207. Photochemical Reactions

Part 60 [1]

The Photorearrangement of a 2,5-Diene-1,7-dione

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Summary. The 2,5-diene-1,7-dione **12** rearranges photochemically to the cyclopentenonyl-cyclopropyl ketone **13**. Dienone **12** does not emit phosphorescence at 78 K. Sensitization and quenching experiments indicate that the photorearrangement occurs in an excited triplet state with E_T between ca. 61–65 kcal/mol according to sensitization data, and between ca. 54–58 kcal/mol according to quenching results. By comparison, the 2,5-dienone **1** behaves similarly with respect to sensitization and quenching of its photorearrangement [3] (indicating $E_T < 61$ and ca. 54–58 kcal/mol, respectively) and to its lack of phosphorescence, while the 2-ene-1,5-dione **8** emits phosphorescence ($E_T = 72.4$ kcal/mol) and sensitization, and quenching data indicate E_T between ca. 68–72 and >61 kcal/mol for its photorearrangement, respectively. It is concluded that the triplet energy of the reactive state of compound **12** extends either over the two enone groups involving strong interaction or is localized on the ring A enone only.

Photoproduct **13** rearranges further to the stereoisomer **14** on direct excitation and sensitization with acetophenone. Thioxanthone as triplet sensitizer and naphthalene as triplet quencher are ineffective. The reverse isomerization process, *i.e.* **14** → **13**, is not observed.

We have reported previously [3] on the photorearrangement of the steroidal 2,5-dienones[1] **1** and **2** (Chart 1). More recently we described [4] the photochemical transformation of the 2-ene-1,5-dione[1] **8**. In both cases the rearrangements involve bonding between the β-carbon of the enone group and the sp^2-hybridized δ-carbon. The structural relationship between products **7**[2] and their precursors **1** and **2** suggests a stepwise rearrangement sequence, while the formation of the major products **3**–**6** could result equally well from concerted cycloadditions of the 1,10-single bond and the 5,6-double bond [5]. For the transformation **8** → **9** + **10**, β,δ-bonding has been shown experimentally to be a discrete primary photochemical process [4b].

The 2,5-diene-1,7-dione[1] **12**, 3,7-dioxo-4,4-dimethyl-17β-acetoxy-$\Delta^{1;5}$-androstadiene, prepared by selective C-2 bromination of compound **8** [4] [6] with pyridine·HBr·Br_2 and dehydrobromination of product **11** with LiBr and Li_2CO_3 in phosphoryl tri-(dimethylamide) (Chart 2), embodies in a formal sense partial structures of both types of ketones, *i.e.* the 2,5-dienone[1] chromophore of **1** and **2** (neglecting the C-7 keto group) and the 2-ene-1,5-dione[1] chromophore of **8** (neglecting the 1,2-double bond). Compound **12** could therefore be expected *a priori* to have the structural capacity to react photochemically according to either or both of the above major pathways, leading to 7-oxo analogues of **3** and **4** or/and 1-dehydro analogues of **9** and **10**.

[1] Numbering chosen to denote the minimum number of carbon atoms between the individual chromophors. The other numbers refer to steroid nomenclature.

[2] It is assumed that each of the ketones **1** and **2** affords specifically one stereoisomer of formula **7** (6β-H and 6α-H, respectively) although no conclusive evidence is available on this point [3].

Chart 1. *Previous Results: Photorearrangements of Compounds* **1** *and* **2** [3], *and* **8** [4]

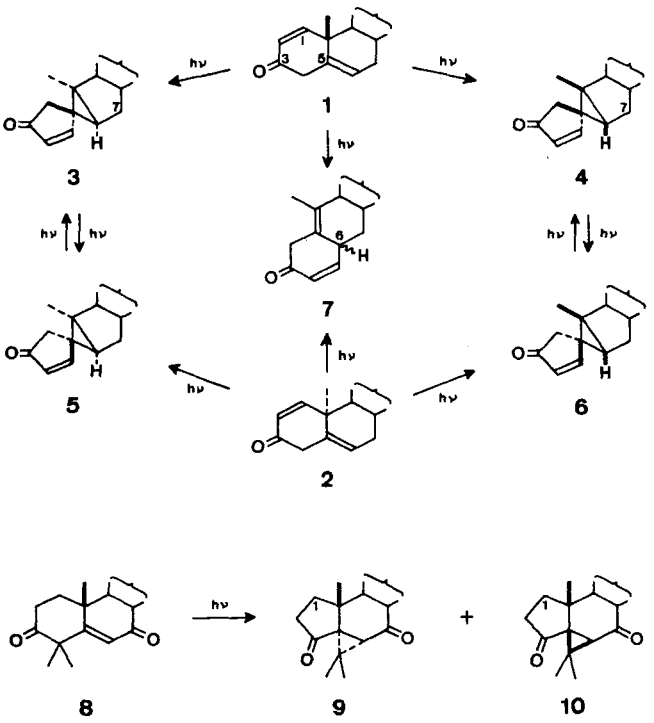
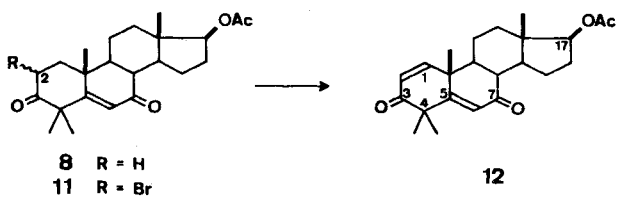


Chart 2.

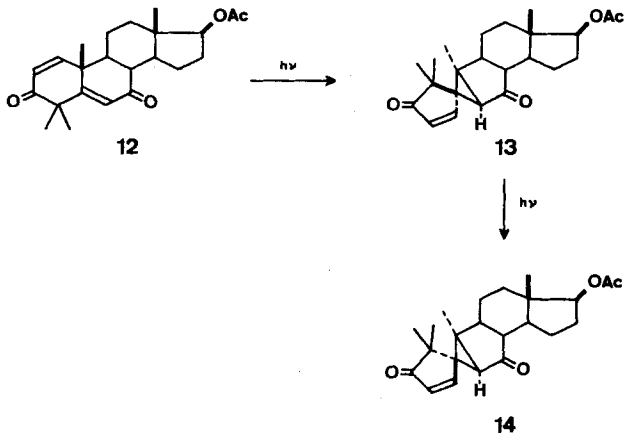


Ultraviolet Irradiation of 3,7-Dioxo-4,4-dimethyl-17β-acetoxy-$\Delta^{1,5}$-androstadiene (12); Results. – Irradiations on an analytical scale of **12** in dioxane and acetonitrile with wavelengths of both 2537 Å and >3400 Å, and in benzene with 3400 Å, gave in each case the same two products. Periodical analyses by thin-layer chromatography revealed that the formation of one product (**13**) sets in prior to the formation of the other one (**14**). In a preparative irradiation experiment, using a 1.7×10^{-2} M benzene solution of **12** and wavelengths of >3400 Å, 40% of photoproduct **13**, 11% of the isomer **14**, and 18% of unreacted starting material (**12**) were isolated in chromatographically pure form.

Irradiations with 2537 Å of the photoproducts in dioxane solutions and analysis by thin-layer chromatography indicated that **13** isomerized to **14**, and that **14** converted

into two other, as yet unidentified products. A preparative run with **13** gave 19% of the isomer **14** and 3% of starting material (**13**), after substantial losses on chromatography.

