recombination ratio for cyclohexyl radicals, which is 1.3.[7] There are more equations (A–I) than unknowns, and the set is easily solved; the redundancy supplies a check for internal consistency. The important yield values are

$$G_7 \equiv G_m(H_2) \equiv G_m(C_6H_{10}) = 1.0 \qquad G_8 = 2.3$$

$$G_b = G(H) = 2.1 \qquad G_3 = 1.0\text{–}1.4$$

$$G_4 = 3.4$$

The two values of G_3 come from (F) and (G), and the agreement reflects the amount of internal consistency in the calculations. The values of these yields are in reasonable accord with those to be expected from the literature and from comparison with other experiments. G_7 is the "molecular" yield of hydrogen or cyclohexene; our value of 1.0 is lower than that observed by Cher for cyclohexene–cyclohexane solutions[2] (where the solute is acting solely as a radical scavenger, and little energy transfer occurs) of 1.66. A lowering of the molecular yield would be expected since the value of $G_8 = 2.3$ shows that a considerable amount of energy transfer must be taking place. In fact, if the value of G_a is taken to be 5.4, then the value of G_7 should be $(3.1/5.4) \times 1.66 = 0.96$, which is in excellent agreement with the experiment. The value of $G(H)$ in the quinone solution is similarly calculated to be 2.1, which compares equally well with $G_b = 2.1$.

The value of 2.3 for G_8, the energy-transfer reaction, is also obtained from $\Delta G(H_2)$, which is $5.4 - 3.1 = 2.3$. The relative values of G_8 and G_3 give the fraction of quinone molecules which accept energy from cyclohexane and then immediately react with cyclohexane according to (3). This fraction is about 1.3/2.3, or

about 0.5; this can be compared with the quantum yield of 0.5 observed for the photochemical reaction (3) although this is not to say that the quinone is necessarily in the same excited state in each case.

We feel that this combination of complete product determination, with the stoichiometric analyses, the tracer experiments, and the demonstration of a pertinent photochemical process, has enabled a firm and complete description of the principal reaction paths in the radiolysis of cyclohexane solutions of quinone. It is evident that both radical scavenging and energy transfer are taking place and that nearly one-half of the excited cyclohexane molecules which would normally dissociate are deactivated by the quinone. One of the most striking features of the analysis is the conclusion that hydrogen atoms are not scavenged by the quinone. The possibility can be considered that (6) is fast enough to consume all the H atoms before they encounter a quinone molecule, as follows. The collision frequency in liquid is about 10^{13} sec.$^{-1}$, and the abundance of quinone molecules in 40 mM solutions is 1/250, so that the collision efficiency of H atoms with C_6H_{12} would have to be better than 1/250 for them all to react with cyclohexane before an encounter with a quinone molecule. The reported[8] collision yield (in gas phase) for the reaction of hydrogen atoms with cyclohexane is much less than this, about 10^{-7} at room temperature. Reaction 6 hardly seems fast enough to explain the facts, and explanation must reside in some peculiarity of the quinone–hydrogen atom interaction.

Acknowledgment. We wish to acknowledge helpful conversations with other members of the North American Aviation Science Center, particularly those with John Y. Yang.

(7) C. E. Klots and R. H. Johnsen, *Can. J. Chem.*, 41, 2702 (1963).

(8) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth and Co. Ltd., London, 1955, p. 177.

A Photoisomerization Reaction of Cyclic Ketones in the Liquid Phase[1]

R. Srinivasan and S. E. Cremer

Contribution from the IBM Watson Research Center, Yorktown Heights, New York. Received November 7, 1964

It has been found that six-, seven-, and eight-membered cyclic ketones, when irradiated as pure liquids with light of 3130 Å., undergo a ring contraction reaction to give the 2-methyl derivative of the cyclic ketone with one less carbon. The reaction accounts for 6% of the cyclohexanone that undergoes photolysis but only 0.2% in cycloheptanone. A variant of this reaction gives 2-n-propylcyclopentanone in the photolysis of cyclooctanone. In cyclohexanone the reaction has a quantum yield of 0.03. This value decreases in solutions of cyclohexanone in cyclohexane. At a given concentration, the addition of cyclohexene has no effect on the yield. Substitution of the ring by a methyl group in the 2-position seems to obscure the reaction, while in the 3-position only one of the two possible dimethylcyclopentanones is formed. In the photolysis of cyclohexanone-2,2,6,6-d_4, the product corresponded to $\overline{COCH(CHD_2)CH_2CH_2CD_2}$. The reaction is believed to involve the transfer of a proton from the 3- to the 2-position in a configuration in which the ring is substantially intact.

