phasized that in the poly(*t*-butyl acrylate) system the *trans* form was found to photoisomerize to the *cis* isomer. The spatial conformation of the three-dimensional *trans* isomer (*gauche*) of the ester is such that the *t*-butylmethyl groups are rotated out of the plane of the carbonyl group[16] leaving the oxygen atom more susceptible to hydrogen bonding. The *cis* isomer cannot hydrogen bond so easily since the methyl groups stagger the carbonyl oxygen. It is apparent that bonding of an intermolecular nature is operative in these carbamate systems. The essential evidence lies in the fact that the (N–H···O=C) bonds are broken upon dilution and the N–H absorbance ratio was temperature dependent in solution.[12a] This is in marked contrast to the polyacrylate system. It is concluded that a dominant factor reducing the type II quantum yield in thin films is due to a releasing of the energy absorbed by the *gauche* isomer *via* some nonradiative process or processes.

Qualitative evidence supporting a relationship between energy dissipation *via* a nonradiative process and hydrogen bonding was advanced by Cowgill[17] in work on fluorescence quenching of tryptophanyl and tyrosyl peptides.

Conclusions

The conclusions may be arrived at by inspection of the data in Table III. The influence of hydrogen bonding on the type II quantum yields from I was found to be dependent on whether the reaction took place in thin films or solution.

TABLE III
COMPARISON OF TYPE II QUANTUM YIELDS FOR THE POLYCARBAMATE AND POLYACRYLATE AT 254-mμ EXCITATION

Compound	Medium	ϕ_{II}	Reactive state
Polyacrylate	Thin film	0.08	$n-\pi^*$
Polycarbamate	Thin film	0.01	$\pi-\pi^*$
Polycarbamate	Alcohol	0.04	$\pi-\pi^*$
Polycarbamate	Hydrocarbon	0.16	$n-\pi^*$

In the solution phase experiments, ϕ_{II} decreased from 0.16 in 3-methylpentane to 0.04 in methyl alcohol. A solvent shift causing an inversion of the $n-\pi^*$ and $\pi-\pi^*$ states was also found to occur. Thus, the variation in ϕ_{II} was explained on the basis of a change in electron density distribution in the excited states. Comparisons of the electronic absorption spectra with the phosphorescence lifetimes gave evidence for this interpretation.

Second, the significant lower quantum yield of I in film form compared to the polyacrylate film or its yield in alcohol was rationalized on the basis of degradation of the excitation energy *via* some radiationless process occurring from a resonance-stabilized hydrogen bonded *gauche* isomer. Evidence for this was found from infrared studies which showed a photochemically inactive, intermolecularly bonded *gauche* isomer. In addition, ϕ_{II} in thin films was found to increase by a factor of 2 in the temperature region ($>T_g$) where the concentration of N–H···O=C bonds decreased by ~10%.

Therefore, the photochemistry of poly(*t*-butyl N-vinylcarbamate) appears to be controlled by the subtle interplay of at least two factors: (1) a solvent effect which changes the character of the lowest reactive state and (2) energy degradation *via* hydrogen bonding. Further experiments that will hopefully clarify the mechanism will be the subjects of further investigations.

Acknowledgments. Dr. H. James Harwood of the University of Akron and Miss Anita VanLaeken of this laboratory are sincerely thanked for the syntheses of I and II, respectively. Informative discussions with Drs. J. B. Flannery, D. L. Stockman, and M. S. Walker are acknowledged with pleasure.

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[17] R. W. Cowgill, *Biochim. Biophys. Acta*, 133, 6 (1967).

Photochemistry of Ketone Polymers.
II. Studies of Model Compounds

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ABSTRACT: Studies of the photolysis of model ketones of the general structure R(C=O)R in hydrocarbon solution show that the type I and type II quantum yields are functions of chain length. The type I quantum yield decreases rapidly, and reaches a limiting value of 0.012. The type II quantum yield decreases slowly and appears to be still decreasing in ketones containing about 40 carbon atoms, where it has a value of 0.06. Although the type II process is insensitive to temperature and solvent viscosity, the type I process depends strongly on both, as might be expected from a process involving radical intermediates. The results of these studies indicate that the photochemistry of the largest of the model compounds is quite similar to that of the ketone polymers studied previously.

