

# Photochemical Reactions of Simple Alicyclic Enones

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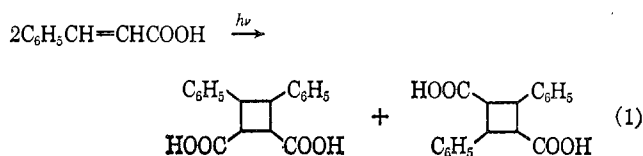
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The photochemistry of 2-cyclopentenone, 2-cyclohexenone, 2-cycloheptenone, 2-cyclooctenone, 1-acetylcyclopentene, 1-acetylcyclohexene, 1-acetylcycloheptene, and 1-acetylcyclooctene is discussed. Only photocycloaddition reactions leading to four-membered carbon rings and *cis-trans* isomerization reactions are considered.

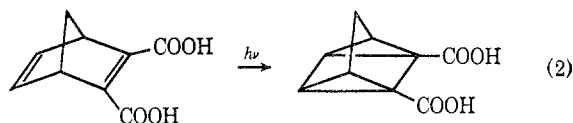
The rising importance of organic photochemistry needs little testimony. The past 10 years have been witness to a burst of enthusiasm by organic chemists for this field of their science. Indeed, for a time the cry of the day was "If you have some of it, irradiate it!" Now that at least some of the heat of the original activity has passed, it would perhaps be useful to review the progress made in one area of photochemistry in the context of its development. It is my purpose in this article to examine, in perspective, the developments of the past decade in the photochemistry of rather simple, cyclic, conjugated ketones with particular reference to light-induced cycloaddition and *cis-trans* isomerization reactions.

The photodimerization of two ethylenic units to form a cyclobutane ring is really an old and familiar reaction in the heritage of organic chemists. Its familiarity derives from the work of a half-century ago by Ciamician and Silber<sup>1</sup> and Stobbe<sup>2</sup> on the photochemistry of stilbene and styrene derivatives. Certainly the most well-known case is the photodimerization of cinnamic acid to the truxinic and truxillic acids (eq 1). It is,

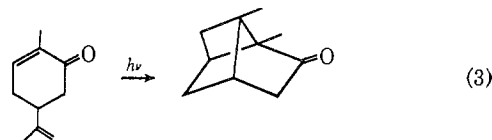


however, most important to realize, if one is to maintain any sense of the historical, that prior to the 1950's very little work had been done on the light-induced cycloaddition reactions of aliphatic, unsaturated carbonyl compounds. The two important reviews on organic photochemistry (there were only very few!) available in the fifties, Mustafa's article<sup>3</sup> and Schönberg's treatise,<sup>4</sup> together devoted only a few pages to cyclobutane formation from aliphatic systems.

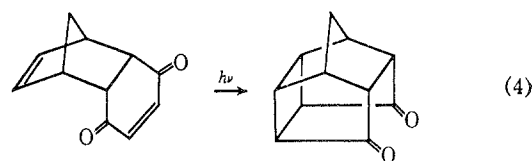
In 1957-1958 the situation started to change rapidly. Cristol at Colorado published his full paper on a norbornadiene-quadricycylene conversion (eq 2),<sup>5</sup> Büchi



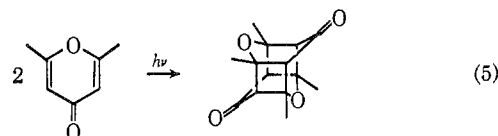
and Goldman at Massachusetts Institute of Technology verified Ciamician's work of 1908 on the carvone-carvonecamphor photoisomerization (eq 3),<sup>6,7</sup>



Cookson and his co-workers at Southampton demonstrated the photoisomerization of the cyclopentadiene-quinone Diels-Alder adduct to the cage isomer (eq 4),<sup>8</sup>



and Yates and Jorgenson at Harvard completed an elegant proof of structure for the photodimer of 2,6-dimethylpyrone first observed by Paternò in 1914 (eq 5).<sup>9</sup> To these observations, which deserve the



accolade "classic reactions," were soon added a variety of other important examples (eq 6-10).

It will not, I hope, escape the reader's attention that many of these photochemical reactions lead into the "cage" system of organic compounds. In fact, except for a very few isolated examples, the progress which has been made in the synthesis of such space-enclosing molecules has been tied very closely to the discovery of these reactions. The synthesis of the cubane system

(1) G. Ciamician and P. Silber, *Ber.*, **35**, 4129 (1902).

(2) H. Stobbe, *ibid.*, **45**, 3396 (1912).

(3) A. Mustafa, *Chem. Rev.*, **51**, 1 (1952).

(4) A. Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958.

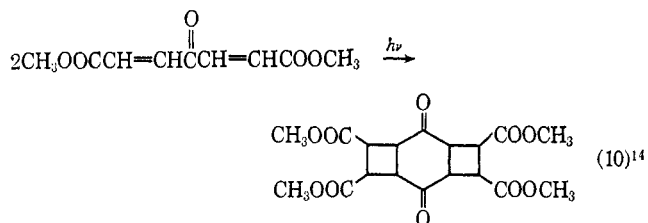
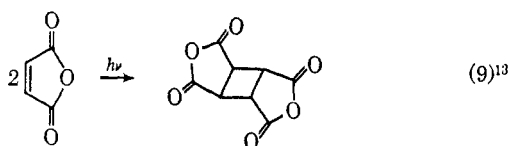
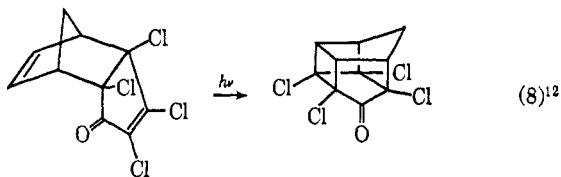
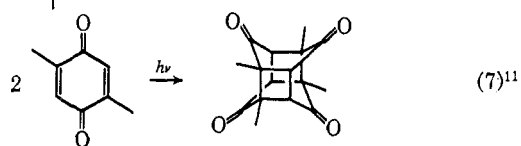
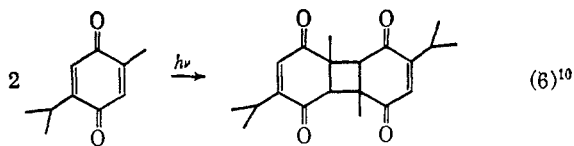
(5) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1951 (1958).