Introduction

Although the photochemical reactions of cyclic ketones in the condensed phase were first studied 50 years ago,[2,3] there has been no systematic study up to

(1) For a preliminary communication, see S. E. Cremer and R. Srinivasan, *J. Am. Chem. Soc.*, 86, 4197 (1964).

(2) G. Ciamician and P. Silver, *Chem. Ber.*, 41, 1071 (1908).

(3) G. Ciamician and P. Silver, *ibid.*, 42, 1510 (1909); 46, 3077 (1913).

now. The reactions in the vapor phase which have been studied in detail[4,5] have demonstrated the effect of pressure quenching of vibrational energy on these molecules. On that basis it can be predicted that the reactions of importance in the condensed phase would not be the same as in the gas phase. This study was undertaken to obtain systematic data on five-, six-, seven-, and eight-membered cyclic ketones. A review of the literature on the photochemistry of these compounds has been published recently.[6]

Experimental

Materials. Commercial samples of cyclohexanone (Baker), cycloheptanone (K and K Laboratories, Aldrich Chemical Co.), cyclooctanone, 2-methylcyclohexanone, and 3-methylcyclohexanone (K and K Laboratories) were distilled on a spinning-band column (18 in.). A middle cut, boiling over a narrow temperature range, was used in each case. Vapor phase chromatographic analysis showed no detectable impurities in any of the samples. Fenchone and β-tetralone were good commercial grade samples (K and K Laboratories) which were used as obtained. Cyclohexanone-2,2,6,6-d_4 was prepared by repeated exchange between cyclohexanone and deuterium oxide in the presence of potassium carbonate as catalyst. Instead of pure cyclohexanone, a solution of the ketone in cyclohexane was used. This procedure kept condensation reactions of the ketone to a minimum. After seven exchanges, about 3.8 of the four exchangeable protons had been replaced by deuterium.

Apparatus. Two experimental systems were used. Photolysis on a preparative scale was conducted in a cylindrical Pyrex cell 10.7 cm. long and 2.7 cm. in diameter. The light source was a 1000-w. GE AH-6 water-cooled, high pressure mercury arc. The lamp and the cell were at the two foci of an elliptical reflector of polished aluminum. The distance from the lamp to the cell was 22 cm. Forced air circulation maintained the temperature of the cell at about 50°. Photolysis on a quantitative basis was conducted in a quartz cell 3.5 cm. in diameter and 0.5 cm. thick. Light from a 500-w. Hanovia high pressure arc was collimated by a quartz lens, filtered through 2 mm. of Pyrex, and used as the source. The intensity of the radiation at 3130 Å. as calibrated with a diethyl ketone actinometer (vapor at room temperature, $\Phi = 0.62$)[7] was 1.7×10^{16} quanta/sec. Even when a 5% solution of cyclohexanone in cyclohexane was used, radiation at 3130 Å. that entered the cell was completely absorbed by the ketone. The solutions were not degassed, but it is unlikely that the results were influenced by oxygen to any extent, as the small amount of oxygen in the condensed phase could not have been readily replaced during photolysis. The solutions were stirred intermittently.

Analysis. In preparative photolysis, work-up of the material was by fractional distillation and preparative gas chromatography. An Aerograph Autoprep fitted with a 20-ft. silicone column was used. In the quantita-

tive studies on cyclohexanone, analysis was carried out on a 2-m. Ucon oil column at 90° fitted to a Perkin-Elmer gas chromatograph.

Results

Products. Photolysis of six-, seven-, and eight-membered cyclic ketones at room temperature as pure liquids gave rise to condensed material as the major product. This material was yellow and gave a green fluorescence when excited by 3130-Å. radiation. There is reason to believe that the presence of the condensed product slowed down the photoisomerization of the ketones. The formation of these high boiling materials was much more rapid in the photolysis of cycloheptanone and cyclooctanone than in cyclohexanone.