Chart 3. *Ultraviolet Irradiation of 3,7-Dioxo-4,4-dimethyl-17β-acetoxy-$\Delta^{1,5}$-androstadiene* (**12**) *and of its Photoisomer* **13**



In view of the fact that the chromatographic separations did not allow a sufficiently reproducible determination of product yields, the analysis of triplet sensitization and quenching experiments was restricted to qualitative estimates, using periodical thin-layer chromatographic screening. The compounds with a ring-A-enone group, **1**, **12** and the model, 3-oxo-17β-acetoxy-Δ^1-5α-androstene, do not show any phosphorescence emission in ether-pentane-ethanol 5:5:2 (EPA) glass at 78 K. Similarly, photoproduct **13** does not phosphoresce. On the other hand, the ring-B-enone **8** was found to emit with $\Phi_P = 0.43$, $\tau_P^{obs} = 32$ ms, and a *O–O* band at 3950 Å ($E_T = 72.4$ kcal/mol) in previous investigations [4] [7]. The photorearrangement **12** → **13** could be sensitized by acetophenone ($E_T = 72.0$ kcal/mol [8]) and thioxanthone [$E_T = 65.5$ kcal/mol [9]), but not by 4,4'-bis(dimethylamino)-benzophenone (*Michler* ketone, $E_T = 61.0$ kcal/mol [9]). High concentrations of naphthalene (1.5 M, $E_T = 60.9$ kcal/mol [9]) and of 1,3-pentadiene (2 M, E_T = ca. 58 kcal/mol [10]) in runs using direct excitation of **12** with wavelengths > 3400 Å did not noticeably affect the rate of rearrangement, while 1 M 1,3-cyclohexadiene ($E_T = 53.3$ kcal/mol [11]) caused partial quenching[3]). Similar experiments were carried out with dienone **1** and enedione **8**. The rearrangement **1** → **3** + **4** was sensitized with acetophenone, thioxanthone and *Michler* ketone. It was unaffected by the addition of naphthalene and 1,3-pentadiene, but quenched completely with 1 M 1,3-cyclohexadiene[3]). The formation of **9** and **10** from **8** was sensitized with acetophenone, but not with benzophenone ($E_T = 67.6$ kcal/mol [8]) and thioxanthone, and was quenched completely with 0.5 M naphthalene [4] and 2 M pentadiene.

[3]) In the presence of 1,3-pentadiene and 1,3-cyclohexadiene, the formation of several new products, arising from reaction of the steroid with diene, was observed in each case, parallel to the isomerizations **1** → **3** + **4** and **12** → **13**.

Excitation with 3660 Å of dienedione **12** in EPA glass at 78 K in the presence of 0.1M naphthalene resulted in sensitized naphthalene phosphorescence, while a sample of dienone **1** + 0.1M naphthalene did not emit.

The isomerization of photoproduct **13** into **14** could be sensitized with acetophenone, but not with benzophenone and thioxanthone, and no quenching of the reaction with 1.5M naphthalene and 2M pentadiene was observed.

Structure Elucidation of Photoproducts 13 and 14. – Among the spectral data which support the assigned structures of photoproducts **13** and **14** are the NMR. *AX* patterns with a coupling constant of 6 cps for the olefinic protons, indicating the presence of a γ,γ-disubstituted cyclopentenone. The UV. absorption maxima at 251 nm (ε 8130 and 8850, respectively) show that the conjugation of the enone chromophore extends to an adjacent cyclopropyl group[4]). The stereoisomerism of the two products is documented by a very close correspondence of the IR. and mass spectra.

The chemical transformations which led to the assignments of structures **13** and **14** are summarized in Chart 4.

The presence of a cyclopropyl ketone is revealed by strong short-wavelength UV. absorptions of the saturated compounds **16** and **24** ($\varepsilon_{210\,nm}$ ca. 4600 and 3840, respectively), by the reductive cleavage of a C–C bond of **13** and **14** (→ **15**), and by the acid-catalyzed isomerizations **13** → **17**, **14** → **25**, and **16** → **8** + **20a**, each of which introduced a new double bond in either the α,β- (**8**, **20a**) or β,γ-position (**17**) to one of the keto groups. The acid treatment of **16** afforded two isomers upon cleavage of the bicyclo[3.1.0]hexanone system: The spirocyclic enedione **20a** (43% yield) results from proton elimination and subsequent migration of the 9,10-double bond into conjugation with the 7-ketone. The second isomer, 3,7-dioxo-4,4-dimethyl-17β-acetoxy-Δ^5-androstene (**8**), which was obtained in 11% yield, results from the (5 → 10)-shift of the methylene group C-1. The steric course of this alkyl 1,2-migration – rear (α) side attack of C-1 at C-10 – provides evidence for the *R* chirality of the spirocarbon C-5 in photoproduct **13**.

The stereochemistry of the bicyclo[3.1.0]hexanone partial structure of **13** is determined by the circular dichroism of compound **22**[5]). The strongly negative *Cotton* effect of the cyclopropyl ketone ($\Delta\varepsilon_{297} = -1.24$) establishes the fusion of the three-membered ring onto the β-face of the 6,10-bond [12]. The fact that compound **15** is formed from both photoproducts **13** (20% yield) and **14** (9% yield) upon reductive cyclopropane cleavage and subsequent oxidation confirms, furthermore, that the fusion between the three- and the five-membered rings of the two compounds is sterically identical. Hence the stereoisomers **13** and **14** differ only with respect to the chirality of the spirocarbon C-5.

Information pertaining to ring sizes is obtained, *inter alia*, from the infrared carbonyl frequencies of compounds **21a** [ν_{CO} = 1670 (cyclohexenone) and 1745 cm^{-1} (cyclopentanone)] and **23** [ν_{CO} = 1715 cm^{-1} (bicyclo[3.1.0]hexan-2-one)].