(6) G. Büchi and I. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957).

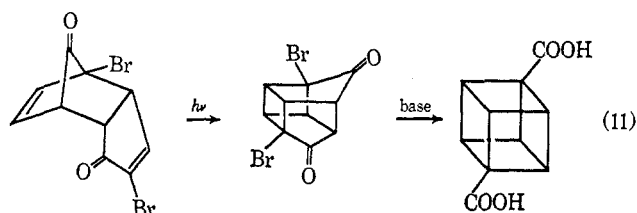
(7) G. Ciamician and P. Silber, *Ber.*, **41**, 1228 (1908).

(8) R. C. Cookson, E. Crundwell, and J. Hudec, *Chem. Ind. (London)*, 1003 (1958).

(9) P. Yates and M. J. Jorgenson, *J. Am. Chem. Soc.*, **80**, 6150 (1958); E. Paternò, *Gazz. Chim. Ital.*, **44**, 1, 151 (1914).

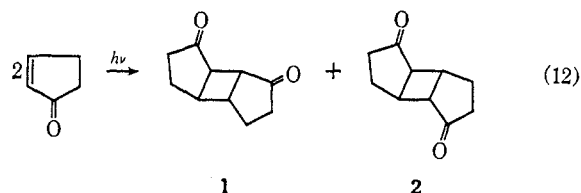


is an appropriate example of the value of such transformations (eq 11).<sup>15</sup>

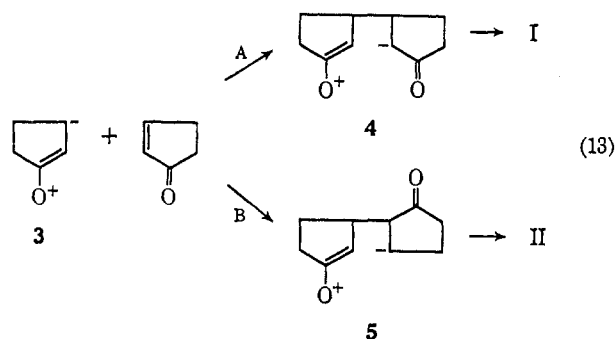


A study of the photochemical behavior of  $\alpha,\beta$ -unsaturated ketones was begun in my laboratory in 1960. The early impetus for this work, before the study became systematic, was the desire to develop an entry into the tricyclo[5.3.0.0<sup>2,6</sup>]decane system which was unknown at that time. It seemed most reasonable to attempt preparation of this ring system by photodimerization of 2-cyclopentenone, the simplest of the stable, alicyclic, conjugated ketones. Indeed, irradiation of cyclopentenone leads quickly and in high yield to a mixture of two (1 and 2, eq 12) of the possible cyclobutane dimers.<sup>16</sup> Rigorous proofs for the structures of these compounds were obtained by (1) referencing them to *cis,anti,cis*-cyclobutanetetra-

carboxylic acid, whose structure was known without ambiguity,<sup>17</sup> and (2) analysis of the nmr spectra of the lactones obtained by peracid oxidation of the dimers.



In the vernacular of photochemistry, photodimer 1 is known as a head-to-head dimer and dimer 2 as a head-to-tail dimer. The nomenclature comes of course from that of free-radical chemists, and in this case defines in part the position of one carbonyl group relative to the other. At the time of this work it was, for good and sound reasons,<sup>18</sup> the generally accepted thought that this aspect of the geometry of the union between monomeric units was determined in straightforward fashion by the electronic effects of substituents on the reaction intermediates. It is known, as I shall discuss later, that the photodimerization of cyclopentenone is the result of attack of a triplet excited state of the ketone on ground-state ketone, but it is still not possible to provide a map of the charge distribution within the excited state at the time of its reaction with the unexcited partner. For the purpose at hand, the polarized form 3 can be taken as one representation. Two nonconcerted pathways (A and B, eq 13) for the dimerization can be written easily.



Interaction of the negative charge with the adjacent carbonyl group should result in some stabilization of intermediate 4 relative to 5. Route A thus seems more attractive than route B; the head-to-head dimer 1 should be the preferred product. The same conclusion can be reached by taking an uncharged diradical as the most representative form of the excited state. If the polarization of the excited state were reversed to that of 3, dimer 2 should be the favored product.

Such simple ideas find neither support nor rejection in practice; the two photodimers of cyclopentenone are not formed in disparate amounts. The precise ratio of the dimers produced on irradiation of cyclopentenone is a gentle function of the properties of the reaction

(10) E. Zavarin, *J. Org. Chem.*, **23**, 47 (1958).

(11) R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 11 (1959).

(12) P. Yates and P. Eaton, *Tetrahedron Letters*, 5 (1960).

(13) G. W. Griffin, J. E. Basinski, and A. F. Velturo, *ibid.*, 13 (1960).

(14) J. Corse, B. J. Finkle, and R. E. Lundin, *ibid.*, 1 (1961).

(15) P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 962, 3157 (1964).

(16) P. E. Eaton, *ibid.*, **84**, 2344 (1962).

(17) R. Criegee and H. Höver, *Ber.*, **93**, 2521 (1960); G. W. Griffin, A. F. Velturo, and K. Furukawa, *J. Am. Chem. Soc.*, **83**, 2725 (1961).

(18) See, for example, F. D. Greene, S. L. Mistrock, and J. R. Wolfe, *ibid.*, **77**, 3852 (1955).