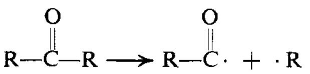
In a previous publication[1] we have described the photochemistry of polymeric ketones synthesized by the copolymerization of ethylene and carbon monoxide. At an early stage in the investigation it became apparent that variations in the molecular weight of the polymer had very little effect on the quantum yields of the processes involved, and yet there was a marked difference between these yields and those for the relatively small organic molecules reported in the literature. It therefore became of interest to establish the molecular

[1] G. H. Hartley and J. E. Guillet, *Macromolecules*, 1, 165 (1968).

weight dependence through a study of model compounds.

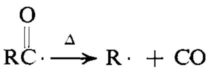
Accordingly a series of symmetrical aliphatic ketones of the general structure RC(=O)R were synthesized and studies made of the variation in quantum yield with changes in the length of the linear alkyl radical R.

Absorption of ultraviolet light by aliphatic ketones leads to dissociation by the Norrish type I free radical process[2]



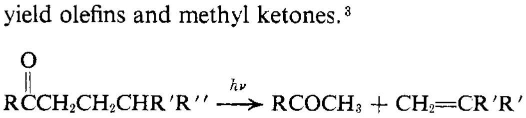
$$R-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-\overset{O}{\overset{\|}{C}}\cdot + \cdot R \qquad (1)$$

At elevated temperatures, the acyl radical can decarbonylate, with the evolution of carbon monoxide.



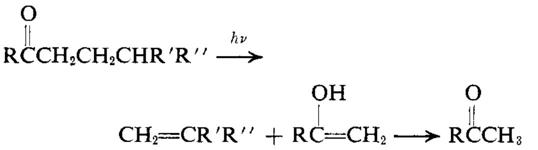
$$R\overset{O}{\overset{\|}{C}}\cdot \xrightarrow{\Delta} R\cdot + CO \qquad (2)$$

Ketones possessing hydrogen-bearing γ-carbon atoms can undergo the Norrish type II photoelimination to yield olefins and methyl ketones.[3]



$$R\overset{O}{\overset{\|}{C}}CH_2CH_2CHR'R'' \xrightarrow{h\nu} RCOCH_3 + CH_2{=}CR'R'' \qquad (3)$$

The type II reaction appears to proceed by intramolecular hydrogen transfer, yielding an enol which rearranges to the final ketone (eq 3a).[4,5] The hydrogen



$$R\overset{O}{\overset{\|}{C}}CH_2CH_2CHR'R'' \xrightarrow{h\nu} CH_2{=}CR'R'' + R\overset{OH}{\overset{|}{C}}{=}CH_2 \longrightarrow R\overset{O}{\overset{\|}{C}}CH_3 \qquad (3a)$$

transfer involves a six-membered cyclic intermediate,[6,7] in either a concerted or a stepwise process.

In addition to the type I and type II reactions, a third primary process has been observed which results in the isomerization of the ketone to a cyclobutanol derivative.[8] However, this reaction has been studied in only a few ketones, and does not appear to be an important process at 3130 Å, the wavelength used in the present work. The two reactions of most importance in polymer systems appear to be types I and II.[1]

Recent quenching studies have confirmed that the type II process at least involves both the singlet and triplet excited states of the ketone.[9,10] For the majority of ketones, however, the extent of the contribution of each state to the reaction is still unknown.

In this paper we shall be primarily concerned with the effects of chain length, temperature, and solvent viscosity on the type I and type II reactions in linear, symmetrical, aliphatic ketones.

