lution of sodium cyclopentadienide. The latter was added to THF (50 mL) containing tungsten hexacarbonyl and the mixture reacted for 12 h. The resulting solution of $Na[C_5H_5W(CO)_3]$ was filtered into a Carius tube containing the thione. The Carius tube was sealed, heated at 110–120 °C for 3 days, and then cooled. The tube was opened and the reaction mixture was worked up as described for the reaction of **5** with **7**, M = Mo, n = 3.

Reaction of Thiobenzophenones (5) with the Methylcyclopentadienyliron Dicarbonyl Anion (11, M = Fe, n = 2). Using NaK (Method A). A solution of methylcyclopentadienyliron dicarbonyl dimer (1.15 g, 3.0 mmol) in THF (50 mL) was stirred with NaK (0.3 mL) at room temperature for 1 h. The solution of $K[CH_3C_5H_4Fe(CO)_2]$ was filtered and the filtrate was reacted with the thiobenzophenone (6 mmol) for 16 h at room temperature. Workup was effected in the same manner as that described for reaction of **5** with **7**, M = Fe, n = 2.

Using 18-Crown-6 (Method C). The procedure described for the reaction of **5** with the cyclopentadienyliron dicarbonyl dimer was utilized here.

Acknowledgments. We are grateful to the National Research Council of Canada, and to Imperial Oil Ltd., for support of this research. We are indebted to Henley and Co., New York, N.Y., for providing generous quantities of hexamethylbicyclo[2.2.0]hexa-2,5-diene, required for the synthesis of **14.**

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A Comparison of the Photoaddition Reactions of Nucleic Acid Nitrogen Bases and Cyclohexenones with Isobutylene. The Role of Rigidity in Product Formation

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Abstract: The acetone-sensitized photoaddition of uracil, thymine, 6-methyluracil, and their 1,3-dimethyl derivatives to isobutylene has been studied and compared with analogous reactions with cyclohexenones. For the nitrogen base systems little regioselectivity was noted since mixtures of cis-fused 7,7-dimethyl- and 8,8-dimethyl-2,4-diazabicyclo[4.2.0]octa-3,5-dione derivatives were formed in good yields. The results for these systems contrast markedly with those for the photoadditions of the analogous cyclohexenones to isobutylene which often yield complex product mixtures. Labeling studies using isobutylene-*1,1-d*$_2$ establish that the ene products formed from the additions of cyclohexenone to isobutylene do not proceed via a symmetrical allylic species. The differences between these two systems are related to the flexibility of the ring systems rather than a marked change in the mechanism of the reaction.

Introduction

The similarity of the photochemistry of nucleic acid nitrogen bases and cyclic enones, while noted by several investigators,[2a,b] was placed on a firm experimental basis by Wagner and Bucheck.[2c] These workers established that the dimerization of cyclohexenone and uracil both proceeded from a triplet state ($E_T \sim 70$ kcal/mol) and followed similar kinetic schemes. Furthermore, they proposed that interaction of the triplet state of the nitrogen base or cyclic enone with a ground state molecule initially produces an exciplex. The exciplex subsequently collapses to give a biradical prior to product formation. This scheme is generalized below. More recently the cycloaddition of triplet 1,3-dimethyluracil to oxygenated olefins has been shown to proceed in a regiospecific manner, a behavior again paralleling that of cyclohexenone.[3] Supporting this formal similarity between the excited state reactions of uracil and cyclohexenone are recent calculations which reveal that the uracil π–π^* transition is largely localized in the enone moiety and that the uracil π–π^* state might best be viewed as an enonelike excited state.[4]

Scheme I. Abbreviated Mechanism for Photochemical Cycloaddition

$C^{*3} + O \rightarrow$ [exciplex]
[exciplex] $\rightarrow$ biradical
biradical $\rightarrow C + O$
biradical $\rightarrow$ products

C = uracil or cyclohexenone
O = olefinic substrate

Our motivation in initiating a study of the cycloaddition reactions of uracil, thymine, and 6-methyluracil to isobutylene was twofold. First, we hoped to utilize analogous photoaddition reactions in the synthesis of modified pyrimidine and nucleoside derivatives.[5] In this context, the complex photoaddition mixtures and low yields of products obtained in irradiations

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Table I. Yields of Cycloadducts from Nitrogen Bases and Isobutylene

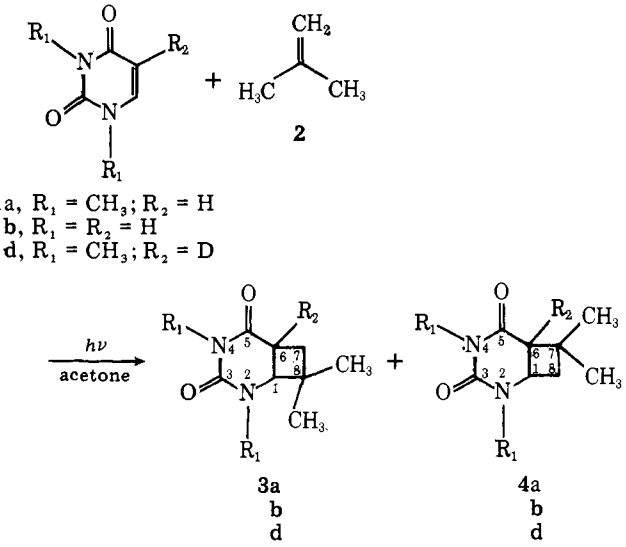
Compd	Isomer ratio 7,7-Dimethyl:8,8-Dimethyl	Yield, %
1a	45:55	76[a]
1b	25:75	92[b]
5a	53:47	90[a]
5b	27:72	92[b]
8a	53:47	72[a]
8b	31:69	97[b]

[a] Isolated yield after chromatography. [b] Yield by VPC employing an internal standard.

of some cyclohexenones and isobutylene[6] suggested a limitation on the photoaddition reactions of uracil and acyclic olefins. Thus, we wished to establish in a simple system what complications could arise in uracil additions to acyclic olefins bearing allylic hydrogens. Second, the mechanistic details of the photoaddition reactions of cyclohexenones to olefins invoked extensive discussion and speculation.[7,8] Two complications in understanding the behavior of cyclohexenone systems are the close positioning of the n-π^* and π-π^* triplets and the geometric distortion in this ring system. In contrast, the nitrogen base systems should have lowest π-π^* triplet states,[4] and the rigidity of the ring system should strongly inhibit pronounced geometric change in the relaxed excited state. Thus, the photoaddition behavior of the nitrogen bases could serve as models for nearly planar π-π^* triplets, and perhaps studies of their photoaddition behavior could aid in dissecting the importance of geometric change in cyclohexenone photoadditions. In view of the formal similarities of uracil and cyclohexenone photochemistry and the published studies and theoretical treatment of the effect of 2- and 3-methyl substitution on the photoreactivity of cyclohexenone,[9] the photoaddition reactions of nitrogen bases and isobutylene would be a most appropriate system for study.

Photochemical Studies

Establishment of Product Orientation. The acetone-sensitized cycloaddition of 1,3-dimethyluracil (**1a**) to isobutylene (**2**) afforded two adducts **3a** and **4a** in a ratio of 55:45 (76% isolated yield). The NMR and mass spectra of these compounds indicated the materials to be cycloadducts of **1a** and **2**; however, we were not confident in assigning the orientation of the particular compounds from spectroscopic data on the protio systems. Thus, the sensitized cycloaddition of **1d** and **2** was studied. For cycloadduct **3d**, H_1 appeared as a singlet as δ 3.58 and the methylene group at C_7 appeared as an AB quartet centered at δ 2.15 (J = 12.5 Hz). By contrast, **4d** showed H_1 as a broad triplet at δ 3.91 and the methylene protons at C_8 as a multiplet centered at δ 2.12.