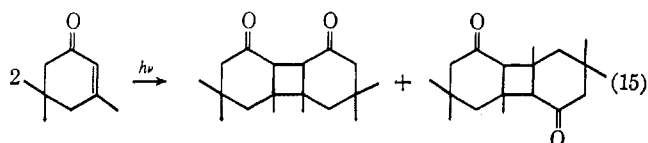
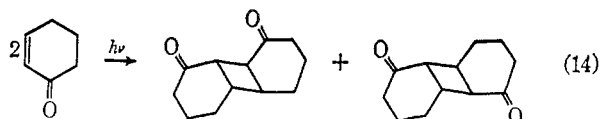
**Table I**  
**Ratio of Photodimers 1 and 2 Produced on Irradiation of**  
**2-Cyclopentenone<sup>a</sup>**

Solvent	Cyclopentenone, M	1:2
Cyclopentenone, neat	12.4	43:57
	10.0	41:59
Benzene	5.0	35:65
	2.0	27:73
	1.1	23:77
	0.093	15:85
1.0 M cyclopentanone in benzene	1.0	27:73
<i>t</i> -Butyl alcohol	1.0	24:76
Ethyl acetate	1.0	30:70
1,4-Dicarbomethoxycyclohexane	1.0	33:67
	10.5	41:59
Methanol	1.0	41:59
	0.1	39:61

<sup>a</sup> The reactions were run to approximately 10% completion using the light from a Hanovia 450-w mercury arc lamp filtered through Pyrex glass.

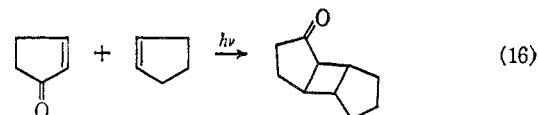
solvent, as recorded in Table I.<sup>19</sup> We shall return to this point later.

Since the time that the structures for the photodimers of cyclopentenone were worked out, proofs for the structures of the dimers of a variety of simple enones have been obtained. I can illustrate here only a small part of this work, and for this I will choose our own work on the dimerization of 2-cyclohexenone,<sup>20</sup> the next member in the homologous series of cyclic enones, and the work of Chapman, *et al.*, with isophorone,<sup>21</sup> which I wish to mention again briefly somewhat later. As will be apparent from the formulations (eq 14 and 15), these dimerizations lead also to mixtures of the head-to-head and head-to-tail products. Once again, solvent effects play a significant role in determining the ratio of products.

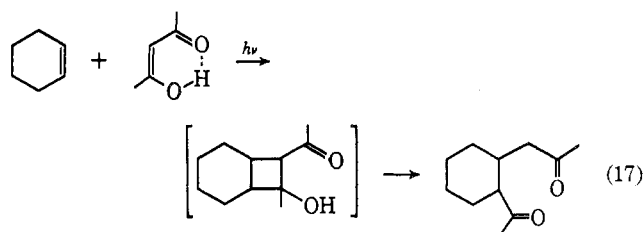


The observation that the carbonyl group in the nonexcited partner in the dimerization reaction does not appear to play an important electronic role in determining the products suggests that it should be possible to intercept the excited enone with olefins

other than those bearing a carbonyl function. Photodimerization would then be only a special case of a more general reaction, intermolecular photocycloaddition. We were able to demonstrate the truth of this proposition in 1962.<sup>22</sup> Irradiation of 2-cyclopentenone dissolved in the simple olefin cyclopentene leads in good yield to the substituted cyclobutane derived from addition of cyclopentenone to cyclopentene (eq 16).



As we have already seen, light-induced cyclobutane formation had been observed to occur *intramolecularly* between an olefin and an  $\alpha,\beta$ -unsaturated ketone as early as 1908 (*e.g.*, eq 3). The proximity of the condensing  $\pi$  systems in these examples might well have special significance in that geometrically enforced orbital overlap could contribute to the ease of reaction. No *intermolecular* analog of such mixed photocondensation reactions had been demonstrated fully prior to the example in eq 16, although de Mayo had proposed somewhat earlier (and later verified) that this reaction took place in his photochemical synthesis of 1,5-diketones (eq 17).<sup>23</sup>



To maintain historical accuracy, it is well that I quote the closing paragraph of the paper which reported the reaction in eq 16: "...attention is drawn to the potential synthetic utility of these photoaddition reactions. We have, for example, used cyclohexene and the butenes successfully as olefinic components. Presumably other  $\alpha,\beta$ -unsaturated carbonyl compounds could replace cyclopentenone. The reaction therefore offers an excellent route to new ring systems."<sup>22</sup> This prophesy has been amply verified. Examples of particular distinction are Corey's extraordinarily fine preparations of caryophyllene (eq 18)<sup>24</sup> and  $\alpha$ -caryophyllene alcohol (eq 19)<sup>25</sup> and White's synthesis of the bourbonenes (eq 20).<sup>26</sup>

Photocycloaddition reactions of  $\alpha,\beta$ -unsaturated ketones are not limited to the use of simple ethylenic substrates. Acetylenes and allenes were shown by us

(19) P. E. Eaton and W. S. Hurt, *J. Am. Chem. Soc.*, **88**, 5038 (1966); J. L. Ruhlen and P. A. Leermakers, *ibid.*, **89**, 4944 (1967).

(20) P. E. Eaton and A. S. Kushner, unpublished results.

(21) D. J. Trecker, A. A. Griswold, and O. L. Chapman, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S28; O. L. Chapman, paper presented at the 20th National Organic Symposium, Burlington, Vt., June 1967.

