Photochemical Reactions of Six β,γ-Cyclopropyl Ketones Derived from Bicyclo[4.2.1]nona-2,4,7-trien-9-one

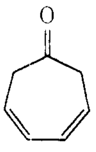
Ioannis M. Takakis and William C. Agosta*

Laboratories of The Rockefeller University, New York, New York 10021

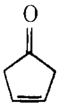
Received October 21, 1978

Simmons–Smith reaction of trienone **4** and its ketal **7** led to the cyclopropyl ketones **5**, **6**, **10**, and **11**; reduction provides **14–17**. The homologous ketone **21** is similarly prepared from **23**. Photolysis of reduced ketones **15** and **16** leads to mixtures of monocyclic olefins through decarbonylation and opening of the cyclopropane rings, and these reactions are rationalized by stepwise biradical pathways. Irradiation of **6** furnishes only the tetrahydronaphthalene **43**, which is considered to result from thermal cyclization of the cyclodecatetraene **42**. Both **5** and **10** undergo decarbonylation with formation of bicyclo[6.1.0]nonatriene **44**. The apparent photostability of **11** is rationalized as the result of a rapid, degenerate 1,3-acyl shift interconverting the enantiomers **11a** and **11b**.

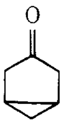
Photochemical decarbonylation of ketones is relatively rare in solution, but it has been recognized for some years that a number of structural features lead to exceptions to this general observation.[1] Among these are the systems represented by 3,5-cycloheptadien-1-one (**1**),[2] 3-cyclopenten-1-one (**2**),[3] and bicyclo[3.1.0]hexan-3-one (**3**)[4] and their derivatives.[5] In this report we describe the preparation and photochemistry of a number of β,γ-cyclopropyl ketones that incorporate one or more of these features and that are accessible from the readily available bicyclic trienone **4**.[6] Photolysis of these compounds typically led to decarbonylation and formation of medium ring unsaturated systems as the primary products.



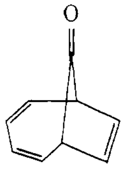
1



2



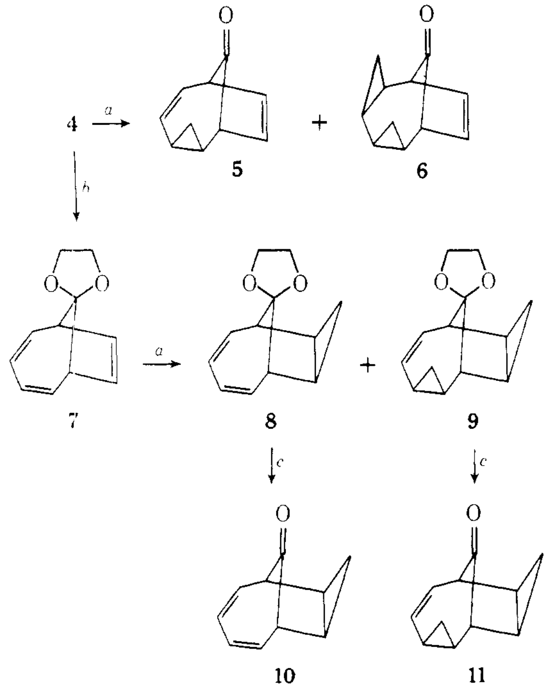
3



4

Preparative Experiments. Simmons–Smith cyclopropanations[7] of **4** and its ketal **7** are summarized in Scheme I. The ketal is available on careful reaction of **4** with ethylene glycol in the presence of a limited amount of *p*-toluenesulfonic acid. Long reaction times or increased amounts of catalyst led to formation of the ketal of 1-indanone (**12**) by way of an acid-catalyzed rearrangement known[6,8] to occur in related compounds of this series. Difficulty in preparing **7** has been noted in the past.[9] The most interesting and synthetically useful finding here is that cyclopropanation of **4** is directed exclusively toward the diene side of the molecule, while ketal **7** reacts preferentially at the isolated double bond. These differences presumably reflect both the nonclassical electronic interaction between the olefinic and carbonyl double bonds of **4**,[6,9] as well as a directive effect of the ketal oxygens in **7**.[10] The structures of the four product ketones **5**, **6**, **10**, and **11** are fully supported by IR and NMR spectroscopic properties recorded in the Experimental Section. As previously noted,[6] the ultraviolet spectrum of trienone **4** is anomalous and substantially different from that of 3,5-cycloheptadien-1-one (**1**). In Table I are presented the ultraviolet spectra of **4**, the related dienone **13**,[9] and the four new ketones; from these data it is clear that, of the new compounds, only ketone **10** retains a spectrum similar to that of **4**. Comparison of the spectra of **10** and **13** suggests some contribution from the cyclopropane electrons of **10** to this chromophore.

Scheme I

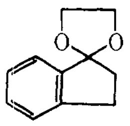


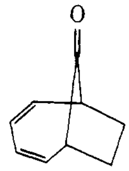
^{a} CH_2I_2, ZnCu. ^{b} H^+, glycol. ^{c} H^+, H_2O.

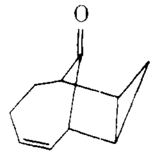
The indicated exo stereochemistry of all the cyclopropyl rings in these products is plausible on the basis of a sterically favored exo approach of the Simmons–Smith reagent in **4** and from the anticipated directive influence of the ketal grouping of **7**. Previous experience[10] had shown, however, that this latter effect fails to control cyclopropanation in two other bicyclic olefinic ketals, and with this in mind we have independently confirmed the assigned strereochemistry through lanthanide-shift NMR experiments. In the NMR spectra of ketones **5** and **10** one of the geminal cyclopropane protons moves rapidly downfield on addition of $Eu(fod)_3$;[11] in spectra of **6** a two-proton signal behaves in a similar manner, and for **11** two separate one-proton signals move rapidly downfield, but at different rates. In all cases the rates of displacement of these signals were greater than those of the adjacent tertiary bridgehead cyclopropane hydrogens. In **5**, **6**, and **10** these rapidly moving signals could be independently ascribed to endo geminal protons by virtue of their relatively small (~4 Hz) trans vicinal coupling constants with the tertiary cyclopropane hydrogens;[12] the spectrum of **11** was too complex to permit this independent assignment. Further confirmation of the cyclopropane stereochemistry of **10** and **11** comes from the relative deshielding of the endo geminal protons in the corresponding ketals **8** and **9**,[13] from independent formation of **11** on Simmons–Smith reaction of **10**, and from other chemical observations described below.

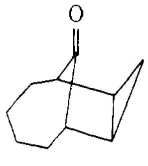
Hydrogenation of **8** over 5% palladium on carbon in meth-

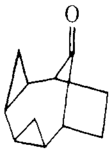
0022-3263/79/1944-1294$01.00/0

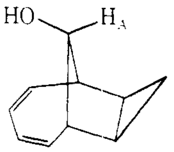

12


13

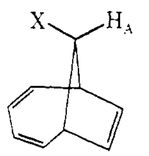

14


15

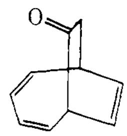

16



17



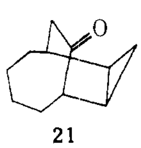
18, X = OH
19, X = H_B

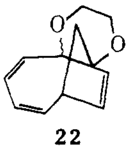

20

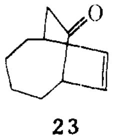
anol could be controlled to permit saturation of one or both double bonds. Deketalization of the products furnished ketones **14** and **15**. Alternatively, **14** was available through partial reduction of dienone **10**. Similar hydrogenation of **6** furnished **16**. The completely reduced ketone **15** was thermally quite stable, being recovered (87%) unchanged after 8 h at ∼250 °C. This behavior strongly favors the assignment of exo stereochemistry to the cyclopropane ring of **15** (and therefore **10**) since the corresponding endo cyclopropyl ketone should decarbonylate readily under much milder conditions.[14,15]

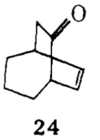
Reduction of **10** with sodium borohydride in methanol gave exclusively the alcohol **17**, the stereochemistry of which was assigned from its NMR spectrum. The carbinyl proton H_A appears at δ 4.18 ppm (dt, J = 12, 5 Hz) in close agreement with the signal for corresponding proton in trienol **18** (4.26, dt, J = 12, 6 Hz).[6,9] Comparison of this latter value with the signals for H_A (1.92, dt, J = 11.3, 6.2 Hz) and H_B (1.30, d, J = 11.3 Hz) in the related hydrocarbon **19**[16,17] had been employed earlier in assigning the stereochemistry of **18**.[6] This stereochemistry for **17** is also in agreement with lanthanide-shifted spectra. With increasing concentration of $Eu(fod)_3$ the original broad four-proton olefin signal splits into two two-proton signals, and these resonances are moved downfield much more rapidly than the cyclopropane signals. The stereospecificity in reduction of **10** to **17** is analogous to that in hydride reduction of **4**, which yields only **18**.[6] Since examination of molecular models suggests considerable steric hindrance by the cyclopropyl methylene group to the required approach of hydride reagent in **10**, this result implies that electronic factors may play a role in determining the course of reduction.

