were degassed and sealed. The tubes were placed around a rotating table and irradiated with 3500-A light. Irradiation was stopped after approximately 20% calculated conversions were reached. The tubes were analyzed by gas chromatography. The relative quantum of formation of **24** to that of **1** was found to be 0.90. Since the quantum yield of the myrcene reaction has been determined (0.023), the quantum yield of formation of **24** is calculated to be 0.021.

Acknowledgment. The part of the work carried out at the California Institute of Technology was supported by a grant from the National Science Foundation.[46]

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[46] This paper has been assigned no. XLV in the series, "Mechanisms of Photochemical Reactions in Solution." Paper XLIV is E. Y. Lam, D. Valentine, and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3482 (1967).

Photochemistry of Cyclopentenone in Various Media

James L. Ruhlen and Peter A. Leermakers

Contribution from the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. *Received April 7, 1967*

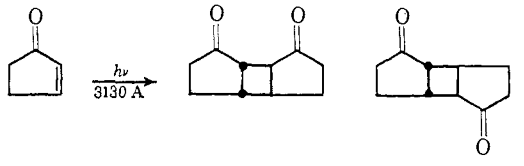
Abstract: Cyclopentenone at various concentrations in several solvents, and in a silica gel–cyclohexane slurry, has been irradicated yielding the *trans syn-* and *anti*-photodimers as well as other products. The excited state responsible for dimerization is the triplet, formed in high quantum efficiency, and lying at about 61 kcal/mole. The ratio of dimers is highly concentration and solvent dependent. On silica gel, photodimerization appears to be virtually completely suppressed; that dimer which does form is apparently formed in the supernatent solvent. An interesting side reaction in cyclohexane solvent, which becomes important when certain sensitizers are used (and also when the medium contains silica gel), is addition of cyclohexane to the carbon–carbon double bond of cyclopentenone.

The photochemistry of conjugated cyclic enones has been the subject of considerable recent activity.[1–4] From these studies a fairly consistent picture of the reaction mechanism appears. Cyclopentenone and cyclohexenone behave in a similar fashion, and it is relatively well established that (1) photodimerization occurs in the triplet state; (2) of the four possible cycloadducts, only the *trans syn* and *anti* are of major importance; and (3) the ratio of *anti* to *syn* is concentration and solvent dependent, with *anti* becoming increasingly important at higher concentrations of enone and with increasing solvent polarity.

Our original purpose in this investigation was to study the effect of physical adsorption (on silica gel) in photodimerization reactions; we felt that physical constraint on a surface could lead either to measurably more efficient cycloaddition, or to drastically reduced efficiency, depending upon the nature of the surface interaction and the chemical mechanism. We chose the cyclopentenone system because previous work[5] had been done on it in solution, and because there existed the possibility that the system might be perturbed enough by adsorption on silica gel so that *cis* as well as *trans* stereochemistry might be observed in the dimerization. Before very long it became apparent that the reaction in solution was complex enough to warrant additional investigation in its own right; in this paper we will attempt to digest the work of others and ourselves on the photochemistry of cyclic enones in solution, and to discuss briefly our results in a somewhat different medium, namely, a cyclohexane–silica gel matrix.

Results

Cyclopentenone undergoes photodimerization at 3130 A as indicated in eq 1, the efficiency of which depends upon several variables. The ratio dimer II/dimer I has been studied as a function of concentration in a variety of solvents: cyclohexane, isopropyl alcohol, ethanol, and methanol. The data are given in Table I.



I II

Table I

	Cyclopentenone concn, *M*			
	Neat	6.2	1.2	0.12
Solvent	Dimer II/dimer I			
(Neat)	1.1			
Cyclohexane		2.0	4.3	6.4
Isopropyl alcohol		1.6	2.2	2.1
Ethanol		1.4	1.7	4.3
Methanol		1.9	1.9	1.9

A. Multiplicity of the Excited Intermediate. In order to investigate the possibility of participation by an excited triplet state intermediate, attempts were made to quench (*i.e.*, inhibit) the dimerization with the triplet quencher *cis*-piperylene (Table II). *cis*-Piperyl-

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[1] J. L. Ruhlen and P. A. Leermakers, *J. Am. Chem. Soc.*, **88**, 5671 (1966).

