV, reaction IV and I)	$-\Delta H_R$ (corr) ^d
1	309.45	4.65	20.17	-
2	291.13	4.02	15.90	-
3	273.08	4.58	-	-
$\overline{\Delta H_R}^e$	287±47	4.4±0.9	18±9	265±48

a All enthalpy values in units of cal/g.

b Symbols stand for: $\Delta H_p(\text{tot}) = \text{uncorrected enthalpy of reaction}$; $\Delta H_R(\text{sol'n I}) = \text{enthalpy of sol'n of I}$; $\Delta H_R(\text{sol'n IV, reaction IV and I}) = \text{enthalpy of sol'n of IV, and enthalpy of reaction of IV and I}$.

c Uncertainties given as 2s.

d Symbol stands for: $\text{corrected enthalpy of isomerization reaction}$; obtained by subtracting enthalpy terms $\Delta H_R(\text{sol'n I})$ and $\Delta H_R(\text{sol'n IV, reaction IV and I})$ from $\Delta H_R(\text{tot})$.

e Symbol stands for the calculated mean enthalpy.

TABLE III

Comparison of ΔH_R Values with Literature at 25°C

Reaction	$-\Delta H_R(\text{expt.})$ [kcal/mol]	$-\Delta H_R(\text{lit.})$ [kcal/mol]	% Difference
$\Delta H_R(\text{sol'n I})$	0.41 ± 0.08	0.497 ± 0.002 ³⁰	19.0
$\Delta H_R(\text{corr.})$	24 ± 4	24 ± 1 ³¹	0.0
		26.2 ± 0.2 ³⁰	9.0

ments, ~10%, appears to be low enough that comparisons can be made with ΔH_R values obtained for other systems in the future.

Thus, the catalyzed reaction of quadricyclene to norbornadiene has been shown to be a reasonably exothermic one, releasing 24 kcal per mole of quadricyclene reacted. This information characterizes the thermodynamics of the retroconversion reaction of quadricyclene to norbornadiene.

Kinetics for the Catalyzed Quadricyclene to Norbornadiene Reaction.

The kinetics for the isomerization reaction of quadricyclene to norbornadiene were investigated using both polymer-bound (V) and unbound (IV) Wilkinson's catalyst. Following the reaction by nmr, the conversion was found to be first-order in quadricyclene. First-order plots were quite good for both types of catalyst, but the reaction using the unbound catalyst (IV) was kinetically well-behaved only to one half-life with catalyzed isomerization finally coming to an end before completion, while the reaction using the polymer-bound catalyst (V) was kinetically well-behaved over several half-lives with almost 100% conversion to norbornadiene. The deviation from first order after one half-life for the conversion utilizing the unbound catalyst (IV) has been rationalized for similar reactions as being due to alteration of the catalyst, thereby mitigating high conversion to norbornadiene.³² Some feature of the conversion using polymer-bound catalyst (V) apparently suppresses the catalyst-altering reactions thereby enabling high conversion to norbornadiene.

Using pseudo-first order rate constants calculated from the plots mentioned above and initial catalyst concentrations, second-order rate constants (k_2) were derived and are shown in Table IV for both types of

TABLE IV

Results and Comparison of Kinetic Measurements of Valence Isomerization of Quadricyclene to Norbornadiene Using Polymer-bound (V) and Unbound (IV) Wilkinson's Catalyst.^{a,b}

Catalyst	$k_2, M^{-1}s^{-1}$	k_{rel}
IV ^c	7.0×10^{-1}	9
V ^d	8.0×10^{-2}	1

a At 35°C; [quadricyclene] = 1 M.

b Estimated rate constant error $\pm 25\%$.

c [catalyst] = $5.49 \times 10^{-4}M$.

d [catalyst] = $1.15 \times 10^{-2}M$.

catalyst. A classical second-order catalytic rate law has been shown to be obeyed in this reaction using similar catalysts.¹³ As shown by the k_{rel} values, the rate of conversion using unbound catalyst is nine times greater than the rate using the polymer-bound catalyst. This would be expected since the catalyst anchored to a polymer support is somewhat sterically-hindered from reaction with the substrate, perhaps causing inefficient substrate diffusion to catalytic sites within the polymer, resulting in a slower rate of isomerization of the quadricyclene. However, the important feature here is that the rate of reaction is not drastically lowered by using the polymer-bound catalyst, as might be expected from consideration of effects such as the steric effect mentioned above. In fact, at the catalyst concentrations and temperature shown in Table IV, the conversion using the polymer-bound catalyst proceeded with a half-life of ~20 minutes. This, along with the better conversion to norbornadiene obtained with the polymer-bound catalyst, makes it an attractive catalyst for use with the norbornadiene-quadricyclene system in a HELEOS-type application.