We were interested in extending these cyclopropanation reactions to the homologous trienone **20**,[6] particularly with the purpose of preparing the simple tricyclic ketone **21**, which was wanted for other investigations. However, products parallel to those from ketone **4** and ketal **7** were not obtained in this second series. Neither ketone **20** nor its α-acetoxy derivative[6] reacted under the Simmons–Smith conditions successful with **4**. Attempts to ketalize **20** with ethylene glycol under the conditions used for **4** or under a variety of other, milder conditions[18] led to a single substance isomeric with the desired ketal, but quite stable to aqueous acid. This stability suggests a molecular rearrangement during reaction of **20** with glycol, and a plausible product that is in accord both with spectroscopic properties and also with previously observed[6] bond switching reactions of carbonium ions related to **20** is the triene ether **22**. Additional work will be necessary, however, to establish the structure of this substance with certainty. The specific problem of preparing **21** was solved through selective hydrogenation of **20** to the tetrahydro ketone **23**. This substance readily yielded an ethylene ketal, which on cyclopropanation and deketalization furnished **21**. These steps closely followed conversion of the lower homologue **24** to **25**;[19] as expected, physical properties of the related compounds of these two series are quite similar.[20]


21


22


23


24

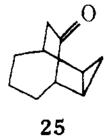

25

Table I. Ultraviolet Spectra of Compounds Related to Ketone 4

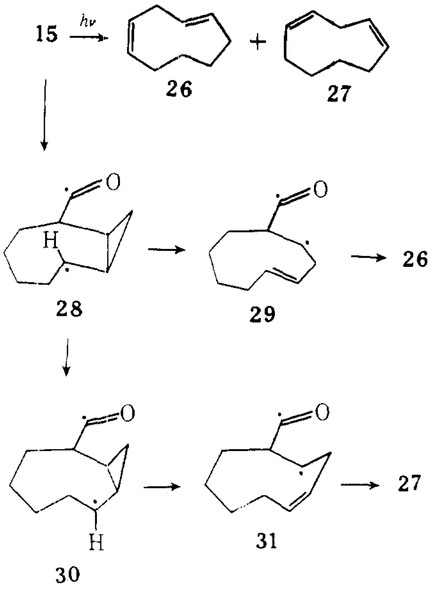
λ_{max}, nm(ε)					
4[a]	**5**[b,d]	**6**[b,e]	**10**[f]	**11**[g]	**13**[c]
	198 (5580)	197 (2770)	196 (3370)	198 (5660)	
216 (3080)	214 sh (3250)				
				232 sh (530)	
			257 (2590)		
269 (4010)			266 (3970)		264 (3300)
277 (3820)			277 (3800)		
				293 (90)	
325 (567)			318 (550)		313 (500)

[a] Reference 6. [b] These ketones showed typical, unenhanced $n\pi^*$ absorption. [c] Reference 9. [d] Registry no. 69140-31-4. [e] Registry no. 69140-32-5. [f] Registry no. 68285-77-8. [g] Registry no. 69140-33-6.

Photochemical Experiments. We turn now to a survey of the photochemical behavior of six of these new cyclopropyl ketones, compounds **5**, **6**, **10**, **11**, **15**, and **16**. Each of these was irradiated in benzene containing 3% methanol through Pyrex (λ >2800 Å) using a 450-W Hanovia lamp;[21] products were separated and purified by vapor phase chromatography (VPC).

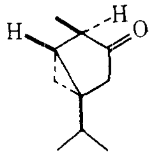
Irradiation of the saturated tricyclic ketone **15** resulted in decarbonylation and fragmentation of the three-membered ring to yield ∼78% of the two 1,4-cyclononadienes **26** and **27** in the ratio ∼69:31 (**26**–**27**).[22] The cis,cis diene **27** was identified by direct comparison with an authentic sample.[23] The cis,trans diene **26** is new and was identified by its spectroscopic properties, which require both diallylic and allylic hydrogen atoms along with both a cis and a trans disubstituted double bond. Data on the time course of the reaction[22] indicate that both dienes are primary products of the photolysis. This conclusion is supported by the observation that exposure of **26** to the reaction conditions led to only slow isomerization to **27** (**26**–**27** 90:10 after 25 h), although we cannot rule out some additional sensitized isomerization of **26** to **27** in the presence of ketone **15**.

Several lines of evidence indicate that **26** is thermodynamically less stable than the cis,cis isomer **27**. Previous studies of the equilibration of various 1,2-, 1,3-, 1,4-, and 1,5-cyclononadienes led to formation of **27** but not **26**.[24,25] From examination of molecular models it appears that **26** is more strained than **27**; in the related monoalkenes it is known from heats of hydrogenation that *cis*-cyclononene is more

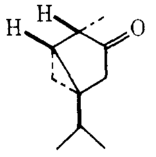


stable ($\Delta\Delta H$) than the trans isomer by 2.9 kcal/mol.[26] These various observations suggest then that photolysis of **15** does not proceed by way of long-lived biradical intermediates and that some detailed explanation for the selective formation of the less stable diene product **26** is desirable.

It appears inappropriate to ascribe this result to a combination of linear and nonlinear (and therefore conrotatory and disrotatory) concerted pathways,[27] such as have been invoked in the decarbonylation of substituted 3-cyclopenten-1-ones,[3] since the exo stereochemistry of the cyclopropane ring is unfavorable for the occurrence of such processes.[15] We suggest, however, that these very structural constraints in **15** permit the operation of a biradical mechanism that leads to selective formation of the trans double bond of **26**. In **15** α cleavage should give an acyl cyclopropylcarbinyl biradical in which the initial geometry, as shown in **28**, is quite favorable for stereoelectronically controlled fragmentation[28] with formation of the trans-homoallyl biradical **29**; decarbonylation of **29** then would furnish **26**.[29] The geometry necessary for formation of the cis,cis diene **27** requires conversion of **28** to the alternative conformer **30**, which can then fragment (**31**)[29] and decarbonylate to yield **27**. This conformational change, however, should be hindered in **28** by transannular interactions in the eight-membered ring, thus permitting preferential, kinetically controlled cleavage to the trans double bond with formation of the observed major product **26**. Our findings here with **15** then provide significant evidence for a biradical pathway in decarbonylation of a derivative of bicyclo[3.1.0]hexan-3-one (**3**). In an earlier study of the photodecarbonylation of (−)-thujone (**32**) and (+)-isothujone (**33**) a biradical mechanism was favored, and only a fortuitous combination of concerted pathways could provide an alternative explanation of the results.[4]

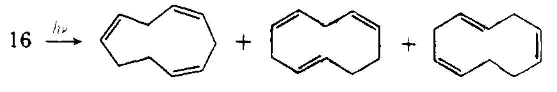


32

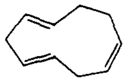


33

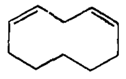
Irradiation of the bis(cyclopropyl) ketone **16** yielded ~50% of a mixture of at least three cyclodecatrienes. The all-cis triene **34** was purified by preparative VPC, but the remaining isomers could not be separated under any conditions tried. Re-exposure of this inseparable mixture of isomers to the photolytic conditions produced no detectable change in its properties. From the data given below, which were obtained on the purified mixture, we conclude that it consists of the cis,cis,trans isomer **35**, the cis,trans,cis isomer **36**, and possibly (but not necessarily) the cis,trans,trans isomer **37**. The 1, 4, 7 positioning of the double bonds in the components of the mixture follows from the absence of an ultraviolet maximum above 200 nm and from a ^{1}H NMR spectrum requiring six olefinic, four allylic, and four diallylic hydrogen atoms [δ 5.42 (m, 6 H), 2.75 (m, 4 H), 2.02 (m, 4 H)]. No other positions of three double bonds in a ten-membered ring satisfy these requirements. Reduction of the mixture with 1 equiv of hydrogen over palladium on carbon furnished a mixture of three cyclodecadienes plus very small amounts of *cis*-cyclodecene and unreacted trienes. The three dienes were separated by preparative VPC and identified as *cis,cis*-1,4-cyclodecadiene (**38**), *cis,trans*-1,5-cyclodecadiene (**39**), and *cis,cis*-1,5-cyclodecadiene (**40**) from their IR and NMR spectra. In each case the NMR spectrum contained resonances for the appropriate number of olefinic, diallylic, allylic, and saturated hydrogens and the IR spectrum showed appropriate bands for cis and trans disubstituted double bonds. The spectra of all three cyclodecadienes were in accord with information on record for these compounds.[30] Since the all-cis triene **34** is absent from the mixture hydrogenated, and since the trienes are all 1,4,7-cyclodecatrienes, formation of **38** and **40** is direct evidence for **35** and **36**, respectively, in the triene mixture. The cis,trans diene **39** could arise from an alternative mode of reduction of **35**, or possibly from the isomeric cis,trans,trans triene **37**. While we suspect that **37** would have separated chromatographically from the structurally more closely related trienes **35** and **36**, as did the all-cis isomer **34**, we cannot rigorously exclude its presence. The structure of **34** is assigned on the basis of NMR evidence similar to that described above for the mixture, along with an IR spectrum that contains strong absorption for cis double bonds at 710 cm^{-1} but no absorption for trans double bonds. From the amount of **34** found, together with the relative amounts of dienes **38**–**40** formed on reduction of the triene mixture, we calculate the following approximate composition of the hydrocarbon products obtained on photolysis of **16**: **34** (2%), **35** (24–30%), **36** (19%), and **37** (0–6%).