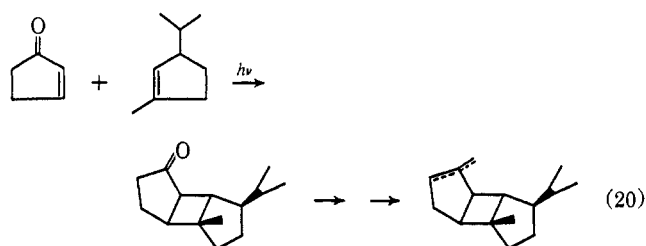
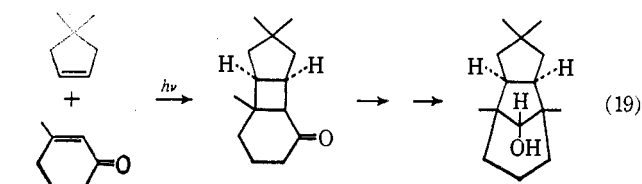
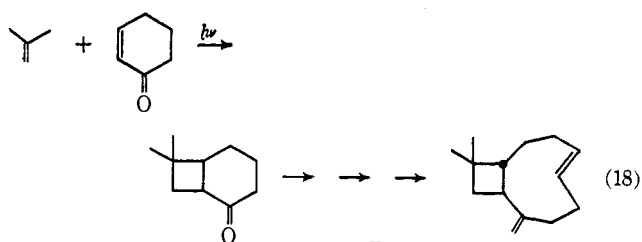
(22) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962).

(23) P. de Mayo, H. Takeshita, and A. B. M. A. Sattar, *Proc. Chem. Soc.*, 119 (1962); P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963).

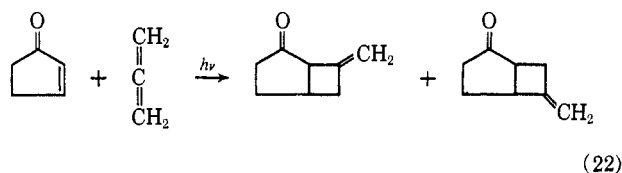
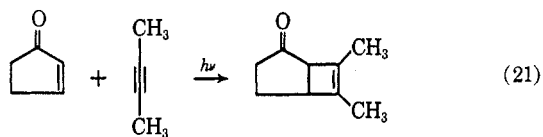
(24) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 485 (1964).

(25) E. J. Corey and S. Nozoe, *ibid.*, **86**, 1652 (1964).

(26) J. D. White and D. N. Gupta, *ibid.*, **88**, 5364 (1966).



in 1964 to be suitable reactants.<sup>27</sup> Photocycloaddition reactions with these substrates lead to substituted cyclobutenes (eq 21) and methylenecyclobutenes (eq 22), respectively.

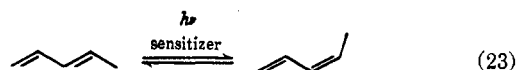


In general the photocycloadditions which we are concerned with here are brought about by light of wavelengths greater than 3000 Å. (In most cases the reactions are conducted in Pyrex vessels; Pyrex is essentially opaque to light below 3000 Å.) This is not to say that the reactions cannot be induced by light of lower wavelength (higher energy), but only that excitation of the  $n-\pi^*$  transition of enones is of sufficient energy (about 87 kcal/mole) to bring about reaction. The initial excitation is to an excited singlet electronic state; excitation from the singlet ground state to a triplet excited state is strongly forbidden. Intersystem crossing of the excited singlet with the triplet state is allowed, however,<sup>28</sup> and there is every reason to believe that most photocycloaddition reactions of simple enones are brought about by a triplet state.

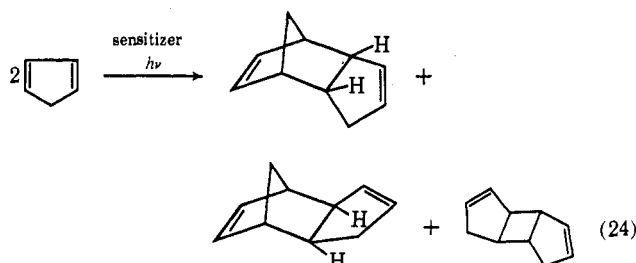
(27) P. E. Eaton, *Tetrahedron Letters*, 4395 (1964); R. Criegee and H. Furrer, *Ber.*, 97, 2949 (1964).

(28) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, 83, 2789 (1961); G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, 83, 2795 (1961).

Irradiation of cyclopentenone in the presence of piperlyene, under conditions such that only cyclopentenone absorbs any of the incident radiation, results in *cis-trans* isomerization of the diene (eq 23). A



similar experiment in which cyclopentadiene is used in place of piperlyene leads to the induced dimerization of this diene (eq 24). In both cases the consumption



of cyclopentenone is small. These observations provide qualitative evidence for the formation of a triplet state of cyclopentenone. Hammond, in part of his pace-setting studies in organic photochemistry, has demonstrated that the transfer of energy from the triplet excited state of a ketone to these dienes leads, *via* the diene triplets, to such isomerization and dimerization reactions.<sup>29</sup>

The intermolecular transfer of energy from the triplet state of cyclopentenone to a diene (a quencher) can compete with other intermolecular reactions of the triplet state. If the photocycloaddition reactions of cyclopentenone were due to attack of triplet enone on the substrate, the efficiency of these reactions would fall off with increasing concentration of quencher. It can be shown by simple kinetic analysis that if a triplet state of cyclopentenone were the *only* excited state participating in the photodimerization, then a plot of the reciprocal quantum yield for dimer formation against quencher concentration would be linear. Relative quantum yield is defined as the quantum yield for dimer formation in the absence of quencher divided by the quantum yield at a particular quencher concentration. Figure 1 depicts the results for the cyclopentenone-piperlyene system; a straight line fits the points well within experimental precision. Had even 5% of the dimerization reaction been caused by singlet cyclopentenone, the line would have curved distinctly in its upper reaches. Such experiments lead cleanly to the conclusion that a triplet state of cyclopentenone is the reactive species in the photodimerization reaction.<sup>19</sup>

The ratio of the two types of dimers, head-to-head and head-to-tail, produced on irradiation of cyclopentenone depends on the solvent and the concentration of cyclopentenone employed in the reaction (Table I). At one time it was thought that this could be taken as *prima facie* evidence for the participation of two dif-

(29) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *ibid.*, 83, 2396 (1961); N. J. Turro and G. S. Hammond, *ibid.*, 84, 2841 (1962).

