H, s), 1.55 (6 H, s), 3.06 (3 H, s); ^{13}C NMR δ 23.4, 24.0, 25.1, 50.4 (OCH_3), 119.9 (C-5), and 133.7 (C-2); MS (CI/NH_3), m/z 162 (M^+). Anal: ($C_6H_{12}N_2O_2$) C, H, N.

Thermolysis of 1 in $(CD_3)_2CO$. Oxadiazoline **1** (20 mg, 1.39×10^{-4} mol) in $(CD_3)_2CO$ (0.5 mL) containing CH_2Cl_2 (internal standard) was sealed into an NMR tube after several freeze-pump-thaw cycles at 10^{-2} torr. The tube was heated at 80 °C for 8 days, at which time the signal from **1** had disappeared. Yields of **2**, acetone, methyl acetate, and propene were determined by NMR at 90 MHz, by using an expanded δ scale and the cut-and-weigh procedure.

Products from analogous thermolysis of **1** (100 mg, 6.9×10^{-4} mol) in acetone-d_6 (3.0 mL) in a Pyrex tube were transferred to a bulb-to-bulb still and the most volatile fraction (propene plus some acetone, ester, and some solvent) was distilled over.

The distillate was used to obtain the ^1H and ^2H NMR spectra of the propene/propene-d_6 mixture and it was injected into the GC-MS system and into the GC-FT/IR system for the mass spectrum and infrared spectrum of the mixture. The remaining distillate was treated with Br_2 in CCl_4 to convert propenes to dibromopropanes, which were collected from a GC column (6 ft × 0.25 in. 20% DEGS, 140 °C, 40 mL min^{-1}) for mass spectrometric analysis.

The distillation residue, containing acetone, methyl acetate, solvent, and high boiling materials, was analyzed by GC (6 ft × 0.25 in. column, 3% OV-17, temperature programmed to 200 °C after 5 min at 35 °C) to determined relative yields, which were converted to absolute yields through correlation with the ^1H NMR assay, as described in the text. Mass spectra of each eluent were obtained on the fly. Acetone, methyl acetate, **3**, **2**, **4**, **5**, and **6** plus **7** were eluted in that order.

Thermolysis of 1 in Acetone. The thermolysis was similar to that described above for the large-scale decomposition in acetone-d_6. Much of the volatile material, including solvent, was separated from the less-volatile products by bulb-to-bulb distillation as already described. Both the distillate and the distillation residue were analyzed with a GC column similar to that used for deuterated products (OV-17, but 10%) from which the components eluted in the same order. Components were collected to determine the ^1H NMR spectra in Table I.

Acknowledgment. Financial support of this work by the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. We are indebted to E. Osei-Twum for many of the mass spectra. The high-field NMR spectra were obtained at the Southwestern Ontario NMR Centre funded by a grant from NSERC.

Registry No. 1, 77879-49-3; **2**, 84369-94-8; **3**, 84369-95-9; **4**, 84369-96-0; **5** (isomer 1), 84369-97-1; **5** (isomer 2), 84369-98-2; **6**, 84369-99-3; **7**, 84370-00-3; $(CD_3)_2CO$, 666-52-4; $(CH_3)_2CO$, 67-64-1; $CH_3CO_2CH_3$, 79-20-9; $H_2C{=}CHCH_3$, 115-07-1; $D_2C{=}CDCD_3$, 1517-52-8.

Regiochemical Control in Intramolecular Photochemical Reactions of 1,5-Hexadien-3-ones and 1-Acyl-1,5-hexadienes

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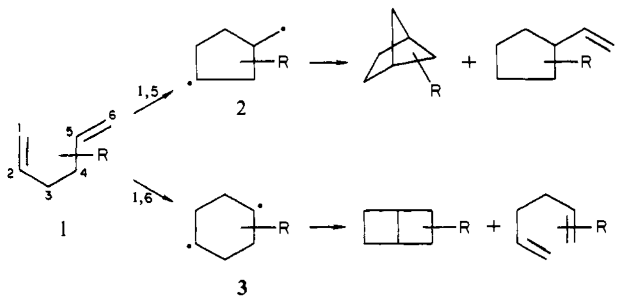
Received July 21, 1982

Abstract: Both 1,5-hexadien-3-ones (**7**) and 1-acyl-1,5-hexadienes (**8**) generally undergo intramolecular photochemical cyclization by way of 1,5 (crossed) closure (see **2**), as do other derivatives of 1,5-hexadienes (**1**). Through study of the photochemistry of 14 members of series **7** and **8**, summarized in Tables I and II, two effects that modify this regiochemistry and favor a shifting to 1,6 (straight) closure (see **3**) were identified. These are alkyl substitution at C(5) and incorporation of the conjugated double bond in a five- or six-membered ring. These effects are additive, and with both present (as in **4** and **19**) regiospecific 1,6 closure can occur. The sources of these effects and implications of these reactions for the mechanism of the intermolecular [2 + 2] cyclization are discussed.

Over the past 15 years numerous inquiries have supported the generalization[1,2] that ultraviolet irradiation of 1,5-hexadienes (**1**) leads preferentially to 1,5 (crossed) closure, with formation of a biradical intermediate **2** that then proceeds to products. All indication of the alternative 1,6 (straight) closure leading to **3** is frequently completely absent, and little or no change results from incorporation of the hexadiene double bonds into more complex systems such as trienes,[2] tetraenes,[3] or α,β-unsaturated ketones[4,5] or esters.[6] Typically **2** collapses to a bicyclo[2.1.1]hexane or, with appropriate substitution, it may disproportionate, while **3** either gives a bicyclo[2.2.0]hexane or fragments to an isomeric 1,5-hexadiene. Various authors have called attention to this "rule of five" and its broad validity over the years,[1,2,7,8] and the few exceptions known[9,10] are reasonably understood to result from special structural features.



In contrast to these generalizations Smith noted some 10 years ago that photolysis of ketone **4** in methanol gave only the two isomers of ester **5**, a result requiring 1,6 closure.[11] Further

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(1) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932.

(2) Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 4936.

(3) White, J. D.; Gupta, D. N. *Tetrahedron* **1969**, *25*, 3331.

(4) Bond, F. T.; Jones, H. C.; Scerbo, L. *Tetrahedron Lett.* **1965**, 4685.

(5) Gibson, T. W.; Erman, W. F. *J. Org. Chem.* **1972**, *37*, 1148.

(6) Scheffer, J. R.; Wostradowski, R. A. *J. Org. Chem.* **1972**, *37*, 4317. Crandall, J. K.; Mayer, C. F. *Ibid.* **1970**, *35*, 3049.

(7) Dilling, W. L. *Chem. Rev.* **1966**, *66*, 373. Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 11 and references cited therein.

(8) The most recent discussions known to us are those of (a) Hoye, T. R.; Martin, S. J.; Peck, D. R. *J. Org. Chem.* **1982**, *47*, 331. (b) Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135.

(9) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 522, 7474 (allylically stabilized radical).

(10) Yoshioka, H.; Mabry, T. J.; Higo, A. *J. Am. Chem. Soc.* **1970**, *92*, 923 (structurally constrained system).

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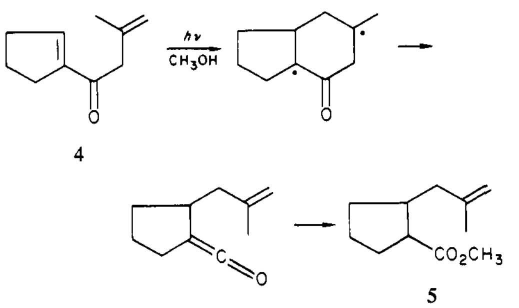
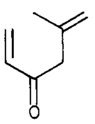
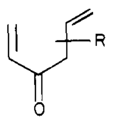
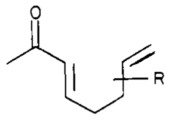


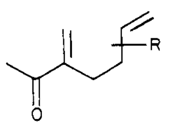

6

investigation revealed that the simple acyclic analogue of **4**, 5-methyl-1,5-hexadien-3-one (**6**), yielded products of both 1,5 and 1,6 closure.[11] The information available before our present study did not clarify the regiochemical questions raised by the behavior of **4** and **6**, despite extensive investigation of the related intermolecular [2 + 2] photocycloaddition between olefin and enone during the past decade.[12,13] It appeared to us that better understanding would come through systematic examination of the effect of structure on regiochemistry in the photochemical reactions of carbonyl-substituted 1,5-hexadienes, and we have now studied these reactions in three classes of relatively simple dienones.