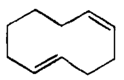
cis,cis,cis-**34** *cis,cis,trans*-**35** *cis,trans,cis*-**36**



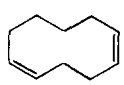
cis,trans,trans-**37**



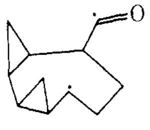
38



39



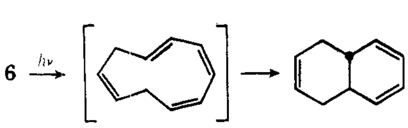
40



41

The stereochemistry of the cyclopropane rings of **16** is unfavorable for concerted decarbonylation, as we noted above for **15**, and the formation of such an assortment of products is indeed in line with a stepwise biradical mechanism. Here again the molecular geometry should favor initial formation of a trans double bond by way of rearrangement of the cyclopropylcarbinyl radical of **41** in its original conformation. The lower yields of trienes isolated from **16** and the only approximate analysis of this product mixture prevent a thorough test of the prediction in this case, but ~60% of the trienes found on decarbonylation of **16** do have a terminal trans double bond.

In contrast to the behavior of **15** and **16**, photolysis of the



42 43

unsaturated bis(cyclopropyl) ketone 6 followed by preparative VPC gave a single product in 80% yield. This was shown to be the tetrahydronaphthalene 43 from the following evidence. Reduction of this hydrocarbon with 3 equiv of hydrogen yields *trans*-decalin unaccompanied by the cis isomer. The positions of the three double bonds were apparent from spectroscopic evidence requiring a cyclohexadiene chromophore [λ_{max} = 259 nm (3540)],[31] olefinic and saturated hydrogens in the ratio 1:1 (^{1}H NMR), and molecular symmetry leading to a five-line ^{13}C NMR spectrum. Triene 43 is the product expected from secondary cyclization of a cyclodecatetraene produced on photochemical decarbonylation and isomerization of 6. The indicated stereochemistry of the unisolated intermediate tetraene 42 is that required for symmetry-allowed,[27] thermal, disrotatory closure to 43. Similar thermal cyclizations of related cyclodecapentaenes to *cis*- and *trans*-9,10-dihydronaphthalenes at temperatures below 0° C[32] and of a conjugated cyclodecatriene at 220° C[33] have been known for some time. The alternative possibility that 43 arises in a secondary conrotatory, photochemical cyclization of an appropriate geometric isomer of 42 seems unlikely. Even in the early stage of photolysis of 6, the only observed product is 43, implying that this is reached by a thermal rather than photochemical path.

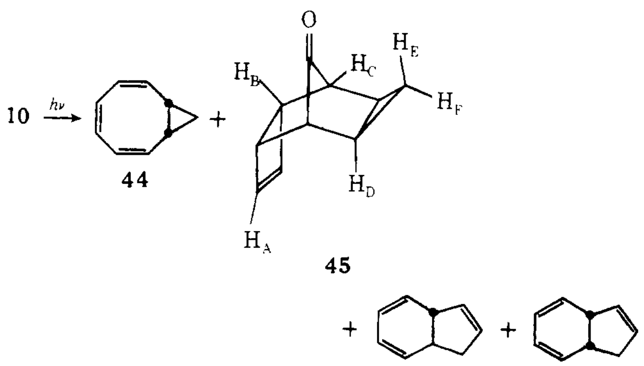
The inferred formation of a single cyclodecatetraene with the stereochemistry shown in 42 suggests that photolysis of 6 is probably mechanistically different from that of 16. Although the presence of a trans double bond in the appropriate position of 42 is in line with the behavior of 15 and 16, it is not obvious in models that stepwise opening of the cyclopropane rings of 6 should lead to a unique product rather than a mixture such as is formed from 16. It seems possible that decarbonylation of 6 is a conrotatory process related to the concerted loss of carbon monoxide believed to occur upon irradiation of simpler 3-cyclopenten-1-ones.[3] More information, including isolation of the primary photoproduct that is the precursor of 43, is needed to clarify this matter.

We turn attention now to the cyclopropyl dienone 10. Irradiation of this ketone followed by preparative VPC furnished *cis*-2,4,6-bicyclo[6.1.0]nonatriene (44, ~46%) and the tetracyclic ketone 45 (5%), along with the secondary products *trans*- and *cis*-dihydroindenes 46 (~3%) and 47 (~7%). The known hydrocarbons 44, 46, and 47 were identified by comparison of their spectroscopic properties with those previously reported.[34] The structure of 45 was assigned through comparison of its IR and NMR spectra with those of the tricyclic model compounds 48[2] and 49,[35] along with the knowledge that cyclization of the butadiene to a cyclobutene is a process common to the photochemistry of 4,[6] its dihydro derivative 13,[2] and other compounds similarly related to 10. In particular the IR carbonyl frequency at 1780 cm^{-1} in 45 compares favorably with 1770 for 48[2] and 1775 for 49,[35] and the value of 4 Hz for the coupling constant J_{BC} in 45 agrees with that of 48 (4.7 Hz) and a number of related compounds,[2] thus indicating that 45 has the same endo stereochemistry of the new cyclobutene ring as do these analogues. Detailed analysis of the 220-MHz NMR spectrum of 45 is given in the Experimental Section.

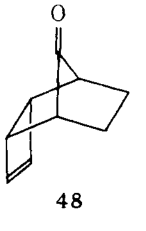
Previous investigations have shown that complex thermal and photochemical interconversions occur among 44, 46, 47, cyclononatetraenes, and other C_9H_{10} hydrocarbons.[34,36] This accounts for the presence of dihydroindenes 46 and 47 among the products from 10, but it also means that it is not yet certain whether photolysis of 10 furnishes initially cyclononatetraene(s) or alternatively leads directly to 44 through simple decarbonylation (or both). However, direct photolysis of dienone 13 rapidly yields 1,3,5-cyclooctatriene as the major product, and both this and related reactions have been regarded as concerted processes.[2] It is then plausible that 10 follow a similar path directly to 44.

Cyclopropyl diene 5 is formally an allylic isomer of 10, so that it was of some interest to compare the behavior of these two compounds and to determine whether they are interconverted by a photochemical 1,3-acyl shift.[5] Irradiation of 5 yielded a mixture of 44, 46, and 47 in essentially the same ratio as these are formed from 10; the amount of 45, however, was only ~1%, or only ~20% as great as from 10. Reaction of 10 is rapid and complete in ~45 min, and the resulting reaction mixture undergoes no detectable change over 7.25 h of additional illumination. Reaction of 5 is much slower and requires ~8 h under identical conditions. Neither starting ketone is detected during reaction of its allylic isomer. From these observations we can conclude firmly that 10 does not rearrange photochemically to the more slowly destroyed 5. However, on the reasonable assumption that isomerization of 5 to 45 does not occur directly, the formation of ~1% of 45 from 5 is evidence that ~20% of the reaction of 5 proceeds by way of prior 1,3-acyl shift to 10. With its much more rapid reaction and much higher extinction coefficient (Table I), the steady state concentration of 10 in photolysis of 5 could well be low enough to remain undetected. The other ~80% of 5 presumably undergoes direct decarbonylation to the same products as does 10.

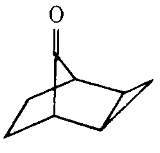
In contrast to the smooth photochemical reactions of the substrates discussed above, ketone 11 is remarkably stable to irradiation. Photolysis under the general conditions previously described, or through quartz, or in acetone as solvent, all for times of 17–19 h, led to virtually no observable reaction and recovery of starting material in high yield. We suggest that this apparent unreactivity is due to a degenerate, energy-wasting 1,3-acyl shift,[5] which merely interconverts the optical antipodes 11a and 11b. This explanation requires that the 1,3-acyl shift be rapid and not pass through a biradical intermediate free to undergo either cyclopropylcarbinyl–homoallyl rearrangement or decarbonylation. In this regard we note our earlier report that irradiation of the simpler β,γ-unsaturated β',γ'-cyclopropyl ketone 50 gives 91% of its isomer 51 through 1,3-acyl shift with no evidence of competing fragmentation of the three-membered ring.[37] We interpreted this behavior



44 45 46 47



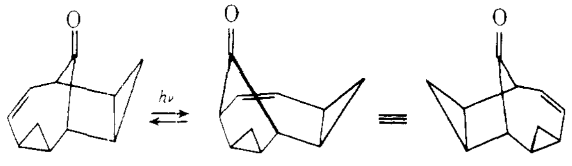
48



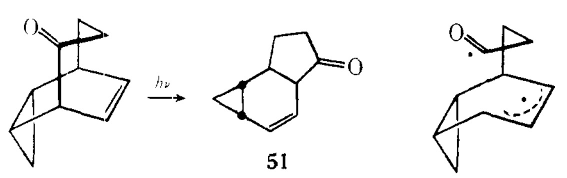
49

as evidence against involvement of biradical **52**, in which the three-membered ring should fragment readily. This behavior of **50** provides useful precedent for the suggested degenerate rearrangement of **11**.