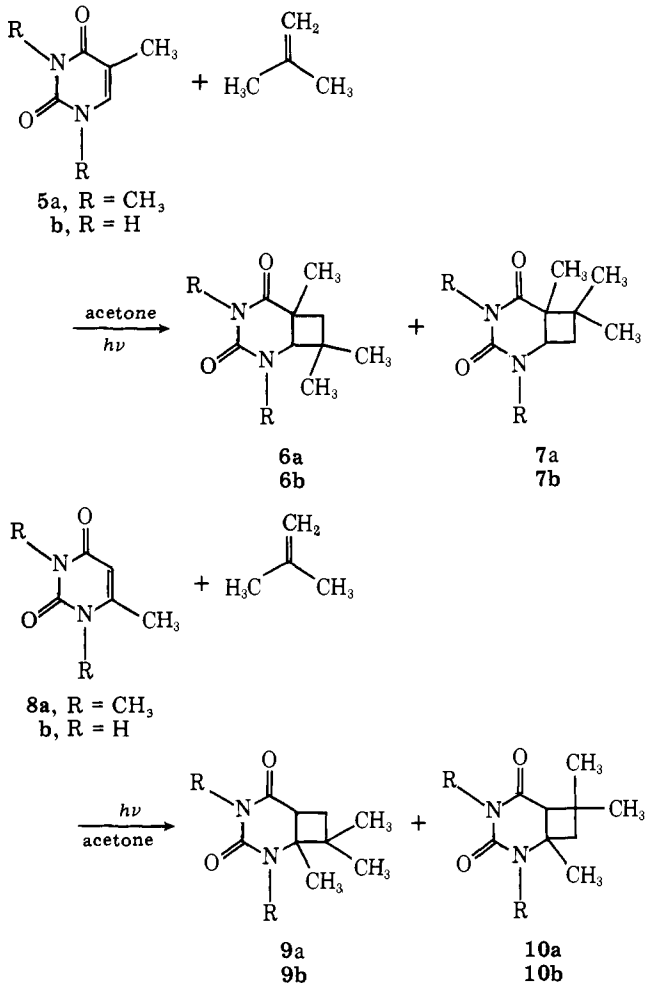
Since we wished to establish for future studies that the potential tautomerization in the parent bases did not dramatically

Table II. NMR Absorptions for Cycloadducts (δ)

Compd	Solvent	C_1	C_6	C_7	C_8
3a	$CDCl_3$	3.55 (d, J = 9.5 Hz)	3.30 (partially obscured)	2.30-1.80 (m)	CH_3- 1.20 (s) CH_3- 1.02 (s)
4a	$CDCl_3$	3.6-4.0 (m)	3.10 (partially obscured m)	CH_3- 1.32 (s) CH_3- 1.10 (s)	2.5-1.6 (m)
6a	$CDCl_3$	3.22 (partially obscured)	CH_3- 1.43 (s)	1.95 (center of AB quartet) J = 12 Hz)	CH_3- 1.19 (s) CH_3- 0.95 (s)
6b	CF_3CO_2H	3.72 (d, J = 4 Hz)	CH_3- 1.62 (s)	2.24 (center of AB quartet) J = 12 Hz)	CH_3- 1.22 (s) CH_3- 1.18 (s)
7a	$CDCl_3$	3.45 (t, J = 7 Hz)	CH_3- 1.33 (s)	CH_3- 1.12 (s) CH_3- 1.06 (s)	2.15 (d of d, J = 7, 13 Hz) 1.75 (d of d, J = 7, 13 Hz)
7b	CF_3CO_2H	3.95 (m)	CH_3- 1.49 (s)	CH_3- 1.26 (s, 6 H)	2.36 (d of d, J = 8, 12 Hz) 2.06 (d of d, J = 8, 12 Hz)
9a	$CDCl_3$	CH_3-1.49 (s)	3.00 (partially obscured m)	2.3-1.7 (m)	CH_3- 1.12 (s) CH_3- 1.07 (s)
9b	CF_3CO_2H	CH_3- 1.48 (s)	3.32 (t, J = 9 Hz)	2.56-2.08 (m)	CH_3- 1.22 (s, 6 H)
10a	$CDCl_3$	CH_3- 1.40 (s)	2.90 (s, partially obscured)	CH_3- 1.30 (s) CH_3- 1.09 (s)	1.97 (center of AB quartet, J = 12 Hz)
10b	CF_3CO_2H	CH_3- 1.63 (s)	3.12 (s)	CH_3- 1.45 (s) CH_3- 1.33 (s)	2.30 (s)

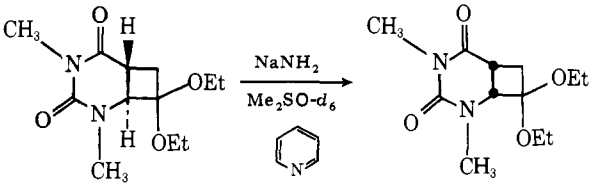
affect photoaddition behavior, the reaction of these compounds with isobutylene was studied. For uracil (**1b**), photoaddition to isobutylene afforded two major products (inferred by NMR) which could not be separated. To identify and analyze the reaction products, the crude irradiation mixture was methylated (sodium hydride and dimethyl sulfate) and the products were characterized as their 1,3-dimethyl derivatives. The formation of **3b** and **4b** in 92% yield indicates that the potential tautomerization of the uracil to the dihydroxypyrimidine form has no major consequence of photoaddition behavior. However, the ratio of regioisomers was somewhat altered (75:25) from the 1,3-dimethyl system (55:45).

For the remaining nitrogen base systems **5** and **8**, acetone-



sensitized addition to isobutylene proceeded smoothly to afford a mixture of cycloadducts which could be separated by a combination of silica gel chromatography and preparative VPC (Table I). In the case of these cycloadducts, the orientation of the nitrogen base vs. isobutylene could be readily established by NMR (Table II).

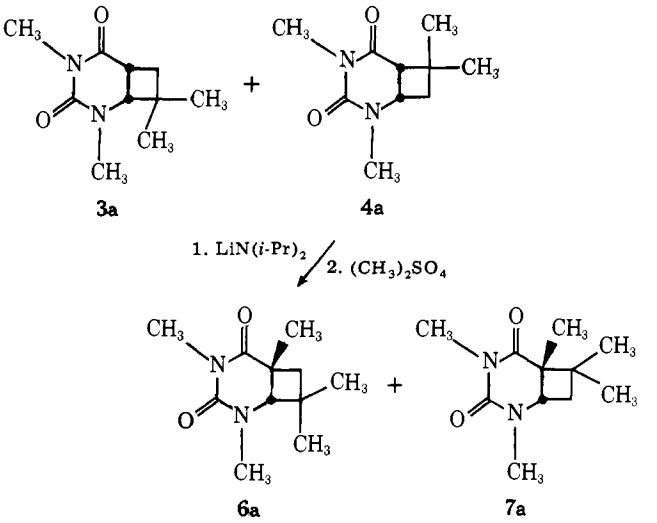
Stereochemistry of the Ring Fusion. Since the major product from photoaddition of cyclohexenone and isobutylene and a minor product from 1,3-dimethyluracil and ketene diethyl acetal possess a trans ring fusion,[3,6] it was imperative to rigorously establish the question of ring stereochemistry for the present cycloadducts. The most obvious approach for adducts **3, 4, 9**, and **10** involved attempted epimerization in base of the more strained trans isomer to the cis isomer. When the known trans compound, **11**,[3] was treated with sodium amide in Me_2SO-d_6 and pyridine, rapid isomerization to **12** occurred, demonstrating the facile isomerization of trans to cis ring fusion under these conditions. When compounds **3a, 4a, 9a,** and **10a** were subjected to the identical reaction conditions, no



11 **12**

change in their NMR spectra resulted,[10] establishing the cis ring juncture for these compounds.