The chemistry of 1,5-hexadien-3-ones (**7**)[14a] and 1-acyl-1,5-hexadienes (**8**) is presented here; the rather different behavior of


7


8

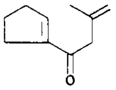
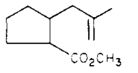
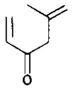
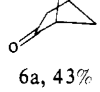
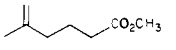
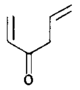
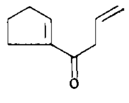
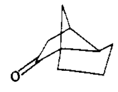
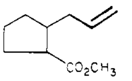
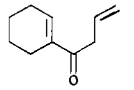
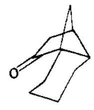
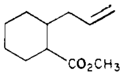
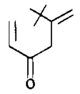
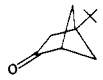
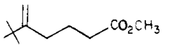
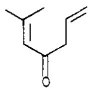
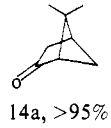
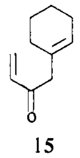
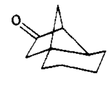
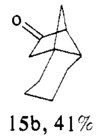
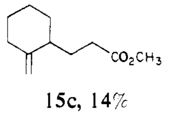

9

2-acyl-1,5-hexadienes (**9**) is reported in the accompanying paper.[14b] Our results and comparisons with earlier work permit useful generalizations about effects of structure on regiochemistry in these systems, are pertinent to the ongoing discussion of the detailed mechanisms of these processes, and raise a number of questions for future study. In addition to their mechanistic implications, these findings may have some practical value, since photocyclization of diene systems is finding increasing use as a synthetic method.[8b,15]

Results

In Tables I and II are gathered data on 14 1,5-hexadien-3-ones (**7**) and 1-acyl-1,5-hexadienes (**8**), most of which were prepared and photolyzed in the present study. Dilute solutions of these compounds in benzene were irradiated through a uranium glass filter (λ > 340 nm), in most cases at ~25 °C. For ketones **7**, which can yield ketenes (as in **4** → **5**), ~4.5% methanol (v/v, ~1.1 M) was added. Under these reaction conditions both saturated ketone products and methyl esters resulting from the trapping of ketenes are photochemically inert. The concentration of substrate ketones was 0.01–0.15 M, with no apparent effect on the results when the concentration was varied. For preparative purposes several of these reactions were also carried out at 80 °C in refluxing benzene. This had only a small effect on the distribution of products or yields, but the reactions were appreciably faster at the higher temperature. Rearrangement of **14** and **17** proceeds at an appreciable rate only at elevated temperature.[19] Products and unreacted starting ketones were isolated by preparative vapor phase chromatography (VPC). Structures of these products and preparation of the starting ketones are discussed below. In the tables products are segregated according to the

Table I. Products of Photolysis of 1,5-Hexadien-3-ones

dienone	ratio 1,5/1,6 closure	product, yield (quantum yield) 1,5 closure	1,6 closure	ref
 4	only 1,6		 cis and trans 4a, ~100%, (0.59)[a]	10
 6	61:39	 6a, 43%	 6b, 27%	10
 10	only 1,5	 10a, 88%[a]		4, 5
 11	43:57	 11a, 39%	 11b, 51%	
 12	93:7	 12a, 40%  12b, 25%	 12c, 5%	
 13	10:90	 13a, 9%	 13b, 82%	
 14	only 1,5	 14a, >95%		
 15	77:23	 15a, 7%  15b, 41%	 15c, 14%	

[a] This work.

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(11) Smith, A. B., III; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 1961.

(12) For recent reviews see: Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152. Caldwell, R. A.; Creed, D. *Ibid.* **1980**, *13*, 45.

(13) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80.

(14) (a) For a preliminary communication see: Agosta, W. C.; Wolff, S. *J. Org. Chem.* **1980**, *45*, 3139. (b) A less detailed discussion of the entire problem is given by Agosta and Wolff: Agosta, W. C.; Wolff, S. *Pure Appl. Chem.* **1982**, *54*, 1579.

(15) Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123. This review contains many references to both synthetic and mechanistic aspects of [2 + 2] photocycloaddition.

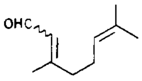
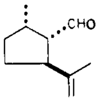
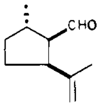
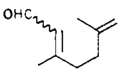
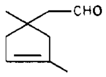
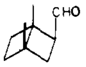
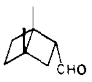
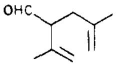
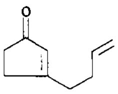
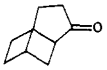
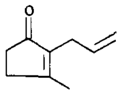
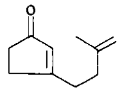
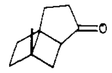
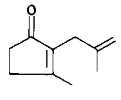
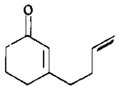
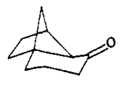
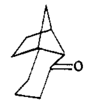
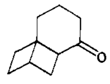
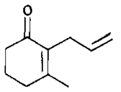
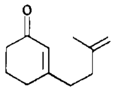
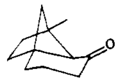
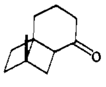
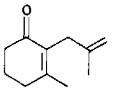
(16) Cookson, R. C.; Hudec, J.; Knight, S. A.; Whitear, B. R. D. *Tetrahedron* **1963**, *19*, 1995. Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1965**, *87*, 1589.

(17) Wolff, S.; Barany, F.; Agosta, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2378.

(18) Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1981**, *46*, 4821.

(19) We confirmed the earlier report (ref 5) that **14** is photochemically unreactive at room temperature.

Table II. Products of Photolysis of 1-Acyl-1,5-hexadienes

acyl diene	ratio 1,5:1,6 closure	product, yield (quantum yield) 1,5 closure	product, yield (quantum yield) 1,6 closure	ref
 16	only 1,5	 16a, 25%  16b, 42%  16c, 5%		16, 17
 17^b	22:78	 17a, 5%  17b, 8%	 17c, 10%  17d, 7%  17e, 3	
 18	10:90	 18a, 7%^{a} (0.010)	 18b, 56%^{a} (0.076)  18c, 8%^{a} (0.011)	18
 19	only 1,6		 19a, 84%^{a} (0.34)  19b, 4%^{a} (0.016)	18
 20	74:26	 20a, 20%  20b, 49%	 20c, 22%  20d, ~2%	
 21	13:87	 21a, 11% (0.067)	 21b, 76% (0.48)  21c, <2%	

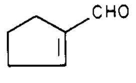
^{a} This work. ^{b} Data are for 80 °C; products were separated and characterized as the corresponding methyl esters.

regiochemistry of closure; the yields given are based on VPC measurements, and ratios of 1,5 and 1,6 closure calculated from these yields are tabulated for convenience. For comparison the tables also contain pertinent information from earlier studies.

The [2 + 2] photocycloaddition reaction is well recognized to be a triplet process,[7] and sensitized rearrangement of ketone **4**[11] and of citral (**16**)[17] was already known to give essentially the same results as direct irradiation. As expected, we found that the cyclopentenone **18** also gives an unchanged distribution of products on acetophenone-sensitized reaction and that direct reaction of **18** is efficiently quenched by 2,3-dimethyl-1,3-butadiene. We have also determined approximate quantum yields for several of these reactions. The data, which are included in Tables I and II, were obtained for benzene–methanol solutions irradiated in a merry-go-round apparatus at ~313 nm (potassium chromate filter,[20a] medium pressure mercury arc), using as a chemical actinometer the concurrent formation of acetophenone from valerophenone.[20] The values recorded are averages for two runs with a precision of ±3% or better.

Preparative Experiments

Synthesis of the desired substrates was straightforward. Ketone **11** was available through addition of allylmagnesium chloride to 1-cyclopentenecarboxaldehyde (**22**) and subsequent oxidation, all following an established procedure.[11] Homologous ketone **12** was prepared by addition of allyl bromide to 1-cyclohexenecarbonitrile (**23**) in the presence of zinc–silver couple,[21] followed by hydrolysis.



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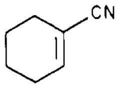

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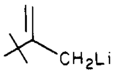

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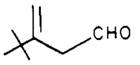

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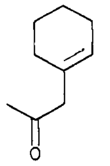

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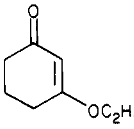

27

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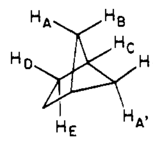
(20) (a) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898. (b) Data obtained for **6** and **10** are not reported here since they show that for these two ketones at 313-nm processes other than those now under discussion become important.

(21) Rousseau, G.; Conia, J. M. *Tetrahedron Lett.* **1981**, *22*, 649.