Photoisomerization of cyclohexanone at 3130 Å. in the pure liquid state gave a product which accounted for ~6% of ketone that disappeared. Its infrared spectrum showed that it was a carbonyl compound (1740 (s) cm.$^{-1}$), presumably a five-membered cyclic ketone. The presence of C–CH$_3$ (1375 cm.$^{-1}$) and –CH$_2$–CO (1407 cm.$^{-1}$) groups was also indicated. It was found that the product was identical with 2-methylcyclopentanone (A) in its infrared spectrum, retention time on a gas chromatographic column, and the melting point and mixture melting point of its semicarbazone. The photoisomerization of cyclohexanone to 5-hexenal was also observed, but the relative importance of this reaction was a function of the extent of photolysis.

Irradiation of cycloheptanone as a pure liquid gave only a minor (<1%) amount of isomeric products. These consisted of 6-heptenal and a compound which accounted for 0.2% of the ketone that was photolyzed. The infrared spectrum of the unknown compound indicated the presence of a carbonyl group (1718 cm.$^{-1}$) and a methyl group (1380 cm.$^{-1}$). The compound was identified as 2-methylcyclohexanone by comparison of its infrared spectrum, retention time on a gas chromatograph, and the melting point of its semicarbazone with those of an authentic sample. 6-Heptenal was formed in smaller yield than 2-methylcyclohexanone. A more important product than either of the isomers was cycloheptanol.

Irradiation of cyclooctanone as a pure liquid gave a mixture of three isomers which together accounted for 2.5% of the ketone that was photolyzed. One of the isomers, which amounted to $^1/_8$ of the total, was an aldehyde (1725, 2710 cm.$^{-1}$) which showed unsaturation (997 (w), 975 (s), 915 (m) (cm.$^{-1}$)). The product may have been *trans*-octenal mixed with some 7-octenal. The major isomer (>$^4/_8$) was a ketone (1741 cm.$^{-1}$) located in a five-membered ring. It had a C-methyl group (1378 cm.$^{-1}$) but no *gem*-dimethyl group. The n.m.r. spectrum showed no unsaturation and protons from τ 7.5 to 9.2. The compound was identified as 2-*n*-propylcyclopentanone by comparison with an authentic sample, which was prepared as described by Chatterjee.[8] The third isomer was also a ketone (1710 cm.$^{-1}$) with a C-methyl group (1375 cm.$^{-1}$). The n.m.r. spectrum showed a broad absorption from τ 7.3 to 8.8 which corresponded to 11 protons while a doublet centered at τ 8.95 corresponded to 3 protons. The structure of 2-methylcycloheptanone would agree

(4) S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **64**, 80 (1942).
(5) R. Srinivasan, *ibid.*, **81**, 1546 (1959); **83**, 4344, 4348 (1961).
(6) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).
(7) K. O. Kutschke, M. H. J. Wijnen, and E. W. R. Steacie, *J. Am. Chem. Soc.*, **74**, 714 (1952).

(8) D. N. Chatterjee, *ibid.*, **77**, 414 (1955).

with these observations. The identity of the compound was proved by a comparison of its properties with those of an authentic sample.[9]

In the photolysis of 2-methylcyclohexanone as a pure liquid no ketonic product was detected. 5-Heptenal, the formation of which has been reported before,[10] was formed in 20% yield. Its infrared spectrum agreed with that described before in all respects except for the absorption at 756 (s) cm.$^{-1}$ which was absent. The n.m.r. spectrum agreed with this identification.

Irradiation of 3-methylcyclohexanone as a pure liquid gave about 1.5% of isomeric products. The major isomer ($^2/_3$) was an aldehyde (1745, 2750 cm.$^{-1}$) with a terminal double bond (1642, 915, 995 cm.$^{-1}$). The n.m.r. showed that it had four sets of protons of relative areas 1:3:5:3 which were located at τ 0.28, 4.50, 7.82, and 9.05. These data show that the product was $CH_2=CHCH_2CH(CH_3)CH_2CHO$ rather than $CH_2=C(CH_3)CH_2CH_2CH_2CHO$. A weak absorption in the infrared at 890 cm.$^{-1}$ may correspond to a $CH_2=C(CH_3)$ group from the latter compound. However, since the integration of the n.m.r. spectrum fitted the first structure very well, the second compound was possibly present only, if at all, in small amounts.