For the thymine adducts, **6a** and **7a,** such a procedure was not applicable so authentic cis-fused compounds were prepared. When a mixture of **3a** and **4a** in dioxane was treated



with lithium diisopropylamide followed by the addition of dimethyl sulfate, **6a** and **7a** were produced in 70% yield. Since it is unreasonable to suppose that trans ring fusions would be produced in these alkylations, the ring fusion in the thymine adducts is cis also. The cis stereochemistry for the adducts **3b, 4b, 6b, 7b, 9b,** and **10b** rests largely on analogy with the results for the 1,3-dimethyl systems. It appears quite unreasonable that the methyl substituents could cause a change in the stereochemistry at the ring fusion.

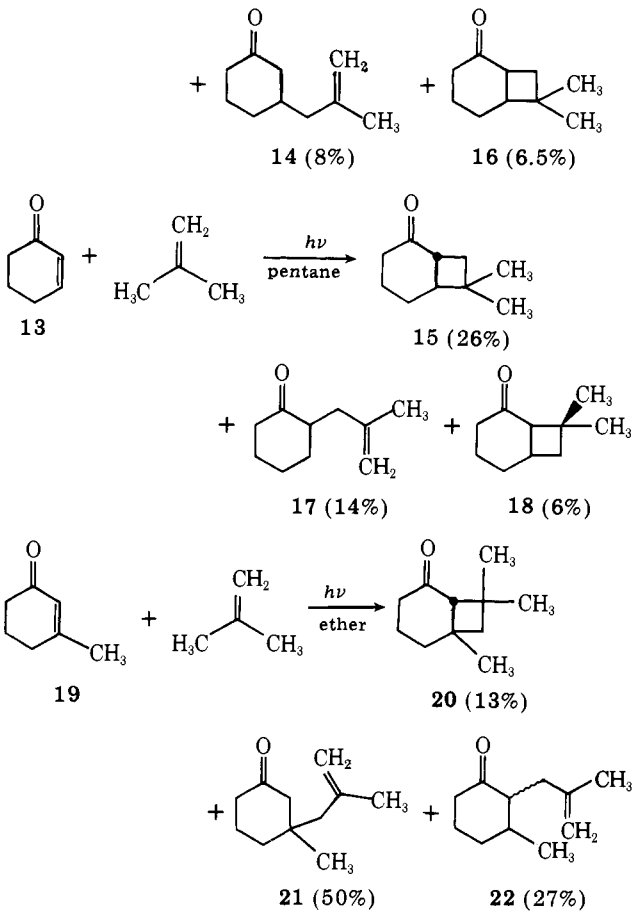
Photoaddition of Cyclohexenone and Isobutylene-*1,1-d*$_2$. A most striking aspect of the photoaddition reactions of the nitrogen bases is the high yield of cycloadducts; we have never detected ene products in any of these systems. By contrast cyclohexenones often afford significant amounts of olefinic products with isobutylene. To understand the photochemistry of these nitrogen bases as compared with cyclohexenones, the mechanism for the formation of ene product (i.e., **14, 17, 21, 22**) was of major interest. One possible mechanism involves disproportionation of biradicals such as **23** and **24**.[6a] The only instance in which fragmentation at the biradical stage has been convincingly established is the photoaddition of cyclohexenone and norbornadiene,[8b] and this may be a somewhat special case.

A second possibility is hydrogen transfer in the exciplexes **25** and **27** to afford radical pairs which then collapse to afford **14** and **17.** There is much precedent for hydrogen abstraction reactions on oxygen of ketones (i.e., **25** → **26**) and recent investigations by Agosta have provided examples of hydrogen abstraction at the β carbon (i.e., **27** → **28**) of an α,β-unsaturated ketone.[11] Such a mechanism could also rationalize the absence of ene products from cyclohexenone–cyclopentene type additions[6a] since a less hindered anti configuration in the exciplex would place the allylic hydrogens quite distant from the carbonyl oxygen and the β carbon. Furthermore, the formation of trans-fused adduct from 4,4-dimethylcyclohexenone and tetramethylethylene could derive from steric hindrance

Table III. ^{13}C NMR Assignments for Compounds 14-18

Position	Shift ( )[1]	Position	Shift ( )[1]	Position	Shift ( )[1]	Position	Shift ( )[1]	Position	Shift ( )[1]
1	211.7 (s)	1	209.3 (s)	1	215.6 (s)	1	212.3 (s)	1	213.6 (s)
2	47.8 (t)	2	48.1 (d)	2	39.6 (d)	2	48.3 (d)	2	53.4 (d)
3	36.7 (d)	3	57.4 (d)	3	45.2 (d)	3	33.2 (t)	3	38.2 (d)
4	31.1 (complex t)	4(5)	29.1 (t)	4(5)	22.7 (t)	4	24.7 (t)	4(5)	27.5 (t)
5	25.1 (" ")	5(4)	25.8 (t)	5(4)	23.1 (t)	5	27.8 (t)	5(4)	19.7 (t)
6	41.4 (" ")	6	40.5 (t)	6	39.6 (t)	6	41.8 (t)	6	41.1 (t)
7[2]	45.1 (" ")	7[2]	35.5 (t)	7[2]	37.5 (t)	7[2]	37.3 (t)	7[2]	26.9 (complex)
8	142.8 (s)	8	39.2 (s)	8	36.3 (t)	8	143.1 (s)	8	37.5 (s)
9	112.3 (t)	9	29.4 (q)	9	30.0 (q)	9	111.6 (t)	9	31.9 (q)
10	22.0 (q)	10	20.3 (q)	10	23.9 (q)	10	22.1 (q)	10	26.6 (complex)

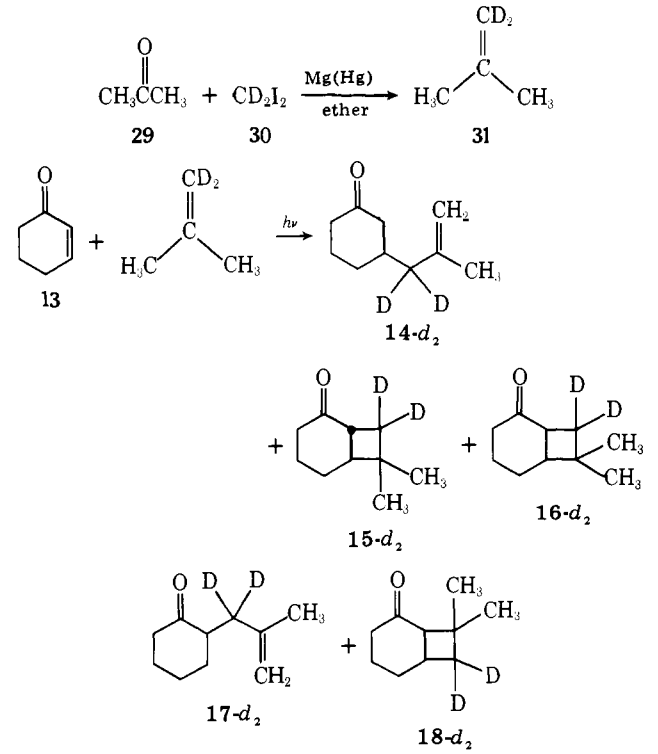
[1] Multiplicity in the off-resonance decoupled spectra.
[2] Signal absent in the deuterated material.



to an appropriate exciplex.[12] In spite of the extensive studies in photoaddition chemistry, we are aware of no labeling study concerning the mechanism of the ene reaction.