For preparation of **13**, 2,3,3-trimethyl-1-butene was first converted[22] to its lithium derivative **24**, and this was treated with gaseous formaldehyde. Oxidation of the resulting alcohol gave **25**; this aldehyde was treated with vinylmagnesium bromide and the product then oxidized to form **13**. Dienone **15** was available through Mannich addition of formaldehyde and diethylamine to 1-cyclohexenylacetone (**26**) followed by destructive distillation. The two cyclohexenones **20** and **21** were prepared by Grignard reaction on 3-ethoxy-2-cyclohexenone (**27**)[23] and subsequent acid hydrolysis.

Structures of Products

All new products reported in Tables I and II have been fully characterized and show spectroscopic properties compatible with their assigned structures.[24] In reaching these assignments we made extensive use of the well-documented differences between the proton nuclear magnetic resonance (NMR) spectra of bicyclo[2.1.1]hexanes[25] and the isomeric bicyclo[2.2.0]hexanes.[26] Detailed analyses of the NMR spectra of these new compounds are given in the Experimental Section. These spectra also permitted determination of the stereochemistry of those tricyclic products incorporating the bicyclo[2.1.1]hexane system. The assignments follow from several spectroscopic properties of the bicyclic system that have been previously discussed.[25] These include the facts that (1) H_A (cf. **28**) is readily identified from its upfield position, (2) H_B is deshielded by an alkyl substituent replacing $H_{B'}$, and (3) ranges for the various possible geminal, vicinal, and long-range proton–proton coupling constants have been established. For **20a,b** and **21a** the task was made simpler by an earlier analysis of spectra and stereochemistry of the closely related heterocyclic compounds **29–31**.[27] Also we found that, in parallel with the reported[27] epimerization of **30** to **29**, exposure of **20b** to methanolic potassium carbonate caused its complete inversion to **20a**. As we have previously noted,[18] the stereochemistry of **18a** could be assigned in turn through spectral comparisons with **20a,b**.



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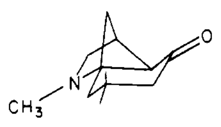

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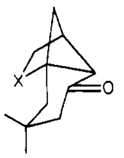
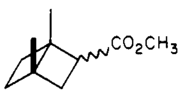
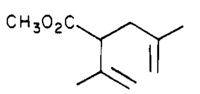


30, X = NCH_3
31, X = O

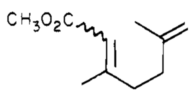
Also important for our structural assignments was the fact that simple bicyclo[2.2.0]hexanes undergo fragmentation at lower temperature (~130–175 °C)[28] than do their [2.1.1] isomers (~330–375 °C).[29] Thus pyrolysis at 190 °C of the mixture of esters **32** derived from **17c,d** yielded as the only products the three carbomethoxy dienes **33** and **34**, which were identified spectroscopically. Similar pyrolysis of **20c** and **21b** caused reversion to the original cyclohexenone in each case. On the other hand, ketones **18a** and **20b** were recovered unchanged after several hours of heating at ~190 °C.



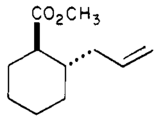
32



33



34, both isomers



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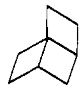
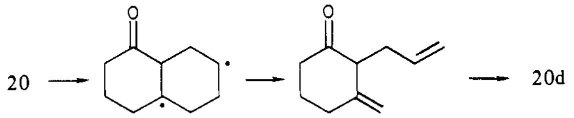


36

Ketone **14a** was independently identified by comparison of its IR spectrum with that of an authentic sample[30] and through its 2,4-dinitrophenylhydrazone.[31] Authentic methyl *trans*-2-allylcyclohexanecarboxylate (**35**) was prepared from the related nitrile; comparison of this substance with **12c** suggested that the photochemically derived material was largely the trans isomer.

In addition, we have previously reported various chemical correlations and transformations in preparation of derivatives of tricyclo[4.2.0.0^{1,4}]octane (**36**) from **18** and **19**.[18] These reactions provided independent rigorous identification of **18b** and also an assignment for **19a**. In turn these ketones were useful for spectral comparisons with other photoproducts in Tables I and II.

Finally, with the exception of four minor enones, all these products are types of compounds expected from biradicals **2** and **3**. The minor enones **18c**, **19b**, **20d**, and **21c** are 1,4- rather than 1,5-dienes, presumably arising through incidental shift of the double bond of an initial β,γ-unsaturated ketone into conjugation; this is illustrated for formation of **20d**. The yields of these minor products obtained preparatively were somewhat higher than those recorded. The accompanying tricyclic photoproducts related to bicyclo[2.2.0]hexane (as **20c**) can open thermally to the biradicals (as **37**) that are precursors of the enones, and the VPC conditions used for preparative separation of the product mixtures caused a small amount of thermolysis of the tricyclic compounds.[32] Under analytic VPC conditions such secondary transformations could be avoided.



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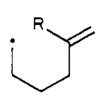
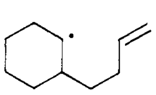


38, R = CH_3
39, R = H



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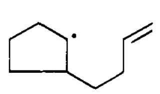

41

Discussion

The results in Tables I and II reveal that alkyl substitution at C(5) of the diene system is accompanied by an increase in the relative amount 1,6 closure. Several examples indicate that substitution at C(1), C(2), or C(6) has no comparable effect, and there is considerable support for this latter conclusion in an earlier study of the photochemistry of 1,5-hexadien-3-ones bearing alkyl substituents at C(1), C(2), C(4), or C(6).[5] This finding is immediately reminiscent of the behavior of alkyl-substituted 5-hexenyl radicals. These species are relatively insensitive to alkyl substitution at all positions except C(5), generally cyclizing highly

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[22] Akiyama, S.; Hooz, J. *Tetrahedron Lett.* **1973**, 4115.

[23] Gannon, W. F.; House, H. O. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 539, and references cited therein.

[24] As noted in Table II, products from **17** were purified and characterized as the corresponding methyl esters rather than as aldehydes **17a–e**, which were not readily separable.

[25] Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1980**, *45*, 1332 and references cited therein.

[26] Srinivasan, R. *J. Am. Chem. Soc.* **1961**, *83*, 4923. Lüttke, W.; Shabacker, V. *Liebigs Ann. Chem.* **1966**, *698*, 86. Srinivasan, R.; Sonntag, F. I. *Tetrahedron Lett.* **1967**, 603. Dauben, W. G.; Chitwood, J. L.; Scherer, K. V., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 1014.

[27] Tamura, Y.; Ishibashi, H.; Hirai, M.; Kita, Y.; Ikeda, M. *J. Org. Chem.* **1975**, *40*, 2702.

[28] Steel, C.; Zand, R.; Hurwitz, P.; Cohen, S. G. *J. Am. Chem. Soc.* **1964**, *86*, 679.

[29] Srinivasan, R.; Levi, A. A. *J. Am. Chem. Soc.* **1963**, *85*, 3363.

[30] Hirata, T.; Suga, T. *J. Org. Chem.* **1971**, *36*, 412. We thank Professor Takayuki Suga for providing this spectrum.

[31] Our derivative had mp 129–130 °C (lit. mp 130.5–131 °C: Meinwald, J.; Gassman, P. G. *J. Am. Chem. Soc.* **1960**, *82*, 2857).

[32] Liquid-phase pyrolysis of **20c** and **21b** causes reversion only to starting cyclohexenones **20** and **21** as noted above, but under VPC conditions both starting and rearranged cyclohexenones are formed. This reaction accounts for the somewhat different yields of **19a,b** originally reported in ref 18.

preferentially in the 1,5 manner.[33] Substitution of a methyl group at C(5), however, introduces a steric effect that dramatically decreases the rate of 1,5-cyclization and concomitantly slightly increases the rate of 1,6 closure. The overall result is that 5-methyl-5-hexenyl (**38**) closes irreversibly at similar rates to cyclopentane and cyclohexane products, while 5-hexenyl (**39**) itself gives virtually only the cyclopentane. Evidence strongly indicating that in the photochemical reaction also much of the effect of substitution at C(5) is steric comes from comparison of the 1,5/1,6 closure ratios for the three hexadienones **10**, **6**, and **13**, where a progressive shift to 1,6 closure accompanies the change of C(5) substituent from hydrogen to methyl to *tert*-butyl. The quantum yield data for **18** and **19** also present a related qualitative similarity to the radical process. Examination of these results shows that the 5-methyl group also slows 1,5 closure and accelerates 1,6 closure in this system. We noted the same effect in preparative photolyses of **10** and **6**; under comparable conditions rearrangement of **10** to **10a** is about sixfold faster than transformation of **6** to **6a**,**b**. Closer comparisons between the radical and photochemical reactions appear unwarranted, since there may be an important mechanistic difference between the two. Radical cyclization is known to be irreversible and under kinetic control,[33] but the initial photochemical cyclization step is possibly reversible.[34] In the photochemical process then substitution at C(5) may favor 1,6 closure not only sterically but also by stabilization of the biradical formed.