The second isomer was a ketone (1748 cm.$^{-1}$) possibly in a five-membered ring. It also had C-methyl groups (1381 cm.$^{-1}$). There was no indication of $>C(CH_3)_2$ or unsaturation in the infrared spectrum. Of the possible structures, 2-ethylcyclopentanone was excluded by comparison with an authentic sample. The n.m.r. spectrum showed two broad absorptions centered at τ 7–9 and 8–9, respectively, of equal area. This spectrum would be in agreement with both 2,4-dimethylcyclopentanone and 2,2-dimethylcyclopentanone. But the splitting of the absorption owing to the methyl groups at τ 8.9 excluded the 2,2-dimethylcyclopentanone structure.

Irradiation of both fenchone and β-tetralone gave no detectable yield of isomeric products although considerable decomposition to give both volatile products (especially in the former instance) and condensed material was evident.

From the irradiation of cyclohexanone-2,2,6,6-d_4, 5-hexenal-d_4 and 2-methylcyclopentanone-d_4 were isolated as products. The n.m.r. spectrum of the ketone showed two regions of broad absorption which were centered at τ 7.9 and 8.9, respectively. It was known from the n.m.r. spectrum of 2-methylcyclopentanone that the latter absorption was due to the protons on the methyl group. The absorption in 2-methylcyclopentanone-d_4 corresponded to one proton. Double irradiation of the sample at 9.2098 Mc. as the second frequency decoupled the splitting owing to the deuterium atoms, and the absorption due to the single proton on the methyl group was resolved into a doublet of coupling constant 6.1 c.p.s., which was identical with the splitting in the methyl group in 2-methylcyclopentanone. This strongly indicated that the structure of the 2-methylcyclopentanone-d_4 that was obtained was

$$\begin{array}{c} O \\ \parallel \\ D_2C{-}\overset{C}{\underset{H_2C{-}CH_2}{\diagdown}}\overset{CH_2H}{\underset{CH}{\diagup}} \end{array}$$
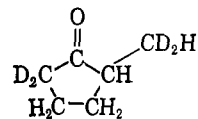
The aldehyde clearly showed the C–H stretch frequency at 2720 cm.$^{-1}$ owing to a –CHO group, and the n.m.r. spectrum showed one aldehydic proton (τ 0.2), only one vinylic proton (τ 4.2), and four protons at τ 8, so that the structure would be $CD_2=CHCH_2CH_2CD_2CHO$.

Rate Studies. In the photolysis of pure liquid cyclohexanone the rate of formation of 5-hexenal at constant absorbed intensity was a maximum at zero time and decreased steadily with increasing time.[1] The formation of 2-methylcyclopentanone showed no such effect but was linear with time. The effect of a nonpolar solvent on the formation of these two products is given in Table I. Included in this table is the effect of cyclohexene.

The quantum yield for the formation of 2-methylcyclopentanone from pure liquid cyclohexanone was 0.03. The quantum yield for 5-hexenal was time dependent, but the maximum value that could be directly determined was 0.26. This is in good agreement with the value reported before.[10] Although in that work it was not realized that the value was time dependent, it can be estimated that it was determined at very low conversion ($\sim 1\%$).

The material yield as a function of time for the formation of 5-heptenal in the photolysis of 2-methylcyclohexanone as a pure liquid is shown in Figure 1.

Vapor Phase Reaction. The photolysis of cyclohexanone in the vapor phase at 3130 Å. at a pressure of 370 mm. at 140° and a pressure of 8.2 mm. at 90° was investigated in two runs. The v.p.c. analysis of the fraction that was condensable at $-78°$ did not indicate the formation of any 2-methylcyclopentanone. On the basis of a quantum yield of unity for Φ_{CO}, it was calculated that the quantum yield for 2-methylcyclopentanone, if formed, would be of the order of 0.01 or less.