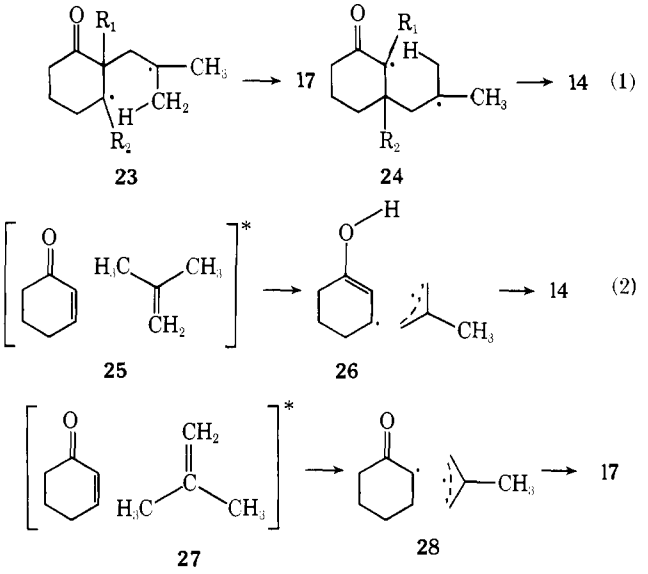
A decision between these two alternative mechanisms for the ene product can be made by the use of labeled isobutylene. The first possibility retains the integrity of the label while the second mechanism should scramble the label over the two allylic positions. Since the ^{13}C resonance of a carbon substituted with deuterium is strongly quenched, we chose isobutylene-*1,1-d*$_2$ as the labeled compound. It was first necessary to determine the ^{13}C NMR spectra of **14–18.** The compounds were obtained by cycloaddition of cyclohexenone to isobutylene and separated by a combination of pressurized liquid chromatography and preparative VPC. The shift assignments (see Experimental Section for details) for the products **14–18** are given in Table III.

Preparation of isobutylene-*1,1-d*$_2$[13] followed by cycloaddition to cyclohexenone produced a product mixture which was separated by preparative VPC into two fractions. The peak of longer retention time contained compounds **14–16** while the faster eluting peak contained **17** and **18.** Comparison of the ^{13}C



NMR spectra of these fractions with those of the pure compounds established for each of the products complete absence of only one carbon resonance. These results then rigorously exclude any mechanism wherein the methylene and methyl carbons of isobutylene become equivalent during the ene reaction. However, the hydrogen transfer mechanism of Scheme II is ruled out only if there is sufficient mobility in the "caged

Scheme II. Mechanistic Considerations for Ene Product Formation



radical pair" to allow carbon–carbon formation at either allylic terminal. While an exact analogy for such mobility is lacking, Engel[14] has established randomization of the terminal carbons of allylic radicals generated from thermal and photochemical decomposition of azo compounds and from photodecarbonylations of ketones. These results strongly suggest that deuterium scrambling would have been observed had allylic radicals been formed in the ene process studied here. While the mechanism involving hydrogen transfer in the exciplex could still operate in other systems,[15] we feel that it is not important in cyclohexenone photochemistry.

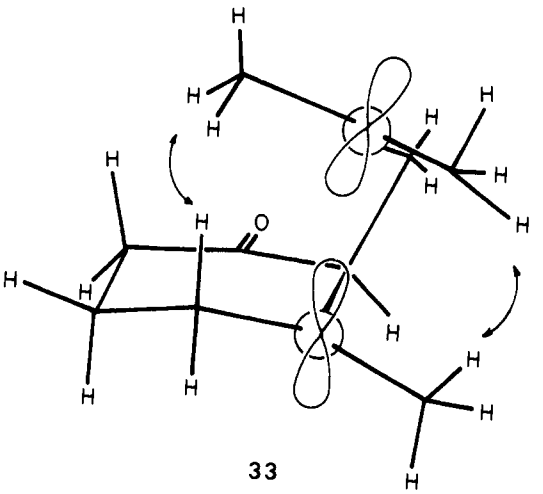
Discussion

The results for the nitrogen bases reported here show several pronounced differences in reactivity from those recorded for cyclohexenones: (1) the substitution of methyl groups for hydrogens on cyclohexenones has a pronounced effect on reactivity and products while for uracil the effect is small; (2) there is predominant formation of cycloadducts in the nitrogen base system, no appreciable other products being detected in this work; and (3) the ring fusion in the nitrogen base cycloadducts is exclusively cis. The origin of these differences is briefly discussed below.

As noted previously, the photoaddition of cyclohexenone and 3-methylcyclohexenone affords cycloadducts together with ene products. By contrast 2-methylcyclohexenone, the thymine analogue underwent very slow photoaddition to isobutylene to produce a minimum of seven unidentified products.[6a] The different effect of the 2-methyl group in the photoaddition reaction of cyclohexenone vs. that of thymine could arise from either its steric or electronic effect, or some combination of the two. Devaquet[9a] has proposed on the basis of calculations that the effect of the 2-methyl group in cyclohexenone is to electronically stabilize an orthogonal triplet state and that this enhances the rate of conversion of the excited triplet to the twisted ground state, cycloaddition being rendered less likely by this process. Should this geometric distortion contribute to decay of triplet excited state to twisted ground state, it would be expected to be much less important for thymine. For this nitrogen base, much less geometric distortion is possible, since the excitation is largely localized in the unsaturated portion of the molecule and the urea moiety has a strong bias toward maintaining planarity. An alternate hypothesis is that a reversible intramolecular hydrogen transfer from the allylic methyl group to the carbonyl in 2-methylcyclohexenone competes with cycloaddition and lowers the efficiency of the process.[16] That thymine would not be similarly deactivated could reflect a lower propensity toward hydrogen abstraction by an amide carbonyl.[17] Regardless of the interpretation, the photoaddition reaction of thymine to isobutylene is not so sensitive to the methyl substituent as the analogous reaction of 2-methylcyclohexenone.

In comparing the photoaddition reaction of 3-methylcyclohexenone and 6-methyluracil to isobutylene, it is instructive to review what are thought to be the key steps in the reaction mechanism. Interaction of the triplet state of the α,β-unsaturated compound with the olefin initially produces an exciplex which subsequently gives rise to a biradical. Should isomeric exciplexes and biradicals be formed in these reactions, then the relative rates of competing reactions should determine the observed products of the system. In this discussion we will assume that competing reactions of isomeric biradicals are a major consideration in understanding this chemistry.

The photocycloaddition reactions of 6-methyluracil (**8**) and 3-methylcyclohexenone (**19**) stand in marked contrast regarding the regioselectivity of the products. Thus for **19** the products derived from the head-to-head biradical predominate and **22** is the only product from a head-to-tail orientation. The failure of **32a** to close reflects the reluctance of two tertiary radicals to couple presumably because of methyl-axial hydrogen and methyl–methyl steric interactions generated in the transition state for ring closure, i.e., **33**.[18] Since the transition



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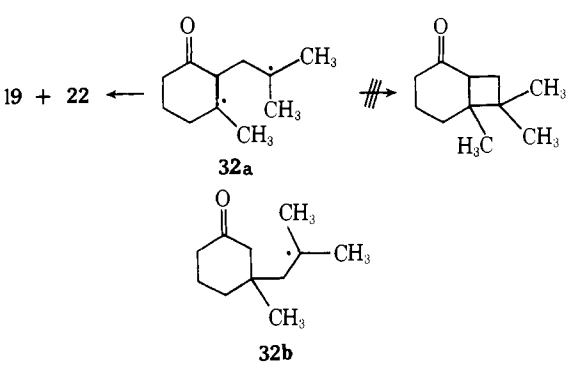
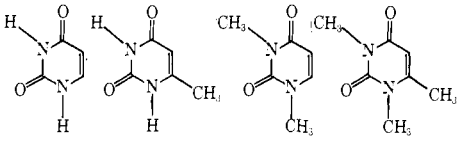
states leading to disproportionation (vida infra) and reversion are relatively insensitive to the additional steric interaction, **22** is formed together with starting material. In contrast to **32a,** the biradical **32b** encounters little additional barrier to closure



