STEROID PHOTOCHEMISTRY

THE PHOTOCYCLOADDITION OF A 3-KETO-4,6-DIENE TO NON-DIELS-ALDER 1,3-DIENES

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Abstract—The addition of linear steroidal dienones to dienes incapable of undergoing Diels-Alder reactions has been studied. Photocycloaddition of the steroid to the dienes yielded three [2 + 2]-adducts: a head-to-tail-*trans*-4 α ,5 β -adduct and two epimeric head-to-tail-*cis*-4 α ,5 α -adducts, thus maintaining the regiospecific addition found in dienone olefin cycloadditions, but losing the stereospecificity.

Recently, we and others have described the regio- and stereospecific photocycloaddition of linear dienones to various cyclic and acyclic olefins, e.g. $1 \rightarrow 2$.¹ The exclusive formation of only the *trans*-isomer from the dienones may be contrasted to that of steroidal 3-keto-4-ene enones which yield a mixture of *cis*- and *trans*-isomers.²

Attempted quenching of the cycloaddition reactions of the dienone lead to the discovery of the cycloaddition of the excited dienone to dienes. The photocycloaddition of dienone 3 to butadiene yielded the trans-Diels-Alder adduct 4 as the major product, together with significant amounts of the ladder compound 5.³ There are few reports in the literature concerning the addition of excited enones to dienes. Cantrell has noted that the photocycloaddition of cyclohexenone and cyclopentenone to a variety of dienes gave almost exclusively [2+2]-addition, although the dienes studied were all capable of undergoing Diels-Alder [4+2]-cycloadditions.⁴ Additionally, the reaction did not appear to be regiospecific since it formed a large number of adducts whose structures were not determined. Cantrell, in the recent full report, has demonstrated that reduction of the isomeric mixture of cyclohexenone-cyclopentadiene adducts lead to the isolation of a trans-fused adduct, which was identical to the trans-adduct formed from cyclohexenone and cyclopentene. However, it was not possible to determine whether the trans-adduct arose from the head-to-tail or the headto-head adduct or a mixture of both.^{4b} Chapman has shown the addition of excited 4,4-dimethylcyclohexenone to isoprene and 2,3-dimethylbutadiene gave regio- and stereospecific cis-[2+2]-adducts. Addition of the enone to 2,5 - dimethyl - 2,4 - hexadiene also gave a [2+2]-adduct.⁵ Since it had already been demonstrated that dienes capable of undergoing the Diels-Alder reaction gave [4+2]-adducts with dienones,^{3,6} we were interested in the photocycloaddition of steroidal dienones to dienes which, because of steric hindrance to the necessary *s*-cis-conformation, were incapable of undergoing the Diels-Alder reaction, and, particularly whether *trans* -[2+2] - adducts would be formed.

The first system investigated was the photocycloaddition of dienone 1 to the symmetrical diene, 2,5 - dimethyl-2,4 - hexadiene. This diene is not known to undergo Diels-Alder reactions without prior rearrangement.⁷ Irradiation of 1 in the presence of this diene gave a smooth and rapid conversion to four adducts. These adducts were separable by column chromatography and will be discussed in order of their elution.

The first compound eluted 6 was identified as a cis-fused $[2+2] - 4\alpha, 5\alpha$ - adduct. The physical properties of 6 showed an unconjugated CO at 1690 cm⁻¹ which had previously been shown to be characteristic of cis-fused cyclobutanes.¹ In support of this observation compound 6 was stable to sodium methoxide in methanol. The NMR spectrum showed two vinyl Me groups and three olefinic





protons. Additionally, the spectrum in hexadeuteriobenzene showed the C - 4β - proton as a singlet indicating a head-to-tail adduct rather than a head-to-head adduct.⁸ The cyclobutane tertiary allylic proton resonated in CDCl₃ at 3.178 (J = 11 Hz). This proton was consistently the farthest downfield of all the aliphatic protons, even farther downfield than the 4β -hydrogen in the $4\alpha,5\beta$ trans - fused compound 8.¹