The photochemical behavior of these six ketones under the conditions employed suggests the following relative rates for the processes observed: decarbonylation of the 3,5-cycloheptadien-1-one system (as **10**) > decarbonylation of the 3-cyclopenten-1-one system (as **5** and possibly **6**) ~ 1,3-acyl shift (as **5** and **11**) > α cleavage and stepwise decarbonylation (as **15** and **16**). This order is in general agreement with available quantitative information and estimates in various other systems,[5] although the lack of concomitant α-cleavage processes in **11** (and also **50**) is exceptional. This survey of the photochemistry of these tri- and tetracyclic ketones provides both insight into the mechanistic pathways followed on irradiation as well as novel entry into several cyclic unsaturated systems.



11a 11b



50 51 52

Experimental Section

Materials and Equipment. These have been previously described.[19] In this work the following VPC columns were used: A, 15–16 g of 20% Carbowax 20 M, 5 ft; B, 33 g of 20% DEGS, 11 ft; C, 25% QF-1, 15 ft; D, 27–28 g of 20% SE-30, 12 ft; E, 15–16 g of 20% SE-30, 7 ft; F, 29 g of 20% DEGS, 9.7 ft; G, 31 g of 20% EGA, 10 ft; H, 14 g of 25% QF-1, 5 ft; I, 14 g of 20% EGS, 5 ft; J, 38 g of 20% DEGS, 12.2 ft; and K, 28 g of 15% SILAR-10 C, 10 ft. Chromosorb P, mesh 60/80, was used as the solid support for columns A, B, F, G, I, J, and K; Chromosorb W, mesh 45/60, was used for columns C, D, E, and H. All columns were constructed of standard aluminum tubing having $^3/_{16}$-in. i.d. Ultraviolet spectra were obtained on a Cary Model 14PM spectrophotometer (95% aqueous EtOH solution). Infrared spectra were recorded on a Perkin-Elmer Model 621 or on a Perkin-Elmer Model 237B grating infrared spectrophotometer. ^{1}H-NMR spectra were obtained on a Varian Model T-60 (60 MHz) instrument; ^{13}C spectra were obtained on a Bruker HX-90 (22.63 MHz) instrument. Exceptions to the above are noted. Unless otherwise noted all pure compounds were obtained as colorless oils.

All photolyses were carried out in benzene (distilled, J. T. Baker) solution containing 3.0% (by volume) methanol through a double Pyrex filter (λ >2800 Å) using a 450-W Hanovia lamp. Details of the procedure are described elsewhere.[21] All yields reported are based on converted starting material. Exceptions of the above are noted.

Cyclopropanation of 4. A mixture of **4** (207 mg, 1.57 mmol) freshly purified by VPC on column A, diiodomethane (1.68 g, 4 equiv), zinc–copper couple (615 mg, 6 equiv), and a catalytic amount of iodine in dry ether (25 mL) was heated at reflux for 41 h.[19] Preparative VPC on column A (165 °C, 74 mL/min) gave *exo*-tricyclo[5.2.1.0^{2,4}]deca-5,8-dien-10-one (**5**) (31 min, 19 mg, 8%) and *exo,exo*-tetracyclo[6.2.1.0^{2,4}0^{5,7}]undec-9-en-11-one (**6**) (47 min, 95 mg, 38%). For **5**: UV λ_{max} (ϵ) 214 sh (3250), 198 (5580) nm; IR 3060 (w), 3020 (m), 3000 (m), 2925 (m), 1780 (m), 1755 (s), 1635 (m), 1145 (m), 1115 (m), 1030 (m), 1015 (m), 975 (w), 945 (w), 925 (w), 905 (w), 880 (w), 845 (m), 700 (m), 675 (m) cm^{-1}; NMR (60 MHz) δ 0.35 (m, 1 H), 0.60–1.60 (m, 3 H), 3.19 (m, 2 H), 5.33–6.47 (m, 4 H). NMR (60 MHz) of **5** (5.3 mg, 0.0363 mmol, 0.0806 M) in the presence of Eu(fod)$_2$ (24.6 mg, 0.0237 mmol, 0.0527 M) δ 2.43 (m, 1 H), 3.03 (m, 1 H), 3.48 (m, 1 H), 5.65 (m, 1 H), 7.67 (m, 2 H), 8.12 (m, 2 H), 8.63 (m, 1 H), 9.02 (m, 1 H).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.90; H, 6.99.

For **6**: mp 55–57 °C; UV λ_{max} (ϵ) 197 (2770); IR 3475 (w), 3060 (m), 3000 (s), 2910 (m), 1805 (w), 1755 (s), 1740 (s), 1665 (w), 1595 (w), 1455 (m), 1375 (w), 1360 (m), 1245 (s), 1195 (w), 1155 (m), 1125 (m), 1105 (m), 1035 (s), 1015 (m), 950 (m), 860 (m), 845 (s), 825 (s), 720 (s), 665 (s), 640 (w) cm^{-1}; NMR (60 MHz) δ 0.17 (m, 2 H), 0.52 (m, 2 H), 1.12 (m, 4 H), 2,92 (m, 2 H), 6.30 (s, 2 H). NMR (60 MHz) of **6** (13.5 mg, 0.0843 mmol, 0.172 M) in the presence of Eu(fod)$_3$ (68.2 mg, 0.0657 mmol, 0.134 M) δ 2.30 (m, 2 H), 3.42 (m, 4 H), 6.68 (m, 2 H), 8.33 (s, 2 H), 9.50 (m, 2 H).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.58. Found: C, 82.48; H, 7.63.

Bicyclo[4.2.1.]nona-2,4,7-trien-9-one Ethylene Acetal (7).[9] Trienone **4** (4.09 g, 30.9 mmol)[6] was ketalized with ethylene glycol (4.0 mL) and *p*-toluenesulfonic acid (72 mg) in refluxing benzene (100 mL), with continuous removal of water, for 2.5 h. Distillation of the crude product gave 4.15 g (76%) of a colorless liquid, bp 78–82 °C (0.4 mm). An excessive amount of catalyst and/or prolonged reaction period led to a mixture of **7** and **12**. A sample of **7** purified by VPC on column A had the following properties: IR 3050 (m), 3020 (s), 2975 (m), 2930 (s), 2875 (s), 1610 (w), 1595 (w), 1335 (s), 1270 (s), 1125 (s), 1100 (s), 1035 (s), 995 (m), 940 (m), 870 (m), 845 (s), 720 (m), 665 (s) cm^{-1}; NMR (60 MHz) δ 2.72 (m, 2 H), 3.83 (s, 4 H), 5.23 (m, 2 H), 5.72 (m, 4 H).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.01; H, 7.08.

Cyclopropanation of 7. A mixture of **7** (1.394 g, 7.911 mmol), diiodomethane (9.42 g, 4 equiv), zinc–copper couple (3.45 g, 6 equiv), and a catalytic amount of iodine in dry ether (55 mL) was heated at reflux for 23 h and worked up as previously described.[19] Preparative VPC on column C (145 °C, 71 mL/min) gave *exo*-tricyclo[4.3.1.0^{7,9}]-deca-2,4-dien-10-one ethylene acetal (**8**) (41 min, 534 mg, 35%), and *exo,exo*-tetracyclo[5.3.1.0^{2,4}.0^{8,10}]undec-5-en-11-one ethylene acetal (**9**) (59 min, 170 mg, 11%). For **8**: UV λ_{max} (ϵ) 287 (1560), 276 (3100), 266 (3330), 260 sh (2790), 198 (2850) nm; IR 3025 (m), 2980 (m), 2950 (m), 2920 (m), 2875 (m), 1595 (w), 1365 (m), 1305 (m), 1265 (m), 1125 (m), 1090 (m), 1030 (s), 1000 (m), 945 (m), 860 (m), 820 (m), 680 (s) cm^{-1}; NMR (60 MHz) δ −0.25 (dt, J = 5.5, 8 Hz, 1 H), 0.70 (dt, J = 5.5, 4 Hz, 1 H), 1.45 (dd, J = 8, 4 Hz, 2 H), 2.02 (m, 2 H), 3.78 (m, 4 H), 5.57 (m, 4 H). Irradiation at −0.25 simplified the absorptions at 0.70 and 1.45. Irradiation at 2.02 simplified the absorption at 1.45. Irradiation at 5.57 caused collapse of m at 2.02 into a sharp s.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.57; H, 7.53.

For **9**: UV λ_{max} (ϵ) 198 nm (7760); IR 3005 (s), 2980 (m), 2950 (m), 2905 (m), 2875 (m), 1645 (w), 1305 (m), 1260 (m), 1120 (s), 1105 (m), 1095 (m), 1045 (m), 1035 (s), 1025 (s), 1005 (m), 940 (m), 820 (m), 700 (m) cm^{-1}; NMR (60 MHz) δ 0.067–1.47 (m, 8 H), 2.20 (d, J = 8 Hz, 1 H), 2.35 (d, J = 3 Hz, 1 H), 3.67 (m, 4 H), 5.17–5.97 (m, 2 H).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.22; H, 7.89.