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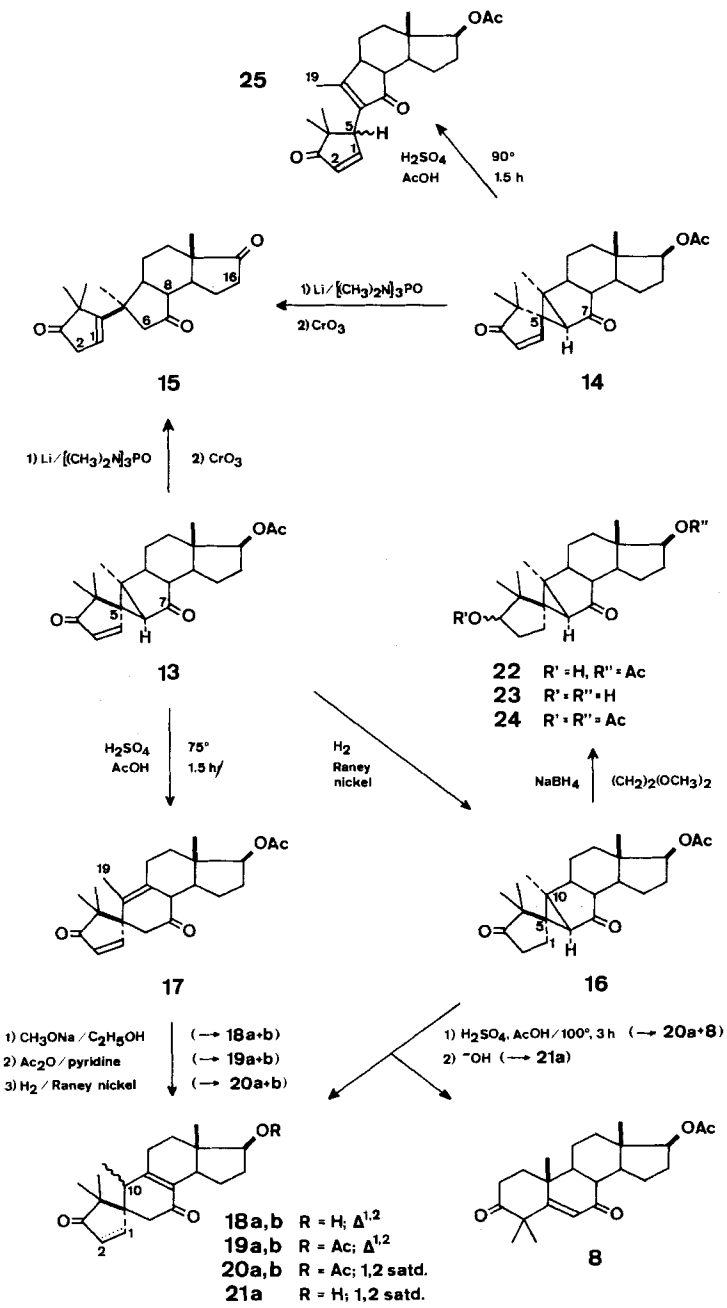
[4]) By comparison, the 7-deoxo analogues **4** and **6** absorb at considerably longer wavelengths (268 nm, ε 10400, and 267 nm, ε 8850, respectively) [3]. It is of interest to note that the additional keto group at C-7 in **13** and **14** decreases the conjugative effect of the three-membered ring on the enone system.

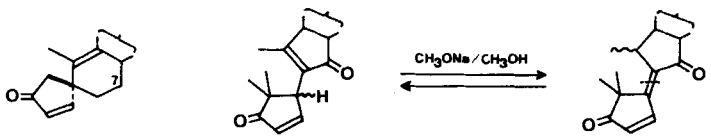
[5]) We thank Professor *G. Snatzke*, University of Bonn, for measuring the circular dichroism of compound **22**.

Chart 4. *Structural Elucidation of Photoproducts* **13** *and* **14**



The double bond of the β,γ-unsaturated cyclopentenone moiety in triketone **15** could not be brought into conjugation by treatment with alkali. Structure **15** is, however, amply secured by the following data: The ring size of the three cyclic ketones is determined by a single strong IR. carbonyl band at 1745 cm^{-1}. In the NMR. spectrum, the four methyl groups appear as singlets at δ 0.78, 1.16, 1.24, and 1.47. The methylene (C-2) and olefinic (C-1) protons give rise to a sharp AX_2 pattern (doublet at δ 2.98 and triplet at 5.90, J = 2 cps). An AX spectrum at δ 2.08 and 2.92 (J = 20 cps) is attributable to the methylene protons at C-6. The chemical shift of the two C-2 protons is in accord with the expected value for a methylene group flanked by a double bond and a keto group. The similarly large down-field shift for one (6β) of the C-6 protons can be attributed to deshielding by the olefinic substituent in the vicinal *cis* position. The location of these five hydrogens relative to the ketone functions is further substantiated by the result of a base-catalyzed hydrogen-deuterium exchange with **15**, which gave a heptadeuterated analogue (ca. 88% 2,2,6,6,8,16,16-d_7, 12% d_6). The deuteration is reflected in the NMR. spectrum by the disappearance of the C-2 and C-6 methylene proton signals (together with the disappearance of the non-resolved signals of another three protons (at C-8 and C-16) in the region between δ 1.8 and 2.6), and by the appearance of a singlet for the olefinic proton at δ 5.82.

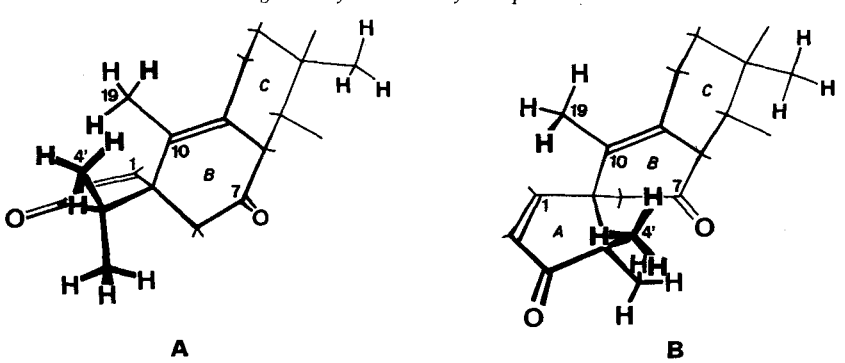
Chart 5.



26 **25** **27**

The ultraviolet absorption maximum at 212 nm (ε 13300) of compound **17** (IR.: ν_{CO} 1715, 1735 (shoulder) cm^{-1}) compares to absorptions of similar cyclopentenones lacking additional unsaturation in ring B [13] but, interestingly, it differs remarkably from the spectrum of the 7-deoxo analogue **26** (Chart 5), which absorbs at 218 and 265 nm (ε 12300 and 1910, respectively) [13]. The position of the tetrasubstituted double bond of **17** is indicated in the NMR. spectrum by a signal at δ 1.47 for CH_3-19 (finely split by homoallylic coupling), which converts to a doublet (at δ 1.15 and 1.23, J = 7 cps) in each of the stereoisomers **19a** and **19b**. The latter result upon treatment of **17** with sodium methoxide and subsequent reacetylation. Selective hydrogenation of

Ring B Conformations of Compound **17**



A **B**

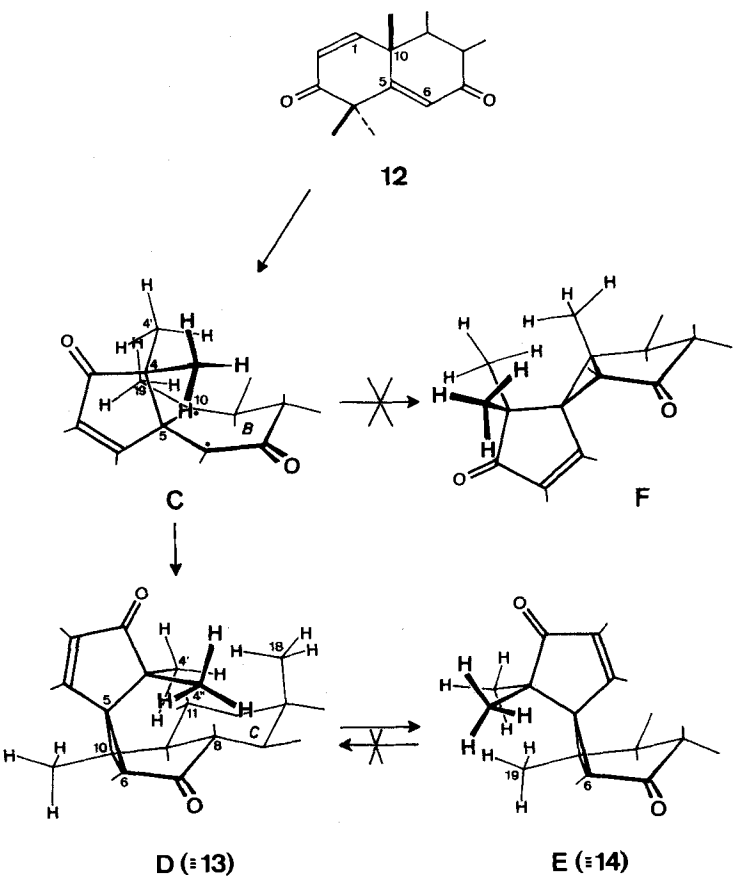
the 1,2-double bond of **19a** and **19b** gave two crystalline dihydro derivatives (**20a** and **20b**, respectively), one of which (**20a**) corresponded to the non-crystalline sample obtained by acid-catalyzed isomerization of **16** with respect to IR., NMR., and mass spectra, and thin-layer chromatography. The UV. difference between **17** and **26** may be explained by a difference in the preferred conformation of ring B in the two compounds. Molecular models show that orbital overlap