A second feature that affects regiochemistry in photolysis of these dienones is incorporation of the conjugated double bond into a five- or six-membered ring. In both classes the smaller ring is considerably more effective in causing increased 1,6 closure, and, where we have comparative data (**19** and **21**), this is accompanied by some reduction in quantum efficiency. This ring effect is roughly additive with the substitution effect just discussed, and in either series **7** or **8** the simultaneous presence of both a methyl group at C(5) and a five-membered ring (cf. **4** and **19**) brings about exclusive 1,6 cyclization. Since C(5) substitution has a qualitatively similar effect on regiochemistry in both radical and photochemical cyclizations, it was natural to inquire whether the ring effect also has a counterpart in the chemistry of 5-hexenyl radicals. The behavior of 2-(3-butenyl)cyclohexyl (**40**) was already on record,[36] and this six-ring radical undergoes overwhelming 1,5 (98%) rather than 1,6 closure. We examined the corresponding cyclopentyl radical **41** and found that it was even more selective for the 1,5 mode, with an upper limit of ~0.5% for 1,6 cyclization.[37] There is then no analogous ring effect in radical cyclization reactions. In the photochemical reactions it presumably reflects a steric requirement for overlap in the initial 1,5 or 1,6 bonding, taken together with the geometry of the reactive excited state of the enone. This effect then is related to the well-recognized facts that enone triplets twist about the carbon–carbon double bond when possible and that incorporation of this double bond in a ring can introduce constraints on the geometry of the triplet that alter excited-state reactivity.[38,39] Such twisting is at least partly responsible for the reduced rate of photolysis noted qualitatively for **6** relative to its cyclopentene analogue **4**.[40]

It is important to note that these two effects on regiochemistry hold equally well for the 1,5-hexadien-3-ones (**7**) and the 1-acyl-1,5-hexadienes (**8**), since the carbonyl group is at the opposite end of the conjugated double bond in the two series. That is, in **7** C(1) is the β-carbon atom of an enone but it is the α-carbon in **8**. Now, most of the compounds in Tables I and II designated "1,5 closure products" are derivatives of bicyclo[2.1.1]hexane and, as such, have two new carbon–carbon bonds, C(1)–C(5), and C(2)–C(6). There are two observations strongly suggesting that in isomerizations to these products the initial bond is indeed formed between C(1) and C(5), and not between C(2) and C(6). First, from appropriate substrates there are in general also formed products of disproportionation (as from **16**), where only one new carbon–carbon bond exists. In most cases on record this bond is C(1) to C(5);[5,41] analogous products with a single new C(2)–C(6) bond are unusual and typically are formed only in low yield. The only example of this latter process in Tables I and II is **17b**.[42] Second, the effect on regiochemistry of an alkyl substituent at C(5) is readily interpretable only if the initial bonding is either C(1)–C(5) or C(1)–C(6), because if the preferred initial bond were C(2)–C(6) in the unsubstituted series, it is not obvious why substitution at C(5) would cause a shift to C(1)–C(6) bonding. We conclude that initial C(2)–C(6) bonding is a minor process in these two classes of dienones. Our observation that the regiochemistry of these photochemical processes is insensitive to reversal of the enone double bond then implies that it is immaterial whether C(1) be the α (in **8**) or the β (in **7**) carbon atom of an enone for initial bonding to occur at this site. Support for this conclusion comes from the relatively high quantum efficiency for regiospecific 1,6 closure of both **4** and **19**, where location of the carbonyl group is the only structural difference in two dienones with identical carbon skeletons. This point is noteworthy because an issue still unsettled in the intermolecular [2 + 2] photocycloaddition reaction between enone and alkene concerns the factors that control the relative orientation of the two addends. One point frequently discussed is whether initial bonding of the alkene occurs selectively to the α- or β-carbon atom of the enone.[15] Our clear results with the intramolecular reaction suggest that initial bonding to either position is feasible in bimolecular systems. This is in agreement with some of the evidence from direct study of the intermolecular process.

In summary, this investigation has demonstrated that the regiochemistry of cyclization of these two classes of carbonyl-substituted hexadienes is strongly influenced by a substitution effect and a ring effect. The "rule of five" can be partially or totally invalidated by appropriate structural modification, predictably and at will. In the following paper we report that in the third related class of dienones, the 2-acyl-1,5-hexadienes (**9**), the situation is quite different.

Experimental Section

Materials and Equipment. General procedures have been previously described.[17] All VPC was carried out by using a Varian Aerograph Model 920 gas chromatograph with one of the following columns: (A) 25% XF-1150, 6 ft; (B) 25% QF-1, 3 ft; (C) 25% QF-1, 10 ft; (D) 25% QF-1, 25 ft; (E) 25% FFAP, 16 ft; (F) 25% FFAP, 33 ft; (G) 25% Carbowax 20 M with 15% $AgNO_3$, 15 ft; (H) 25% CDA, 40 ft; (I) 25% Carbowax 20 M, 5 ft; (J) 25% EGS, 10 ft; (K) 25% QF-1, 4.5 ft. All columns were packed in 0.25-in. aluminum tubing with 45/60 Chromosorb W, except columns A, G, and I, which employed 40/80 Chromosorb P. Uranium glass filters were used in all preparative photolyses. In addition to the aforementioned 60-MHz and 220-MHz NMR spectrometers,[17] a Nicolet/Oxford NT-300 (300-MHz) instrument was also employed. Unless otherwise noted, all pure compounds were obtained as

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[33] Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* **1974**, 2257. Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482. Beckwith, A. L. J.; Lawrence, T.; Serelis, A. K. *Ibid.* **1980**, 484. These articles contain extensive references to pertinent literature. For a more general review, see: Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4.

[34] Direct evidence for reversibility of the intramolecular reaction is lacking. For the bimolecular cycloaddition, reversion is a major source of inefficiency (see ref 15 and 35).

[35] Loutfy, R. O.; de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559.

[36] Beckwith, A. L. J.; Phillipou, G. *J. Chem. Soc., Chem. Commun.* **1973**, 280.

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[40] Another frequently observed consequence is the cis–trans isomerization that accompanies many cyclizations. Photochemical equilibration, for example, of the isomers of citral (**16**) (geranial and neral) is rapid relative to cyclization (ref 17).

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[42] As noted above, the photolysis of **17** reported in Table II was carried out at 80 °C; at room temperature the yield of **17b** drops to ~4%. Two additional examples of the minor 2,6 closure (yields of 3–5%) are given in ref 17.

colorless oils; products are usually listed in order of their elution upon VPC.

1-(1-Cyclopentenyl)-3-buten-1-one (11). This ketone was prepared in the same manner as **4**.[11] Addition of 1-cyclopentenecarboxaldehyde (**22**, 1.85 g, 19.3 mmol) to a suspension of allylmagnesium chloride, prepared from Mg (1.97 g, 0.081 mol) and allyl chloride (6.2 g, 81 mmol) gave 2.74 g of the carbinol, which was used without further purification; IR 3600 (w), 3070 (w), 2925 (s), 2840 (s), 1637 (m), 905 (m) cm^{-1}. The alcohol (2.74 g) was oxidized by the complex prepared[43] from CrO_3 (12.00 g, 120 mmol) and pyridine (19 g, 240 mmol) in CH_2Cl_2 (300 mL). Bulb-to-bulb distillation gave 1.411 g (54%) of **11**: bp 85–95 °C (10 mm); IR 3070 (w), 2965 (s), 1670 (s), 1635 (m), 920 (m) cm^{-1}; NMR (60 MHz) δ 6.62 (m, 1 H), 6.25–5.50 (m, 1 H), 5.25–4.82 (m, 2 H), 3.32 (ddd, J = 6, 1, 1 Hz, 2 H), 2.67–1.42 (m, 6 H); mass spectrum, m/z 136.0897 (M$^+$, calcd for $C_9H_{12}O$, 136.0888).

Photolysis of 11. VPC analysis (column A, 150 °C) of the irradiation of **11** (246 mg) in C_6H_6 (65 mL)–CH_3OH (3 mL) indicated complete conversion of starting ketone to two products in 1.5 h. Preparative VPC afforded a pure sample of each. The first product (51%) was methyl 2-allylcyclopentanecarboxylate, **11b**: IR 3070 (w), 2945 (s), 1736 (s), 1641 (w), 1429 (m), 1187 (s), 1158 (s), 982 (w), 907 (m) cm^{-1}; NMR (60 MHz) δ 6.07–5.37 (m, 1 H), 5.13–4.72 (m, 2 H), 3.62 (s, 3 H), 2.95–2.52 (m, 1 H), 2.5–1.02 (m, 9 H); mass spectrum, m/z 168.1151 (M$^+$, calcd for $C_{10}H_{16}O_2$, 168.1150). The second product (39%) was **11a**: IR 2955 (s), 1759 (s), 1412 (w), 1250 (w), 1051 (w), 987 (w) cm^{-1}; NMR[44] (220 MHz) δ 2.59 (m, H_C), 2.47 [dd, J_{DE} = 14.9, J_{CE} (or J_{CD}) = 0.4 Hz, H_E (or H_D)], 2.42–1.71 (m, 9 H), 1.39 (ddd, J = 5.2, 8.4, 13.6 Hz, 1 H); mass spectrum, m/z 136.0896 (M$^+$, calcd for $C_9H_{12}O$, 136.0888).