32a

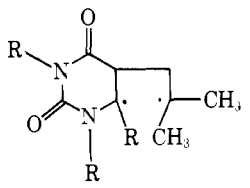
32b

Table IV. Steric effects on Regioselectivity in the Photoaddition of Isobutylene to Methyl-Substituted Uracils

				
	1b	**8b**	**1a**	**8a**
Cycloadducts ratio head-to-tail/ head-to-head	3.2	2.2	1.2	0.88

or disproportionation; thus products derived from this orientation are favored. For the nitrogen base system no axial hydrogens are present, so there is no pronounced barrier to closure of the head-to-tail biradical. Furthermore, disproportionation products would not be expected since the transition state for disproportionation is not readily obtained (vide infra). At most, if steric interactions were introduced at N_1 or C_6 in the nitrogen bases, an increased preference for the head-to-head cycloadduct would be expected. This is indeed precisely what is observed in comparing the regioselectivity of the series **1b, 8b, 1a,** and **8a** (Table IV).

The Absence of Ene Products. Since the deuterium labeling studies using isobutylene-d_2 have ruled out a radical pair mechanism, the absence of ene products in the nitrogen base system most reasonably derives from a lack of disproportionation of the uracil-derived 1,4 biradicals, **34** and **35.** The failure



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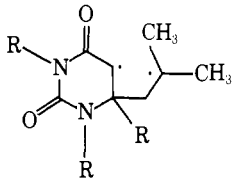
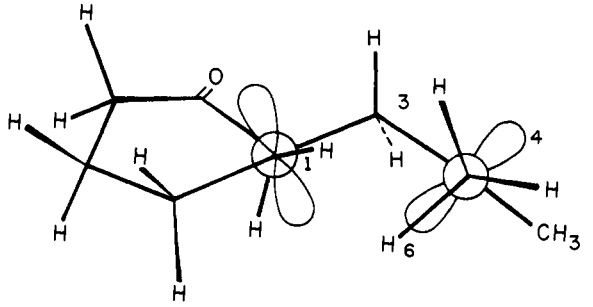


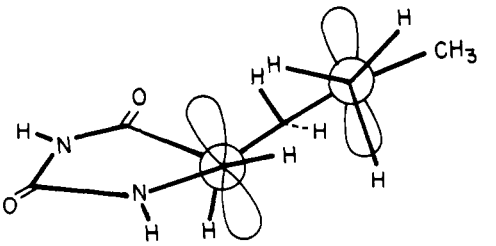
35

of **34** and **35** to disproportionate may arise from an inability to achieve the proper transition state for hydrogen transfer. In the cyclohexenone–isobutylene system a reasonable transition state is one in which biradicals **23** and **24** adopt a six-membered ring chair conformation. Critical to the transfer are the requirements that p orbital "1" complete the chair and that p orbital "4" eclipse H_6. The cyclohexenone-derived biradical, i.e., **36,** can readily achieve this transition state with a chair



36

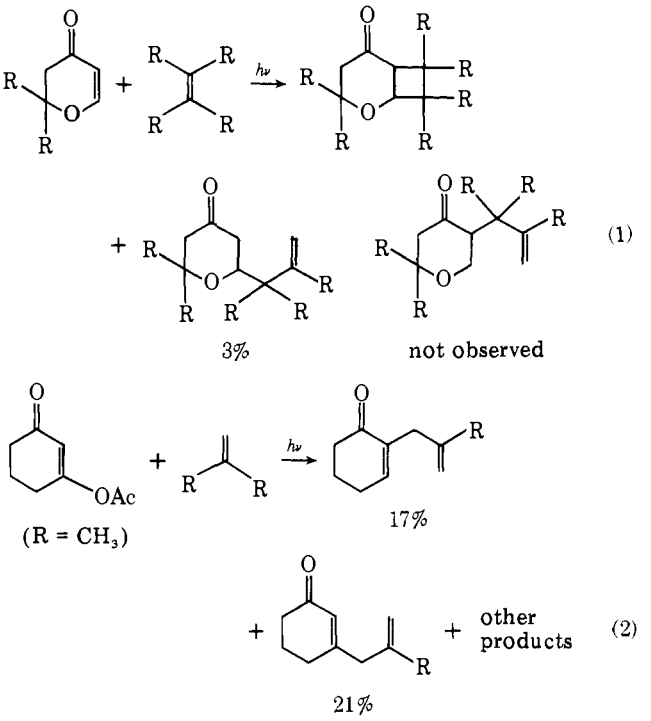
conformation of its cyclohexanone ring, and H_6 is transferred to the bottom lobe of p orbital "1".[19] In contrast the uracil-derived biradical, i.e., **37,** cannot achieve this transition state because the more rigid and nearly planar uracil ring holds p orbital "1" nearly parallel to H_6, and transfer to the bottom lobe of the orbital is not possible. While rotation of the methyl group would allow transfer of H_6 to the top lobe of the p orbital in a boat transition state, H_6 would then be orthogonal to p



37

orbital "4". Such transition state arguments are applicable to both biradicals **34** and **35.**

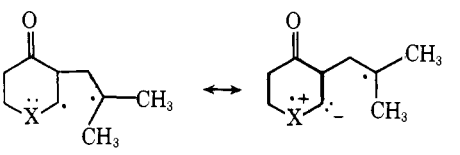
A second possibility for the absence of ene products in the nitrogen base system is the alteration of biradical reactivity (i.e., **34**) by the adjacent heteroatom. Thus Margaretha[8f] has recorded that oxaenone systems, for which a biradical can attain the appropriate transition state for disproportionation, afford only small amounts of ene products. On the other hand, Cantrell[6b] observed little, if any, effect with an adjacent heteroatom. Thus to what extent a zwitterionic biradical contributor effects disproportionation is not clear.[20] Charge-separated structures should be more important contributors for systems of eq 1 than for those of eq 2 or the work presented



(1)

(2)

here and may play a role in determining both regioselectivity and products in the photoaddition reaction.



(3)

In the uracil system, however, the absence of ene products even from the head-to-head biradical (i.e., **35**), which does not have an adjacent heteroatom, is consistent with a steric effect in which the nearly planar and rigid uracil ring prevents both biradicals from achieving the appropriate transition state for disproportionation.

The Nature of the Ring Fusion. Finally, the absence of significant amounts of trans-fused cycloadducts in this system is reasonably attributed to the barrier to geometric distortion of the nitrogen base ring system as discussed above. It would

appear that trans-fused cycloadducts will generally not be favored under most conditions in these systems.

Summary

This work shows that methyl substitution at the olefinic carbon exhibits no dramatic effect on the photocycloaddition reactions of nitrogen bases with isobutylene, in marked contrast to the cyclohexenone series. The different effect of methyl substitution in the two systems is attributed to the conformational flexibility of the carbocyclic ring vs. the more rigid pyrimidione moiety rather than any basic change in mechanism. The clean, high-yield cycloadditions of the nitrogen bases, uncomplicated by ene product formation, indicate that these reactions are excellent processes for synthetic modifications of pyrimidiones and good candidates for mechanistic studies of photocycloaddition reactions.