[2] P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966).

[3] P. De Mayo, J. Pete, and M. Tchir, private communication.

[4] E. Y. Lam, D. Valentine, and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3482 (1967).

[5] P. E. Eaton, *ibid.*, **84**, 2344 (1962).

Table II

	Cyclopentenone concn, M			
	Neat	6.2	1.2	0.12
Dimer yield suppression factor	1.34	1.45	1.45	7.9

ene has an excited triplet level at 57 kcal/mole and does not absorb light at 3130 A. However, if one irradiates a solution containing a species (in this case, cyclopentenone) which is producing triplets by intersystem crossing from the singlet, piperylene will quench the cyclopentenone triplets at a nearly diffusion-controlled rate *provided the cyclopentenone triplets have a long enough reactive lifetime so that other triplet-destroying pathways are not competitive with quenching by the piperylene.* Thus, if dimerization is taking place partially or wholly *via* a triplet mechanism, addition of piperylene to the reaction mixture should inhibit production of dimer. Cyclohexane solutions 0.1 M in *cis*-piperylene and of various cyclopentenone concentrations were irradiated for 3 hr with 3130-A light. Absorption of light by quencher was negligible, the enone accounting for essentially all light absorption. The total yield of dimer produced in these solutions was then compared by vapor chromatographic (vpc) analysis with that produced in solutions of corresponding cyclopentenone concentrations without the quencher (Table II). Production of dimer was, in fact, reduced by addition of quencher. Experiments of this type, using higher concentrations of piperylene, have been reported by Eaton,[2] and support a mechanism proceeding wholly *via* a triplet state intermediate.[6]

Table III presents the results of irradiation of cyclopentenone in the presence of various energy transfer agents. Although cyclopentenone absorbs some of the incident light, "sensitizers" were chosen such that most of the light is absorbed by the energy transfer agent. Thus, if the latter were not acting as a *sensitizer* (but rather, if anything, as a quencher), or if dimerization were not proceeding *via* a triplet state intermediate, one should observe a decrease in dimer yield due to the light-filtering action of the sensitizer. Cyclohexane solutions 0.12 M in cyclopentenone and 0.1 M in energy transfer agent were irradiated for 3 hr at 3130 A. The dimer yield was compared with that obtained without energy transfer agent in a solution of the same cyclopentenone concentration which had been irradiated under the same conditions for the same length of time (Table III).

Table III

Energy transfer agent	Triplet energy, kcal/mole	% absorption due to energy transfer agent	Effect on dimer yield
Xanthone	74.2	99	None[a]
Acetophenone	73.6	52	None
Benzophenone	69	80	Uncertain[b]
Naphthalene	61	<30	85% reduction
Nitrobenzene	60	>95	95% reduction
2-Acetonaphthone	59	...	90% reduction

[a] Eaton[2] was the first to use xanthone as a sensitizer for cyclopentenone. His results agree with ours. [b] Benzophenone appeared on the vpc at the same point as dimer II; however, dimer I was reduced by about 65%.

Adequate interpretation of the quenching and sensitization experiments above is facilitated in part by knowledge of two important parameters: the triplet energy of cyclopentenone, and the efficiency of crossover from the cyclopentenone n,π^* singlet to the n,π^* triplet.

B. Cyclopentenone Triplet Energy. Attempts were made to observe either phosphorescence or fluorescence from cyclopentenone in an EPA glass at 77°K, and met with failure. Apparently other workers have met with similar results.[3] Hence measurement of the cyclopentenone triplet energy was made by an indirect method,[7] namely, that involving use of the enone as a sensitizer to establish a photostationary state of the piperylenes. Benzene solutions 0.10 M in cyclopentenone and 0.2 M in either *cis*- or *trans*-piperylene upon irradiation yielded a photostationary mixture containing 59–60% *trans* isomer. This is a precise value obtained from several experiments. This value implies a triplet energy (E_T) of 61 ± 1 kcal/mole for cyclopentenone. Hammond[4] has obtained an E_T of 61 ± 1 kcal/mole for 2-cyclohexenone by similar techniques. Thus it is verified that (1) cyclopentenone has a sufficiently high E_T to make the piperylene quenching data meaningful (because its E_T is higher than that of the piperylenes), and (2) acetophenone, xanthone, and benzophenone should have sufficiently high triplet energies to sensitize the dimerization, provided the reaction proceeds *via* a triplet intermediate.