1-(1-Cyclohexenyl)-3-buten-1-one (12). To a mixture of 1-cyclohexenecarbonitrile (2.14 g, 20 mmol) and activated Zn (1.75 g) in anhydrous ether was added allyl bromide (3.24 g, 26.8 mmol) according to the procedure of Conia.[21] Bulb-to-bulb distillation (110–130 °C, 0.5 mm) gave 379–544 mg (13–18%) of an oil which required further purification by VPC (column B, 125 °C): IR 3100 (w), 2955 (s), 1659 (s), 1636 (m), 1177 (m), 987 (w), 912 (m) cm^{-1}; NMR (60 MHz) δ 6.68 (m, 1 H), 6.25–5.52 (m, 1 H), 5.07 (br s, 1 H), 4.97–4.72 (m, 1 H), 3.24 (ddd, J = 1, 1, 7 Hz, 2 H), 2.48–1.32 (m, 8 H); mass spectrum, m/z 150.1048 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1044).

Photolysis of 12. Irradiation of **12** (144 mg) in C_6H_6 (70 mL)–CH_3OH (3 mL) was monitored by VPC (column C, 150 °C), which indicated the formation of three products after 16 h. The first (5%) was identified as **12c** upon comparison of NMR and IR spectra with those of an authentic sample of **35** described below. The second product (25%) was identified as **12b**: IR 3005 (m), 2955 (s), 1755 (s), 1448 (w), 1023 (w) cm^{-1}; NMR[44] (300 MHz) δ 2.81 (m, H_C), 2.06 (ddd, H_D, J_{DE} = 16.1, J_{BD} = 4.4, J_{CD} = 1.0 Hz), 2.00–1.95 (m, 2 H), 1.91–1.83 (m, 2 H), 1.75–1.66 (m, 1 H), 1.63 (d, H_A, J_{AB} = 6.8 Hz), 1.55–1.02 (m, 6 H); mass spectrum, m/z 150.1069 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1045). The third product (40%) was **12a**: IR 2950 (s), 1755 (s), 1442 (w), 1260 (w), 991 (w), 906 (w) cm^{-1}; NMR (300 MHz) δ 2.61 (m, H_B), 2.48 (ddd, H_C, J_{BC} = 3.6, J_{CD} = 1.4, J_{CE} = 1.4), 2.20 (ddd, H_E, J_{DE} = 15.6, J_{CE} = 1.4, J_{BE} = 1.1), 2.09 (ddd, H_D, J_{DE} = 15.5, J_{CD} = 1.4, J_{BD} = 4.7 Hz), 1.95–1.19 (m, with dd at 1.36, H_A, $J_{AA'}$ = 6.3, J_{AB} = 7.7 Hz, 9 H), 1.01–0.85 (m, 1 H); mass spectrum, m/z 150.1046 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1044).

Methyl *trans*-2-Allylcyclohexanecarboxylate (35). To a solution of tosylmethyl isocyanide (3.81 g, 19.5 mmol) and 2-allylcyclohexanone[45] (2.01 g, 15 mmol) in $(CH_3)_2SO$ (25 mL) containing CH_3OH (0.25 mL) was added *t*-BuOK (4.55 g, 40.5 mmol) in $(CH_3)_2SO$ (15 mL) according to the published procedure.[46] Bulb-to-bulb distillation afforded **23** (1.41 g, 63%), bp 140–150 °C (20 mm). An analytical sample was obtained by preparative VPC (column B, 110 °C): IR 3100 (w), 2955 (s), 2870 (m), 2245 (w), 1639 (m), 1445 (m), 988 (m), 910 (s) cm^{-1}; NMR (60 MHz) δ 6.07–5.33 (m, 1 H), 5.27–4.82 (m, 2 H), 3.0–0.83 (m, with br s at 2.82, 12 H). Anal. ($C_{10}H_{15}N$) C, H, N.

The nitrile (500 mg, 3.35 mmol) and KOH (3 g) in ethylene glycol (10 mL)–H_2O (2 mL) was heated at reflux under a N_2 atmosphere for 24 h. The mixture was cooled, diluted with H_2O, and washed with Et_2O. The aqueous phase was acidified and extracted with Et_2O. The extracts were dried and treated with diazomethane. Bulb-to-bulb distillation gave 444 mg of **35** (73%), bp 140–150 °C (10 mm). Further purification was achieved by preparative VPC (column C, 140 °C): IR 3100 (w), 2955 (s), 2870 (m), 1733 (s), 1636 (w), 1443 (m), 1426 (m), 1256 (s), 904 (m) cm^{-1}; NMR (60 MHz) δ 6.02–5.33 (m, 1 H), 5.08–4.68 (m, 2 H), 3.6 (s, 3 H), 2.7–0.7 (m, 12 H). Anal. ($C_{11}H_{18}O_2$) C, H.

4,4-Dimethyl-3-methylenepentanal (25). For 1.5 days 2,3,3-trimethyl-1-butene (5.92 g, 60 mmol) was treated with *n*-BuLi (21 mL of a 2.4 M solution, 50 mmol) in the presence of tetramethylethylenediamine (5.81 g, 50 mmol) according to the method of Akiyama and Hooz.[22] The reaction mixture was cooled to 0 °C, and gaseous formaldehyde generated by the thermal depolymerization of paraformaldehyde (3.0 g) was introduced. The mixture was added to ice/H_2O and extracted with Et_2O. The combined extracts were washed with dilute HCl, H_2O, dilute $NaHCO_3$, and brine and dried. Distillation gave 1.936 g (30%) of a fraction, bp 73–82 °C (20 mm). VPC analysis (column C, 110 °C) indicated two components in an approximate ratio of 12:1. The major, first eluted component was collected and identified as 4,4-dimethyl-3-methylene-1-pentanol: IR 3660 (w), 3375 (m), 3120 (w), 2990 (s), 2890 (m), 1630 (m), 1360 (m), 1040 (s), 888 (m) cm^{-1}; NMR (60 MHz) δ 4.97 (s, 1 H), 4.73 (br s, 1 H), 3.70 (br t, J = 6.5 Hz, 2 H), 2.32 (t, J = 6.5 Hz, 2 H), 1.62 (br s, 1 H), 1.08 (s, 9 H). Anal. ($C_8H_{16}O$) C, H. The alcohol (897.5 mg, 7 mmol) was oxidized by the method of Ratcliffe and Rodehorst.[43] Preparative VPC (column C, 110 °C) gave pure **25**: IR 3120 (w), 2985 (s), 2830 (w), 2735 (w), 1725 (s), 1630 (w), 1360 (m), 895 (m) cm^{-1}; NMR (60 MHz) δ 9.45 (t, J = 2.5 Hz, 1 H), 5.3 (s, 1 H), 4.82 (s, 1 H), 3.03 (d, J = 2.5 Hz, 2 H), 1.08 (s, 9 H); mass spectrum, m/z 126.1061 (M$^+$, calcd for $C_8H_{14}O$, 126.1045).

5-*tert*-Butyl-1,5-hexadien-3-one (13). The crude aldehyde **25** was added to vinylmagnesium bromide (13 mL of a 1.1 M solution, 14.3 mmol) at 0 °C. Standard workup gave the alcohol (1.10 g): IR 3650 (w), 3115 (w), 2980 (s), 1630 (m), 1360 (m), 982 (w), 918 (w), 885 (w) cm^{-1}. The alcohol was oxidized with the complex prepared from CrO_3 (4.8 g) and pyridine (7.59 g) in CH_2Cl_2 (120 mL).[43] Bulb-to-bulb distillation gave **13** (458 mg, 43% from 4,4-dimethyl-3-methylene-1-pentanol), bp 110 °C (15 mm). Further purification was achieved by VPC (column C, 140 °C): IR 3115 (w), 2985 (s), 1696 (s), 1678 (m), 1616 (m), 1398 (m), 1360 (m), 898 (m) cm^{-1}; NMR (60 MHz) δ 6.62–5.9 (m, 2 H), 5.58 (dd, J = 3, 9 Hz, 1 H), 4.98 (s, 1 H), 4.63 (br s, 1 H), 3.17 (m, 2 H), 1.08 (s, 9 H); mass spectrum, m/z 152.1196 (M$^+$, calcd for $C_{10}H_{16}O$, 152.1201).