***exo*-Tricyclo[4.3.1.0^{7,9}]deca-2,4-dien-10-one (10).** Acetal **8** (171 mg, 0.899 mmol) was hydrolyzed by stirring it with an equivolume solution of 10% aqueous HCl–methanol at room temperature for 15 h. Preparative VPC on column D gave 109 mg (83%) of a white solid: mp 70–71 °C (sealed tube): UV λ_{max} (ϵ) 318 (550), 277 (3800), 266 (3970), 257 (2590), 196 (3370) nm; IR 3495 (w), 3065 (w), 3030 (m), 2985 (w), 2940 (w), 1825 (w), 1795 (w), 1755 (s), 1715 (w), 1595 (w), 1440 (w), 1235 (w), 1150 (m), 1040 (m), 1020 (w), 990 (w), 960 (w), 925 (w), 855 (m), 825 (m), 710 (m), 685 (m), 665 (w) cm^{-1}; NMR (60 MHz) δ −0.32 (dt, J = 6.5, 4 Hz, 1 H), 0.28 (dt, J = 6.5, 7.5 Hz, 1 H), 1.85 (dd, J = 7.5, 4 Hz, 2 H), 2.62 (m, 2 H), 5.63 (m, 4 H). Partial NMR (60 MHz) (20.4 mg, 0.140 mmol, 0.264 M) in the presence of Eu(fod)$_3$ (78.5 mg, 0.0757 mmol, 0.143 M) δ 2.02 (dt, J = 6.5, 7.5 Hz, 1 H), 3.76 (dt, J = 6.5, 4 Hz, 1 H), 4.32 (dd, J = 7.5, 4 Hz, 2 H).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 81.98; H, 6.99.

***exo,exo*-Tetracyclo[5.3.1.0^{2,4}.0^{8,10}]undec-5-en-11-one (11).** Acetal **9** (80 mg, 0.392 mmol) was deketalized with an equivolume solution of 10% aqueous HCl–methanol. Purification by VPC on column A gave 44 mg (70%) of a white solid: mp 31–34 °C (sealed tube); UV λ_{max} (ϵ) 293 (90), 232 sh (530), 198 (5660) nm; IR 3065 (w), 3020 (w), 3000 (w), 2920 (w), 1750 (s), 1640 (w), 1445 (w), 1255 (w), 1235 (w), 1160 (w), 1120 (w), 1040 (w), 1030 (m), 1020 (w), 965 (w), 890 (w), 855 (w), 710 (m) cm^{-1}; NMR (60 MHz) δ 0.13 (m, 2 H), 0.60–1.57 (m, 6 H), 2.60 (d, J = 8 Hz, 1 H), 2.77 (d, J = 4 Hz, 1 H), 5.37–6.10 (m, 2 H). NMR (60 MHz) (17.9 mg, 0.112 mmol, 0.220 M) in the presence of Eu(fod)$_3$ (74.0 mg, 0.0713 mmol, 0.140 M) δ 2.67 (m, 2 H), 3.32–4.42 (m, 5 H), 7.02 (m, 1 H), 8.27 (m, 2 H), 10.3 (d, J = 8 Hz, 1 H), 10.7 (d, J = 4 Hz, 1 H).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.52; H, 7.61.

Cyclopropanation of dienone **10** (22 mg, 0.150 mmol) with diiodomethane (4 equiv) and zinc–copper couple (8 equiv) for 21 h gave largely starting **10** and a small amount of **11**.

***exo*-Tricyclo[4.3.1.0^{7,9}]dec-2-en-10-one (14).** Partial hydrogenation of **8** with 5% Pd/C in methanol followed by preparative VPC on column A gave the ethylene acetal of **14** as a colorless liquid: IR 3005 (m), 2970 (m), 2940 (m), 2910 (s), 2820 (m), 1655 (w), 1640 (w), 1445 (m), 1420 (m), 1310 (m), 1210 (m), 1160 (m), 1120 (s), 1095 (m), 1035 (s), 1000 (m), 940 (m), 895 (m), 810 (m), 710 (w), 660 (m), 645 (m) cm^{-1}; NMR (60 MHz) δ 0.30 (m, 1 H), 0.60–1.37 (m, 3 H), 1.37–2.70 with major absorption of 2.08 (m, 6 H), 3.72 (m, 4 H), 5.33 (m, 1 H), 5.60 (m, 1 H). Irradiation at 0.93 simplified the absorptions at 0.30 and 2.08. Irradiation of 2.08 caused collapse of m at 5.33 into s and simplified the absorption at 5.60.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.84; H, 8.55.

Deketalization of the acetal with an equivolume solution of 10% aqueous HCl–methanol and subsequent purification by VPC on column A afforded **14**: IR 3060 (w), 3010 (w), 2980 (w), 2920 (m), 2830 (w), 1750 (s), 1650 (w), 1430 (m), 1170 (m), 1155 (m), 1040 (m), 985 (w), 850 (w), 695 (w), 645 (m) cm^{-1}; NMR (60 MHz) δ −0.10 (m, 1 H), 0.70 (m, 1 H), 1.10 (m, 2 H), 2.27 (m, 6 H), 5.50 (m, 2 H).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.03; H, 8.21.

Ketone **14** could also be prepared by partial hydrogenation of **10** under the same conditions.

***exo*-Tricyclo[4.3.1.0^{7,9}]decan-10-one (15).** Hydrogenation of **8** (118 mg, 0.620 mmol) with 5% Pd/C (51 mg) in methanol (10 mL) followed by preparative VPC on column A gave 90 mg (75%) of the ethylene acetal of **15** as a colorless liquid: IR 3005 (m), 2945 (s), 2915 (s), 2855 (s), 1450 (m), 1445 (m), 1375 (m), 1325 (m), 1270 (m), 1180 (m), 1165 (m), 1115 (s), 1080 (m), 1050 (m), 1025 (s), 990 (s), 940 (m), 880 (m), 830 (m), 805 (m), 670 (m) cm^{-1}; NMR (60 MHz) δ 0.37 (m, 1 H), 0.90 (m, 3 H), 1.10–2.13 with major absorptions at 1.63, 1.93 (m, 10 H), 3.73 (s, 4 H).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.42; H, 9.54.

This acetal (55 mg, 0.283 mmol) was deketalized with an equivolume solution of 10% aqueous HCl–methanol and purified by VPC on column A to give 32 mg (75%) of a colorless semisolid. In a different experiment, hydrogenation of **8** and deketalization of the crude product followed by VPC isolation gave **15** (70%, based on **8**): mp 36–38 °C (sealed tube); IR 3455 (w), 3060 (w), 3020 (w), 2980 (w), 2920 (s), 2855 (m), 1745 (s), 1455 (m), 1440 (m), 1290 (w), 1280 (w), 1195 (w), 1165 (m), 1055 (m), 1040 (w), 1025 (m), 1010 (w), 975 (w), 905 (w), 670 (w), 660 (m) cm^{-1}; NMR (60 MHz) δ −0.058 (m, 1 H), 0.58–1.00 (m, 1 H), 1.00–2.11 with major absorption at 1.61 (m, 10 H), 2.33 (m, 2 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.77; H, 9.24.

***exo,exo*-Tetracyclo[6.2.1.0^{2,4}.0^{5,7}]undecan-11-one (16).** Hydrogenation of **6** (43 mg, 0.27 mmol) with 5% Pd/C (50 mg) in methanol (5.0 mL) followed by preparative VPC gave 40 mg (92%) of a white solid: mp 61–63 °C (sealed tube); IR 3065 (w), 3000 (m), 2950 (m), 2870 (w), 1755 (m), 1740 (s), 1460 (w), 1445 (w), 1375 (w), 1360 (w), 1345 (w), 1300 (w), 1235 (w), 1200 (w), 1170 (w), 1130 (w), 1060 (w), 1035 (m), 1025 (m), 845 (w) cm^{-1}; NMR (60 MHz) δ −0.083 (m, 2 H), 0.20–1.60 (m, 6 H), 1.60–2.80 with major absorptions at 2.02, 2.45 (m, 6 H).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.36; H, 8.67.

***exo*-Tricyclo[4.3.1.0^{7,9}]deca-2,4-dien-*syn*-10-ol (17).** Dienone **10** (61.7 mg, 0.422 mmol) was reduced with $NaBH_4$ as described[6] for the reduction of **4**. Preparative VPC on column A (140 °C, 78 mL/min) yielded two fractions identified as starting **10** (86 min, 20.4 mg) and **17** (74 min, 31.1 mg, 74% based on unrecovered **10**). For **17**: mp 30–31 °C (sealed tube); IR 3560 (m), 3450 (w), 3060 (w), 3020 (s), 3000 (m), 2945 (m), 2910 (m), 1595 (w), 1455 (w), 1425 (m), 1405 (m), 1390 (w), 1310 (m), 1265 (m), 1245 (m), 1225 (m), 1110 (s), 1105 (s), 1090 (s), 1055 (m), 1015 (m), 965 (m), 880 (m), 870 (m), 830 (m), 690 (s) cm^{-1}; NMR (60 MHz) δ from −0.37 to 0.30 (m, 2 H), 1.50 (dd, J = 8, 4 Hz, 2 H), 1.87 (d, J = 12 Hz, 1 H), 2.75 (m, 2 H), 4.18 (dt, J = 12, 5 Hz, 1 H), 5.77 (m, 4 H). Partial NMR (60 MHz) (13.8 mg, 0.0931 mmol, 0.217 M) in the presence of Eu(fod)$_3$ (63.1 mg, 0.0608 mmol, 0.141 M) δ 1.48 (m, 1 H), 2.38 (m, 1 H), 4.32 (dd, J = 8, 4 Hz, 2 H), 9.6 (m, 2 H), 10.0 (m, 2 H), 10.4 (m, 2 H), 18.4 (br, 1 H), hydroxyl signal not recorded.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.09; H, 8.22.