C. Intersystem Crossing Efficiency. Triplet counting (measurement of singlet–triplet crossover efficiency) by the technique of Lamola and Hammond[8] depends on the comparison of the rates of photoisomerization of *cis*-piperylene obtained using benzophenone as sensitizer and the compound in question as sensitizer. Since the singlet–triplet crossover efficiency for benzophenone is known to be unity, a lower rate of photoisomerization of piperylene using cyclopentenone as sensitizer indicates a crossover efficiency of less than unity, *provided that some other triplet consuming process, such as photoreaction, is not competing with energy transfer.* Usually, such competition is trivial and thus not important, but it will be seen that it is important in the case of cyclopentenone. The triplet counting experiment was carried out under two sets of conditions. In one set a solution 0.60 M in benzophenone and 0.10 M in *cis*-piperylene was irradiated for 1 hr with 3130-A light, and resulted in 17.5% isomerization to the *trans* isomer. A benzene solution 0.33 M in cyclopentenone and 0.10 M in *cis*-piperylene was irradiated under the same conditions and for the same length of time, resulting in 7.5% isomerization. Correcting for back-reaction,[8] these values indicate a singlet–triplet crossover efficiency of 0.39 for cyclopentenone. In the other set, benzophenone was 0.30 M, cyclopentenone was 0.50 M, and *cis*-piperylene was 0.20 M. From the latter experiment, a value of 0.66 was obtained for the crossover efficiency. (Note that so long as cyclopentenone or benzophenone is the only species absorbing light, a concentration of

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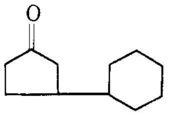
(6) Eaton plotted $1/\Phi_{rel}$ *vs.* piperylene concentration. The linearity of this plot supports this view. From his values, a reactive lifetime of 5×10^{-10} sec, under the conditions of his experiment, may be derived.

(7) *Cf.* G. S. Hammond, *et al., J. Am. Chem. Soc.,* **86,** 3197 (1964).

(8) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.,* **43,** 2129 (1965).

0.1 *M* suffices to absorb essentially all of the incident light, so above 0.10 *M* the choice of sensitizer concentration is really arbitrary.) Quite obviously this value will continue to increase at even higher piperylene concentrations, and is thus unreliable in the present case. De Mayo[3] reports a value "close to unity" using the same technique, but does not specify conditions. Implications of these experiments will be treated in the discussion.

D. Side-Reaction Product. When cyclopentenone is irradiated in cyclohexane an easily isolable byproduct (III) in addition to the dimers is formed. The relative amount of III that is formed is dependent on enone concentration, and on the sensitizer employed, if any. In the presence of acetophenone it is a major product. The infrared spectrum of the compound showed a large peak at 1745 cm^{-1}, indicating a saturated, cyclic ketone, probably in a five-membered ring. The nmr spectrum was not very helpful: absorption was limited to the saturated hydrocarbon region (around τ 8). The ultraviolet spectrum was compatible with the infrared indication that the compound was a ketone. Mass spectral data indicated a parent peak at 166 mass units, with the major fragment species at 83 mass units. Carbon-hydrogen analysis also indicated that III was a 1:1 adduct of cyclopentenone and cyclohexane. From mechanistic considerations and on the basis of the above data, structure III was assigned.