Experimental Section

Apparatus. The ketones were photolyzed with the 3130-Å line of the mercury emission spectrum. The lamp used was a 250-W, medium-pressure (30 atm) compact source mercury arc, Type ME/D (Associated Electrical Industries Ltd.). The rest of the apparatus, including the filters and light monitoring system, have been described previously.

Procedure. A quartz cell, path length 20 mm, was filled with 20 ml of pure solvent, and the intensity of the lamp measured at the temperature of the experiment. Enough ketone was then added to make a 0.1 *M* solution, which was mixed by a stream of nitrogen. Air was removed from the solution by alternate applications of vacuum and a slight positive pressure of nitrogen. The solution was then photolyzed under nitrogen, the cell being sealed by a Teflon stopcock. After photolysis (to about 5% conversion), the ketone solution was replaced by pure solvent, and the intensity of the lamp checked.

Analysis. After photolysis the ketone solutions were analyzed on a Perkin-Elmer Model 800 gas chromatograph, using dual flame ionization detectors and $^{1}/_{8}$ in. × 5 ft columns (5% w/w silicone SE30 on Chromosorb G.). The photolysis products were measured by comparing their peak areas with the peak areas obtained from standard solutions containing known concentrations of the products. The peak areas were measured by a disk integrating unit attached to the chromatograph recorder.

Carbon monoxide evolution from the ketone photolyses was measured, in a separate series of experiments, as described previously.[1] Ultraviolet absorption spectra of the ketones and solvents were run on a Bausch and Lomb Spectronic 505 double beam spectrophotometer. Solvent viscosities were measured using a Desreux viscometer.

Materials. The solvents used in the photolyses were purified by distillation and/or filtration through silica gel columns until they were completely transparent over the whole range of wavelengths passed by the filter system. Analyses were performed on the Perkin-Elmer Model 800 gas chromatograph.

With the exception of 4-heptanone and 5-nonanone, all the ketones were prepared by the method of Davis and Shultz,[11] in which a carboxylic acid RCOOH is refluxed with iron powder. Decarboxylation of the resulting salt forms the ketone RC(=O)R in good yield and high purity. The ketones were either distilled or extracted from the reaction mixture and purified by redistillation or recrystallization. The 5-nonanone was Eastman Kodak White Label grade, and the 4-heptanone was Eastman Kodak Practical grade, distilled under vacuum through a dewar column. With the exception of 5-nonanone (purity 99.5%), the minimum purity in each case was 99.9 mol %.

Results and Discussion

Dependence of Quantum Yield on Chain Length. The ketones studied were all aliphatic, linear and symmetrical. They ranged in size from a total chain length of 7 carbon atoms (4-heptanone), to a total chain length of 43 carbon atoms (22 -tritetracontanone).

Figure 1 shows the effect of increasing chain length on the type II quantum yield for photolysis in paraffin oil solution at 70°. ϕ_{II} appeared to decrease quite regularly with increasing chain length, and was still as high as 0.06 in 22-tritetracontanone. Furthermore, even at chain lengths of this magnitude the type II quantum yield had not yet reached a limiting value and was still slowly decreasing. The value of 0.025 re-

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(2) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 379.

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(5) R. Srinivasan, *ibid.*, **81**, 5061 (1959).

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(7) W. Davis, Jr., and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **60**, 2153 (1947).

(8) N. C. Yang and D. D. H. Yang, *ibid.*, **80**, 2913 (1958).

(9) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(10) T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

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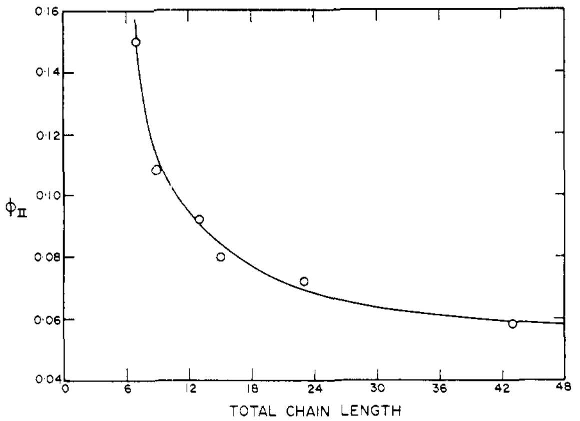


Figure 1. Type II quantum yield (ϕ_{II}) as a function of chain length; temperature, 70°; solvent, paraffin oil.