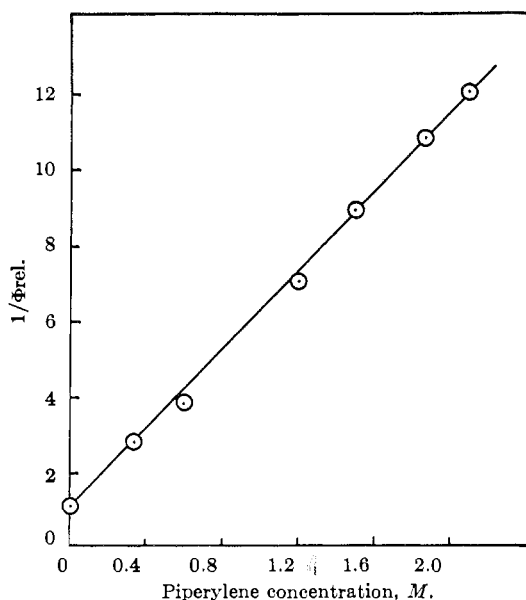


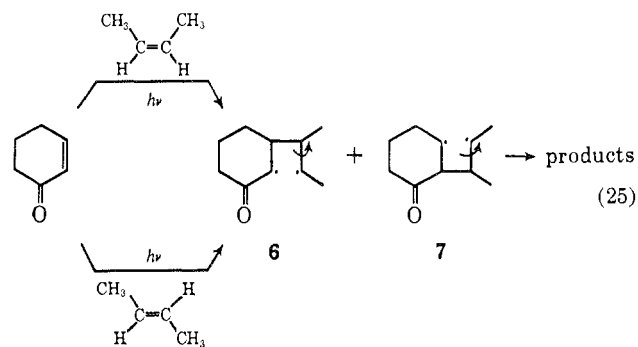
Figure 1. The reactions were run using benzene solutions 3.0 *M* in cyclopentenone and were taken to 11% completion with 3130-Å light. The piperylene used contained 26% *cis* isomer.

ferent excited states in the product-forming reactions. Such an interpretation however cannot be reconciled economically with other available data. The ratio of dimers formed has been shown to be independent of the method of triplet generation (*i.e.*, direct or sensitized), independent of the concentration of sensitizer, independent of the concentration of quencher (piperylene), and unaffected by the presence of an additional reactant (cyclopentene) which diverts triplet cyclopentenone from the dimerization process into the reaction of eq 16.<sup>19</sup> The photodimerization of cyclopentenone involves the union of two polar molecules. It is not surprising that the formation of the more polar dimer, II, is favored somewhat in the more polar solvents. There is no compelling reason to explain the solvent effect on the dimerization of cyclopentenone in terms other than those normally applied to the reactions of ground-state molecules. It appears, in turn, that the concentration dependence is no more than a manifestation of a solvent effect; that is, the character of the solvent is dependent on the concentration of cyclopentenone. As should be apparent from Table I, the concentration effect can be mimicked by altering the solvent. In particular, note that the ratio of dimers produced on irradiation of 1 *M* cyclopentenone in benzene 1 *M* in cyclopentanone is identical with that for irradiation of 2 *M* cyclopentenone in benzene. As might be expected, the concentration effect is most noticeable in nonpolar solvents.

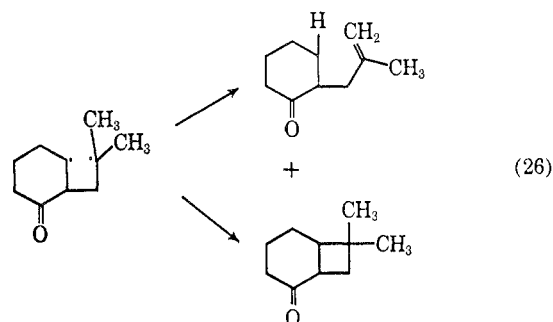
de Mayo has studied the photocycloaddition reactions of cyclopentenone with olefins and has concluded that triplet cyclopentenone is responsible for these reactions also.<sup>30</sup> It is reassuring to note that in the reactions

with nonpolar olefins the solvent effect on the direction of reaction is quite small. Hammond has shown that cyclohexenone photodimerization is a triplet-state reaction,<sup>31</sup> and Chapman has demonstrated that the same is true for reactions of isophorone.<sup>21</sup> Some evidence taken to indicate that more than one triplet is involved in the dimerization of isophorone has been uncovered.<sup>21</sup> This observation is surely of great significance, but as of the writing of this account insufficient information is available to justify discussion.

Two new carbon-carbon bonds are formed in the photocycloaddition reactions of interest to us here. It is generally assumed that these bonds are not formed concertedly. This formulation is derived primarily from Corey's observation that the same set of products is produced from the photoreaction of 2-cyclohexenone with either *cis*- or *trans*-2-butene.<sup>32</sup> The result indicates that the stereochemical integrity of the butene isomers is lost in a common reaction intermediate (**6** and/or **7**, eq 25), as might be predicted for a reaction brought about by a triplet. More detailed work is called for to strengthen this conclusion; in particular, pairs of stereoisomeric olefins substituted by polar groups should be examined.