III

III is produced in dilute solutions of cyclopentenone alone in cyclohexane, in cyclohexane solutions containing cyclopentenone and benzophenone or acetophenone, and in cyclopentenone-silica gel-cyclohexane slurries. The III yield, as might be expected, is an inverse function of cyclopentenone concentration. In 0.12 *M* solutions of cyclopentenone in cyclohexane, the yield of III is about 15% (for an average of three runs) that of the total dimer; in 0.60 *M* solution, the value is about 0.05%, and III is not observed at higher concentrations. When the 0.12 *M* solution is made 0.1 *M* in acetophenone, the yield of III rises to 130% that of the total dimer (the absolute yield of which, however, remained the same as that without acetophenone). Similar increases in the III yield were obtained with addition of benzophenone. When the reaction is carried out in a cyclopentenone-silica gel-cyclohexane slurry, relative yields of III are higher than those obtained in cyclopentenone-cyclohexane solutions of corresponding "concentration," the yield at 0.12 *M* "concentration" being about 80% that of the dimer. ("Concentration" refers to the cyclopentenone concentration of the solution which is mixed with silica gel to produce the slurry.)

Cyclohexane solutions 0.1 *M* in cyclopentenone were irradiated while saturated with oxygen, which is known to be an excellent radical scavenger. The yield of III thus produced from a solution 0.12 *M* in cyclopentenone was 6% that of the dimer yield, which represents a reduction of by more than one-half the value (15%) obtained using a 0.12 *M* solution without oxygen. This supports the view that III is formed *via* a free-radical chain mechanism.

E. Irradiation in Cyclohexane-Silica Gel. Irradiation of cyclopentenone in silica gel-cyclohexane slurrys resulted in drastically reduced dimer yield and relatively increased yields of other products, including III and probably polymeric material. II/I ratios were about the same as those obtained in solutions of the same enone "concentration," except at very low concentrations. By measuring the ultraviolet absorption of the supernatant liquid above silica gel slurries containing cyclopentenone, it was found that the enone is not completely adsorbed in the matrix at "concentrations" of 0.1 *M*. At this concentration about 1% of the enone is not adsorbed. Since the dimer yield obtained on irradiation of such a slurry was about 40-fold less than that obtained in solution of the same concentration, it appears reasonable that little dimerization is taking place among the adsorbed molecules. Rather, the bulk of the dimerization is probably taking place among nonadsorbed liquid-phase molecules, and the principal process in the adsorbed phase thus appears to be reaction between cyclohexane and cyclopentenone to produce III.

Discussion

It is the present opinion of others[2-4] and ourselves that cyclic enones such as cyclopentenone undergo photocycloaddition in the triplet state. Although the dimer ratio is concentration dependent, the work of Eaton and Hurt[2] and Lam, Valentine, and Hammond[4] nullifies our earlier preliminary hypothesis that the singlet state might be important at high concentrations,[1] with phasing in of a triplet mechanism at lower concentrations (where, presumably, a longer lifetime would be necessary for the bimolecular reaction). The ratio of dimer II to dimer I is substantially smaller in polar solvents than in cyclohexane, so that a reasonable conclusion is that the transition state leading to polar dimer I is relatively stabilized in polar solvents. The concentration dependence in cyclohexane reflects decreasing macroscopic and microscopic polarity as the cyclopentenone concentration is reduced.

The experiments with energy transfer agents (Table III) require some discussion. Xanthone has a high triplet energy, and in solutions containing it and cyclopentenone with virtually all light absorbed by xanthone, the absolute dimer yield and relative quantum yield of dimers are no different than in solutions containing no sensitizer. With acetophenone as sensitizer the dimer yields are also unchanged even though acetophenone absorbs only about one-half the incident light. The latter experiment is compelling evidence that the intersystem crossing efficiency in cyclopentenone must be near unity. Direct measurement of the intersystem crossing efficiency in cyclopentenone by chemical methods was relatively fruitless, except that it pointed to the extreme rapidity of the photodimerization process. Values for crossover efficiency of 0.39 and 0.66 using 0.1 and 0.2 *M* piperylene, respectively, were obtained. The technique used in these crossover efficiency measurements assumes that the triplets being "counted" exist long enough for near-diffusion-controlled quenching by piperylene to be the major reactive pathway. This is the case with the standard, benzophenone, which has a lifetime on the order of 10^{-6} sec. Thus the most reasonable explanation for the concentration dependence of the above measurements is probably that cyclopentenone triplets are produced with very nearly unit efficiency, but, since dimerization is competitive with quenching by piperylene, the efficiency measuring technique used does not apply. Thus it should be possible to reach a limiting piperylene concentration at which a value of close to unity would be obtained. However, that concentration would have to be very high indeed, for Eaton[2] finds that with a piperylene concentration of 2.0 *M*, dimer yield is reduced by only a factor of 12 over that with no quencher. From Eaton's experiments a *reactive* lifetime of cyclopentenone of 5×10^{-10} sec (at moderate cyclopentenone concentrations) is obtained. This will be competitive with near-diffusion-controlled quenching by piperylene.