Table I. Rates of Formation of 2-Methylcyclopentanone (MCP) and 5-Hexenal (H) as a Function of Time[a]

Time, min.	Product	Pure cyclohexanone	50% solution	5% solution	50% with 10% cyclohexene
		Rate, μmoles/min. $\times$ 10^{4b}			
100	MCP	...[c]	...[c]	...[c]	
	H	63.40	41.35	1.89	N.d.[d]
200	MCP	4.96	4.14	0.20	
	H	30.33	27.57	0.62	N.d.
400	MCP	5.24	4.14	0.18	
	.H	17.64	0.99	0.56	N.d.
1000	MCP	5.51	4.45	...[e]	4.48
	H	4.41	0.55	...	...
1600	MCP	5.68	4.41		
	H	2.21	~ 0		

[a] Solvent: cyclohexane; high pressure mercury arc; Pyrex filter (2 mm.). Solutions not degassed; intermittent stirring. [b] Since determinations were not made at identical time intervals in all four instances, the values reported here have been interpolated from experimental values. [c] Too small to be measurable. [d] N.d. = not determined. [e] The decomposition of cyclohexanone was 40% at this point; since the photolysis of the primary products was observed, quantitative data were not obtained at higher conversions.

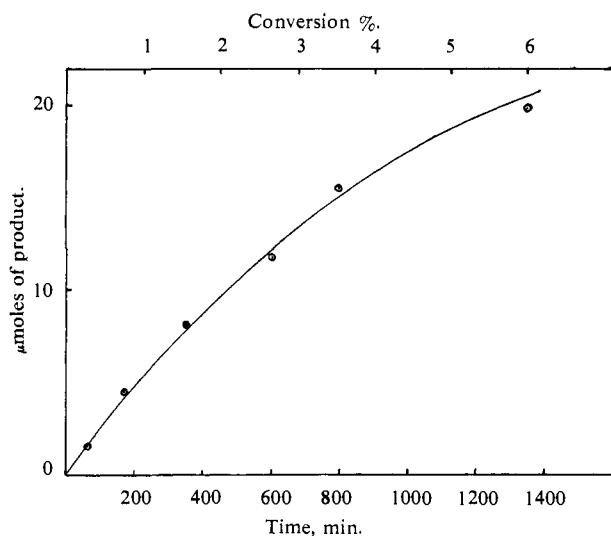(10) R. Srinivasan, *J. Am. Chem. Soc.*, 81, 2601 (1959).

Figure 1. Yield of 5-heptenal in the photolysis of 2-methylcyclo-hexanone at 3130 Å. as a pure liquid. Conversion refers to ketone that had been photolyzed. At the point marked with a filled circle the quantum yield was 0.48.

Discussion

The data indicate that six-, seven-, and eight-membered cyclic ketones undergo a general photochemical reaction which can be written as
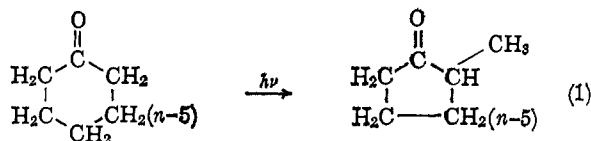

It is unfortunate that the reaction could not be studied in the vapor phase as it would then have been possible to obtain evidence for its mechanism which would have been unequivocal. As it is, the possibilities that have to be considered are that the reaction is a primary process or that the reaction is derived from an initial product of photolysis by a secondary photochemical reaction. The data in Table I indicate that the formation of the ring-contracted product from cyclohexanone is linear with time at conversions from 3 to 10%. However, when about 1 or 2% of the starting material had disappeared, there was too little of the 2-methylcyclopentanone to measure with any accuracy. As a result, it is not possible to be certain that the linear plot for the formation of the ring-contracted product passed through the origin. However, it can be argued that, when only 1% of the starting material had decomposed, it is unlikely that the products that are formed (assuming that they are carbonyl compounds) absorb more than 1% of the radiation at 3130 Å. On that basis it seems likely that reaction 1 is a primary process.[11]

The mechanism of reaction 1 is of interest. The net process can occur in one of two ways, which are shown by the arrows and dotted lines