Closely following 6 was another $cis - 4\alpha, 5\alpha - [2+2]$ adduct 7. The NMR again showed three vinyl protons and two olefinic Me groups. The spectrum run in hexadeuteriobenzene possessed a singlet resonance for the C- 4β -hydrogen at 2-48 δ , indicating that 6 and 7 are epimeric at the vinylic cyclobutane carbon.[†] The stereochemistry of the vinyl substituents on the cyclobutane ring was assigned on the basis of the ratio of 6 to 7 (1:10). Molecular models indicate severe steric interaction of the substituted vinyl group with the steroidal axial hydrogens at C-1 and C-9 in 6, and the absence of any appreciable steric interactions in 7 where the vinyl group

[†]The convention to denote epimeric stereochemistry in these adducts is to use a dotted line when the alkyl substituent projects under the steroid AB-rings (*endo*) and a heavy solid line when the alkyl substituent projects away from the steroid AB-rings (*exo*).



projects away from the steroid. These assignments although plausible mechanistically have to be regarded as tentative in the absence of any more compelling evidence.

Continued elution gave a mixture from which the *trans*-fused compound could be isolated by crystallization. The IR showed the characteristically high absorption at 1725 cm⁻¹ for the cyclohexanone CO group in these compounds.¹⁹ The mother liquor from 8 was shown by NMR to consist of a 1:2 mixture of 8 and its $4\beta,5\beta$ -epimer 9. Sodium methoxide in methanol smoothly converted this mixture into 9 in virtually quantitative yield. The ORD showed the usual change from a strongly positive Cotton effect for 8 to a negative Cotton effect for 9 upon epimerization.¹²

A Cope reaction on 7 was attempted with the idea that the *trans*, *trans*-cyclooctadiene 10 might close to give a ladder compound due to the extreme proximity of the two double bonds and the rigidity of the system.¹⁰ However, refluxing a sample of 7 in a variety of solvents gave no reaction, until approx. 250° where a slow cycloreversion to the starting dienone 1 occurred.

The other non - Diels-Alder - 1,3 - diene studied was 4 - methyl - 1,3 - pentadiene.⁷ The photocycloaddition of 6-dehydrotestosterone acetate 3 to this diene proceeded rapidly to yield four adducts. The adducts were isolated





by column chromatography. The first adduct eluted was the cis - $4\alpha.5\alpha$ - 11 as indicated by an unconjugated CO group and a positive Cotton effect in ORD. The NMR spectrum demonstrated that a [2+2]-cycloaddition across the unsubstituted diene double bond had occurred since there were three olefinic protons and two vinyl Me groups. The spectrum in hexadeuteriobenzene moved the C - 4β - proton out of the methylene manifold to 2.558 where it appeared a broadened doublet $(J \cong 8 \text{ Hz})$. Inspection of a model showed that the protons in the methylene group adjacent to C-4 form dihedral angles of 30° and 90°, which indicates that the C-4 proton should couple strongly with one proton and weakly, or not at all, with the other. Thus demonstrating that 11 was a head-to-tail adduct.¹¹ Again the tertiary allylic cyclobutane proton resonated as a broad multiplet centered at 3·33δ.

The next compound eluted was the major $cis - 4\alpha, 5\alpha$ epimer 12. Compound 12 showed a positive Cotton effect and an unconjugated CO in the IR as well as three olefinic protons and two vinyl Me groups in the NMR. The NMR spectrum of 12 in hexadeuteriobenzene demonstrated that 12 was a head-to-tail adduct epimeric with 11. The C - 4 β proton appeared as a broadened doublet at 2.38 δ $(J \cong 6.5$ Hz). Both 11 and 12 were stable to methanolic sodium methoxide and could be regenerated after reacetylation.

The $4\alpha,5\beta$ - trans - adduct 13 was eluted next. Compound 13 showed the typical CO absorption at 1720 cm⁻¹ for trans-fused compounds.¹⁹ The NMR spectrum showed two vinyl Me groups and three olefinic protons. The C-4 β proton in 13 appeared as a triplet (J = 8 Hz) in hexadeuteriobenzene at 2.50 δ . Molecular models indicate a dihedral angle of 180° and 25° between the C - 4 β - proton and the adjacent methylene protons; indicating maximum coupling.¹¹ Compound 13 was relatively unstable and epimerized readily to the 4 β ,5 β -epimer 14. Repeated attempts at obtaining the ORD/CD spectrum of 13 resulted in obtaining only the spectrum of 14. The isolation of a large amount of 14 was indicative of the instability of 13. Compound 14 was a glass and could



not be induced to crystallize, although it analyzed correctly and possessed the appropriate spectral properties. Additionally, 14 could be prepared from 13 with sodium methoxide in methanol; followed by reacetylation.