between the 1,2- and 9,10-double bonds of compound **26** is possible in the half-chair like conformation of ring B where the olefinic C-1 adopts the quasi-axial position. The corresponding conformation of compound **17** (*cf.* **A**) is highly destabilized by severe non-bonding repulsion between one of the geminal methyl groups at C-4 and methyl C-19. Considerable steric relief is achieved by flipping of ring B into the alternative half-chair like conformation **B**, where the olefinic C-1 is now equatorial on ring B. In this form, however, the two double bonds are sufficiently separated in spatial orientation to prevent any significant π interaction.

The acid-catalyzed isomerization of photoproduct **14** gave an oily mixture of two (C-5)-diastereoisomers **25** (IR.: 1240, 1590, 1635, 1705, 1710, 1735 cm^{-1}) which could not be separated. The *AMX* patterns of the protons at C-1, C-2 and C-5, and the C-19 methyl signals appear in the NMR. spectrum with only slight chemical shift differences for each isomer. Analysis and structural assignments were possible using extensive decoupling techniques on samples of **25** in $CDCl_3$ and C_6D_6 solutions. In a 0.01N solution of sodium methoxide in methanol, an equilibrium between **25** and its linear conjugated dienedione **27** was reached, with ultraviolet absorption maxima at 242 ($\varepsilon = 9300$) and 305 nm ($\varepsilon = 4660$), which remained unchanged on acidification with acetic acid.

Discussion of the Photochemical Results. – The structural aspect of the rearrangement of the 2,5-diene-1,7-dione[1]) **12** to compound **13** represents a close analogy to the phototransformation of the 2,5-dienones[1]) **1** (→ **3**) and **2** (→ **6**). However, while

Chart 6. *Stereomodels of the Photoisomers of* **12**



these latter isomerize to two stereoisomers each (**3**/**4** and **5**/**6**, respectively), compound **F** (Chart 6), which would correspond to photoproducts **4** and **5**, could not be found among the irradiation products of **12**.

The available data on reaction **12** → **13** do not allow to distinguish between a stepwise rearrangement – involving sequential $\beta \rightarrow \delta$ bonding between C-1 and C-5 in the primary photochemical step, breaking of the 1,10-bond, and ring closure between C-6 and C-10, as discussed previously [3] as a possible mechanistic route for **1** and **2** – and a concerted addition of the 1,10-single bond and the 5,6-double bond in a $\pi^2s + \sigma^2s$ mode [5]. A possible rationale for the preference of photoproduct **13** (*cf.* **D**) over the stereoisomer **F** can be seen in the increase of steric crowding between the methyl groups C-4′ (β-oriented) and C-19 in either of the transition states leading to compound **F**. Biradical **C** (shown in the ring B conformation which provides for maximum orbital overlap in the α-keto radical group), one of the intermediates in the stepwise mechanistic alternative for **12** → **13**, may serve to illustrate this point. The formation of **F** requires that C-5 moves downwards with the two methyls C-4′ and C-19 passing through a coplanar alignment of C-4′, -4, -5, -10, and -19. In this conformation the steric repulsion between the two methyl groups is quite large. In the alternative upwards movement of C-5, leading to **D**, maximum steric interactions (CH_3-4′ *vs.* CH_3-18 and the axial hydrogens on C-8 and C-11, and CH_3-4″ *vs.* CH-8) are reached only in the final product.

The apparent irreversibility of the isomerization **13** → **14** (*cf.* **D** → **E**) is again in contrast to the earlier findings concerning the photostationary equilibria between the photoproducts in the 7-deoxo series (**3** $\rightleftharpoons h\nu \rightleftharpoons$ **5** and **4** $\rightleftharpoons h\nu \rightleftharpoons$ **6**). Here also, the results may reflect a preference of **E** over **D** for steric reasons only. The reaction presumably involves photolytic opening of either the 5,10- or 6,10-cyclopropane bond, rotation around the remaining one of these bonds, and reclosure. Judging from molecular models, the non-bonding interactions of the geminal methyl groups in **D** with the ring C environment are considerably greater than those in **E** with CH_3-19 and CH-6. Reclosure to **E** should therefore be greatly favoured.

The results of sensitization and quenching experiments with compounds **1**, **8**, and **12** indicate that in each case reaction occurs from a triplet-excited state. The energy of the reactive state of dienedione **12** can be estimated to lie between 53.5 (E_T of 1,3-cyclohexadiene) and 58 kcal/mol (E_T of 1,3-pentadiene) according to quenching data, and close to 61 kcal/mol according to the sensitization data with thioxanthone and *Michler* ketone, and the sensitized phosphorescence of naphthalene. The same criteria for dienone **1** give very similar triplet energy ranges. The successful sensitization of reaction **1** → **3** + **4** with *Michler* ketone and the failure of **1** to sensitize emission from naphthalene seems to indicate, in this context, that E_T of **1** is only marginally lower than E_T of **12**. The energy of the reactive triplet of **8** is located between 67.6 (E_T of benzophenone) and 72.0 kcal/mol (E_T of acetophenone) according to sensitization, and $>$ 60.9 kcal/mol (E_T of naphthalene) according to quenching, which agrees well with the value of 72.4 kcal/mol for the lowest emitting triplet state of **8** [4] [7][6]).

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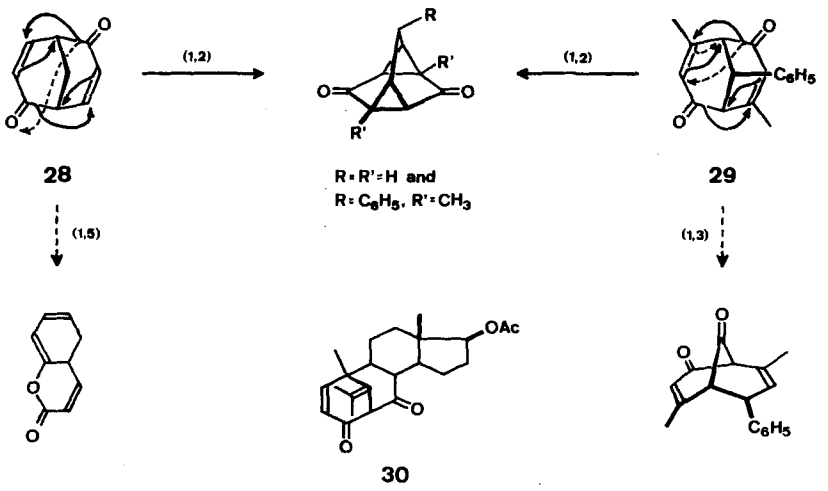
[6]) *De Mayo & al.* [14][7]) found recently that the energies which are transferred from triplet-excited cyclic enones to stilbene may be several kcal/mol lower than the values determined from phosphorescence data. For further comments on these findings, see reference [7].