Experimental Section[20]

Cycloaddition of 1,3-Dimethyluracil (1a) and 1,3-Dimethyluracil-5-*d* (1d) to Isobutylene. A solution of 2.5 g (0.018 mol) of **1a** and 30 mL of isobutylene in 600 mL of 7:2 acetone-water was irradiated at −5 °C. After 8 h of irradiation, VPC analysis showed loss of the **1a** and formation of three product peaks in the ratio 39:61:7. The smallest peak was observed to decrease in size upon treatment of the reaction mixture with pyridine; this presumed trans adduct was not investigated. NMR analysis of the crude reaction mixture after removal of the solvent showed the two major components to be in the ratio 55:45. Elution of the crude, oily mixture through a short silica gel column with ether afforded 2.68 g (76%) of clear photoproduct mixture, from which the major product **3a** could be isolated by fractional crystallization from ether-pentane at −78 °C. The mother liquors from this crystallization were subjected to preparative gas chromatography in order to isolate a sample of the 45% product.

The crystalline, 55% product (2,4,8,8-tetramethyl-2,4-diazabicyclo[4.2.0]octane-3,5-dione, **3a**) was recrystallized from pentane and had mp 97-98 °C; IR (KBr) 5.92, 6.04, 6.78, 7.14, 7.68, 7.85, 8.26, and 9.35 μ; spectrum *m/e* 196 (P, 2.1%); 140 [retro (2 + 2), 100%].

Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.27. Found: C, 61.22; H, 8.44; N, 13.82.

The 45% product (2,4,7,7-tetramethyl-2,4-diazabicyclo[4.2.0]-octane-3,5-dione, **4a**)was a clear syrup: IR (neat) 5.89, 6.01, 6.75-7.30 (br str), and 7.77 μ; mass spectrum *m/e* 196.1211 (P, calcd 196.1215, 1.2%), 140 [retro (2 + 2), 100%].

Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.25. Found: C, 61.61; H, 8.21; N, 13.88.

In order to to verify the above structural assignments, 1,3-dimethyluracil-5-*d* (**1d**)[3b] was added to isobutylene under the conditions used for **1a** and the two major products were isolated by preparative gas chromatography.

Compound **3d**, the 55% product, had mp 97-98 °C; NMR ($CDCl_3$, 100 MHz) δ 3.58 (s, 1 H), 3.25 (s, 3 H), 3.02 (s, 3 H), 2.15 (AB q, J = 12.5 Hz, 2 H), 1.23 (s, 3 H), and 1.05 (s, 3 H).

Compound **4d** was a clear syrup: NMR ($CDCl_3$, 100 MHz) δ 3.91 (m, 1 H), 3.25 (s, 3 H), 2.95 (s, 3 H), 2.12 (center of m, 2 H), 1.8-2.4 (AB of ABX, m, 2 H), 1.34 (s, 3 H), and 1.11 (s, 3 H).

Cycloaddition of 1,3-Dimethylthymine (5a) to Isobutylene. A solution of 2.5 g (0.016 mol) of **5a** and 30 mL of isobutylene in 550 mL of 7:2 acetone-water was irradiated at −5 °C for 5.0 h. VPC analysis of the reaction mixture indicated ca. 5% of **5a** remaining and four products in the ratio 53:47:2:3. NMR analysis of the oily reaction mixture after removal of solvent showed two major products in the ratio 55:45. The crude product mixture was chromatographed on 200 g of silica gel (3 by 55 cm), elution proceeding as follows: 25% ether-hexane, 750 mL, nil; 33% ether-hexane, 1 L, nil; 40% ether-hexane, 450 mL, nil; 40% ether-hexane, 400 mL, 1.02 g of a 80:20 mixture of **6a** and **7a**; 40% ether-hexane, 350 mL, 1.0 g of a 1:1 mixture of **6a** and **7a**; 40% ether-hexane, 600 mL, 1.08 g of a 20:80 mixture of **6a** and **7a**. The total yield of photoproducts was 3.10 g (90%).

The fraction enriched in the 45% product was rechromatographed on silica gel (100 g, 33% ether-hexane elution) to afford a sample of pure 2,4,6,8,8-pentamethyl-2,4-diazabicyclo[4.2.0]octane-3,5-dione (**6a**), which was further purified by molecular distillation at 60 °C (0.05 mmHg). The clear, syrupy product crystallized upon standing and was recrystallized from ether-pentane: mp 63-65 °C; IR (neat) 5.87, 6.02, 6.7-7.3 (br, struct), 7.85, and 9.52 μ; mass spectrum *m/e* 210 (P, absent), 154 [retro (2 + 2), 100%].

Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.62; H, 8.66; N, 13.21.

The fraction enriched in the 55% product was a rechromatographed as above to afford a sample of material of ca. 92% purity which was further purified by preparative VPC to give pure 2,4,6,7,7-pentamethyl-2,4-diazabicyclo[4.2.0]octane-3,5-dione (**7a**) as a clear oil: IR (neat) 5.88, 6.00, 6.75-7.30 (br m), 7.82, and 9.33 μ; mass spectrum *m/e* 210 (P, 0.01%), 145 (P − 15, 0.03%), 154 [retro (2 + 2), 100%].

Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.75; H, 8.74; N, 12.99.

Cycloaddition of 1,3,6-Trimethyluracil (8a) to Isobutylene. A solution of 3.0 g (0.019 mol) of **8a** and 30 mL of isobutylene in 900 mL of 2:7 water-acetone was held at −5 °C and irradiated for 10 h, when VPC analysis indicated ca. 80% consumption of **8a** and formation of two products in the ratio 53:47. NMR analysis of the crude mixture after removal of solvent showed, in addition to unchanged **8a**, two products in the ratio 54:46. The crude oily mixture was triturated with ether and cooled to afford 0.5 g of unreacted **8a**. The mother liquors were then chromatographed on 300 g of silica gel (5 by 60 cm). Elution proceeded as follows: 25% ether-hexane, 3 L, nil; 30% ether-hexane, 4 L, nil; 40% ether-hexane, 1.25 L, nil; 40% ether-hexane, 2.1 L, 0.79 g of the 54% product, **10a**, as a crystalline solid. Recrystallization of this material from ether-pentane afforded white needles: mp 93-95 °C; IR (KBr) 5.91, 6.08, 6.90, 7.57, 8.54, 9.85, 9.95, and 13.30 μ; mass spectrum *m/e* 210 (P, 0.4%), 195 (P − 15, 0.4%), 154 [retro (2 + 2), 100%], 56 (C_4H_8, 20%).

Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.22. Found: C, 62.94; H, 8.65; N, 13.17.

Continued elution with 40% ether-hexane, 2 L, gave 0.87 g of a ca. 1:1 mixture of **9a** and **10a** and 3 L, 0.61 g, of the 46% product, **9a**, as an oil. The total yield of adducts was 2.26 g (72%). Final purification of **9a** was effected by molecular distillation (80 °C, 0.1 mm) to afford a clear syrup: IR (neat) 5.88, 6.02, 6.85, and 7.52 μ; mass spectrum *m/e* 210 (P, 0.6%), 195 (P − 15, 0.3%), 154 [retro (2 + 2), 100%], 56 (C_4H_8, 50%).

Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63, N, 13.22. Found: C, 63.02; H, 8.83; N, 12.67.

Cycloaddition of Uracil (1b) to Isobutylene. A solution of 200 mL of acetone-water (4:1), 10 mL of isobutylene, and 0.5 g (4.46 mmol) of **1b** was irradiated for 9 h after which time UV analysis at 260 nm indicated complete disappearance of uracil. VPC analysis of the reaction mixture showed only one unresolved product in 92% yield. Removal of the solvent afforded a white solid which was recrystallized from hexane-ethyl acetate to afford a solid mixture of adducts which could not be separated by VPC. Thus analysis was accomplished by methylation of the reaction mixture followed by VPC analysis of the methylated adducts.