Compound 12 was irradiated in an attempt to close the two proximate double bonds in another attempt to form ladder compounds. Irradiation under a variety of sensitized and unsensitized conditions resulted either in recovery of 12 or complete degradation of the starting material.

It was previously demonstrated that the photocycloaddition of excited steroidal linear dienones to nonsymmetrical olefins gave only a single $4\alpha,5\beta$ - trans isomer. Any accompanying cis-isomer was found to be 48.58, and attributable to epimerization of the transadduct.1 This is remarkable regio- and stereospecificity for a photochemical cycloaddition. From the observed trans- product and the cycloaddition of the dienone to dienes, several points can be inferred about the excited dienone. Excitation of the dienone leads to twisting about the C-4, C-5 double bond; the olefinic hydrogen becoming pseudo-4 β in the process. The excited dienone can then either form a complex with an olefin and collapse directly to the trans-fused cyclobutane.¹² Alternatively, the excited dienone can add to an olefin to form a diradical which is suitably disposed to closure to the transcyclobutane. However, the rate or ring closure must be at least two orders of magnitude faster than rotation about the newly formed single bond between C-4 and the olefin to avoid formation of the cis-cyclobutanes.

Since the two dienes studied are incapable of assuming the necessary s-cis-conformation necessary for forming Diels-Alder adducts, they may be viewed as simple olefins with very strong electron donating groups. From the formation of only one trans-cyclobutane of the two possible head-to-tail adducts, the approach of the diene to the dienone is highly ordered, although this may be due to steric interactions of the diene with the steroid B-ring and the angular Me group. The approach of the excited dienone to the diene would be in a symmetricantisymmetric manner where one of the diene double bonds would be orthogonal to the plane of the steroid and the remainder of the diene above the plane of the steroid. Then a complex A could form (presumably an exiplex⁵) which could collapse to the trans-product B. Additionally, due to the strong electron delocalization properties of the two incipient allyl radicals, a portion of A could leak to form an oriented diradical C where the radical derived



from the diene is still orthogonal to the plane of the steroid. The newly formed bond in C could then rotate to form D where the diene derived radical is parallel to the α -side of the steroid. At the same time, the indicated single bond in D could rotate, followed by ring closure to form the epimeric *cis*-fused cyclobutanes E. Alternatively, the dienone and diene could form the diradical C directly, which could collapse ($C \rightarrow B$), or rotate and collapse to the observed products ($C \rightarrow D \rightarrow E$). Although the formation of only *trans*-fused cyclobutanes from olefins as diverse as ethylene, cyclopentene, norbornene and ketene diethyl acetal argues for complex formation with collapse directly to products.^{16.5}

The results obtained show that for the first time in dienone photocycloadditions with dienes, *trans*-fused cyclobutanes have been formed. The cycloadditions are regiospecific forming [2+2] - head - to - tail adducts, but the stereospecific formation of only *trans*-fused [2+2]-adducts has been lost.

EXPERIMENTAL

General. M.ps were taken on a Thomas-Hoover Uni-Melt capillary apparatus and are uncorrected. IR spectra were run in KBr unless otherwise noted, and UV spectra were run in MeOH and are not reported if only $n \rightarrow \pi^{*}$ absorption were observed. A Varian Associates A-60 or HA-100 spectrophotometer was used to record spectra. All spectra were run in CDCl, soln, using TMS as an internal standard unless otherwise noted. ORD/CD curves were run on a Jasco ORD/UV-5 spectrometer.

Irradiation of dienone 1 with 2,5 - dimethyl - 2,4 - hexadiene. The dienone 1 (10.0 g, 29.4 mmol)[®] was dissolved in 160 ml EtOAc and 35 ml 2,5 - dimethyl - 2,4 - hexadiene (Chemical Samples, 99%) added. A slow stream of argon was passed through the soln while irradiating with a 450 W medium pressure mercury arc (Pyrex filter) for 11 hr. The solvent was removed under reduced pressure and the residue chromatographed on 1500 g of E. Merck silica.