[7]) We thank Professor *P. de Mayo* for communicating these results prior to publication.

The similar behaviour of the reactive states of compounds **1** and **12** may be due to an accidental proximity of the triplet energies of the two species, with ^{3}**1** possessing an excited 2,5-dienone[1]) and ^{3}**12** an excited system corresponding to two strongly coupled conjugated enones. Another possibility is, however, that also in the transformation of the dienedione **12** the reaction is initiated by the separately excited Δ^1-3-keto group, which would suggest that the analogy of the photorearrangements **1** → **3** + **4** and **12** → **13** is not confined to the overall structural changes, but pertains also to the mechanism of the reactions. This conclusion has further support in the lack of phosphorescence emission from both ring-A-enones (**1** and **12**) and from the model Δ^1-3-ketone, 3-oxo-17β-acetoxy-Δ^1-5α-androstene, considering the fact that the ring-B-enone of **8** does phosphoresce. It appears then that, whichever enone chromophore of **12** is excited primarily, energy is possibly localized (*inter alia*, by intramolecular transfer from the ring-B-enone moiety) in the lower-energy ring-A-enone triplet prior to photochemical reaction.



Knott & Mellor [15] reported recently photorearrangements of the bicyclo[3.3.1]-nona-3,7-diene-2,6-diones **28** and **29**, which provide for an interesting comparison of the photochemical pathways in **28**/**29** and in our dienedione **12**. The bicyclic compounds were found to undergo three types of rearrangements altogether: two consecutive 1,2-acyl shifts, a 1,3-acyl shift, and a 1,5-acyl shift. Bonding between the β-carbons of the enone groups – the exclusive process in the steroid **12** – is clearly less favourable in the bicyclic compounds for structural reasons. On the other hand, 1,2- and 1,3-acyl shifts would be feasible structurally for **12**, and a 1,2 shift has been observed, in fact, in the case of **8** (→ **9** + **10**), whose carbocyclic system is related to that of **12**. This reaction is initiated by breaking a σ-bond in γ,δ-position to the excited enone. Quite possibly this is also the case in (part of) the reactions of **28** and **29**, while for **12** an α-cleavage of an excited enone involving the 3,4-bond would be required for 1,*n*-acyl shifts (1,2 shift → 1-dehydro analogues of **9** and **10**; 1,3 shift → bridged diketone **30**). Our results indicate that such a photolytic enone α-cleavage is much less

efficient at best than the bonding process between the β-carbons of the two enone groups in **12**.

The multiplicity requirements of reaction **13** → **14** are less stringently defined by the available data. The successful sensitization with acetophenone demonstrates that the isomerization is possible in the triplet-excited state which appears to lie between 68 and 72 kcal/mol, considering the failure of benzophenone as a sensitizer. The absence of quenching effects may simply reflect that the cyclopropane opening (cleavage of the 5,6- or 5,10-bond) and reclosure occurs in the triplet state at a rate faster than diffusion control. Alternatively, this reaction may proceed in the triplet- (on sensitization) and the singlet-excited state (mainly on direct excitation). The fact that **13** neither phosphoresces nor sensitizes phosphorescence of 0.1M naphthalene in EPA glass at 78K indicates that any triplet formed is very short-lived.

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Experimental. – *General remarks.* Unless stated otherwise, the work-up of crude reaction mixtures involved addition of ethyl acetate, washing of the organic layer with water to the neutral point, drying over anhydrous $MgSO_4$, and evaporation of the solvent *in vacuo* in a rotatory evaporator.

Silica gel *Merck* (0.05–0.2 mm) was used for *preparative column chromatography*, and *Merck* Plates F_{254} (silica gel) for *thin-layer chromatography* (tlc.). The tlc. spots were located by the use of UV. light and by spraying the dried plates with conc. H_2SO_4 and subsequent heating.

Melting points were measured in open capillaries and are not corrected. $[\alpha]_D$ values were determined in CH_2Cl_2 solutions in a 5 cm tube.

UV. spectra: λ_{max} are given in nm (ε values in parantheses). – *IR. spectra:* ν_{max} in cm^{-1}. All IR. spectra were measured in CCl_4 solution. – *NMR. spectra:* $CDCl_3$ solution unless stated otherwise; 60 or 100 MHz. Chemical shifts are given in δ values, with $(CH_3)_4Si$ as the internal standard. Abbreviations: *s* (singlet), *d* (doublet), *t* (triplet), *m* (multiplet), *b* (broad), *J* (coupling constant in cps). Proton integration of each signal is in agreement with the given assignments.

3,7-Dioxo-4,4-dimethyl-17β-acetoxy-$\Delta^{1,5}$-androstadiene (**12**). 2.85 g (8.4 mmol) of pyridine·HBr·Br_2 were added to an ice-cooled solution of 3.0 g (8.1 mmol) of 3,7-dioxo-4,4-dimethyl-17β-acetoxy-Δ^5-androstene (**8**) [4] [6] in 80 ml CH_2Cl_2. After 1 h at room temperature the reaction mixture was taken up in ethyl acetate and washed with dil. $NaHCO_3$ solution and with H_2O. The resulting *2ξ-bromo-3,7-dioxo-4,4-dimethyl-17β-acetoxy-Δ^5-androstene* (**11**) showed IR. bands at 1240, 1620, 1675, 1735 (broad) cm^{-1}. The material was dissolved in 50 ml phosphoryl tri-(dimethylamide) and 2 g LiBr and 4 g Li_2CO_3 were added. After 1 h at 100° the mixture was worked up. Two crystallizations of the crude product from CH_2Cl_2–CH_3OH gave 2.682 g (89% yield) of **12**. M.p. 200–201°. $[\alpha]_D = +45°$ ($s = 0.94$). IR.: 1240, 1610, 1630, 1675, 1695, 1735. UV. (C_2H_5OH): 235 (12700), 333 (238). NMR.: 0.90/*s*, CH_3-18; 1.37+1.45+1.50/3 *s*, CH_3-4′, -4″, and -19; 2.05/*s*, 17-$OCOCH_3$; ca. 4.65/*bt*, CH-17; 6.00/*s*, CH-6; 6.06+6.95/2*d*, $J = 10.4$, CH-2 and -1. Mass spectrum: $M^+ = 370$. $C_{23}H_{30}O_4$ Calc. C 74.56 H 8.16% Found C 74.43 H 8.11%

UV. Irradiations. – a) *Preparative irradiation of* **12**. A solution of 974 mg (2.6 mmol) of **12** in 150 ml benzene was placed in a cylindrical flask equipped with a magnetic stirrer and a central immersion well holding a 80 W medium pressure mercury lamp (Q81, *Quarzlampen GmbH.*, Hanau). The immersion well was water-cooled through an inner jacket and contained a filter solution of 750 g NaBr and 8 g $Pb(NO_3)_2$ per liter water in an outer jacket (wavelength cut-off at 340 nm). After 1 h irradiation the benzene solution was evaporated *in vacuo*, and the residue was chromatographed on 100 g silica gel with hexane-acetone 6:1. The following fractions were obtained:

1. 175 mg **12** (18%).