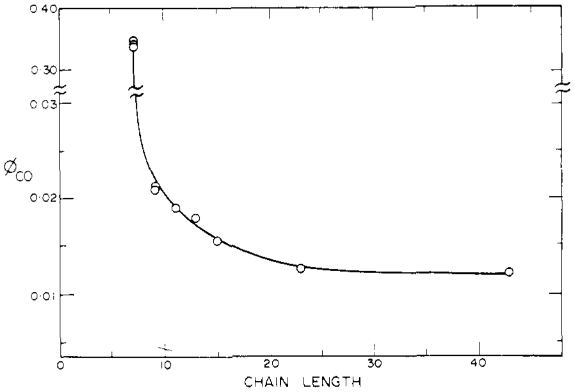


Figure 2. Quantum yield for carbon monoxide evolution (ϕ_{CO}) as a function of chain length; temperature, 120°; solvent, paraffin oil.

ported for the type II quantum yield of a 1 mol % ethylene–carbon monoxide copolymer is therefore of the expected order of magnitude for a very long chain ketone.[1]

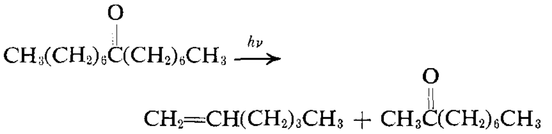
The above behavior can be contrasted with that of the type I reaction. Figure 2 shows the quantum yields of carbon monoxide evolution from photolyses of the ketones in paraffin oil at 120°. At this temperature the acyl radicals produced by the type I reaction should decompose quantitatively and the quantum yield for carbon monoxide evolution will be very nearly equal to that for the type I bond breaks. It can be seen that as the chain length of the ketone increases, ϕ_{co} quickly drops to a limiting value (0.012) and that the major decrease occurs between 4-heptanone (di-*n*-propyl ketone), and 5-nonanone (di-*n*-butyl ketone).

Calvert and Nicol[12] investigated the vapor phase photodecomposition of a number of propyl ketones. Their results show that at a temperature of 150°, the substitution of one butyl group for a propyl group in di-*n*-propyl ketone lowers the carbon monoxide quantum yield by a factor of about 4, their values for 4-heptanone and 4-octanone being 0.37 and 0.10, respectively. This was explained by Wagner and Hammond,[13] who pointed out that abstraction of a secondary γ-hydrogen atom, such as in 2-hexanone, should be easier than abstraction of a primary γ-hydrogen, such as in 2-pentanone, with the result that the type II reaction should be faster than the type I. Their quenching experiments showed that such was the case.[9] It is interesting to note therefore, that the type II quantum yield for 4-octanone is higher than that for 4-heptanone, although 4-octanone has a lower total quantum yield for reaction.[12]

In the present work, it seems reasonable to expect that 5-nonanone, with its secondary γ hydrogens, would have a higher type II rate constant than 4-heptanone. Figures 1 and 2 show, however, that the type II quantum yield for 5-nonanone is smaller than that for 4-heptanone, and that the type I quantum yield is lower by a factor of about 16. This is presumably a result of an increased rate of radiationless deactivation in 5-nonanone, compared to 4-heptanone.

From the above discussion we can provide a possible qualitative explanation for the difference in behavior between 4-heptanone and 5-nonanone. The type I and type II are probably competitive with each other and with the processes of radiationless deactivation. Energy dissipation by nonradiative processes occurs more rapidly in 5-nonanone, but since the type II reaction is also faster, the type II quantum yield is less affected than that for the type I reaction. Also, since the quantum yields continue to decrease with increasing chain length, reaction must become even less efficient in the long-chain ketones, compared with the processes of radiationless deactivation.