Elution with EtOAc-light petroleum (1:9) gave 437 mg (0.97 mmol, 3%) of cis - [2+2] - adduct as a non-crystalline oil. Compound 6 exhibits: γ_{CHCF_3} 1775, 1690 cm⁻¹; NMR & 6-04 (d, 1H), 5-71 (m, 1H), 5-34 (d, 1H), 3-16 (d, J = 11 Hz, 1H), 1-80 (broad s, 3H, vinyl -CH₃), 1-65 (broad s, 3H, vinyl -CH₃), 1-22 (s, 3H), 0-97 (s, 3H), 0-90 (s, 3H), 0-70 (s, 3H); [C₄D₄] 5-0-6-0 (m, 3H), 3-14 (d, J = 11 Hz, 1H), 2-64 (s, 1H, 4 β -H), 1-69 (d, 3H, vinyl -CH₃), 1-53 (d, 3H, vinyl -CH₃), 1-25 (s, 3H), 0-94 (s, 3H), 0-85 (s, 3H), 0-61 (s, 3H); [α]³⁵/₂₅ = +76.6° ± 2-0° [C = 0.107% (CHCl₃)]; [α]₂₅₀ +631°, a = +11; [θ]₃₀₂ +1036°, a calcd = +13. (Found: C, 80-24; H, 9-70. Calcd. for C₃₀H₄₂O₃: C, 79-95; H, 9-39%).

Continued elution gave an intermediate fraction of 470 mg containing both *cis*-isomers, followed by 3.51 g (7.8 mmol, 26%) of 7: m.p. 154-7° (ether-light petroleum); γ 1780, 1700 cm⁻¹, NMR δ 5-67 (dd, J = 6.2 Hz, 1H), 5-13-6-00 (m, 2H), 3-28 (d, J = 10.5 Hz, 1H), 1-72 (d, $J \approx 1$ Hz, 3H, vinyl -CH₃), 1-68 (d, $J \approx 1$ Hz, 3H, vinyl -CH₃), 1-02 (s, 3H), 0-97 (s, 3H), 0-95 (s, 3H), 0-78 (s, 3H); [CaDa] 5-51 (dd, J = 6.2 Hz, 1H), 5-17 (m, 2H), 3-20 (d, J = 10.5 Hz, 1H), 1-67 (d, $J \approx 1$ Hz, 3H), 1-53 (d, $J \approx 1$ Hz, 3H), 1-11 (s, 3H), 0-98 (s, 3H), 0-83 (s, 3H), 0-67 (s, 3H); $[\alpha]_{2}^{2} \pm 55.5^{\circ}$ [C = 0-119% (CHCl₃)]; [ϕ]₃₋₅₅ + 2253°, [ϕ]₂₋₅₀ 0°, a = +36; [θ]₂₋₅₆ + 3988°, a calcd = +49. (Found: C, 79-91; H, 9-36. Calcd. for C₃₋₀H₄₂O₃: C, 79-95; H, 9-39%).

Elution with EtOAc-light petroleum (15:85) gave a mixture of 5-15 g of the *trans*-8 and its *cis* - 4 β ,5 β - epimer 9. Crystallization from ether gave 3-20 g (8.7 mmol, 29%) of the pure *trans*-isomer 8: m.p. 174-5°; γ 1770, 1725 cm⁻¹; NMR & 6.08 (s, 2H, C-6,7 vinyl protons), 5.00 (d of m, $J \cong 10$ Hz, 1H, trimethyl vinyl proton), 2-95 (d, J = 10 Hz, 1H, cyclobutane proton), 2-80 (s, 1H, C-4 β -proton),

^{*}A referee requested the $\pi\pi^*$ and $n\pi^*$ absorptions of the dienone. The $\pi\pi^*$ absorption is at 282 nm (ϵ 27000). The $n\pi^*$ is not resolved in methanol, although ORD measurements indicate that it occurs around 360 nm.¹⁴ The UV spectrum in benzene shows the $n\pi^*$ transition at 350 nm (ϵ 90).