Attempted Ketalization of 20. A mixture of **20**[6] (2.19 g, 15.0 mmol), ethylene glycol (4.0 mL), and *p*-toluenesulfonic acid (62 mg) in benzene (100 mL) was heated at reflux with continuous removal of water for 3 h. Workup and distillation gave 2.28 g (80%) of product, bp 88–92 °C (0.4 mm). The same product was also obtained under a variety of other conditions.[18] This substance had the following properties: IR 3060 (w), 3030 (m), 2955 (m), 2935 (m), 2890 (m), 2865 (m), 2850 (m), 1645 (w), 1610 (w), 1445 (m), 1390 (m), 1360 (m), 1265 (m), 1240 (m), 1100 (s), 1080 (s), 1030 (m), 995 (s), 965 (m), 950 (s), 915 (m), 900 (m), 700 (s) cm^{-1}; NMR (60 MHz) δ 1.45 (dd, J = 12, ~1 Hz, 1 H), 2.40–3.97 with s at 3.63 (m, 7 H), 4.97–6.23 (m, 6 H).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.60; H, 7.48.

Bicyclo[4.2.2]dec-9-en-7-one (23). Trienone **20**[6] (213 mg, 1.46 mmol) was reduced with 2.2 equiv of hydrogen over 5% Pd/C (25 mg, pre-equilibrated with hydrogen) in methanol (10 mL) at room temperature and atmospheric pressure (hydrogenation time ~0.5 h). Preparative VPC on column A (150 °C, 78 mL/min) afforded a white solid identified as **23** (40 min, 97 mg, 44%) and five additional unidentified fractions (97 mg, 44%) of greater retention times. The reaction was equally satisfactory on a 1.0-g scale. For **23**: mp 141–143 °C (sealed tube); IR 3030 (m), 2920 (s), 2860 (m), 1750 (w), 1710 (s), 1645 (w), 1455 (m), 1445 (m), 1440 (m), 1400 (m), 1355 (w), 1235 (m), 1185 (w), 1125 (m), 1100 (w), 1065 (w), 845 (w), 685 (w) cm^{-1}; NMR (60 MHz) δ 0.50–2.17 with major absorption at 1.65 (m, 8 H), 2.30 (m, 2 H), 2.80 (m, 2 H), 5.70 (dd, J = 10, 6 Hz, 1 H), 6.18 (dd, J = 10, 7 Hz, 1 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.63; H, 9.36.

Bicyclo[4.2.2]dec-9-en-7-one Ethylene Acetal. Ketalization of **23** (109 mg) with ethylene glycol and *p*-toluenesulfonic acid in refluxing benzene for 17 h as described above gave a viscous oil which was purified by VPC on column E to obtain 129 mg (91%) of a colorless liquid: IR 3025 (m), 2920 (s), 2850 (m), 1650 (vw), 1460 (w), 1435 (m), 1385 (w), 1370 (w), 1340 (w), 1305 (w), 1240 (w), 1134 (m), 1105 (s), 1095 (s), 1030 (m), 1015 (m), 985 (w), 955 (w), 940 (w), 915 (w), 845 (w) cm^{-1}; NMR (60 MHz) δ 0.99–2.96 with major absorption at 1.59 (m, 12 H), 3.86 (s, 4 H), 5.77 (m, 2 H).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.10; H, 9.32.

***exo*-Tricyclo[4.3.2.0^{7,9}]undecan-10-one (21).** A mixture of the above crude ketal (~600 mg), diiodomethane (2.42 g, 3 equiv), zinc–copper couple (1.18 g, 6 equiv), and a catalytic amount of iodine in ether (30 mL) was heated at reflux for 22 h.[19] After workup, the crude product was hydrolyzed by stirring overnight with an equivolume solution of 10% aqueous HCl–THF at room temperature, and the crude product was purified by preparative VPC on column E (160 °C, 78 mL/min) to obtain a white solid (17 min, 24 mg) identified as recovered ketone **23** (95% conversion for three steps), a second white solid (32 min, 309 mg, 66% based on consumed **23**) identified as **21**, and an unidentified colorless liquid (65 min, 92 mg). For **21**: mp 150–153 °C (sealed tube); IR 3065 (w), 3000 (m), 2925 (s), 2855 (m), 1700 (s), 1455 (m), 1440 (m), 1415 (w), 1380 (w), 1360 (w), 1340 (w), 1330 (w), 1325 (w), 1285 (w), 1235 (w), 1230 (w), 1185 (w), 1135 (w), 1085 (w), 1075 (w), 1015 (m), 1005 (w), 850 (w), 820 (w) cm^{-1}; NMR (60 MHz) δ 0.20–2.17 (m, 14 H), 2.37–2.98 (m, 2 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.59; H, 9.81.

Photolysis of *exo*-Tricyclo[4.3.1.0^{7,9}]decan-10-one (15). Ketone **15** (84 mg, 0.56 mmol, 0.021 M, 27.0 mL solution) was irradiated in the usual manner.[21] Samples were withdrawn at appropriate intervals and analyzed by VPC on column C (initial column temperature and flow rate 90 °C, 78 mL/min, respectively, raised to 160 °C and 113 mL/min after 58 min) using *p*-xylene (36 min) and *o*-methylacetophenone (97 min) as internal area standards. Conversion after 44 h was 81%, with products **26** and **27** formed in the ratio 69:31 and a total yield of 84%. Data on yields and conversion at other times have been reported.[22] The major product (47 min) was identified as *cis,trans*-1,4-cyclononadiene (**26**): IR 3010 (s), 1665 (w), 1625 (w), 975 (s), 700 (s) cm^{-1}; IR (CS_2) 785 (m), 735 (m) cm^{-1}; NMR δ 0.67–3.27 with major absorptions at 1.08, 1.37, 1.78, 1.92, 2.27, and 2.77 (m, 10 H), 5.52 (m, 4 H).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.42; H, 11.50.

The minor product was identified as *cis,cis*-1,4-cyclononadiene (**27**) by comparison of IR and NMR spectra with those of the authentic diene.[23]

Photolysis of *cis,trans*-Cyclononadiene (25). *cis,trans*-Cyclononadiene **26** (3.5 mg, 0.029 mmol, 0.0048 M) was irradiated for 25.0 h in benzene–3% methanol (6.0 mL). VPC analysis on column C with *p*-xylene as internal area standard indicated starting **26** (86%) and **27** (9.2%).

Photolysis of *exo,exo*-Tetracyclo[6.2.1.0^{2,4}.0^{5,7}]undecan-11-one (16). Ketone **16** (110 mg, 0.678 mmol, 13.6 mM, 50.0 mL solution) was irradiated for 66 h. Preparative VPC on column F (initial column temperature 88 °C, raised to 160 °C after 53 min, 71 mL/min) afforded starting **16** (91 min, 3.8 mg, 96% conversion), four unidentified fractions totaling 6.0 mg, a colorless liquid identified as a mixture of **35, 36,** and possibly **37** (39 min, 40.5 mg, 46%), and a second colorless liquid identified as **34** (48 min, 1.8 mg, 2.1%). For **35–37:** UV λ_{max} (ϵ) 198 (11 990); IR 3005 (s), 2975 (m), 2930 (s), 2890 (m), 2860 (m), 2835 (m), 1665 (w), 1635 (w), 1450 (m), 1440 (m), 1430 (m), 1200 (w), 1175 (w), 1070 (w), 1010 (w), 965 (w), 915 (m), 905 (m), 890 (w), 700 (s) cm^{-1}; NMR (60 MHz) δ 2.02 (m, 4 H), 2.75 (m, 4 H), 5.42 (m, 6 H).

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.28; H, 10.43.

For **34:** IR 3005 (s), 2955 (m), 2925 (m), 2895 (m), 2860 (m), 1655 (w), 1640 (w), 1465 (m), 1450 (m), 1430 (m), 940 (m), 915 (m), 885 (m), 710 (s), 695 (m) cm^{-1}; NMR (60 MHz) δ 2.17 (m, 4 H), 2.78 (m, 4 H), 5.32 (m, 6 H).

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.56; H, 10.17.

Irradiation of Mixture 35–37: Mixture **35–37** (11.4 mg, 0.0849 mmol, 4.24 mM, 20.0 mL solution) was irradiated for 47.0 h under the above conditions. Analytical VPC on column F indicated less than ~2% isomerization to **34.** The NMR and infrared spectra of the major fraction were identical with those of the starting mixture.