The value of 61 kcal/mole obtained for the triplet energy of cyclopentenone is also worthy of discussion. If this value is correct, and if the reaction proceeds exclusively *via* the triplet (as it probably does), then the reaction should be sensitized by benzophenone, whose efficiency as an energy transfer donor has long been established. While the total dimer yield in runs with benzophenone could not be measured due to vpc peak interference between benzophenone and dimer II, dimer I was reduced by about 65% (see Table III). In none of the sensitization experiments which have been carried out was the dimer *ratio* affected by addition of sensitizer. Hence one may fairly safely conclude that dimerization is decreased on addition of benzophenone, and it is decreased to an extent close to that accounted for by the competitive absorption of incident light by the benzophenone. De Mayo, *et al.*,[3] find that the cycloaddition of cyclopentenone to olefins may be sensitized by acetophenone, but not by benzophenone. The indirect method of triplet energy measurement admits of anomalies, and cyclopentenone could be one of these anomalies. The fact that photodimerization is competitive with piperylene quenching (see the previous paragraph) should not invalidate the photostationary-state technique for measuring triplet energies, but in any event the experimental results are contradictory. However, the value for cyclopentenone obtained by piperylene isomerization is in excellent agreement with Hammond's[4] value of 61 kcal for cyclohexenone using three different olefin isomer pairs. It is intuitively reasonable that cyclohexenone and cyclopentenone should possess similar excited states. At this time a definitive statement regarding the energy of the triplet state of cyclopentenone cannot be made.

The photochemical behavior of cyclopentenone in a cyclohexane–silica gel slurry[9] is easily rationalized. In the adsorbed state the enone molecules are tightly bound to the polar surface disallowing bimolecular cycloaddition except for those few molecules fortuitously situated such that the steric requirements for addition are met prior to absorption of a photon. Undoubtedly nearly all of that small amount of dimer that does form is formed in the supernatant solution phase. Formation of the cyclohexane adduct III probably can take place on the surface since cyclohexane will be weakly bound if at all.

Experimental Section

Materials. Cyclopentenone was obtained from K & K Laboratories, Plainview, N. J., and from Aldrich Chemical, Milwaukee, Wis. It was twice distilled at ~34° under aspirator pressure (15–25 mm), and stored at Dry Ice temperatures over molecular sieve granules. Spectrograde cyclohexane, benzene, and methanol from Baker Chemicals were used as received. Reagent grade 2-acetonaphthone and isopropyl alcohol from Baker Chemicals were used as received. Reagent grade benzophenone and xanthone were obtained from Matheson Coleman and Bell and were used without further purification. Reagent grade acetophenone, naphthalene, and nitrobenzene were used as received from Eastman Organic Chemicals. Silica gel was activated by heating for 12 hr or more at 175° and stored in a dessicator. *cis*-Piperylene (1,3-pentadiene), obtained from Frinton Laboratories, S. Vinetown, N. J., contained less than 1% of the *trans* isomer and was used without further purification. Technical grade piperylene, containing mostly the *trans* isomer, was obtained from Matheson Coleman and Bell and used as received.

Irradiation of Solutions. In general, irradiations were carried out in Pyrex tubes, using a 450-w Hanovia mercury arc lamp with a solution filter to eliminate all light but a band around the 3130-A line. The solution filter was composed of 20.75 g of $CoSO_4 \cdot 7H_2O$ and 72.5 g of $NiSO_4 \cdot 6H_2O$ in 250 ml of distilled water. Unless otherwise specified, the solvent for all irradiations of cyclopentenone may be assumed to be cyclohexane. In instances in which equal irradiation of several samples was desired, a "merry-go-round" apparatus was used. which carried the sample tubes around the lamp throughout the period of irradiation.