Such diradical intermediates have been used as well to account quite economically for the olefinic by-products formed in the photocycloaddition of cyclopentenone or cyclohexenone with isobutylene (*e.g.*, eq 26). Corey has pointed out that this explanation is more attractive than one in which these olefins are produced by hydrogen atom transfer from isobutylene to excited enone followed by radical combination, for if cyclopentene is used in place of isobutylene little hydrogen abstraction occurs.<sup>32</sup>



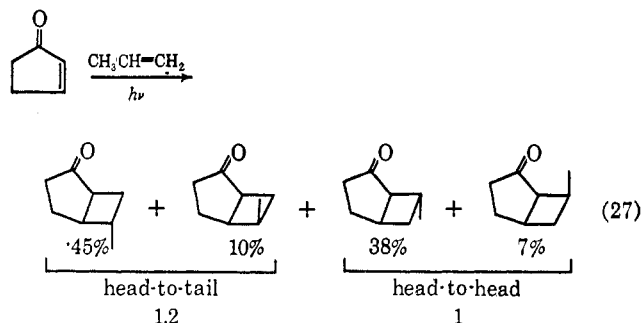
(30) P. de Mayo, J.-P. Pete, and M. Tahir, *J. Am. Chem. Soc.*, **89**, 5712 (1967). It is included in this paper that the lowest triplet state of cyclopentenone is inactive in these reactions and that it is a higher energy triplet state that effects cycloaddition. This possibility is of great interest and warrants further study.

(31) E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

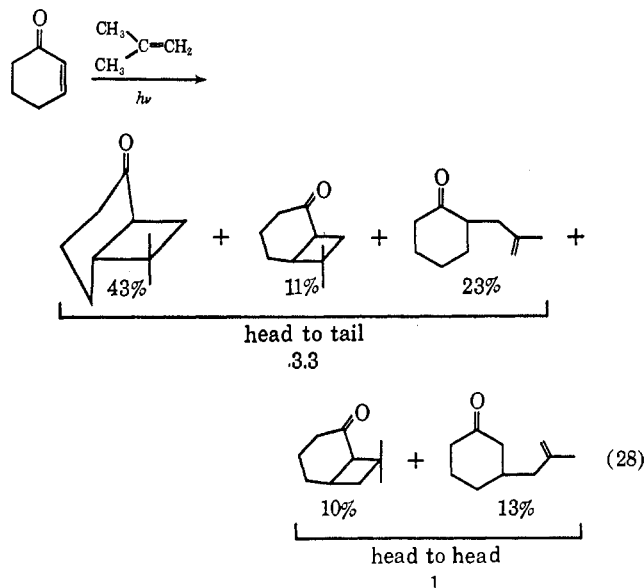
(32) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964).

Much effort has been put into determining the effects of enone or substrate substituents on the outcome of photocycloaddition reactions. From this work certain operational definitions sometimes useful in predicting the applicability of the reaction to problems in synthesis have emerged.

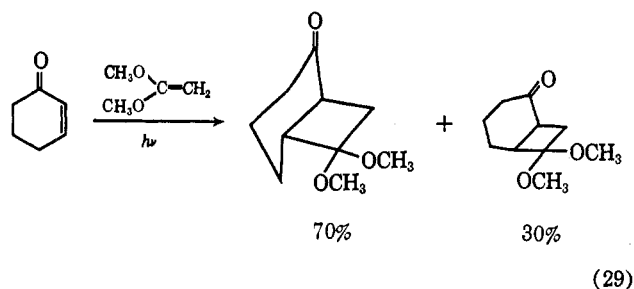
The direction of photocycloaddition, that is, head-to-head *vs.* head-to-tail, is not particularly influenced by substituents on the olefinic substrate except in those cases in which the olefin carries a powerful electron-donating group. Thus, the reaction of cyclopentenone with propylene leads to an about even distribution of the head-to-head and head-to-tail products (eq 27).<sup>33</sup> Some preference for head-to-tail addition can be



discerned in the cycloaddition of cyclohexenone with isobutylene (eq 28);<sup>32</sup> but the factor is really rather small, a point that has not been fully appreciated. Note that I have included the olefinic products in calculating this factor; these compounds probably arise from the same intermediates that lead to the cyclobutanes.



The reactions of olefins bearing an ethereal oxygen substituent lead preferentially (and in some cases exclusively) to the head-to-tail products (eq 29).<sup>32</sup> On the other hand, as we have already seen, olefins bearing electron-withdrawing groups (the substrates in photodimerization) do not react selectively to

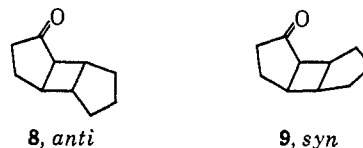


form products of reversed geometry (*e.g.*, eq 12, 14, and 15). Preliminary evidence has been presented to show that the major products from the reaction of cyclohexenone with acrylonitrile (electron-withdrawing group) are head-to-head, but the head-to-tail product(s) is also formed in not inconsiderable amounts.<sup>32</sup> Solvent effects on this reaction between polar molecules have yet to be evaluated.

Some measurements have been made on the efficacy of various olefinic substrates in competition for the enone excited state. It would seem from the limited data available that electron-releasing groups enhance somewhat the reactivity of olefins, and, conversely, electron-withdrawing substituents depress reactivity. For example, cyclopentenone and cyclohexenone react on irradiation with 1,1-dimethoxyethylene about five times faster than with cyclopentene;<sup>32</sup> the reaction of cyclopentenone with cyclopentene is about three times faster than photodimerization.<sup>34</sup> These relative rate factors are not large.

Corey has chosen to call the reactive state of an excited enone entering a photocycloaddition reaction "moderately electrophilic."<sup>32</sup> This terminology is suitable, but only if one holds carefully in mind the fact that in many of their reactions these moderate electrophiles exhibit preferences orders of magnitude less well developed than those of full-blown electrophilic species.

Steric factors certainly play a significant role in determining the products of photocycloaddition reactions. The dimerizations of cyclopentenone and cyclohexenone and the addition of cyclopentenone to cyclopentene lead to at least a tenfold predominance of products of *anti* configuration (*e.g.*, 8) over the *syn* isomers (*e.g.*, 9). In these cases the *syn:anti* ratio is fixed immediately upon formation of the first of the two new carbon-carbon bonds to be formed. In the addition of cyclopentenone to propylene (eq 27) products of the *anti* configuration are favored by 3:1. As the addition here is to an acyclic olefin, the geometry of the products may be fixed after the first bond has formed, but this is not necessary.