2. 107 mg *3,7-Dioxo-4,4-dimethyl-17β-acetoxy-1(10→5β)-abeo-6β,10β-cyclo-Δ^1-androstene* (**14**) (yield 13% of converted starting material). M. p. 207–208° (2 cryst. from hexane-CH_2Cl_2; 71 mg). $[\alpha]_D = -162°$ ($c = 1.0$). UV. (C_2H_5OH): 251 (8850). IR.: 1240, 1580, 1720, 1740. NMR.:

0.85+1.08+1.22+1.48/4*s*, CH_3-4′, -4″, -18, and -19; 2.04/*s*, 17-OCOCH$_3$; ca. 4.7/*bt*, CH-17; 6.35+7.76/2*d*, J = 6, CH-2 and -1. Mass spectrum: M^+ = 370.

$C_{23}H_{30}O_4$ Calc. C 74.56 H 8.16% Found C 74.30 H 8.10%

3. 395 mg *3,7-Dioxo-4,4-dimethyl-17β-acetoxy-1(10→5α)*-abeo-*6β,10β-cyclo-Δ*^{1}*-androstene* (**13**) (yield 49% of converted starting material). M.p. 214–215° (2 cryst. from hexane-CH_2Cl_2; 294 mg). $[\alpha]_D = -2°$ (c = 1.23). UV. (C_2H_5OH): 251 (8130). IR.: 1240, 1595, 1720, 1740. NMR.: 0.84+1.07+1.40+1.55/4*s*, CH_3-4′, -4″, -18, and -19; 2.06/*s*, 17-OCOCH$_3$; ca. 4.7/*bt*, CH-17; 6.26+7.19/2*d*, J = 6, CH-2 and -1. Mass spectrum: M^+ = 370.

$C_{23}H_{30}O_4$ Calc. C 74.56 H 8.16% Found C 74.59 H 8.23%

b) *Irradiations of* **12** *on analytical scale.* 1% Solutions of **12** were irradiated for 1 h with 253.7 nm (low pressure mercury lamp NK 6/20, *Quarzlampen GmbH.*, Hanau) in dioxane and acetonitrile, and with < 340 nm (lamp and filter as in run a) in dioxane, acetonitrile, and benzene. In each case, tlc. analysis showed that the two *photoproducts* **13** *and* **14** were formed. Product **13** appeared before **14** became visible. Traces of other materials became visible at large conversions.

c) *Irradiation of* **13** *and* **14**. 1% Solutions of **13** and **14** in dioxane were irradiated with 253.7 nm. Tlc. indicated that **13** was partly isomerized to **14**, and that **14** gave no **13** but other unknown products.

In a preparative run a solution of 144 mg (0.39 mmol) of **13** in 32 ml dioxane was irradiated with 253.7 nm. After 4.5 h the solvent was evaporated *in vacuo*, and the residue was chromatographed on 14 g silica gel with benzene-ethyl acetate 10:1. 4 mg (3%) of starting material (**13**) and 27 mg (19%) of **14** (identified by mixed m.p., $[\alpha]_D$, and UV., IR., NMR., and mass spectra) were obtained.

d) *Experiments with triplet sensitizers and quenchers.* Degassed (three freeze-thaw cycles at 10^{-5} Torr) solutions of ketones **1**, **8**, **12**, and **13** in neat benzene and in the presence of sensitizers and quenchers were irradiated in a turn-table reactor equipped with a 125 W medium pressure mercury lamp, a filter jacket (cut-of at 340 nm), and magnetic stirring of each sample tube. Further experimental details and results are summarized in the Table. Isolation of material contained in

Triplet Sensitization and Quenching Experiments of the Phototransformations of **1**, **8**, **12**, *and* **13** [a]

	Photoisomerization [b]			
	1→**3**+**4**	**8**→**9**+**10**	**12**→**13**	**13**→**14**
Sensitizer [c]				
Acetophenone [E_T = 72.0 kcal/mol], 1M [d]	x	x	x	x
Benzophenone [E_T = 67.6 kcal/mol], 1.5M [d]		o		o
Thioxanthone [E_T = 65.5 kcal/mol], 0.05M [d]	x	o	x	o
4,4′-Bis-(dimethylamino)-benzophenone (*Michler*-Ketone) [E_T = 61.0 kcal/mol], 0.01M [e]	x		o	
Quencher				
Naphthalene [E_T = 60.9 kcal/mol], 0.5M [e]		x [f]		
Naphthalene [E_T = 60.9 kcal/mol], 1.5M [e]	o		o	o
1,3-Pentadiene [E_T = ca. 58 kcal/mol], 2M [e]	o [g]	x	o [g]	o
1,3-Cyclohexadiene [E_T = 53.5 kcal/mol], 1M [e]	x [g]		x [h]	

[a] Photolyses in benzene solutions with wavelengths < 340 nm; qualitative analyses only by periodical tlc. during the irradiations and comparison with runs without sensitizer or quencher.
[b] x = sensitization or complete quenching observed; o = sensitization or quenching not observed.
[c] ≳98% of incident light absorbed by sensitizer.
[d] 0,001M Steroid.
[e] 0.01M Steroid.
[f] See reference [4a].
[g] Formation of adducts between ketone and diene.
[h] Partial quenching; formation of adducts between ketone and diene.

an additional tlc. spot formed in the system **12** + 1,3-pentadiene, gave *m/e* 438 (M^+, $C_{28}H_{38}O_4$) in the mass spectrum, corresponding to an addition product of **12** + diene. The NMR. indicated the presence of several components. Corresponding results were also obtained in the systems **1** + 1,3-pentadiene, **1** + 1,3-cyclohexadiene [mass spectrum: *m/e* 408 (M^+, $C_{27}H_{36}O_3$)], and **12** + 1,3-cyclohexadiene.

Triketone **15**. – a) *From photoproduct* **13**. 500 mg Li were dissolved in 10 ml phosphoryl tri-(dimethylamide) and 10 ml ether under an Ar atmosphere. 100 mg (0.27 mmol) of **13** in 2 ml phosphoryl tri-(dimethylamide) and 20 ml ether were added dropwise with stirring. After the immediate work-up the crude product was dissolved in 20 ml acetone and oxidized for 3 min at room temperature with *Jones* reagent (8N CrO_3 in 8N H_2SO_4). The oxidation was stopped by the addition of CH_3OH. The work-up and filtration of the crude material through neutral Al_2O_3 (activity III) in CH_2Cl_2 gave 50 mg which were chromatographed on 5 g silica gel in benzene-ethyl acetate 8:1. 20 mg (23%) of *triketone* **15** were obtained. M.p. 186–188° (3 cryst. from acetone-hexane; 11 mg). $[\alpha]_D = +166°$ ($c = 0.6$). IR.: 1745. NMR.: 0.78 + 1.16 + 1.24 + 1.47/4*s*, CH_3-4′, -4″, -18, and -19; 2.08 + 2.92/2*d*, $J = 20$, CH_2-6; 2.98/*d*, $J = 2$, CH_2-2; 5.90/*t*, $J = 2$, CH-1; the coupling of the CH_2-6 *AX* system and of the CH-1/CH_2-2 *ABX* system was ascertained by double resonance experiments. Mass spectrum: $M^+ = 328$.