Methylation of Uracil–Isobutylene Reaction Mixture. To 100 mg (0.59 mmol) of the above recrystallized mixture suspended in 2 mL of dry benzene was added 150 mg (3.12 mmol) of sodium hydride (50% emulsion in mineral oil). This was stirred until the evolution of hydrogen ceased, then 0.665 g (5.27 mmol) of dimethyl sulfate was added, and the reaction mixture heated to reflux and then stirred for 4 h at room temperature. After quenching with water, workup afforded 153 mg of a yellow oil which showed two components by VPC. Preparative VPC of this material showed the major component to be **3a** and the minor component to be **4a** by comparison of the IR spectra of the materials with authentic samples. The VPC yield of the methylation reaction was 72%.

To determine the adduct ratio, the crude reaction mixture was subjected to the methylation procedure and the analysis performed by VPC, giving a ratio of 75:25 for **3a** and **4a**. This ratio is in good agreement with that determined by NMR integration of the methyl resonances in the crude unmethylated reaction mixture. Thus the NMR (pyridine, 100 MHz) showed two methyl resonances of equal intensity at δ 0.94 and 1.04 (assigned to the major adduct) and two methyl resonances of equal intensity at δ 1.16 and 1.18 (assigned to the minor adduct) in a ratio of 76:24.

Cycloaddition of Thymine (5b) to Isobutylene. A solution formed from 150 mL of acetone-water (4:1), 6.53 g (0.12 mol) of isobutylene, and 400 mg (3.17 mmol) of **5b** was cooled to −7 °C and irradiated for

8 h, after which time UV analysis at 260 nm indicated the disappearance of starting material. Solvent removal in vacuo afforded 585 mg of white solid which by VPC analysis was a 72:27 mixture of photoadducts (92% VPC yield). The major product was most readily obtained by fractional recrystallization of the photolysis mixture from water. Thus, two careful crystallizations afforded 101.5 mg (17.6%) of **6b**: mp 240-241 °C; IR (KBr) 5.82, 5.88, 7.25, 7.60, 7.96, 8.12, and 8.30 μ; NMR (CF_3CO_2H, 100 MHz) δ 9.36 (br s, 1 H), 7.46 (br s, 1 H), 3.72 (d, J = 4 Hz, 1 H), 2.44 (center of AB, J = 14 Hz, 1 H), 2.03 (center of AB, J = 14 Hz, 1 H), 1.62 (s, 3 H), 1.22 (s, 3 H), and 1.18 (s, 3 H).

Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.31; H, 7.76; N, 15.37. Found: C, 59.01; H, 7.76; N, 15.10.

The minor product, **7b**, was obtained by preparative VPC separation of the mother liquors and was recrystallized from ethyl acetate: mp 255-256 °C; IR (KBr) 5.90, 7.78, 8.10, and 8.39 μ; NMR (CF_3CO_2H, 100 MHz) δ 9.47 (br s, 1 H), 7.49 (br s, 1 H), 3.95 (m, 1 H), 2.36 (A of ABX, q of d, J = 8, 12 Hz, 1 H), 2.06 (B of ABX, q of d, J = 8, 12 Hz, 1 H), 1.49 (s, 3 H), and 1.26 (s, 6 H).

Cycloaddition of 6-Methyluracil (8b) to Isobutylene. A solution of 160 mL of acetone-water (4:1), 10 mL of isobutylene, and 500 mg (3.96 mmol) of **8b** was irradiated for 8 h after which time UV analysis indicated complete disappearance of starting material. Analysis of the crude reaction mixture by VPC revealed that two products were produced in a ratio of 69:31 (VPC yield, 97%). The crude reaction mixture was separated on column A. The major adduct, **9b**, was recrystallized from ethyl acetate: mp 197-198.5 °C; IR (KBr) 5.82, 5.89, 6.75, 6.89, 7.60, and 7.67 μ; NMR (CF_3CO_2H, 100 MHz) δ 9.50 (br s, 1 H), 7.44 (br s, 1 H), 3.32 (t, J = 9 Hz, 1 H), 2.08-2.56 (m, 2 H), 1.48 (s, 3 H), and 1.22 (s, 6 H).

Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.31; H, 7.76; N, 15.37. Found: C, 58.75; H, 7.65; N, 15.26.

The minor product was crystallized from ethyl acetate: mp 219-220 °C; IR (KBr) 5.82, 5.95, 7.57, 7.62, 8.55, 9.44, and 11.79 μ; NMR (CF_3CO_2H, 60 MHz) δ 9.44 (br s, 1 H), 7.34 (br s, 1 H), 3.25 (s, 1 H), 2.30 (s, 2 H), 1.63 (s, 3 H), 1.45 (s, 3 H), and 1.33 (s, 3 H).

Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.31; H, 7.76; N, 15.37. Found: C, 58.88; H, 7.85; N, 15.13.

Establishment of Conditions for Epimerization and Attempted Epimerization of Adducts 3a, 4a, 9a, and 10a. A solution of 15 mg (0.06 mmol) of **11** in 0.5 mL of pyridine containing 3% Me_2SO-d_6 was transferred to an NMR tube and its spectrum recorded. To this solution was added 15 mg (0.4 mmol) of sodium hydride and after 5 min the NMR spectrum rerun. This spectrum was identical with that of the cis isomer, **12**, When this procedure was repeated for the mixtures of adducts **3a** and **4a**, and **9a** and **10a**, no spectral changes were observed in the NMR.

Conversion of Adducts 3a and 4a to Adducts 6a and 7a. A solution of lithium diisopropylamide was formed by addition of 0.75 mL (1.5 mmol) of 2 M butyllithium in hexane to 151.5 mg (1.5 mmol) of diisopropylamine in 1.5 mL of dry dioxane. To this solution was added 58.8 mg (0.3 mmol) of a mixture of **3a** and **4a** and the mixture allowed to stir for 5 min. Then 400 mg (3.3 mmol) of dimethyl sulfate was added and the reaction mixture stirred for 2 h. The reaction mixture was then quenched with water and concentrated to yield an oil which was extracted with ether. VPC analysis using bis[2-2-(methoxyethoxy)ethyl] ether as a standard showed two components having retention times identical with those of **6a** and **7a** (70%). Preparative VPC isolation of these two components (10 ft by $\frac{1}{4}$ in. SE-30 on 60/80 Chromosorb G at 165 °C) and comparison of their IR and NMR spectra with those of authentic **6a** and **7a** rigorously established their structures.

Photoaddition of Isobutylene-*1,1-d*$_2$ to Cyclohexenone. A mixture of 6.3 lb of mercury and 8.16 g of magnesium was heated under nitrogen for 0.5 h during which time the amalgam formed. The mixture was cooled to room temperature and 240 mL of anhydrous ether added. To this stirred mixture were added 45.27 g (0.17 mol) of dideuteromethylene iodide (>98% d_2) and 9.17 g (0.16 mol) of acetone in 200 mL of anhydrous ether over a period of 2.5 h, during which a gentle stream of nitrogen was passed through the solution and the isobutylene formed trapped in 100 mL of hexane cooled to −70 °C. After the addition was complete the solution was refluxed for 1.5 h to remove any dissolved isobutylene. The hexane solution was diluted to 150 mL with cold hexane, 0.9 g of cyclohexenone added, and the solution irradiated with Corex-filtered light for 13 h. The solvent was distilled off and collected at −70 °C and the residue molecularly distilled to afford 0.46 g of cycloadduct mixture. Preparative VPC (10 ft by $\frac{1}{4}$ in., 3% QF-1 on 60/80 Chromosorb G at 110 °C) separated this mixture into two fractions. Fraction 2 contained **14–16**, while fraction 1 contained **17** and **18**. The fractions were then analyzed by ^{13}C NMR.