The photocycloaddition reactions of 2-cyclohexenone

(33) P. E. Eaton and N. Heap, unpublished results.

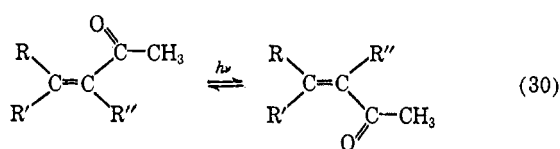
(34) P. E. Eaton and W. S. Hurt, unpublished results.

sometimes lead to products in which the six- and four-membered rings are fused *trans* as well as to the thermodynamically more stable *cis*-fused adducts.<sup>32</sup> This seems to be true only if the olefinic substrate is not substituted by electron-withdrawing groups, for the addition of cyclohexenone to acrylonitrile and the dimerization of cyclohexenone lead only to *cis*-fused compounds. In the addition of 1,1-dimethoxyethylene (eq 29), the *trans*-fused product is favored by 2:1. In the reaction with isobutylene (eq 28), the *trans*-fused, head-to-tail product predominates over the *cis*-fused epimer by 4:1. It has been obvious for a long time that this point must have special significance, but as yet no explanation which has been put forth can be considered sufficient.

Substitution of a methyl group for hydrogen at either the  $\alpha$ - or  $\beta$ -vinyl carbon of 2-cyclohexenone markedly affects the photochemical behavior of the system. The reaction of 2-methyl-2-cyclohexenone with isobutylene is extremely complex and is reported to lead to at least seven products.<sup>32</sup> 3-Methyl-2-cyclohexenone, on the other hand, reacts quite smoothly with isobutylene, but the head-to-head product is formed predominantly rather than the head-to-tail isomer produced as the major product in the cycloaddition of unsubstituted cyclohexenone with isobutylene.<sup>32</sup> Isophorone, a 3-methyl-2-cyclohexenone, does however react with isobutylene to give head-to-tail adducts predominantly.<sup>21</sup>

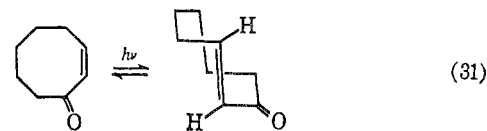
In the opinion of this author, with apologies to my less conservative colleagues, no really satisfying theory has yet been put forth to draw together all the observations made thus far on the photocycloaddition reaction. Ignoring the awkward question as to whether or not these observations can be tied together in the grand manner, I can hope that the design and performance of new and more subtle experiments will remedy this. Fortunately, at least from the utilitarian's point of view, the lack of any real understanding in depth has not interfered too seriously with the use of these reactions by synthetic organic chemists, nor has it delayed the discovery of other interesting and important processes in the photochemistry of enones.

As we have seen, cyclopentenones and cyclohexenones readily undergo a variety of photocycloaddition reactions. On the other hand, it is well known that the primary photochemical reaction of most acyclic enones is *cis-trans* isomerization about the double bond (eq 30). Apparently intermolecular cyclo-

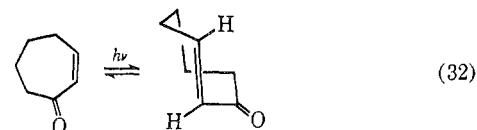


addition reactions cannot compete with this intramolecular process. No evidence has yet been found for the *cis-trans* isomerization of cyclopentenone or cyclohexenone; the process is probably not geometrically permissible.

In early 1964 we were able to establish that *cis*-2-cyclooctenone could be equilibrated photochemically with the previously unknown *trans* isomer (eq 31).<sup>35</sup>



In 1965 we<sup>36</sup> and Corey with his co-workers<sup>37</sup> demonstrated that a similar isomerization took place on irradiation of *cis*-2-cycloheptenone (eq 32). These



isomerizations take precedence entirely over the photochemical reactions characteristic of cyclopentenone and cyclohexenone. Nor true photocycloaddition reactions can be observed. Although dimerization and addition reactions do occur, these have been shown unequivocally to be reactions of *trans*-2-cyclooctenone and *trans*-2-cycloheptenone that occur readily *in the dark*. Irradiation of the *cis* isomers in the presence of piperylene or cyclopentadiene leads neither to sensitized isomerization of piperylene nor to sensitized dimerization of cyclopentadiene, in contrast to the corresponding experiments with the five- and six-membered cyclic enones. The intramolecular *cis-trans* isomerization of cyclooctenone and cycloheptenone, presumably *via* the triplet state, is very much faster than either intermolecular energy transfers or cycloadditions. Photochemical *cis-trans* isomerization can no longer be considered a remarkable process *per se*. What is notable is that this reaction dominates the photochemistry of the medium-ring cycloalkenones and provides exceptionally easy access to compounds of great interest.

It is clear that the flexibility of the ring determines the photochemical behavior of the simple cycloalkenones. A triplet state is responsible for the intermolecular reactions induced on irradiation of cyclopentenone or cyclohexenone, whereas the ground-state *trans* isomer produced photochemically accounts for the reactions of cycloheptenone and cyclooctenone. We are now studying the photochemistry of the 1-acetylcycloalkenes, acetylcyclopentene through acetylcyclooctene.<sup>34</sup> In these  $\alpha,\beta$ -unsaturated ketones, the vinyl carbon atoms are part of the ring system, but the  $sp^2$ -hybridized carbon of the carbonyl group is external to it. Thus, the ring is less rigid than it is in the cycloalkenone of corresponding ring size.