$C_{21}H_{28}O_3$ Calc. C 76.79 H 8.59% Found C 76.73 H 8.65%

Triketone **15** showed no intensified UV. absorption above 225 nm in methanolic 0.01N CH_3ONa solution.

b) *From photoproduct* **14**. 102 mg (0.26 mmol) of **14** were subjected to the procedure described above. 15 mg (18%) of *triketone* **15** were obtained. The samples from the two preparations were dentified by mixed m.p., $[\alpha]_D$, IR., NMR., mass spectrum, and tlc.

Base-catalyzed deuteration of triketone **15**. A solution of 10 mg of **15** in 1 ml dioxane + 1 ml D_2O containing 1% KOH was refluxed for 2 h under argon. The work-up with ethyl acetate and D_2O and chromatography of the crude product (9.4 mg) on 1 g silica gel with hexane-acetone 4:1 gave 2 mg of *deuterated* **15**. Mass spectrum: 88% d_7 ($M^+ = 335$), 12% d_6. NMR. (100 MHz, using CAT for 2.5 h): the former *t* at 5.9 appeared as *s* at 5.82, and the *d* at 2.08, 2.92, and 2.98 had disappeared. The deuterated material was indistinguishable from **15** by tlc.

3,7-Dioxo-4,4-dimethyl-17β-acetoxy-1 (*10* → *5α*)-abeo-*6β,10β-cyclo-androstane* (**16**). 53 mg (0.14 mmol) of **13** were hydrogenated for 20 min on *Raney* nickel in 6 ml C_2H_5OH. Two crystallizations of the crude product from hexane-CH_2Cl_2 gave 44 mg **16**. M.p. 178–179°. $[\alpha]_D = +40°$ ($c = 1.0$). UV. (iso-octane): end absorption ε_{210} 4600. IR.: 1240, 1720, 1745. NMR.: 0.80 + 1.18 + 1.33 + 1.45/4*s*, CH_3-4′, -4″, -18, and -19; 2.05/*s*, 17-OCOCH$_3$; ca. 4.6/*bt*, CH-17. Mass spectrum: $M^+ = 372$.

$C_{23}H_{32}O_4$ Calc. C 74.16 H 8.66% Found C 74.01 H 8.72%

3,7-Dioxo-4,4-dimethyl-17β-acetoxy-1 (*10* → *5α*)-abeo-$\Delta^{1;9,10}$-*androstadiene* (**17**). 76 mg (0.21 mmol) of **13** were dissolved in 7.6 ml of a 0.5% solution of H_2SO_4 in CH_3COOH and heated to 75° for 1.5 h. The reaction mixture was poured into a saturated $NaHCO_3$ solution. Work-up and filtration of the crude product in CH_2Cl_2 through neutral Al_2O_3 (activity III) gave 71 mg which were chromatographed on 8 g silica gel in hexane-acetone 8:1. 43 mg (57%) **17** were obtained. M.p. 123 to 124° (3 cryst. from hexane-acetone; 35 mg). $[\alpha]_D = +197°$ ($c = 1.66$). UV. (iso-octane): 212 (13300). IR.: 1240, 1595, 1715, 1735 (shoulder). NMR. ($CDCl_3$): 0.84 + 0.98 + 1.04/3*s*, CH_3-4′, -4″, and -18; 1.47/finely split *s*, CH_3-19; 2.04/*s*, 17-OCOCH$_3$; 2.53 + 2.61/central two peaks of CH_2-6 *AX* pattern; ca. 4.7/*bt*, CH-17; 6.25 + 7.23/2*d*, $J = 6$, CH-2 and -1; (C_6D_6): 0.72 + 0.81 + 1.02/3*s*, CH_3-4′, -4″, and -18; 1.12/finely split *s*, CH_3-19; 1.67/*s*, 17-OCOCH$_3$; 2.18 + 2.20/central two peaks of CH_2-6 *AX* pattern; ca. 4.7/*bt*, CH-17; 5.95 + 6.55/2*d*, $J = 6$, CH_2-2 and -1. Mass spectrum: $M^{+\cdot} = 370$.

$C_{23}H_{30}O_4$ Calc. C 74.56 H 8.16% Found C 74.54 H 8.10%

Acid-catalyzed isomerization of compound **16**. 75 mg (0.21 mmol) of **16** were dissolved in 8 ml of a 0.5% solution of H_2SO_4 in CH_3COOH and heated to 100° for 3 h. The reaction mixture was poured onto a saturated $NaHCO_3$ solution and worked up. Filtration of the crude product through neutral Al_2O_3 (activity III) in CH_2Cl_2 gave 59 mg which were chromatographed on 35 g silica gel in benzene-ethyl acetate 10:1. 8.4 (11%) mg of *3,7-dioxo-4,4-dimethyl-17β-acetoxy-*Δ^5-*androstene* (**8**) (identified with authentic material by mixed m.p., IR., NMR., mass spectrum, and tlc.) and 32 mg of *3,7-dioxo-4,4-dimethyl-17β-acetoxy-1* (*10* → *5α*)-abeo-$\Delta^{8,9}$-*10ξ-androstene* (**20a**) were obtained. Sample

20a could not be crystallized; it contained a yellow impurity which could not be removed. UV. (C_2H_5OH): 252 (8130). IR.: 1240, 1615, 1670, 1740. NMR.: 0.86+1.02+1.10/3*s*, CH_3-4′, -4″, and -18; 1.28/*d*, *J* = 8, CH_3-19; 2.02/*s*, 17-OCOCH_3; ca. 4.7/*bt*, CH-17. Mass spectrum: M^+ = 372 ($C_{23}H_{32}O_4$). The IR., NMR., and mass spectra, and tlc. of this sample corresponded to those of the crystalline compound **20a** described below.

3,7-Dioxo-4,4-dimethyl-17β-hydroxy-1 (10→5α)-abeo-*Δ⁸,⁹-10ξ-androstene* (**21a**). 28 mg (0.075 mmol) of the oily sample **20a** (see above) were hydrolyzed overnight at room temperature in 2 ml of a saturated methanolic K_2CO_3 solution. The crude product (22 mg) was chromatographed on 2.5 g silica gel in benzene-ethyl acetate 4:1. 13 mg (52%) of non-crystalline **21a** were obtained. UV. (C_2H_5OH): 254 (7250). IR.: 1610, 1670, 1745, 3600. NMR.: 0.70+1.02+1.08/3*s*, CH_3-4′, -4″, and -18; 1.27/*d*, *J* = 7, CH_3-19; ca. 3.7/*bt*, CH-17. Mass spectrum: M^+ = 330 ($C_{21}H_{30}O_3$).

3,7-Dioxo-4,4-dimethyl-17β-acetoxy-1 (10→5α)-abeo-*Δ¹;⁸,⁹-10ξ-androstadienes* **19a** *and* **19b**. A solution of 240 mg (0.65 mmol) of **17** and 240 mg CH_3ONa in 20 ml C_2H_5OH was refluxed under argon for 1 h. The crude *product mixture* (**18a+b**) had IR. bands at 1620, 1667, 1720, 3600, and tlc. showed one spot. The mixture was treated with 3 ml of acetic anhydride-pyridine 1:1 at room temperature, then taken to dryness by azeotropic distillation with toluene, and the residue was filtered through neutral Al_2O_3 (activity III) in CH_2Cl_2. Chromatography of the eluate (204 mg) on 20 g silica gel in hexane-acetone 4:1 gave the *two (C-10)-diastereoisomeric 3,7-dioxo-4,4-dimethyl-17β-acetoxy-1 (10→5α)*-abeo-*Δ¹;⁸,⁹-androstadienes:*

1. 13 mg of a mixture of **19a+19b**.