(11) The possibility that the unsaturated aldehydes which are formed in these systems are the intermediates in reaction 1 can be ruled out, as in common with other unsaturated carbonyl compounds these aldehyde products are very stable to photoisomerization.
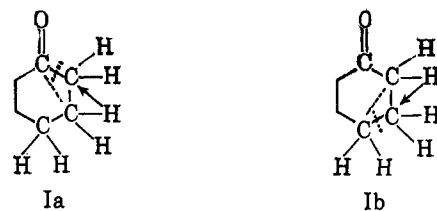
In the photolysis of cyclohexanone-2,2,6,6-d_4, these processes would lead to
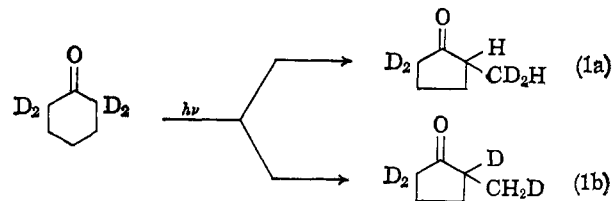
The structure that was actually found is in accord with (1a). In view of this, the observation that 3-methylcyclohexanone gives only one of the two possible products may be interpreted to mean that the methyl group in the 3-position not only reduces the number of hydrogens available for transfer (in which case at least some of the second product may be formed) but actually blocks the reaction. This in turn would mean that the cyclic structure is carried throughout the reaction, a situation that also appears to prevail in the formation of the unsaturated aldehydes. More complex reaction mechanisms which involve the transfer of an H atom, first to a carbonyl group and then to an adjacent carbon atom, seem to have little merit. A mechanism in which a methyl radical is formed and then migrates would be contrary to the observation that the addition of cyclohexene, which is an efficient free-radical scavenger, has no effect on the rate of reaction 1 in cyclohexanone. One of the surprising aspects of reaction 1 is that it involves a hydrogen migration between two atoms which are not part of the chromophore that causes the absorption of a photon.[12] The isomerization of cyclooctanone to 2-propylcyclopentanone can also be visualized as a (1a) or (1b) type of transfer except that a δ-carbon instead of a β-carbon is involved.

It has been found that cyclopentanone emits only fluorescence but no phosphorescence in the vapor phase; however, it emits both in the pure liquid phase.[16,17] The first part of this statement is also consistent with the interpretation of the photochemistry which requires that three primary processes occur from one excited state, presumably a singlet.[5] The results obtained here with pure liquid cyclohexanone suggest that more than one excited state may be involved in the condensed-phase reactions although this may not be true of the vapor phase processes. This is convincingly indicated by the fact that the formation of 2-methylcyclopentanone is linear with time while the formation of 5-hexenal levels off when its concentration is about

(12) A similar mechanism has been suggested for the Norrish Type II process.[13] It has been found to be at variance with the facts.[14,15]

(13) This mechanism has been discussed by J. N. Pitts, Jr., J. Chem. Educ., 34, 112 (1957).

(14) R. Srinivasan, J. Am. Chem. Soc., 81, 5061 (1959).

(15) G. R. Macmillan, J. G. Calvert, and J. N. Pitts, Jr., ibid., 86, 3602 (1964).

(16) S. R. La Paglia and B. C. Roquitte, Can. J. Chem., 41, 287 (1963).

(17) S. R. La Paglia and B. C. Roquitte, J. Phys. Chem., 66, 1739 (1962).

0.5% of cyclohexanone. If this is due to a quenching reaction between the 5-hexenal and excited cyclohexanone, it must not extend to the excited state which undergoes reaction 1. On this basis, while it is not possible to identify the states, it can at least be said that two different electronically excited states must be responsible for the formation of 5-hexenal and 2-methylcyclopentanone in the condensed phase. The decrease in the yield of both isomers on the addition of increasing amounts of cyclohexane is probably due to a photoaddition reaction between cyclohexanone and the solvent.[18]

In every one of the monocyclic ketones that were studied, the well-known photoisomerization reaction which leads to unsaturated, open-chain aldehydes was also observed. A few comments on this reaction which, in general, can be written as
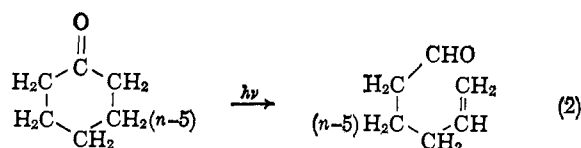
can be made from the new data that were obtained in the present study. The probable mechanism of this