Product Analyses. Dimer ratios and relative yields, as well as by-products, were analyzed by vapor phase chromatography (vpc), using a 6-ft 15% Carbowax 20M column. For separation of dimers and by-products, the column was run at ~240°; for monitoring cyclopentenone disappearance, temperatures around 130° were used. Dimers I and II were correlated with their vpc peaks by following the product work-up described by Eaton[6] and injecting the individual dimers into the vpc.

Piperylene Quenching. Triplet quenching experiments were carried out using *cis*-piperylene at 0.1 *M* concentration, and cyclopentenone concentrations ranging from neat to 0.12 *M*. Solutions were irradiated for 3 hr on the "merry-go-round" with 3130-A light. The effect of added piperylene upon dimer yield was determined by comparison with yields obtained in solutions containing cyclopentenone only, at corresponding concentrations, which were irradiated under exactly the same conditions and for the same length of time. In general, it was necessary to concentrate the irradiated solutions by a factor of 10 when the initial cyclopentenone concentration was less than 1.0 *M*, before vpc analysis. This concentration was accomplished by means of a dry air jet at room temperatures.

Energy Transfer Experiments. Photosensitization experiments employed solutions 0.12 *M* in cyclopentenone and 0.10 *M* in sensitizer (or quencher, depending upon relative triplet levels). Per cent absorption due to energy transfer agent was calculated using extinction coefficients measured at 3130 A on a Perkin-Elmer Model 202 ultraviolet spectrometer. Solutions were irradiated for 3 hr with 3130-A light, using the "merry-go-round" apparatus. Acetophenone, xanthone, benzophenone, nitrobenzene, naphthalene, and 2-acetonaphthone were used as transfer agents in separate experiments. The effect of added transfer agent upon dimer yields was determined in the same manner as in the quenching experiments.

Luminescence Spectra. Attempts to measure phosphorescence and fluorescence of cyclopentenone were made using an Aminco-Bowman spectrophosphorimeter. Cyclopentenone was added to EPA (ether–isopentane–ethanol) in concentrations ranging from 0.001 to 0.1 *M*. These solutions were cooled to a glass at 77°K, and emission measurements were attempted with a range of excitation wavelengths spanning the absorption spectrum of cyclopentenone.

Determination of Cyclopentenone Triplet Energy. Triplet energy measurements were carried out on cyclopentenone by irradiating benzene solutions which were 0.2 *M* in *cis*-piperylene and 0.1 *M* in cyclopentenone. Samples were irradiated with 3130-A light until further isomerization of the piperylene no longer took place with further irradiation. The same was done using technical grade piperylene containing mostly *trans*-piperylene. The resulting photostationary *cis*/*trans* piperylene ratios were then analyzed using

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[9] For a discussion of spectroscopic and photochemical behavior of organic molecules adsorbed on silica gel, see P. A. Leermakers, H. T. Thomas, L. D. Weis, and F. C. James, *J. Am. Chem. Soc.*, **88**, 5075 (1966).

a 12-ft β,β'-oxydipropionitrile (25%) column at 60°. The experiment was carried out in duplicate on two separate occasions.

Triplet Counting. Singlet–triplet crossover efficiency experiments were carried out using the technique of Lamola and Hammond. This determination was done in duplicate, on two separate occasions. On the first occasion, a benzene solution 0.60 *M* in benzophenone and 0.10 *M* in *cis*-piperylene was irradiated for 1 hr with 3130-A light on the "merry-go-round," and the extent of isomerization to the *trans* isomer was measured using the β,β'-oxydipropionitrile column at 60°. A benzene solution 0.33 *M* in cyclopentenone and 0.10 *M* in *cis*-piperylene was also irradiated under the same conditions and for the same length of time. The extent of isomerization thus produced was compared with that obtained using the benzophenone solution. On the second occasion, the solutions were 0.30 *M* in benzophenone, 0.50 *M* in cyclopentenone, and 0.20 *M* in *cis*-piperylene.