Dependence of Quantum Yield on Temperature and Solvent Viscosity. The effect of temperature and solvent viscosity on quantum yield was investigated for one of the ketones, 8-pentadecanone (di-*n*-heptyl ketone). The type II reaction of this ketone produces 1-hexene and 2-nonanone.



$$CH_3(CH_2)_6\overset{O}{\overset{\|}{C}}(CH_2)_6CH_3 \xrightarrow{h\nu} CH_2{=}CH(CH_2)_3CH_3 + CH_3\overset{O}{\overset{\|}{C}}(CH_2)_6CH_3 \quad (4)$$

Table I shows the quantum yields obtained for these products from photolyses of 8-pentadecanone in paraffin oil solution. It can be seen that the type II reaction in 8-pentadecanone is not strongly temperature dependent. If we define an apparent activation energy by the equation $\phi = \phi_0 e^{-E/RT}$ then a log plot (Figure 3) of the quantum yields in Table I gives a value of E of approximately 1 kcal/mol. This insensitivity to temperature change is a characteristic of the type II reaction in ketones which possess only one type of γ hydrogen. Ethylene–carbon monoxide copolymers also show this temperature independence of ϕ_{II}.[1]

TABLE I
PHOTOLYSIS OF 8-PENTADECANONE TYPE II QUANTUM YIELDS

	Quantum yields	
Temp, °C	1-Hexene	2-Nonanone
30	0.066	0.067
60	0.068	0.067
90	0.091	0.086
120	0.087	0.091
145	0.092	0.102

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(12) C. H. Nicol and J. G. Calvert, *J. Org. Chem.*, **89**, 1790 (1967).

(13) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 4009 (1965).

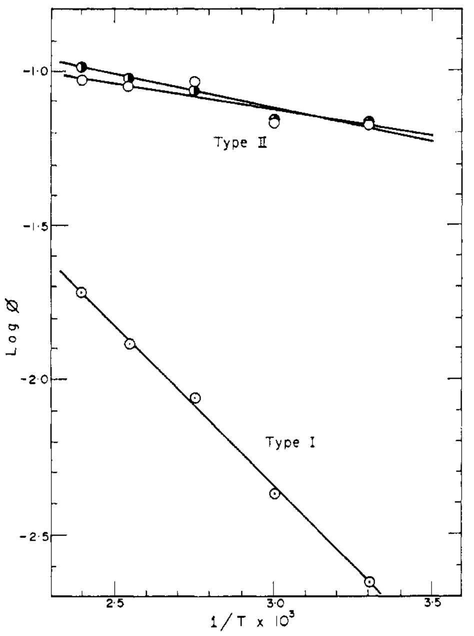
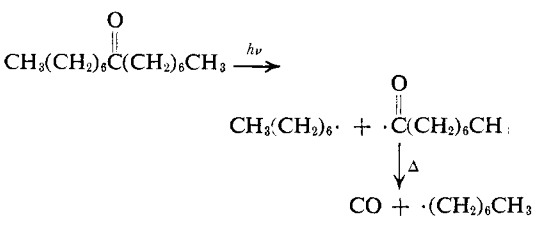


Figure 3. Log (quantum yields) *vs.* $1/T$ for 8-pentadecanone photolyzed in paraffin oil solution: ○, log ϕ_{hexene}; ◑, log ϕ_{nonanone}; ⊙, log ϕ_{heptane}.

At 90°, a change in the solvent viscosity from 4.1 (paraffin oil) to 0.22 cP (heptane) produced no detectable change in quantum yield, indicating that the type II reaction in 8-pentadecanone is not viscosity dependent.