Photolysis of 13. Irradiation of **13** (173 mg) in C_6H_6 (66 mL)–CH_3OH (3 mL) in the usual fashion was nearly complete after 45 h. Preparative VPC (column C, 140 °C) yielded **13b** and **13a** in 82% and 9% yield, respectively. Data for methyl 6,6-dimethyl-5-methyleneheptanoate (**13b**): IR 3110 (w), 2985 (s), 1739 (s), 1631 (w), 1431 (m), 1360 (m), 889 (m) cm^{-1}; NMR (60 MHz) δ 4.88 (s, 1 H), 4.7 (br s, 1 H), 3.6 (s, 3 H), 2.42–1.67 (m, 6 H), 1.05 (s, 9 H). Anal. ($C_{11}H_{20}O_2$) C, H. Data for 4-*tert*-butylbicyclo[2.1.1]hexan-2-one (**13a**): IR 2985 (s), 1762 (s), 1473 (m), 1358 (m), 1212 (w), 1138 (w), 1019 (w) cm^{-1}; NMR (220 MHz) δ 2.66 (t, J = 2.6 Hz, 1 H), 2.01–1.93 (m, 4 H), 1.48 (m, 2 H), 0.92 (s, 9 H); mass spectrum, m/z 152.1207 (M$^+$, calcd for $C_{10}H_{16}O$, 152.1201).

6-Methyl-1,5-heptadien-4-one (14). Oxidation of the corresponding alcohol[5] (2.524 g, 20 mmol) with the complex prepared[43] from CrO_3 (12.0 g, 120 mmol) and pyridine (19.0 g, 240 mmol) in CH_2Cl_2 gave **14** (1.253 g, 50%), bp 79–82 °C (30 mm), with spectral data consistent with that previously reported.[5]

Photolysis of 14. In agreement with previous experience,[5] no reaction was observed upon irradiation of **14** in C_6H_6 at 25–30 °C. VPC analysis (column D, 162 °C) of the course of photolysis of **14** (500 mg) in refluxing *p*-xylene (50 mL) indicated slow formation of one product. After 5 days, conversion of starting material was nearly complete; preparative VPC furnished **14a** (~95%): IR[30] 2960 (s), 1762 (s), 1385 (w), 1368 (w), 1240 (w), 1127 (w) cm^{-1}; NMR:[47] 2,4-dinitrophenylhydrazone, mp 129–130 °C (lit.[31] mp 130.5–131 °C).

1-(1-Cyclohexenyl)-3-buten-2-one (15). A mixture of **26** (5.53 g, 40 mmol, commercially available), 37% aqueous formaldehyde (6.48 g, 80 mmol), and diethylamine hydrochloride (8.77 g, 80 mmol) in ethanol (5 mL) containing 15 drops of concentrated HCl was heated on a steam bath for 3 days. The mixture was destructively distilled up to 260 °C. The distillate was dissolved in pentane, washed with dilute HCl, H_2O, $NaHCO_3$, and brine, and dried. Short-path distillation afforded 595 mg of an oil that upon further purification by preparative VPC (column E, 183 °C) gave **15**: IR 2935 (s), 2850 (m), 2838 (m), 1695 (s), 1613 (m), 1390 (m), 975 (m), 940 (m) cm^{-1}; NMR (60 MHz) δ 6.68–6.00 (m, 2 H), 5.83–5.33 (m, 2 H), 3.10 (s, 2 H), 2.33–1.32 (br m, 8 H); mass spectrum, m/z 150.1051 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1044).

Photolysis of 15. A solution of **15** (235 mg) in C_6H_6 (200 mL)–CH_3OH (6 mL) was irradiated in the usual fashion. VPC analysis (column C, 150 °C) indicated after 5 h that no starting material re-

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(44) Location of H_A–H_E is given in **28**.

(45) Lorette, N. B.; Howard, W. L. *J. Org. Chem.* **1961**, *26*, 3112; "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 25.

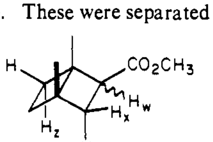
(46) Oldenziel, O. H.; Van Leusen, D.; Van Leusen, A. M. *J. Org. Chem.* **1977**, *42*, 3114.

(47) For discussion of the 600-MHz NMR spectrum of **14a** see ref 25.

mained and two major products had formed. The first, formed in 14% yield, was identified as **15c**: IR 3070 (w), 2935 (s), 2855 (m), 1741 (s), 1160 (m), 880 (m) cm^{-1}; NMR (60 MHz) δ 4.67 (m, 1 H), 4.58 (m, 1 H), 3.63 (s, 3 H), 2.47–1.0 (br m, 13 H); mass spectrum, m/z 182.1300 (M$^+$, calcd for $C_{11}H_{18}O_2$, 182.1307). The second component was a mixture of **15a** and **15b**; these were separated on column F (190 °C). Data for **15a** (7%): IR 3000 (w), 2932 (s), 2865 (w), 1762 (s), 1438 (m), 1290 (m), 1113 (m), 1010 (m), 980 (m) cm^{-1}; NMR[44] (220 MHz) δ 2.63 (m, H_B), 2.52 (d, H_C, J_{BC} = 2.6 Hz), 2.12 (d, H_D, J_{DE} = 15.3 Hz), 1.89–1.03 (m, 11 H); mass spectrum, m/z 150.1048 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1044). Data for **15b** (41%): IR 2935 (s), 2862 (m), 2850 (m), 1762 (s), 1440 (w), 1085 (m), 1018 (m), 980 (m) cm^{-1}; NMR[44] (220 MHz) δ 2.79 (dd, H_C, J_{BC} = $J_{B'C}$ = 1.9 Hz), 2.21 (ddd, H_D, J_{DE} = 16.2, J_{CD} = 4.8, J_{BD} = 1.0 Hz), 1.87–1.70 (m, 6 H), 1.64–1.10 (m, 6 H); mass spectrum, m/z 150.1033 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1044).

***cis*- and *trans*-3,6-Dimethyl-2,6-heptadienal (17).** To a suspension of NaH (4.4 g, 60% oil dispersion, 0.11 mol) in dry dimethoxyethane (175 mL) was added triethyl phosphonoacetate (23.54 g, 0.105 mol) and then 5-methyl-5-hexen-2-one (10.0 g, 0.089 mol) according to the procedure of Wadsworth and Emmons.[48] Distillation afforded 12.23 g (75%), bp 98–104 °C (8 mm), of a mixture of the cis and trans ethyl esters: IR 3100 (w), 3000 (s), 2955 (s), 1720 (s), 1648 (s), 1218 (s), 1138 (s), 886 (m) cm^{-1}. Anal. ($C_{11}H_{18}O_2$) C, H. To a solution of the esters (3.65 g, 20 mmol) in pentane (60 mL), magnetically stirred and cooled to −30 °C under a N_2 atmosphere, was added diisobutylaluminum hydride (43 g of a 20% hexane solution, 60 mmol) over a period of 1.33 h. The reaction mixture was stirred 20 min at −30 °C and was allowed to warm to −5 °C, where it was maintained for 1.5 h. Excess hydride was destroyed with CH_3OH (5 mL). The mixture was poured onto cold 5% HCl and was extracted with Et_2O. Removal of solvent yielded 2.831 g of the alcohols: IR 3655 (m), 3375 (br), 3100 (m), 2955 (s), 1645 (m), 880 (s) cm^{-1}. Oxidation of the crude alcohols using the Ratcliffe–Rodehorst procedure[43] (20-mmol scale) afforded 2.17 g (79%) of **17**, bp 85–90 °C (10 mm). Purification of each isomer (cis:trans 1:3) was achieved by preparative VPC (column C, 150 °C). ***cis*-17**: IR 3070 (w), 2965 (m), 2745 (w), 1680 (s), 1650 (w), 1635 (w), 1390 (m), 1372 (m), 1150 (m), 885 (s) cm^{-1}; NMR (60 MHz) δ 9.83 (d, J = 7.5 Hz, 1 H), 5.80 (br d, J = 7.5 Hz, 1 H), 4.73 (br s, 2 H), 2.85–2.15 (m, 4 H), 1.97 (d, J = 1.5 Hz, 3 H), 1.78 (d, J = 0.5 Hz, 3 H); mass spectrum, m/z 138.1029 (M$^+$, calcd for $C_9H_{14}O$, 138.1045). ***trans*-17**: IR 3065 (w), 2930 (w), 2840 (m), 2755 (w), 1683 (s), 1650 (m), 1635 (m), 1615 (m), 1190 (m), 1118 (m), 885 (s) cm^{-1}; NMR (60 MHz) δ 9.86 (d, J = 7.5 Hz, 1 H), 5.77 (dq, J = 1.0, 7.5 Hz, 1 H), 4.68 (br s, 2 H), 2.27 (s, 4 H), 2.17 (d, J = 1.0 Hz, 3 H), 1.75 (br s, 3 H). Anal. ($C_9H_{14}O$) C, H.