Analysis of By-Product III. III was trapped from the vpc outlet, using the Carbowax 20M column at ~200°. The material thus obtained was then subjected to nuclear magnetic resonance analysis on a Varian A-60A spectrometer. Infrared analysis was carried out with a Perkin-Elmer Model 421 infrared spectrophotometer. Ultraviolet spectra were taken using a Perkin-Elmer Model 202 ultraviolet spectrophotometer. Carbon–hydrogen analysis was done by Eastman Kodak Research Laboratories, Rochester, N. Y. Mass spectral data were obtained through the courtesy of N. J. Turro at Columbia University.

Irradiation on Silica Gel. The behavior of cyclopentenone on silica gel was studied using slurries produced by intimate mixing of activated silica gel and solutions of cyclopentenone in cyclohexane. These slurries were in general irradiated in ~100-ml lots on the Hanovia lamp. Since the slurry was placed in the outer jacket of the lamp which normally contained the solution filter (*vide supra*), the only light filtration employed in irradiation of slurries was that provided by a Pyrex filter which cut out all light below about 3000 A. After irradiation, the slurry was removed and extracted with a 1:1 mixture of methanol and chloroform. The combined washings and supernatant cyclohexane solution originally remaining above the slurry were concentrated at room temperature under aspirator pressure, by a factor of about 100. This resulting mixture was then analyzed as usual by vpc, using the Carbowax 20M column at 240°.

Extent of Adsorption of Cyclopentenone on Silica Gel. This value was measured by comparing the ultraviolet spectra of the original cyclopentenone solution with that of the supernatant liquid above a slurry produced by combination of 0.50 g of activated silica gel and 1.0 ml of cyclopentenone solution.

Irradiation of Oxygenated Cyclopentenone Solutions. Oxygen gas was continuously bubbled through a solution of cyclopentenone in cyclohexane throughout irradiation for 3 hr. The solution was kept cold by surrounding it with an ice bath. The composition of the resulting solution was then compared with that of a nonoxygenated one of the same concentration, by vpc. The Carbowax 20M column was used as usual.

Acknowledgments. We are indebted to Dr. N. J. Turro for obtaining the mass spectrum of III and to Dr. J. A. Leermakers for C and H analyses of III. We also thank Dr. G. W. Griffin for authentic samples of I and II. Financial support was provided by National Institutes of Health (Grant GM 13592-01) and the American Chemical Society Petroleum Research Fund. Finally, we wish to thank Professors G. S. Hammond and P. De Mayo for prepublication copies of their results.

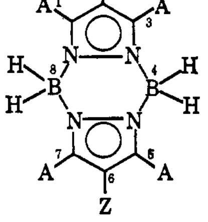
Boron–Pyrazole Chemistry. III. Chemistry of Pyrazaboles

S. Trofimenko

Contribution No. 1282 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.
Received May 19, 1967

Abstract: Pyrazaboles react with halogens and with some active hydrogen compounds to yield 4,8-di- and 4,4,8,8-tetrasubstituted derivatives. Diverse C-substituted derivatives were prepared by direct synthesis with subsequent reactions at the functional groups. The wide variety of transformations carried out indicates considerable stability of the pyrazabole ring system.

Pyrazaboles (I) are a novel class of remarkably stable boron heterocycles.[1,2] In the first paper of this series the synthesis and properties of pyrazaboles of structures I and II were discussed. These compounds were obtained by the reaction of appropriately substituted pyrazoles with borane complexes or with trialkyl- or triarylboranes, respectively. Although widely applicable, such a synthetic approach, henceforth referred to as "direct synthesis," still had some limitations. For instance, some borane or pyrazole components were not readily available; and certain borane–pyrazole combinations were incompatible. Hence, additional routes to pyrazaboles containing diverse boron and carbon substituents were of interest. This paper is concerned with two aspects of pyrazabole chemistry: (a) substitution chemistry of pyrazaboles and (b) chemical transformations of functionally substituted pyrazaboles which maintain the intact ring system.



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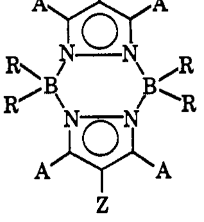

II

R = alkyl, aryl
A = H, alkyl, aryl, halogen
Z = H, R, NO_2, CN, halogen

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[1] S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966).

[2] S. Trofimenko, *ibid.*, **89**, 3165 (1967).