1.67 (broad s, 6H), 1.21 (s, 3H), 1.16 (s, 6H), 0.87 (s, 3H); $[C_{\bullet}D_{\bullet}]$ 5.87 (q with secondary splitting, 2H, C-6,7), 5.09 (d of m, $J \approx 10$ Hz, 1H, vinyl proton), 2.89 (d, J = 10 Hz, 1H, cyclobutane proton), 2.62 (s, 1H, C-4 β -proton), 1.62 (d, J = 1, 3H, vinyl methyl), 1.56 (d, J = 1, 3H, vinyl Me), 1.42 (s, 3H), 1.17 (s, 3H), 0.93 (s, 3H), 0.78 (s, 3H); $[\alpha]_{D}^{25} = -73.5^{\circ}$ [C = 1.035% (CHCl₃)]; $[\phi]_{150} + 19648^{\circ}$, a calcd. = +240 (Found: C, 79.87; H, 9.42. Calcd. for C₃₀H₄₂O₃: C, 79.95; H, 9.39%).

The NMR spectrum of the mother liquor residue from 8 indicated a 1:2 mixture of the trans-isomer and its epimer. The residue was dissolved in 175 ml MeOH and 3.0 g MeONa added. After stirring magnetically overnight, 500 ml of dil. HCl was added and the MeOH removed under reduced pressure to give 1.8 g (2.8 mmol, 10%) of the cis - 4,6,5,6 - epimer 9: m.p. 155-7°; y 1785, 1700 cm^{-1} , NMR & 6.01 (dd, J = 10.2 Hz, 1H, C-7 proton), 5.53 (d, J = 10 Hz, 1H, C-6 proton), 5.38 (broad d, J = 10 Hz, 1H, vinyl-proton), 3.15 (d, J = 10 Hz, 1H, cyclobutane proton), 1.73 (d, $J \cong 1$ Hz, vinyl-Me), 1.65 (d, $J \cong 1$ Hz, vinyl-methyl), 1.16 (s, 3H), $0.97 (s, 3H), 0.95 (s, 3H), 0.72 (s, 3H); [C_6D_6] 5.98 (dd, J = 10.2 Hz, J)$ 1H), 5.48 (broad d, J = 10 Hz, 1H), 5.38 (d with secondary splitting, $J \approx 10$ Hz, 1H), 2.95 (d, J = 10 Hz, 1H), 2.52 (s, 1H, C- 4α -proton), 1.68 (d, $J \approx 1$ Hz, 3H), 1.58 (d, $J \approx 1$ Hz, 3H), 1.15 (s, 3H), 1.00 (s, 3H), 0.82 (s, 3H), 0.63 (s, 3H); $[\alpha]_{D}^{22} = -64.0^{\circ}$ $[C = 0.111\% (CHCl_3)]; [\phi]_{306} - 6129^{\circ}, [\phi]_{274} - 1082^{\circ}, a = -50; [\theta]_{290} - 5227^{\circ}, a \text{ calcd.} = -64. (Found: C, 80.17; H, 9.45. Calcd. for$ C30H42O3: C, 79.95; H, 9.39%).

Elution with EtOAc-light petroleum (1:1) gave back 1.39 g (4.1 mmol, 14%) of starting dienone 1.

Attempted Cope reaction with 7. A soln of 269 mg of 7 was refluxed in toluene for 20 hr. TLC and NMR examination indicated starting material remained accompanied by a trace of dienone. Equivalent results were obtained using xylene. However, when mesitylene was used as solvent, a smooth cycloreversion to starting dienone occurred and 111 mg of dienone 1 was recovered upon thick layer chromatography.

Irradiation of 6-dehydrotestosterone acetate 3 with 4 - methyl -1,3 - pentadiene. A soln of 3 (10.0 g, 30.6 mmol) in 160 ml EtOAc and 25 ml 4 - methyl - 1,3 - pentadiene (Chemical Samples, 99%), was irradiated, under N_2 , with a 450 W medium pressure lamp (Pyrex filter) for 4.5 hr. The solvent was removed under reduced pressure and the residue chromatographed on 1400 g of E. Merck silica.