Photolysis of 17. A solution of the aldehydes (1.057 g) in C_6H_6 (130 mL) was irradiated at reflux for 24 days at which time VPC analysis (column B, 120 °C) indicated no remaining **17**. After removal of solvent, the product mixture was oxidized and esterified as described previously.[17,49] Analytical VPC (column G, 150 °C) indicated the presence of three compounds. The first component was **17Ea** (5%): IR 2975 (s), 2895 (m), 1734 (s), 1447 (m), 1428 (m), 1370 (m), 1306 (m), 1218 (s), 1036 (m) cm^{-1}; NMR[44] (220 MHz) δ 3.58 (s, 3 H), 1.79 (t, $H_{B'}$, J ~ 1 Hz), 1.69–1.63 (m, 2 H), 1.45–1.38 (m, 2 H), 1.24 (s, 6 H), 1.08 (d, H_A, J = 6.1 Hz), 0.95 (dt, H_B, J = 2.5, 6.1 Hz); mass spectrum, m/z 168.1159 (M$^+$, calcd for $C_{10}H_{16}O_2$, 168.1150). The second component was a mixture of **17Ec–e**. These were separated on column H (145 °C).



Eluted first was **17Ee** (≡ **33**; 30%): IR 3100 (w), 2990 (m), 2972 (m), 1738 (s), 1645 (m), 1430 (m), 1151 (s), 890 (s) cm^{-1}; NMR (220 MHz) δ 4.82 (m, 2 H), 4.70 (br s, 1 H), 4.65 (br s, 1 H), 3.61 (s, 3 H), 3.17 (dd, J = 6.3, 8.9 Hz, 1 H), 2.51 (dd, J = 8.9, 14.5 Hz, 1 H), 2.18 (dd, J = 6.3, 14.5 Hz, 1 H), 1.74 and 1.71 (2 br s, 6 H); mass spectrum, m/z 168.1158 (M$^+$, calcd for $C_{10}H_{16}O_2$, 168.1151). Data for **17Ec** (10%): IR 2975 (s), 2885 (m), 1737 (s), 1429 (m), 1374 (w), 1187 (s), 1164 (s), 1034 (m) cm^{-1}; NMR[50] (220 MHz) δ 3.62 (s, 3 H), 2.86 (dd, H_W, J_{WX} = 8.0, J_{WY} = 10.8 Hz), 2.49 (dd, H_X, J_{WX} = 7.9, J_{XY} = 12.5 Hz), 2.21–1.64 (m, 5 H), 1.13 (s, 3 H), 1.02 (s, 3 H); mass spectrum, m/z 168.1165 (M$^+$, calcd for $C_{10}H_{16}O_2$, 168.1150). Data for **17Ed** (7%): IR 2973 (s), 2883 (m), 1737 (s), 1429 (m), 1348 (m), 1164 (s) cm^{-1}; NMR (220 MHz) δ 3.60 (s, 3 H), 3.06 (dd, H_W, J_{WX} = 7.3, J_{WY} = 7.4 Hz), 2.32 (ddd, H_Z, J = 1.4, 6.9, 12.1 Hz), 2.24–1.84 (m, 5 H), 1.04 (s, 3 H), 0.90 (s, 3 H); mass spectrum, m/z 168.1105 (M$^+$, calcd for $C_{10}H_{16}O_2$, 168.1150). The third component (column G) was **17Eb**: IR 3065 (w), 2975 (s), 2940 (s), 2865 (s), 1737 (s), 1432 (m), 1202 (s), 1150 (m), 1010 (m) cm^{-1}; NMR (60 MHz) δ 5.1 (m, 1 H), 3.58 (s, 3 H), 2.55–1.55 (m with s at 2.3 and br s at 1.67, 9 H), 1.13 (s, 3 H); mass spectrum, m/z 168.1164 (M$^+$, calcd for $C_{10}H_{16}O_2$, 168.1150).

Pyrolysis of 17Ec,d. A benzene (1 mL) solution of **17Ec** (~10 mg) in an evacuated, sealed tube was heated at 190 °C for 3 h. Analysis of the pyrolysate by VPC (column C, 145 °C) indicated the presence of the following compounds (*E*)-3,6-dimethyl-2,6-heptadienoic acid methyl ester, 15%; **17Ec** (and **17Ed**), 9%; **17Ee**, 32%; and (*Z*)-3,6-dimethyl-2,6-heptadienoic acid methyl ester, 44%. The *E* and *Z* esters were identified by comparison with authentic samples prepared as described below. The pyrolysate obtained after identical treatment of **17Ed** afforded the same products in the following amounts: *E* ester, 24%; **17Ed** (and **17Ec**), 26%; **17Ee**, 24%; *Z* ester, 26%.

Methyl (*E*)- and (*Z*)-3,6-Dimethyl-2,6-heptadienoate (34). A mixture of (*E*)- and (*Z*)-**17** (496 mg) was oxidized with excess Jones's reagent[51] in acetone (35 mL) for 1.5 h at 25 °C. The usual workup followed by base extraction, acidification, and extraction with ether gave 231 mg of acidic material that was esterified with diazomethane. Preparative VPC (column C, 140 °C) gave the two esters. Data for *E* isomer: IR 3100 (w), 3000 (m), 2970 (m), 1725 (s), 1645 (m), 1440 (m), 1225 (m), 1160 (s), 880 (m) cm^{-1}; NMR (300 MHz) δ 5.65 (br s, 1 H), 4.71 (br s, 2 H), 3.67 (s, 3 H), 2.76 (t, J = 8.0 Hz, 2 H), 2.13 (t, J = 8.0 Hz, 2 H), 1.90 (br s, 3 H), 1.77 (br s, 3 H). Anal. ($C_{10}H_{16}O_2$) C, H. Data for *Z* isomer: IR 3100 (w), 2970 (m), 1723 (s), 1650 (m), 1430 (m), 1220 (s), 1140 (s), 887 (m) cm^{-1}; NMR (60 MHz) δ 5.63 (br s, 1 H), 4.68 (br s, 2 H), 3.63 (s, 3 H), 2.27–2.12 (m, 7 H), 1.73 (br s, 3 H); mass spectrum, m/z 168.1146 (M$^+$, calcd for $C_{10}H_{16}O_2$, 168.1150).

3-(3-Butenyl)cyclohex-2-enone (20). Ketone **27** was added to a solution of 3-butenylmagnesium bromide [prepared from Mg (1.034 g, 0.0425 mol) and 4-bromo-1-butene (4.73 g, 35 mmol)]. Standard workup gave 4.94 g, which was dissolved in CH_3OH (50 mL) and treated with 1 M oxalic acid (5 mL) for 1.5 h at 25 °C. Extraction with pentane and distillation of the residue after removal of solvent gave **20** (2.328 g, 62%) bp 72–74 °C (0.5 mm): IR 3100 (w), 2950 (m), 1673 (s), 1640 (w), 1627 (w), 1320 (w), 1248 (w), 1183 (w), 914 (m), 882 (w) cm^{-1}; NMR (60 MHz) δ 6.15–5.35 (m with br s at 5.7, 2 H), 5.18–4.77 (m, 2 H), 2.48–1.72 (m, 10 H). Anal. ($C_{10}H_{14}O$) C, H.

Photolysis of 20. Irradiation of **20** (217 mg) in C_6H_6 (68 mL) was complete in 16 h. Preparative VPC (column I, 167 °C) yielded two components. The first was **20a** (20%): IR 2980 (s), 2900 (s), 2870 (w), 1713 (s), 1455 (m), 1315 (w), 1303 (m), 1195 (m), 1182 (m), 1108 (m) cm^{-1}; NMR[44] (220 MHz) δ 2.78 (m, H_C), 2.27–1.59 (m, 12 H), 0.81 (dd, H_A, J_{AB} = 7.8, $J_{AA'}$ = 7.8 Hz); mass spectrum, m/z 150.1050 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1045). The second component was a mixture of **20b–d**. Pyrolysis of a C_6H_6 solution of this mixture (73 mg) yielded **20**, **20b**, and **20d**. These were separated on column C (135 °C) to give **20b** (49%): IR 2980 (s), 2970 (s), 2900 (s), 1719 (s), 1419 (m), 1364 (m), 1298 (m), 1169 (m), 1050 (m) cm^{-1}; NMR[44] (220 MHz) δ 2.68 (br s, $H_{B'}$), 2.33–1.26 (m, 12 H), 1.19 (dd, H_A, J_{AB} = 6.1, J_{AC} = 0.9 Hz); mass spectrum, m/z 150.1046 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1045). Data for **20d**: IR 3100 (w), 2955 (m), 2895 (m), 1669 (s), 1627 (m), 1425 (m), 1375 (m), 984 (w), 900 (m) cm^{-1}; NMR (60 MHz) δ 5.97–5.33 (m, 1 H), 5.07–4.63 (m, 2 H), 2.98 (br d, J = 6 Hz, 2 H), 2.5–1.6 (m with s at 1.9, 9 H); mass spectrum, m/z 150.1048 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1045).