The results obtained thus far from studies of the photoproduction of quadricyclene and the thermodynamics and kinetics of the catalyzed retroconversion reaction forming norbornadiene strongly indicate that this system has high potential for use in HELEOS.

Exploration of the Dewar Pyridone (VII, R=CH₃) and 4 + 4 Dimer (VIII, R=CH₃) to N-methyl-2-Pyridone (VI, R=CH₃) Conversion. The results obtained by analyzing the N-methyl-2-pyridone (VI, R=CH₃) system will now be discussed and used as the basis for choosing the system better suited

for application in HELEOS.

The isomerization of VII and VIII to VI ($R=CH_3$) was attempted using a variety of catalysts at ambient and elevated temperatures. Both VII and VIII resisted catalytic reversion to VI at temperatures up to 100°C using high catalyst concentrations (~ 5 mol %) of PdCl_2 , $\text{Rh}_2(\text{NOR})_2 \text{Cl}_2$, $\text{Rh}(\text{P}\emptyset_3)_3 \text{Cl}$, CuSO_4 , AgNO_3 , $\text{CF}_3\text{CO}_2\text{H}$, H_2SO_4 , and *p*-toluenesulfonic acid. Both VII and VIII are also thermally stable at and below 100°C , the thermal isomerization of VII to VI proceeding with a half-life of 142 hours at 100°C .¹⁹

The extreme reluctance of the Dewar pyridone and the 4 + 4 dimer to isomerize is somewhat surprising in view of the facile catalyzed ring openings of substituted Dewar-benzenes such as the Rh(I) catalyzed conversion of hexamethyl-Dewar-benzene to hexamethyl benzene.³³ Reasons for the markedly low reactivity of VII and VIII in comparison with substituted Dewar-benzenes may include the following. First, the presence of the carbonyl group(s) in VII and VIII might be responsible for a rate retardation of up to three orders of magnitude, as noted for similar reactions with compounds containing a carbonyl group.^{16,34} This deceleration has been rationalized in terms of electronic and steric factors,³⁵ and could be an important factor here. Second, although the conversion of VII and VIII to VI possesses a large potential exothermicity, a more important factor controlling the rates of transition-metal-catalyzed valence isomerizations has been theorized to be the degree and kind of local bond deformation that is present in the strained reactant. A change of three orders of magnitude in the rate of conversion can occur by changing the degree of local bond angle deformation and the number of deformed

bonds in the reactant.³² This dependence of the rate of isomerization on local bond angle deformation has been related to the ability of the strained ring to form bonds with the transition metal in the role of a base, oxidizing agent, nucleophile, or electron donor, thereby effecting a ring opening reaction forming the low energy valence isomer.³² It appears that high energy content is a necessary but not sufficient condition for the exothermic valence isomerizations to occur with an appreciable rate. Thus, the bond angle requirements for facile reaction of substrate with metal catalyst may not be met for the Dewar pyridone or 4 + 4 dimer reaction, accounting for the lack of reactivity with this system. Finally, the effect of solvent on the rate of conversion was not investigated, and could play some part in the rate retardation.

Thus, due to effects such as those discussed above, the Dewar pyridone and 4 + 4 dimer system has been shown not to undergo facile catalyzed retroconversion to the starting pyridone VI at temperatures at or below 100°C. The thermodynamics of the thermal isomerization were not investigated, since the instruments for measuring such heat changes at elevated temperatures were not readily available. However, failure of the Dewar pyridone and 4 + 4 dimer to isomerize via transition metal catalysts under 100°C probably eliminates that system from further consideration for application in HELEOS unless some way is found to alter the effects discussed earlier so as to allow the catalyzed retroconversion to VI to occur with an appreciable rate.

CONCLUSION

From the results obtained, the model system consisting of norbornadiene (I) and quadricyclene (II) was shown to be well-suited for use in a HELEOS-type application, both in terms of production of fuel and the reactivity of the fuel under catalytic conditions to reform the starting compound and subsequently release heat. The pyridone system consisting of N-methyl-2-pyridone (VI), Dewar pyridone (VII), and the 4 + 4 dimer (VIII, R=CH₃) was shown not to undergo the catalytic retroconversion reaction necessary for application in HELEOS. This illustrates the fact that, although many compounds appear to be capable of undergoing the valence isomerization reactions necessary for implementation in HELEOS (depicted earlier by equation 1), many factors are involved and indeed only a rather small group of compounds may actually be found that are useful in this application. The future uncovering and evaluation of these compounds may perhaps provide a system better suited than the model system investigated here for use in HELEOS. It is hoped that through continued research such as this, such a solar energy storage plan can become a viable part of the world's future energy resources.

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