Elution with EtOAc-light petroleum (1:19) gave 335 mg (0.82 mmol, 2.7%) from which 240 mg of 11 could be crystallized: m.p. 100-2° (MeOH); γ_{CHCl_3} 1730, 1695 cm⁻¹; NMR δ 5.86 (dd, J = 9, 2.5 Hz, 1H, C-7), 5.32 (d, 2H, C6-H, J = 9 Hz, vinyl hydrogen), 4.76 (t, 1H, C17 α -H), 3.25 (broad m, 1H, cyclobutane H), 2.01 (s, 3H, -OAc), 1.71 (broad s, 3H, vinyl Me), 1.58 (broad s, 3H, vinyl Me), 0.82 (s, 3H, C18-Me), 0.72 (s, 3H, C19-Me); [C₆D₄] 5.73 (dd, J = 9, 2.5 Hz, 1H, C7-H), 5.25 (d, 2H, C6-H and vinyl-H), 4.79 (t, 1H, C17 α -H), 1.73 (s, 3H, -OAc), 1.55 (s, 3H), vinyl Me), 1.48 (s, 3H, vinyl methyl), 0.78 (s, 3H), 0.67 (s, 3H); [ϕ]₃₀₄ +1541°, [ϕ]₃₀₄ 0°, [ϕ]₃₀₅ -1067°, a = +26; [θ]₂₀₅ +2105°, a calcd. = +26. (Found: C, 78.84; H, 9.14. Calcd. for C₂₇H₃₈O₃: C, 78.98; H, 9.33%).

Closely following 11, 1.797 g (4.4 mmol, 14%) of 12 were eluted: m.p. 131-3° (MeOH-water), γ 1745, 1700 cm⁻¹, NMR & 5.64 (s, 2H, C6, C7-H), 5.11 (d with secondary splitting, $J \cong 8$ Hz, vinyl -H), 4.61 (t, 1H, C17 α -H), 3.42 (broad m, cyclobutane-H), 2.03 (s, 3H, -OAc), 1.68 (d, $J \cong 1$ Hz, 3H, vinyl -Me), 1.60 (d, $J \cong 1$ Hz, 3H, vinyl -Me), 0.80 (s, 3H), 0.77 (s, 3H); [C₄D₄] 5.52 (s, 2H, C6,7-H), 5.16 (d, $J \cong 8$ Hz, vinyl -H), 4.75 (t, 1H, C17 α -H), 3.36 (broad m, 1H), 2.38 (d, J = 6.5 Hz, 1H, 4 β -H), 1.73 (s, 3H, -OAc), 1.62 (d, $J \cong 1$ Hz, 3H, vinyl -Me), 1.46 (d, J = 1 Hz, 3H, vinyl -Me), 0.77 (s, 3H), 0.68 (s, 3H); [β_{1299} +2435°, [β_{1280} +2269°, a = +2; [θ_{1283} + 1200°, a calcd. = +15. (Found: C, 78.91; H, 9.30. Calcd. for C₂₇H₃₈O₃: C, 78.98; H, 9.33%). Compound 12 could be saponified with MeONa in MeOH and then reacetylated with pyridine- Ac_2O to reform 12.

Elution with EtOAc-light petroleum (1:9) gave 561 mg (1.4 mmol, 4.5%) of 13: m.p. 101-5° (MeOH); γ 1735, 1720 cm⁻¹; NMR δ 5.86 (dd, J = 11.2 Hz, 1H, C7-H), 5.66 (d, J = 11 Hz, C6-H), 5.23 (d with secondary splitting, $J \cong 8$ Hz, 1H, vinyl-H), 4.65 (t, 1H, C17 α -H), 3.18 (t with secondary splitting, $J \cong 8$ Hz, 1H, cyclobutane-H), 2.02 (s, 3H, -OAc), 1.65 (broad s, 3H, vinyl -CH₃), 1.58 (d, $J \cong 1$ Hz, 3H, vinyl -Me), 0.83 (s, 3H), 0.70 (s, 3H); [C₆D₆] 5.92 (dd, 1H), 5.49 (d, 1H), 5.34 (d, 1H), 4.75 (t, 1H), 3.18 (t, $J \cong 8$ Hz, 1H, cyclobutane-H), 2.50 (t, J = 8 Hz, 1H, C-4 β -H), 1.77 (s, 3H, -OAc), 1.62 (broad s, 3H), 1.50 (d, $J \cong 1$ H, 3H), 0.77 (s, 3H), 0.60 (s, 3H). Compound 13 is very sensitive and epimerizes very readily. Despite repeated attempts to obtain its ORD and CD spectra, only the spectrum of the 4β , 5β - cis - isomer 14 was obtained. (Found: C, 79.80; H, 9.42. Calcd. for C₂₇H₃₈O₃: C, 78.98; H, 9.33%).