(18) At first sight, it may seem surprising that the photoaddition reaction between cyclohexanone and solvent is not replaced in the pure liquid by an equally efficient bimolecular process between two ketone molecules. However, a collision between an excited ketone molecule and another ketone molecule may lead to energy transfer without addition, at least some of the time. Even in the pure liquid, the isomerization products are formed only in poor yield compared to the condensation products.

reaction has already been suggested to be a transfer of the hydrogen atom from the β- to the carbonyl carbon before or at the same time as the ring is broken.[6] In line with this, it was found that the aldehyde from 2-methylcyclohexanone was exclusively *trans*-5-heptenal. The uncertainty concerning the peak at 756 cm.$^{-1}$ that was reported earlier[10] has now been removed. The aldehydes from 2-*n*-propylcyclopentanone and 2-ethylcyclopentanone have also been found[19] to be exclusively the *trans* compounds as shown by the intense absorption at about 975 cm.$^{-1}$ and no strong or medium absorption from 900 to 680 cm.$^{-1}$. The specificity of the reaction is shown by the fact that 2-methylcyclohexanone gives none of the 6-heptenal although the methyl group is also β to the carbonyl group; 2-ethylcyclopentanone gives only 4-heptenal and no 5-heptenal while 2-*n*-propylcyclopentanone gives only 4-octenal and no 5-octenal. These observations on the five-membered cyclic ketones have made arguments concerning the role of axial and equational protons in this reaction (in six-membered cyclic ketones) superfluous. Lastly, the self-quenching of reaction 2 by the aldehyde that is formed seems strong in terminally unsaturated aldehydes but less so in other unsaturated aldehydes. The existence of this effect explains the failure to obtain substantial yields of the aldehyde by reaction 2 in preparative scale photolysis.

(19) S. E. Cremer and R. Srinivasan, unpublished results.

An Electron Spin Resonance Study of the Anion Radicals of 9,10-Diazaphenanthrene, 2,2'-Bipyrimidine, and $\Delta^{2,2'}$-Biisobenzimidazolylidene

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Contribution from the Department of Chemistry, Cornell University, Ithaca, New York. Received December 3, 1964

Electron spin resonance spectra were obtained for the anion radicals of 9,10-diazaphenanthrene, 2,2'-bipyrimidine, and $\Delta^{2,2'}$-biisobenzimidazolylidene in dimethylformamide solution. Polarographic data were obtained for reduction of the neutral polyazines as well as for related hydrocarbons. The ^{14}N coupling constant for the 9,10-diazaphenanthrene anion is 5.27 ± 0.04 gauss (two equivalent nuclei with $I = 1$); four proton coupling constants, each corresponding to two equivalent protons, have the values 3.58 ± 0.03, 2.83 ± 0.03, 0.77 ± 0.01, and 0.283 ± 0.003 gauss. The ^{14}N coupling constant in the anion radical of 2,2'-bipyrimidine is $1.40_5 \pm 0.03$ gauss and the two proton coupling constants are 4.98 ± 0.04 (two equivalent protons) and $0.14_5 \pm 0.01$ gauss (four equivalent protons). For the anion radical of $\Delta^{2,2'}$-biisobenzimidazolylidene the nitrogen coupling constant is 2.97 gauss and the two proton coupling constants (each corresponding to four equivalent protons) are 1.40 and 0.83 gauss. The ^{14}N coupling constants are discussed in relation to values reported for other azine anion radicals.

Introduction

The catalog of azine anion radicals studied by electron spin resonance (e.s.r.) spectroscopy has grown rapidly over the past 3 years. The anion radical of 4,4'-bipyridine was examined in 1961 by Ward[1] and subsequently by Carrington and Santos-Veiga.[2] E.s.r. studies have also been done on the anion radicals of 2,2'-

(1) R. L. Ward, *J. Am. Chem. Soc.*, 83, 3623 (1961).
(2) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, 5, 21 (1962).