The type I reaction in 8-pentadecanone produces heptyl radicals and carbon monoxide. The heptyl radicals can abstract hydrogen to form heptane. The quantum yield for heptane formation was measured in the photolysis of 8-pentadecanone in paraffin oil solution, and the results are shown in Table II. The quantum yield increases rapidly with temperature. Furthermore, a log plot (Figure 3) of the values obtained is quite linear, the slope corresponding to an apparent activation energy of 4.8 kcal/mol.



$$CH_3(CH_2)_6\overset{\overset{O}{\|}}{C}(CH_2)_6CH_3 \xrightarrow{h\nu} CH_3(CH_2)_6\cdot + \cdot\overset{\overset{O}{\|}}{C}(CH_2)_6CH_3 \quad (5)$$
$$\downarrow \Delta$$
$$CO + \cdot(CH_2)_6CH_3$$

The carbon monoxide quantum yields for 8-pentadecanone in a number of solvents and at various temperatures are shown in Table III. At moderate temperatures (60°), the quantum yield decreased with increasing solvent viscosity, which would be expected if a cage mechanism was involved. The differences between the quantum yields were small, however, and of the same order as the probable experimental error, although the trend was perhaps significant.

TABLE II
PHOTOLYSIS OF 8-PENTADECANONE. QUANTUM YIELD FOR HEPTANE FORMATION

Temp, °C	$\phi \times 10^2$
30	0.22
60	0.42
90	0.87
120	1.4
145	1.9

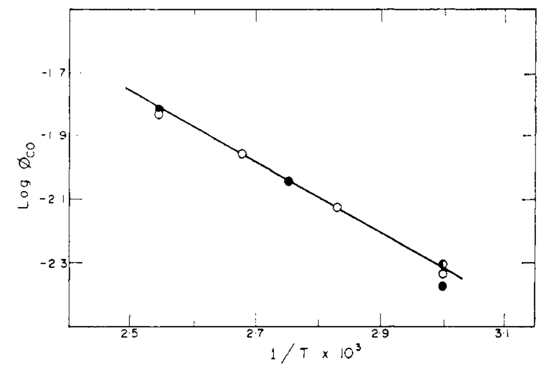


Figure 4. Log ϕ_{CO} for 8-pentadecanone: ◑, heptane solvent; ○, dodecane solvent; ●, paraffin oil solvent.

At higher temperatures the effect of solvent viscosity was even less pronounced, and a log plot of the quantum yields (Figure 4) shows that the solvent appeared to have little influence on the temperature dependence of the carbon monoxide quantum yield. The apparent activation energy calculated from Figure 4 was 5.0 kcal/mol. Conceivably, long chain hydrocarbon solvents could inhibit the type I reaction by the formation of a "cage" in which only a few segments of any one solvent molecule were involved. Under such conditions, beyond a certain limit, increases in the molecular complexity of the solvent would increase the viscosity, but would be virtually without influence on the quantum yield.

Since the production of a molecule of carbon monoxide is accompanied by the formation of two heptyl radicals, then, if the only reaction of a heptyl radical was to abstract a hydrogen atom from the solvent, it would be expected that the quantum yield for heptane formation would be at least twice that for carbon monoxide production.

An examination of Tables II and III shows that such is not the case and that ϕ_{CO} is generally of the same order as ϕ_{heptane}. The heptane product was measured by gas–liquid partition chromatography, and the silicone SE30 liquid phase used would not have resolved 1-heptene and *n*-heptane. Consequently, disproportionation between a heptyl radical and another radical

TABLE III
PHOTOLYSIS OF 8-PENTADECANONE. CO QUANTUM YIELDS

Solvent	Temp, °C	Solvent viscosity, cP	$\phi_{CO} \times 10^2$
n-Heptane	60	0.28	0.49
Dodecane	60	0.73	0.46
Paraffin oil	60	9.2	0.42
Dodecane	80	0.58	0.75
Paraffin oil	90	4.1	0.90
Dodecane	100	0.47	1.1
Dodecane	120	0.40	1.5
Paraffin oil	120	2.1	1.5

would not have changed the apparent heptane quantum yield.