Continued elution gave 5.54 g (13.6 mmol, 44%) of the $4\beta_5\beta_{epimer}$ 14 as a non-crystalline glass: γ_{CHC13} 1740, 1710 cm⁻¹; NMR δ 6.03 (dd, J = 10, 2 Hz, 1H, C7-H), 5.68 (broad d, $J \cong 8$, 1H, vinyl -H), 5.35 (d, J = 10 Hz, 1H, C6-H), 3.56 (broad m, 1H, cyclobutane H), 2.06 (s, 3H, 17 β -OAc), 1.67 (s, 3H, vinyl -Me), 1.58 (s, 3H, vinyl -Me), 0.87 (s, 3H), 0.72 (s, 3H); $[\phi]_{son} = -3632^\circ$, $[\phi]_{280} -2000^\circ$, a = -16; $[\theta]_{291} = -2278^\circ$, a calcd. = -28. (Found: C, 78.73; H, 9.37. Calcd. for C₂₇H₃₈O₃: C, 78.98; H, 9.33%).

MeONa in MeOH cleaved the 17-acetate in 13 to give the free alcohol which also could not be crystallized. Reacetylation with Ac₂O-pyridine regenerated 14.

Continued elution gave back 3.84 g (35%) of starting dienone 3.

Attempted ring-closure in 12. (a) A soln of 863 mg of 12 in 200 ml of acetone were irradiated for 6 hr under N_2 with a 200 W medium pressure mercury arc (Pyrex filter) at which TLC indicated no reaction had occurred and starting material was recovered. (b) 934 mg of 12 was irradiated under N_2 in 300 ml EtOAc and 10 ml p-xylene with a 450 W medium pressure mercury arc (quartz filter) for 2 hr. Thin layer examination indicated that the molecule had completely decomposed under irradiation. (c) The material from part a was dissolved in 300 ml of acetone and irradiated under N_2 for 2 hr with 450 W mercury arc (Vycor filter). Under these conditions, the molecule was completely degraded.

REFERENCES

- ¹G. R. Lenz, Tetrahedron 28, 2211 (1972); ^bM. B. Rubin, D. Glover and R. G. Parker, Tetrahedron Letters 1075 (1964); ^cM.
- B. Rubin and T. Maymon, Israel J. Chem. 8, 717 (1970).
- ²G. R. Lenz, Tetrahedron 28, 2195 (1972).
- ³G. R. Lenz, Tetrahedron Letters 3027 (1972).
- ⁴⁴T. S. Cantrell, Chem. Commun. 1656 (1970); ⁵T. S. Cantrell, J. Org. Chem. 39, 3063 (1974).
- ⁵O. L. Chapman and D. S. Weiss, Org. Photochem. 3, 225 (1973).
- G. R. Lenz, unpublished results.
- ¹A. S. Onishchenko, *Diene Synthesis* pp. 8–16. Israel Program for Scientific Translations, Jerusalem (1964).
- ⁸N. S. Bhacca and D. H. Williams, Applications of NMR Spectroscopy in Organic Chemistry p. 172. Holden-Day, San Francisco (1964).
- *E. J. Corey, J. D. Bass, R. LaMahieu and R. Mitra, J. Am. Chem. Soc. 86, 5570 (1964).
- ¹⁹S. J. Rhoads, Molecular Rearrangements (Edited by P. de Mayo), Vol. 1, p. 684. Wiley, New York (1963).
- ^{11°} M. Karplus, J. Chem. Phys. 30, 11 (1959); ^bI. Fleming and D. H. Williams, *Tetrahedron* 23, 2747 (1967); ^cH. Weitkamp and F. Korte, *Ibid.* Suppl. 7, 75 (1966); ^dF. A. Cotton and B. A. Frenz, *Ibid.* 30, 1587 (1974).
- ¹²P. de Mayo, Accounts Chem. Res. 4, 41 (1971).
- ¹³P. Crabbé, Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry, p. 226. Holden-Day, San Francisco (1965).