Treatment of the three-component mixture with K_2CO_3 in aqueous CH_3OH for 4 days at 25 °C gave, after VPC on column I, **20a** and a mixture of **20c,d**. The latter were separated as above (column C) to give pure **20c** (20%): IR 2960 (s), 2870 (m), 1705 (s), 1455 (m), 1433 (m), 1311 (m), 1285 (m), 897 (m) cm^{-1}; NMR (220 MHz) δ 2.77 (d, J = 5.8, 9.2 Hz, 1 H), 2.52–1.63 (m, 12 H), 1.39 (m, 1 H); mass spectrum, m/z 150.1043 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1045).

3-(3-Methyl-3-butenyl)cyclohex-2-enone (21). Addition of **27** (5.61 g, 40 mmol) to a solution of isopentenylmagnesium bromide [from Mg (1.581 g, 0.065 mol) and 4-bromo-2-methyl-1-butene (8.20 g, 55 mmol)] followed by treatment of the alcohol with 1 M oxalic acid as described above for **20** gave **21** (5.248 g, 80%): bp 78–79 °C (1 mm); IR 3095 (w), 2950 (s), 1674 (s), 1627 (m), 1372 (m), 1342 (m), 1320 (m), 1187 (m), 882 (s) cm^{-1}; NMR (60 MHz) δ 5.70 (br s, 1 H), 4.67 (br s, 2 H), 2.55–1.55 (m, with br s at 1.75, 13 H). Anal. ($C_{11}H_{16}O$) C, H.

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(48) Wadsworth, W. S., Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733.

(49) Compounds **17Ea–e** are the carboxylic acid methyl esters thus prepared that correspond to aldehydes **17a–e**.

(50) Location of H_W–H_Z is given in the adjacent structure.

(51) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2548. Djerassi, C.; Engle, R. R.; Bowers, A. *J. Org. Chem.* **1956**, *21*, 1547.

Photolysis of 21. Irradiation of **21** (180 mg) in benzene (65 mL) in the usual fashion was complete in 15 h. Preparative VPC (column J, 160 °C) afforded two products. **21a** (11%): IR 2970 (s), 2885 (s), 2860 (w), 1712 (s), 1375 (m), 1340 (m), 1310 (m), 1182 (m), 1152 (m), 1090 (m), 1048 (m) cm^{-1}; NMR[44] (220 MHz) δ 2.25–1.46 (m, 12 H), 1.33 (s, 3 H), 0.88 (dd, H_A, J_{AB} = 7.0, $J_{AA'}$ = 8.2 Hz); mass spectrum, *m/z* 164.1192 (M^+, calcd for $C_{11}H_{16}O$, 164.1201). **21b** (76%): IR 2955 (s), 1707 (s), 1366 (w), 1312 (w), 1285 (w), 880 (w) cm^{-1}; NMR (220 MHz) δ 2.73 (dd, *J* = 6.1, 9.1 Hz, 1 H), 2.43 (dd, *J* = 9.2, 12.4 Hz, 1 H), 2.33 (dddd, *J* = 1.6, 3.6, 3.6, 15.2 Hz, 1 H), 2.15–1.62 (m, 9 H), 1.42–1.28 (m, 1 H); mass spectrum, *m/z* 164.1197 (M^+, calcd for $C_{11}H_{16}O$, 164.1201).

Pyrolysis of 21b. Pyrolysis of 50 mg in C_6H_6 (4 mL) in a sealed, evacuated tube at 175 °C for 3 h yielded (VPC analysis) only **21** and ~20% unreacted **21b**.

Quantum Yield Measurements. Solutions of the dienones were prepared in benzene–CH_3OH (95:5), and 3.0 mL of each solution was placed in a separate 13 × 100 mm Pyrex test tube fitted with a constricted neck. Each sample was degassed by purging with N_2 for 10 min before sealing. These samples were irradiated on a merry-go-round apparatus simultaneously with 0.1 M solutions (3.0 mL) of valerophenone in CH_3CH_2OH or C_6H_6 using the output of a 450-W Hanovia medium-pressure mercury lamp filtered through a 1-cm path of 0.002 M K_2CrO_4 in 1% aqueous K_2CO_3. Yields of the dienone products and acetophenone were determined by calibrated VPC on column K. Total conversion was kept below 10%.

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Intramolecular Photochemical Reactions of 2-Acyl-1,5-hexadienes

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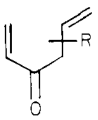
Abstract: Photolysis of the 2-acyl-1,5-hexadienes **6–11** (Table I) leads to regiospecific crossed cyclization, yielding derivatives of bicyclo[2.1.1]hexane. Unlike dienones of the related classes **1** and **2**, neither substitution at C(5) nor the presence of a ring influences the regiochemistry. Quantum yields for **9** and **10** also show an insensitivity to C(5) substitution and are six- to tenfold lower than for comparable dienones **1** and **2**. It is suggested that initial cyclization in these systems occurs from C(2) to C(6), rather than C(1) to C(5) as is preferred in **1** and **2**.

In the preceding paper[1] we reported on control of the regiochemistry of photochemical cyclization of 1,5-hexadien-3-ones (**1**)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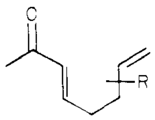
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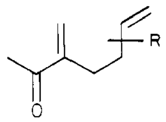
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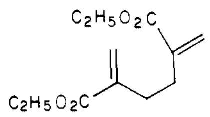

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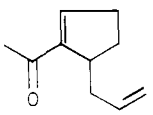
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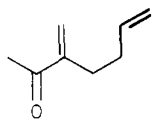
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and 1-acyl-1,5-hexadienes (**2**) both through alkyl substitution at C(5) and also by incorporation of the conjugated double bond into a five- or six-membered ring. The "rule of five"[2] operates in the absence of these structural features, but with either of them present both modes of closure occur. The effects are roughly additive, and incorporation of both a C(5)-methyl group and a five-membered ring in either **1** or **2** leads to regiospecific 1,6 cyclization. Upon completing these studies with **1** and **2** we wished to extend our effort to a third type of hexadiene, 2-acyl-1,5-hexadienes (**3**), particularly because rather less was known about the photochemistry of these compounds. We were aware of only three relevant examples, **4**,[3] **5**,[4] and **6**,[5,6] all of which undergo only crossed closure from the triplet state. Of these, **4** and **5** appear to depart from the rules operating in ketones of types **1** and **2**, since **4** has a substituent at C(5) and **5** has its conjugated double bond in a cyclopentene ring. Unfortunately, however, these two compounds have features that render interpretation of this regiochemical behavior problematic. Diester **4** has two conjugated double bonds rather than one enone and one simple alkene, and the particular location of the cyclopentene ring in **5** may well introduce steric constraints absent in other substrates. We have now investigated several dienones of type **3** to test the operation of the substitution and ring effects discovered in **1** and **2**.[1] Our findings are reported below.

Results

We have prepared and photolyzed dienones **7–11** listed in Table I along with earlier results with **6**[5] for comparison. Unless otherwise noted below, conditions and methods used were those described in detail in the preceding paper.[1] Ketone **7** was reactive only at elevated temperature. Triplet sensitization for **6** and **7** is necessary to avoid singlet reactions,[6] and irradiation of sensitizer acetophenone and **7** at 80 °C leads to extensive hydrogen ab-

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[1] Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983** (preceding paper in this issue).

[2] Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932. Liu, R. S. H.; Hammond, G. S. *Ibid.* **1967**, *89*, 4936.

[3] Bloomfield, J. J.; Owsley, D. C. *Tetrahedron Lett.* **1973**, 1795. Reaction of **4** was triplet sensitized through irradiation in acetonitrile containing benzophenone.

[4] Cormier, R. A.; Agosta, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 1867.

[5] Cormier, R. A.; Schreiber, W. L.; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 4873. Cormier, R. A.; Agosta, W. C. *Ibid.* **1974**, *96*, 618.

[6] Open-chain α-methylene ketones undergo intramolecular hydrogen abstraction from the singlet state, but their triplet [2 + 2] photocycloaddition reactions may be efficiently sensitized.[5]

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