Partial Hydrogenation of Mixture 35–37. The mixture (69.1 mg, 0.515 mmol) was hydrogenated with ~1 equiv of hydrogen over 5% Pd/C (17 mg) in cyclohexane (10 mL) at room temperature and atmospheric pressure. Careful distillation of the solvent at atmospheric pressure, followed by preparative VPC on column J (88 °C, 71 mL/min), afforded starting **35–37** (57 min, 1.6 mg, 98% conversion), *cis*-cyclodecene (29 min, ~2 mg, ~3%, identified from NMR spectrum and by comparison of IR spectrum with the published curve[38]), a partially resolved mixture of *cis,cis*-1,5-cyclodecadiene (**40,** 36 min) and *cis,trans*-1,5-cyclodecadiene (**39,** 38 min) [total of 24.3 mg, 35%, ~3.5:1 (**40–39**)], and *cis,cis*-1,4-cyclodecadiene (**38,** 47 min, 22.4 mg, 33%). To obtain analytically pure samples of the 1,5-dienes, their mixture was further separated on column K (88 °C, 72 mL/min) to give *cis,cis*-1,5-cyclodecadiene (**40,** 35 min) as a white solid and *cis,-trans*-1,5-cyclodecadiene (**39,** 40 min) as a colorless liquid. For **40:**[30] mp 28–29 °C (sealed tube, previously reported[30] as a liquid); IR 2990 (s), 2950 (s), 2910 (s), 2875 (s), 2845 (s), 1650 (vw), 1450 (s), 1340 (w), 1320 (w), 1255 (w), 1155 (w), 1020 (w), 1000 (w), 845 (w), 700 (s) cm^{-1}. The NMR spectrum of this material compared favorably with those reported.[30] For **39:**[30] IR 3025 (w), 2995 (m), 2975 (m), 2920 (s), 2845 (m), 1660 (w), 1440 (m), 1435 (m), 960 (m), 900 (w), 685 (m) cm^{-1}; NMR (60 MHz) δ 1.50 and 2.07 (m, 12 H), 5.13 (m, 4 H). For **38:**[25] IR 3000 (s), 2970 (m), 2915 (s), 2845 (s), 1655 (w), 1470 (m), 1440 (m), 1390 (w), 1350 (w), 1320 (w), 1250 (w), 1040 (w), 970 (w), 925 (m), 865 (m), 700 (s) cm^{-1}; NMR (60 MHz) δ 1.43 (m, 6 H), 2.30 (m, 4 H), 2.77 (dd, J = 8, 8 Hz, 2 H), 5.35 (m, 4 H).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.11; H, 11.67.

Photolysis of *exo,exo*-Tetracyclo[6.2.1.0^{2,4}.0^{5,7}]undec-9-en-11-one (6). Ketone **6** (69.7 mg, 0.435 mmol, 0.0174 M, 25.0 mL solution) was irradiated for 8.7 h. Preparative VPC on column F (initial column temperature 87 °C, raised to 160 °C after 42 min, 78 mL/min) gave 1,4,4aα,8aβ-tetrahydronaphthalene (**43**) (34 min, 38.1 mg, 80%) and starting **6** (78 min, 12.2 mg, 82% conversion). For **43:** UV λ_{max} (ϵ) 259 (3540), 198 (5920) nm; IR 3050 (w), 3025 (s), 2990 (w), 2960 (w), 2900 (s), 2880 (s), 2830 (s), 2810 (m), 1650 (w), 1430 (m), 1175 (w), 1140 (w), 1090 (w), 980 (m), 865 (w), 685 (s) cm^{-1}; NMR (60 MHz) δ 2.12 (m, 6 H), 5.65 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ_{Me_4Si} 32.0, 36.0, 124.2, 126.7, 132.0.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.73; H, 9.12.

Hydrogenation of **43** (10 mg, 0.076 mmol) over 5% Pd/C (~5 mg) in methanol (1 mL) at room temperature and ~1 atm, followed by preparative VPC, gave a colorless liquid (7 mg, 70%) that had identical physical and spectroscopic properties with those of an authentic sample of *trans*-decalin and different from those of an authentic sample of *cis*-decalin.

Photolysis of *exo*-Tricyclo[5.2.1.0^{2,4}]deca-5,8-dien-10-one (5). Ketone **5** (49.9 mg, 0.341 mmol, 11.4 mM, 30.0 mL solution) was irradiated for 8.0 h. Preparative VPC on column J (injector temperature, ~35 °C; column temperature, 55 °C; detector temperature, 50 °C; flow rate 182 mL/min; filament current, 175 mA) afforded *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**44,** 140 min): IR 3065 (w), 2995 (s), 1635 (s), 1610 (w), 1445 (w), 1225 (w), 1120 (m), 1020 (m), 995 (w), 940 (w), 835 (m), 680 (s) cm^{-1}; the 60-MHz NMR spectrum of this material was identical with the curve published for authentic **44.**[34] Preparative VPC of the photolysate soltuion on column F (initial column temperature 75 °C, raised to 150 °C after 57 min, 78 mL/min) afforded **5** (89 min, 1.6 mg, 97% conversion), **46** (21 min, ~3%), **47** (35 min, ~7%), **44** (52 min, ~46%, contaminated with variable amounts of **47** presumably formed in detector), and **45** (78 min, ~1%). In another experiment the time course of the reaction was followed; **45** increased steadily over 7 h, and **10** was never observed. The *trans*-dihydroindene **46** was identified from its NMR spectrum:[34] (220 MHz) δ 1.99–2.09 (m, 1 H), 2.17–2.34 (m, 2 H), 2.82 (br d, J = 19 Hz, 1 H), 5.77–5.96 and 6.21–6.49 (2 m, 6 H). This sample was contaminated with an unidentified impurity. The cis isomer **47** was identified through identity of its 60-MHz NMR spectrum with the curve published[34] and from its IR spectrum: 3050 (s), 3030 (s), 2905 (s), 2845 (s), 1585 (w), 1445 (w), 1365 (w), 1330 (w), 940 (m), 700 (s) cm^{-1}. **45** was identified from the following data: IR 3105 (w), 3065 (w), 3035 (m), 2990 (m), 2940 (m), 1780 (s), 1755 (m), 1735 (m), 1445 (w), 1295 (m), 1250 (w), 1210 (w), 1155 (w), 1115 (m), 1070 (w), 1035 (m), 960 (m), 900 (w) cm^{-1}; NMR (220 MHz) δ 0.331 (dt, J = 6.8, 3.5 Hz, 1 H, H_E), 0.459 (dt J = 6.8, 6.8 Hz, 1 H, H_F), 1.04 (dd, J = 6.8, 3.5 Hz, 2 H, H_D), 2.28 (d, J = 4 Hz, 2 H, H_C), 2.98 (d, J = 4 Hz, 2 H, H_B), 6.26 (s, 2 H, H_A).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.01; H, 7.06.

Photolysis of *exo*-Tricyclo[4.3.1.0^{7,9}]deca-2,4-dien-10-one (10). Ketone **10** (59.7 mg, 0.408 mmol, 20.4 mM, 20.0 mL solution) was irradiated for 45.0 min as described for **5** above. Preparative VPC on columns J and F was carried out as for **5** with essentially identical results, except that **45** was isolated in 5.4% yield. The time course of the photolysis of **10** was followed over 8.0 h. Isomeric ketone **5** was not observed; the concentration of **45** increased over the first 45 min of reaction and then remained unchanged throughout the remainder of the irradiation.

Irradiation of *exo,exo*-Tetracyclo[5.3.1.0^{2,4}.0^{8,10}]undec-5-en-11-one (11). Irradiation of **11** (9.2 mg. 0.057 mmol, 10 mL solution) under the standard conditions through Pyrex for 18.1 h, or through quartz for 17.4 h, followed by VPC analysis, gave only recovered starting material. Irradiation of a similar acetone solution through Pyrex for 19.1 h followed by VPC analysis indicated the formation of only very small amounts of at least three compounds that were not identified.

Acknowledgments. We thank Mr. William Rosenstein for technical assistance, Mr. S. T. Bella for microanalyses, Mr. William Wittbold for 220-MHz NMR spectra, and the National Science Foundation (Grants CHE74-21436 and CHE78-01575) as well as the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The 220-MHz NMR spectra were obtained on an instrument at The Rockefeller University and operated by a consortium supported in part by NSF Grant PCM77-07671.

Registry No.—**4,** 34733-74-9; **7,** 53555-54-7; **8,** 68285-76-7; **9,** 69140-34-7; **12,** 172-13-4; **14,** 69140-35-8; **14** ethylene acetal, 69140-36-9; **15,** 68285-75-6; **15** ethylene acetal, 69177-21-5; **16,** 69140-37-0; **17,** 69140-38-1; **20,** 36628-97-4; **21,** 69140-39-2; **22,** 69140-40-5; **23,** 69140-41-6; **23** ethylene acetal, 69140-42-7: **26,** 33530-61-9; **27,** 6731-21-1; **34,** 69140-43-8; **35,** 69140-44-9; **36,** 69140-45-0; **37,** 69140-46-1; **38,** 58266-32-3; **39,** 1124-78-3; **40,** 31821-17-7; **43,** 69140-47-2; **44,** 26132-66-1; **45,** 69140-48-3; **46,** 3074-50-8; **47,** 24778-81-2; diiodomethane, 75-11-6; *cis*-cyclodecene, 935-31-9.

References and Notes

(1) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31,** 1393 (1966); for more recent work on photodecarbonylation, see D. S. Weiss, *Mol. Photochem.*, **8,** 477 (1977), and references cited therein.

(2) D. I. Schuster and C. W. Kim, *J. Am. Chem. Soc.*, **96,** 7437 (1974), and references cited therein.

(3) T. R. Darling, J. Pouliquen, and N. J. Turro, *J. Am. Chem. Soc.*, **96,** 1247 (1974), and references cited therein.

(4) R. S. Cooke and G. D. Lyon, *J. Am. Chem. Soc.*, **93,** 3840 (1971), and references cited therein.