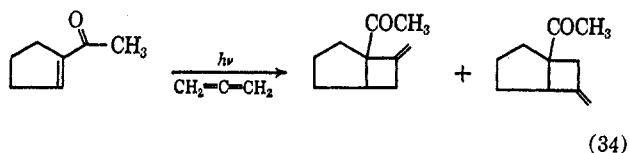
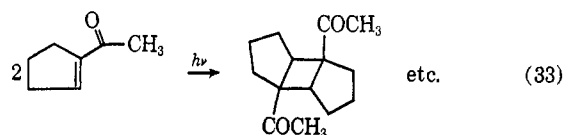
Irradiation of 1-acetylcyclopentene leads to results very similar to those obtained on irradiation of cyclopentenone or cyclohexenone. Photodimerization oc-

(35) P. E. Eaton and K. Lin, *J. Am. Chem. Soc.*, **86**, 2087 (1964); see also ref 34.

(36) P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965).

(37) E. J. Corey, M. Tada, R. LeMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965).

curs readily (eq 33), as does photocycloaddition to olefins, acetylenes, and allenes (e.g., eq 34). Dienes



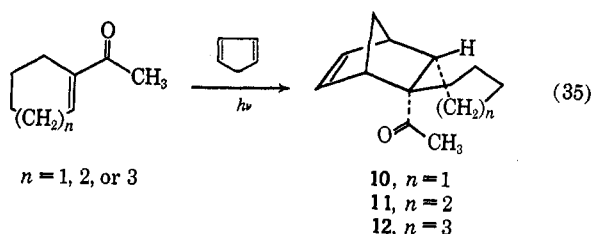
quench the photochemical reactions of acetylcyclopentene. In the case of piperylene, *cis-trans* isomerization of the diene occurs; when cyclopentadiene is used, dimerization of the diene is the major reaction observed. Although the evidence is more qualitative, it appears that a triplet state is responsible for the light-induced, intermolecular reactions of acetylcyclopentene, as it is for those of cyclopentenone and cyclohexenone.

The photochemical behavior of the higher acetylcycloalkene homologs is very different from that of acetylcyclopentene, cyclopentenone, or cyclohexenone, but it bears a definite similarity to that of cycloheptenone and cyclooctenone. We have, I believe, sufficient circumstantial evidence to permit the tentative conclusion that 1-acetylcyclohexene,<sup>38,39</sup> -cycloheptene, and -cyclooctene undergo *cis-trans* isomerization on irradiation. Let me make it clear that although this interpretation is both rational and economic, it is nonetheless still speculative.

Acetylcyclohexene, acetylcycloheptene, and acetylcyclooctene are not effective sensitizers for the isomerization of piperylene or the dimerization of cyclopentadiene. *cis-trans* isomerization of the enone would be expected to be faster than intermolecular energy transfer. Irradiation of each of these enones in neat cyclopentadiene leads to the production in good yield of the Diels-Alder adducts **10**, **11**, and **12**, respectively (eq 35). The structure of compound **12** has been proven. Note the *trans* fusion of the ring systems, as would be expected from a Diels-Alder reaction with a *trans* olefin. Compounds **10** and **11** have chemical properties similar to those of **12**, and quite different from those of both *cis*-fused Diels-Alder adducts of cyclopentadiene to *cis*-1-acetylcyclooctene. However, the assignments of structure to **10** and **11** must still be considered tenta-

(38) Cf. R. A. Schneider and J. Meinwald, *J. Am. Chem. Soc.*, **89**, 2023 (1967). The explanation given in this paper for the observation that 1-acetylcyclohexene reacts on irradiation with isobutylene to give only olefinic product rather than cyclobutanes is weakened considerably by the fact that 60% of the products from the photoreaction of 1-acetylcyclooctene with isobutylene are the expected cyclobutanes.<sup>34</sup>

(39) B. J. Ramey and P. D. Gardner [*ibid.*, **89**, 3949 (1967)] have suggested recently that *trans*-1-acetylcyclohexene might be involved in the photochemical addition of alcohols to acetylcyclohexene.



tive. Although cyclopentadiene does not react in the dark with any of the acetylcycloalkenes at a significant rate, addition of cyclopentadiene to a solution of acetylcyclooctene after this solution has been exposed to ultraviolet light leads (in the dark!) to the formation of compound **12** (about 3% conversion). Similar experiments with acetylcycloheptene and acetylcyclohexene fail to produce **10** or **11**, but one would expect that the lifetime of the *trans* isomers of these enones would be much shorter than that of the *trans* isomer of acetylcyclooctene.

We have been able to demonstrate by ultraviolet spectroscopy that irradiation of 1-acetylcyclooctene leads to its equilibration with a new compound of higher extinction coefficient than the starting material at 322  $m\mu$ . This material decays in the dark at room temperature; 50% of the absorption attributable to it disappears in about 30 min. The decay is very slow, however, at Dry Ice temperature. Presumably, it is the same material that gives rise to adduct **12** on addition of cyclopentadiene to preirradiated solutions of acetylcyclooctene. A similar spectroscopic result has been obtained by irradiating isopentane solutions of acetylcycloheptene, but only at very low temperatures. The material produced by this irradiation has quite a strong absorption peaking at 282  $m\mu$  but extending well into the  $n-\pi^*$  absorption of the starting material. Fifty per cent of this absorption disappears in 6 min at  $-155^\circ$ .

The labile compounds seen in these spectroscopic experiments are taken to be the *trans* isomers of the corresponding *cis*-1-acetylcycloalkenes. The enhanced extinction coefficient of their absorption in the 300- $m\mu$  region over that of the *cis* isomer may be due to a reduction in the symmetry forbiddenness of the  $n-\pi^*$  transition caused by a small torsional distortion in the p-orbital overlap at the strained *trans* double bond. A simple extrapolation of the lifetimes of these compounds shows us that we have not yet reduced the time constants of our experiments sufficiently to detect *trans*-1-acetylcyclohexene spectroscopically. This, along with the additional experiments needed to secure these conclusions, remains for the future. So too does an inquiry into the nature of "*trans*" double bonds in strained rings.

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