Assignment of ^{13}C Shifts. The chemical shifts of the ene products **14** and **17** were assigned using 1- and 2-methylcyclohexanones as models and the expected shifts of the olefinic side chain. For the bicyclic ketones **15**, **16**, and **18**, the chemical shifts of methyl-substituted *tert*-butylcyclohexanones were calculated using the chemical shifts of 2- and 3-*tert*-butylcyclohexanone[22] and the methyl substituent parameters for substituted cyclohexanes.[23] The chemical shifts of the bicyclic ketones were then assigned using the trends shown by the model compounds in conjunction with the multiplicities of the peaks from off-resonance decoupling experiments and second-order effects shown by some of the multiplets. The high-field methyl group in each isomer was assigned as the endo methyl group.

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(18) (a) R. A. Schneider and J. Meinwald, *J. Am. Chem. Soc.*, 89, 2023 (1967); (b) R. H. Hesse, *Adv. Free-Radical Chem.*, 1, 83 (1969); (c) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, and R. G. Zepp, *J. Am. Chem. Soc.*, 94, 7500 (1972).
(19) There are in fact two different chair transition states possible for these hydrogen transfers corresponding to the *cis*- and *trans*-decalin analogues described on p 2028 of ref 18a. The *trans*-decalin analogue is shown but the conclusions are the same regardless of which one is used. The structures depicted were constructed from models using the standard bond lengths for cyclohexanone and the bond lengths for the uracil cycloadducts determined by x-ray crystallography.[3b]
(20) For a discussion of the dramatic effect of a heteroatom on biradical behavior see P. J. Wagner and M. J. Thomas, *J. Am. Chem. Soc.*, 98, 241 (1976).
(21) General procedures: Melting points were taken in open capillaries in a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were taken in the indicated phase on Perkin-Elmer Model 137 or 467 spectrophotometers. Proton magnetic resonance spectra were recorded in the indicated solvent at 60 and 100 MHz on Varian A-60A and Jeolco MH-100 instruments. ^{13}C NMR spectra were measured on a Bruker HX-90. Spectra are reported in δ units with reference to internal tetramethylsilane. Mass spectra were obtained with an AEI-MS9 spectrometer using an ionizing potential of 70 eV. All irradiations were carried out with Corex-filtered light from a 450-W Hanovia medium-pressure source. The vessel containing the reaction mixture was held at −5 to 0 °C with an acetone–ice bath and a dry ice reflux condenser. Gas chromatographic analyses in the 1,3-dimethyl systems were performed on a 5 ft by 1/8 in. column of 3% SE-30 on 100/120 mesh Varaport 30 (110–150 °C), while analyses on the unmethylated systems were performed on a 13 ft by 1/8 in. column of 5% SE-30 on DMSC-treated 60/80 mesh Chromosorb G at 185 °C. Preparative scale gas chromatography utilized either a 20 ft by 3/8 in. column of 5% DMSC-treated 60/80 mesh Chromosorb G (column A) or a 12 ft by 1/4 in column of 20% Carbowax 20M on 60/80 Chromosorb P at 220 °C (column B). Elemental analysis was performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, or Heterocyclic Chemical Corp., Harrisonville, Mo., on sublimed or molecularly distilled pure samples.
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Copper(I) Catalysis of Olefin Photoreactions. Photorearrangement and Photofragmentation of Methylenecyclopropanes

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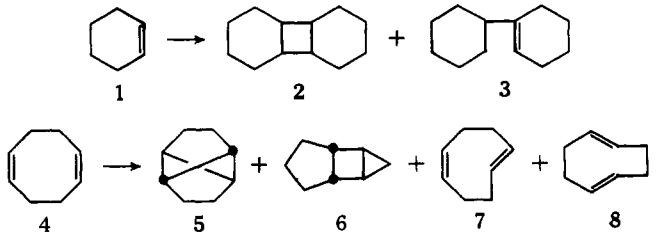
Abstract: Methylenecyclopropanes, 7-methylenebicyclo[4.1.0]heptane (**14**) and 8-methylenebicyclo[5.1.0]octane (**15**), undergo a variety of novel carbon skeletal reorganizations upon photolysis (254 nm) in the presence of copper(I) trifluoromethanesulfonate. Thus, **14** gives bicyclo[4.2.0]oct-1(8)-ene (**17**), *unsym*-pentamethyleneallene (**18**), 3-vinylcyclohexene (**19**), and 1-vinylcyclohexene (**20**); and **15** gives bicyclo[5.2.0]non-1(9)-ene (**22a**), bicyclo[5.2.0]non-1-ene (**22b**), *unsym*-hexamethyleneallene (**23**), and bicyclo[6.1.0]non-1-ene (**24**). Photofragmentation products, acetylene, and cyclohexene (**1**) or cycloheptene (**21**) are also obtained from **14** or **15**, respectively. The fate of the olefinic methylene group was traced by determining the position of deuterium labeling in the products from copper(I)-promoted photorearrangement of 7-(dideuteriomethylene)bicyclo[4.1.0]heptane (**16**).

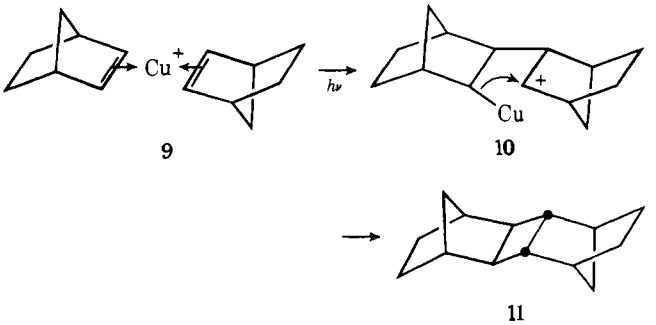
Introduction

Copper(I) salts promote a large variety of olefin photoreactions including both inter-[1] and intramolecular[2,3b] [2 + 2] cycloadditions to give cyclobutanes (e.g., **2** and **5**), and cis–trans isomerization[3] (e.g., **4** → **7** and **8**). Products of other



less general reaction types (e.g., **3** and **6**) have also been found. Some mechanistic details of these reactions are known. Thus, there is evidence that initial cis–trans isomerization to yield copper complexes of reactive *trans*-cycloolefin intermediates may be important in some [2 + 2] cycloadditions (e.g., **1** → **2** and **4** → **5**).[1b,3b] A recent investigation of the mechanism of some intermolecular, copper(I)-catalyzed [2 + 2] photocycloadditions showed that these photodimerizations involve photoexcitation of a 2:1 olefin–Cu(I) complex, and that both C=C bonds *must be coordinated to the same Cu(I)* to undergo photodimerization.[1b] However, the precise nature of the olefin–catalyst–light interaction responsible for reaction remains unknown.

Olefin photoreactions which are catalyzed by salts of copper(I) are especially interesting since the salts form well-characterized olefin complexes,[4] and since the olefin–metal interaction undoubtedly plays a key role in the photochemical process. An organocopper(I) carbenium ion **10** was suggested as a possible intermediate for the photodimerization of norbornene which gives **11** from the 2:1 olefin copper complex **9**.[1a]



The present study of photolysis of methylenecyclopropanes in the presence of copper(I) was inspired by the organocopper(I) carbenium ion hypothesis. Thus, copper catalysis of olefin photoreactions may involve preliminary photocupration, that is, light-induced transformation of a η^2-copper(I) olefin complex into a η^1-β-copper(I) carbenium ion intermediate. This would produce either cyclopropyl (**12**) or cyclo-

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