(5) For recent reviews and extensive references to the photochemistry of β,γ-unsaturated ketones in general, see K. Schaffner, *Tetrahedron*, **32,** 641 (1976); K. N. Houk, *Chem. Rev.*, **76,** 1 (1976); W. G. Dauben, G. Lodder, and J. Ipaktschi, *Top. Curr. Chem.*, **54,** 73 (1975).

(6) (a) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Am. Chem. Soc.*, **94,** 5366 (1972); we have been asked to point out that in ref 22 of this paper the designations H_a and H_b are interchanged relative to the definitions previously given in the text. (b) J. B. Press

and H. Shechter, *J. Org. Chem.*, **40**, 2446 (1975); A. Diaz, J. Fulcher, R. Cetina, M. Rubio, and R. Reynoso, *ibid.*, **40**, 2459 (1975).
(7) H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, *Org. React.*, **20**, 1 (1973).
(8) D. C. Sanders and H. Shechter, *J. Am. Chem. Soc.*, **95**, 6858 (1973).
(9) D. I. Schuster and C. W. Kim, *J. Org. Chem.*, **40**, 505 (1975).
(10) For previous examples of such directive effects in the cyclopropanation of olefinic ketals, see A. de Meijere, C. Weitemeyer, and O. Schallner, *Chem. Ber.*, **110**, 1504 (1977), and I. M. Takakis and W. C. Agosta, *J. Org. Chem.*, **43**, 1952 (1978). The latter paper also describes two cases in which these effects are not observed.
(11) Eu(fod)$_3$ is tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octandionato)europium.
(12) A similar effect is seen in derivatives of simpler but structurally related ring systems: S. C. Clarke, K. J. Frayne, and B. L. Johnson, *Tetrahedron*, **25**, 1265 (1969). A more general discussion with references is given by L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Oxford, 1969, pp 286 and 287.
(13) For earlier examples of this effect in geometrically related systems see M. A. Battiste and M. E. Brennan, *Tetrahedron Lett.*, 5857 (1966).
(14) B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Am. Chem. Soc.*, **89**, 5964 (1967); R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970); S. C. Clarke and B. L. Johnson, *Tetrahedron*, **27**, 3555 (1971).
(15) W. L. Mock, *J. Am. Chem. Soc.*, **92**, 6918 (1970).
(16) M. Roberts, H. Hamberger, and S.Winstein, *J. Am. Chem. Soc.*, **92**, 6346 (1970).
(17) H. Tsuruta, K. Kurabayashi, and T. Mukai, *Tetrahedron Lett.*, 3775 (1967); W. Grimme, *Chem. Ber.*, **100**, 113 (1967).
(18) Conditions tried included ethylene glycol with: (1) pyridinium chloride as catalyst, R. Rausser, A. M. Lyncheski, H. Harris, R. Grocela, N. Murrill, E. Bellamy, D. Ferchinger, W. Gebert, H. L. Herzog, E. B. Hershberg, and E. P. Oliveto, *J. Org. Chem.*, **31**, 26 (1966); (2) *p*-toluenesulfonic acid, selenium dioxide, and methyl orthoformate in chloroform, E. P. Oliveto, H. Q. Smith, C. Gerold, L. Weber, R. Rausser, and E. B. Hershberg, *J. Am. Chem. Soc.*, **77**, 2224 (1955); (3) *p*-toluenesulfonic acid and methyl orthoformate, A. de Meijere, C. Weitemeyer, and O. Schallner, *Chem. Ber.*, **110**, 1504 (1977).
(19) I. M. Takakis and W. C. Agosta, *J. Org. Chem.*, **43**, 1952 (1978).
(20) The photochemistry of **21** and **25** is discussed by I. M. Takakis and W. C. Agosta, *J. Am. Chem. Soc.*, in press.
(21) Conditions used were those given in detail by W. C. Agosta and S. Wolff, *J. Am. Chem. Soc.*, **98**, 4182 (1976). Methanol was added to trap any ketenes that might be formed.
(22) A preliminary report on the photochemistry of **15** has appeared: I. M. Takakis and W. C. Agosta, *Tetrahedron Lett.*, 2387 (1978).
(23) This was prepared by thermolysis of *cis,cis*-bicyclo[6.1.0]non-2-ene as described by D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966), and R. W. Thies, P.-K. Hong, R. Bushwell, and J. L. Boop, *J. Org. Chem.*, **40**, 585 (1975).
(24) D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *J. Am. Chem. Soc.*, **85**, 1553 (1963).
(25) R. Vaidyanathaswamy and D. Devaprabhakara, *Ind. J. Chem.*, **13**, 873 (1975).
(26) R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79**, 4133 (1957).
(27) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(28) S. J. Cristol and R. U. Barbour, *J. Am. Chem. Soc.*, **90**, 2832 (1968); J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 1877, 1879 (1969); E. C. Friedrich, *J. Org. Chem.*, **34**, 528 (1969); W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *ibid.*, **34**, 2512 (1969); A. L. J. Beckwith and G. Phillipou, *Chem. Commun.*, 658 (1971); B. Maillard, D. Forrest, and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 7024 (1976).
(29) Biradicals **29** and **31** are shown as discrete intermediates for clarity only; decarbonylation concerted with fragmentation of the initial biradical (i.e., **28** → **26**, and **30** → **27**) need not be excluded. (See in this regard ref 4.)
(30) For **38:** see ref 25. For **39:** J. G. Traynham, G. R. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967). For **40:** J. G. Traynham and H. H. Hsieh, *Tetrahedron Lett.*, 3905 (1969), and H. Gotthardt and G. S. Hammond, *Chem. Ber.*, **109**, 3767 (1976).
(31) The similarly situated chromophore of *trans*-1,1-dimethyl-8,9-dihydroindene is reported to absorb at 259.5 nm (3300): S. W. Staley and T. J. Henry, *J. Am. Chem. Soc.*, **91**, 1239 (1969).
(32) E. E. van Tamelen and T. L. Burkoth, *J. Am. Chem. Soc.*, **89**, 151 (1967); S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969).
(33) P. Radlick and W. Fenical, *Tetrahedron Lett.*, 4901 (1967).
(34) For **44:** T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964). For **46:** J. Schwartz, *Chem. Commun.*, 833 (1969), and ref 31 for alkylated derivatives. For **47:** P. Radlick and G. Alford, *J. Am. Chem. Soc.*, **91**, 6529 (1969).
(35) R. E. Pincock and J. Haywood-Farmer, *Tetrahedron Lett.*, 4759 (1967).
(36) E. Vogel, *Angew Chem.*, **73**, 548 (1961); S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969), and references cited therein.
(37) I. M. Takakis and W. C. Agosta, *Tetrahedron Lett.*, 531 (1978).
(38) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *J. Am. Chem. Soc.*, **74**, 3636 (1952).

4′-Substituted Nucleosides. 4. Synthesis of Some 4′-Hydroxymethyl Nucleosides[1]

Raymond D. Youssefyeh,[2] Julien P. H. Verheyden,* and John G. Moffatt

Contribution No. 140 from the Institute of Molecular Biology, Syntex Research, Palo Alto, California 94304

Received August 3, 1978

Two complementary routes have been developed for the synthesis of 4-(acetoxymethyl)-1,2,3,5-tetra-*O*-acetyl-D-*erythro*-pentofuranose (**9**). The first of these involves a mixed aldol condensation between 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdofuranose and formaldehyde which gives, as its major product, 4-(hydroxymethyl)-1,2-*O*-isopropylidene-β-L-*threo*-pentofuranose (**5a**). Inversion of configuration at C_3 is achieved via an oxidation–reduction sequence, and subsequent acetolysis furnishes **9**. A more efficient route to **9** involves a mixed aldol condensation between 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*ribo*-pentodialdofuranose (**12a**) and formaldehyde followed by debenzylation, acetylation, and acetolysis. The condensation of **9** with a number of purine and pyrimidine bases and their analogues led to the preparation of a variety of 4′-hydroxymethyl nucleosides that have been screened for potential biological activities.

Recent work from this Laboratory has led to the development of methods for the synthesis of ribonucleosides substituted at the 4′ position by fluoro,[1,3] methoxyl,[4,5] and azido[5] groups. Most of these aspects have been reviewed.[6] Nucleosides such as those above bearing electronegative substituents at $C_{4'}$ are frequently rather labile, particularly when the hydroxyl functions are all unsubstituted.[1,3-6] Hence, it was of interest to undertake the synthesis of nucleosides bearing stable carbon–carbon linked substituents at the $C_{4'}$ position. Such syntheses could, in principle, be carried out via addition reactions to the vinyl ether function of 4′,5′-unsaturated nucleosides, this method being the one used successfully for the preparation of the 4′-fluoro, -methoxy, and -azido compounds. Preliminary attempts to introduce, e.g., a 4′-cyano function by this route were not, however, overly promising.

An alternate approach for the introduction of 4′ substituents is based upon the reactions of nucleoside 5′-aldehydes, a subject that has been of interest to us for some years.[7] This approach has been carried on in parallel with that reported in the present paper and is described separately.[8c] This latter work did, indeed, lead to the preparation of several 4′-hydroxymethyl nucleosides via crossed aldol condensations between suitably protected nucleoside 5′-aldehydes and formaldehyde.[8b,c] As an alternative to this introduction of a $C_{4'}$

0022-3263/79/1944-1301$01.00/0