Other possible reactions of the heptyl radical are (a) recombination with another heptyl radical to give tetradecane

$$R\cdot + R\cdot \longrightarrow RR \qquad (6)$$

or (b) recombination with a solvent radical formed by hydrogen abstraction in the sequence

$$R\cdot + SH \longrightarrow RH + S \qquad (7)$$

$$S\cdot + R\cdot \longrightarrow RS \qquad (8)$$

$$S\cdot + S\cdot \longrightarrow SS \qquad (9)$$

Tetradecane was definitely not formed in the reaction (it is easily detectable in the reaction mixture by gas chromatography) and consequently no heptyl radicals are consumed by process a. This is not unexpected, since the concentration of primary radicals is very low and their lifetime short, so the probability of recombination of primary radicals after the escape from the solvent "cage" is negligible.

On the other hand the radical formed by attack on the solvent, mineral oil (a highly branched saturated hydrocarbon), is likely to be much more stable, and consequently the processes described by eq 8 and 9 are much more favorable under the experimental conditions. Unfortunately, the products formed would not be detectable by gas chromatography, and hence final proof of this mechanism is not available from experiments of this type. However, in the absence of a plausible alternative it does seem reasonable to attribute the discrepancy between the carbon monoxide and heptane quantum yields to removal of heptyl radicals by reaction 8. It is obvious that in such a case, the yield of heptane is not a good measure of the quantum yield for the type I process. This difficulty could be resolved by carrying out the photolysis in a solvent in which the product RS could be estimated by gas chromatography or other means.

From the above results, it may be concluded that for linear, symmetrical, aliphatic ketones, the type I and type II quantum yields are functions of chain length, and that both decrease with increasing chain length. The type I quantum yield decreases rapidly and reaches a limiting value of 0.012. The major change occurs between $R = 3$ and $R = 4$ (4-heptanone and 5-nonanone). The type II quantum yield decreases slowly and appears to be still decreasing in ketones of about 40 carbon atoms in length, where it has a value of 0.06. The type II process is not sensitive to changes in temperature or solution viscosity. The type I quantum yield, on the other hand, is temperature dependent, but also does not appear to be affected by solvent viscosity. The type I quantum yields and activation energies for the two higher ketones studied are quite similar to those obtained for ketone polymers, and hence no additional effect would be expected from a further increase in molecular weight. On the other hand ϕ_{II} appears to be still a function of chain length even for the largest ketone used in this study and a further reduction may be expected as the molecular weight is increased.

Acknowledgment. This work was supported by research grants from Dunlop Research Ltd. and the Province of Ontario, whose support is gratefully acknowledged.

Polymerization and Structure of Allyl-Substituted Cyclopentadienes

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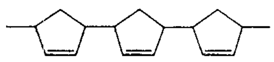
ABSTRACT: The related diene monomers, allylcyclopentadiene, methallylcyclopentadiene, and allylmethylcyclopentadiene, the last two of which have not previously been reported in the literature, were synthesized and characterized as their Diels–Alder adducts with tetracyanoethylene. Polymerizaton of these monomers was carried out with boron trifluoride as catalyst; all three polymers were soluble in organic solvents such as benzene. The structures of the polymers were determined by nmr spectroscopy and it was shown that the proportion of the 1,4 structure increased with increasing steric hindrance in the monomer.

Two extremes of structure are observed in the polymerization of cyclopentadiene under normal conditions. These are a 1,4 enchainment (A) and a 1,2 enchainment (B). The proportions of these two units can be estimated by using nmr spectra of the polymer.[1] Aso and Ohara have also determined the structure of polyallylcyclopentadiene prepared by a cationic mechanism and found it to consist of about equal amounts of the 1,4 structure (II) and the 1,2 structure (III), and no other structures such as I.[2] The isomer distribution in allylcyclopentadiene, however, was not determined.



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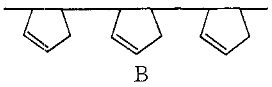

B

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(1) C. Aso, T. Kunitake, K. Ito, and Y. Ishimoto, *J. Polym. Sci., Part B*, **4**, 701 (1966).

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