2. 79 mg (33%) **19a**, m.p. 183–184° (3× cryst. from acetone-hexane; 61 mg). $[\alpha]_D$ = −50° (*c* = 0.36). IR.: 1240, 1615, 1670, 1725, 1745. UV. (C_2H_5OH): broad absorption, with λ_{max} at ca. 238 (11500) and ca. 250 (shoulder, 10400). NMR.: 0.87 (3H)+1.09 (6H)/2*s*, CH_3-4′, -4″, and -18; 1.15/*d*, *J* = 8, CH_3-19; 2.08/*s*, 17-OCOCH_3; ca. 4.8/*bt*, CH-17; 6.20+7.63/2*d*, *J* = 6, CH-2 and -1. Mass spectrum: M^+ = 370.

$C_{23}H_{30}O_4$ Calc. C 74.56 H 8.16% Found C 74.38 H 8.17%

3. 48 mg (25%) **19b**, m.p. 200–201° (3× cryst. from acetone-hexane; 23 mg). $[\alpha]_D$ = −29° (*c* = 0.32). UV. (C_2H_5OH): broad absorption, with λ_{max} at ca. 224 (9800) and ca. 250 (8400). IR.: 1240, 1610, 1665, 1720, 1740. NMR.: 0.83 (3H)+1.10 (6H)/2*s*, CH_3-4′, -4″, and -18; 1.23/*d*, *J* = 7, CH_3-19; 2.15/*s*, 17-OCOCH_3; ca. 4.8/*bt*, CH-17; 6.20+7.60/2*d*, *J* = 6, CH-2 and -1. Mass spectrum: M^+ = 370 ($C_{23}H_{30}O_4$).

3,7-Dioxo-4,4-dimethyl-17β-acetoxy-1 (10→5α)-abeo-*Δ⁸,⁹-10ξ-androstenes* **20a** and **20b**. – a) 33 mg (0.09 mmol) of **19a** in 5 ml C_2H_5OH were hydrogenated over *Raney* nickel for 2 min. Filtration through Celite and evaporation of the solvent, followed by two crystallizations from CH_2Cl_2-hexane, gave 27 mg (81%) **20a**, m.p. 183–184°. $[\alpha]_D$ = −60° (*c* = 0.26). UV. (C_2H_5OH): 252 (8650). IR., NMR., and mass spectra, and tlc. were identical with those of the non-crystalline material **20a** obtained from **16** (see above.).

$C_{23}H_{32}O_4$ Calc. C 74.16 H 8.66% Found C 74.02 H 8.70%

b) Hydrogenation of 24 mg (0.06 mmol) of **19b**, as described above in a), gave 13 mg (54%) of **20b** after two crystallizations from CH_2Cl_2-hexane. M.p. 162–163°. $[\alpha]_D$ 0° (0.37). UV. (C_2H_5OH): 252 (8600). IR.: 1240, 1615, 1670, 1745. NMR.: 0.84+0.92+1.01/3*s*, CH_3-4′, -4″, and -18; 1.18/*d*, *J* = 7, CH_3-19; 2.07/*s*, 17-OCOCH_3; ca. 4.7/*bt*, CH-17. Mass spectrum: M^+ = 372.

$C_{23}H_{32}O_4$ Calc. C 74.16 H 8.66% Found C 74.26 H 8.68%

3ξ-Hydroxy-4,4-dimethyl-7-oxo-17β-acetoxy-1 (10→5α)-abeo-*6β,10β-cyclo-androstane* (**22**). 396 mg (1.06 mmol) of **16** were reduced with 400 mg (10.5 mmol) $NaBH_4$ in 40 ml 1,2-dimethoxyethane for 13 min at room temperature. Work-up and chromatography of the crude product on 35 g silica gel in benzene-ethyl acetate 8:1 recovered 153 mg **16** (39%) and gave 151 mg **22** (39%) which could not be crystallized. Circular dichroism[5]: $\Delta\varepsilon_{224}$+4.45, $\Delta\varepsilon_{297}$−1.24 (C_2H_5OH). IR.: 1240, 1720, 1740, 3600. NMR.: 0.81 (3H)+0.93 (3H)+1.36 (6H)/3*s*, CH_3-4′, -4″, -18, and -19; 2.05/*s*, 17-OCOCH_3; 3.70/*bm*, CH-3; ca. 4.7/*bt*, CH-17. Mass spectrum: M^+ = 374 ($C_{23}H_{34}O_4$).

A solution of 5 mg **22** in 1.5 ml acetone was reoxidized with *Jones* reagent at room temperature for 1 min. Work-up and filtration of the crude product through neutral Al_2O_3 (activity III) gave *diketone* **16** (identification by IR., NMR., and tlc.).

3ξ,17β-Dihydroxy-4,4-dimethyl-7-oxo-1(10→5α)-abeo-*6β,10β-cyclo-androstane* (**23**). 4.5 mg of **22** were hydrolyzed in 2 ml of a saturated methanolic K_2CO_3 solution at room temperature over night under Ar atmosphere. The resulting *dihydroxy-cyclopropyl ketone* **23** had IR. bands at 1715 and 3600 cm^{-1}. Mass spectrum: $M^+ = 332$ ($C_{21}H_{32}O_3$).

3ξ,17β-Diacetoxy-4,4-dimethyl-7-oxo-1(10→5α)-abeo-*6β,10β-cyclo-androstane* (**24**). 40 mg of **22** were acetylated in 3 ml acetic anhydride-pyridine 1:1 at room temperature for 1 day. The solvents were removed azeotropically with toluene at 12 Torr. Filtration of the residue in CH_2Cl_2 through neutral Al_2O_3 (activity III) gave 30 mg (66%) **24** which could not be crystallized. UV. (isooctane): end absorption ε_{210} 3840. IR.: 1240, 1720, 1740. NMR.: 0.80+1.02+1.32+1.38/4*s*, CH_3-4′, -4″, -18, and -19; 2.03+2.08/2*s*, 3- and 17-OCOCH_3; ca. 4.7/*b*, CH-3 and -17. Mass spectrum: $M^+ = 416$ ($C_{25}H_{36}O_5$).

(C-5)-Diastereoisomeric acetoxy-dienediones **25**. 81 mg of **14** were dissolved in 8 ml of a 0.5% solution of H_2SO_4 in CH_3COOH and heated to 90° for 1.5 h. The reaction mixture was poured onto a saturated $NaHCO_3$ solution and worked up. Filtration of the crude product in CH_2Cl_2 through neutral Al_2O_3 (activity III) and chromatography on 8 g silica gel in benzene-ethyl acetate 8:1 gave 49 mg (60%) of a *ca. 1:1 mixture of the stereoisomers* **25** which could not be crystallized. [α] = +255° (*c* = 1.0). UV. (C_2H_5OH): 238 (15200). IR.: 1240, 1590, 1635, 1705, 1710, 1735. NMR. ($CDCl_3$, 100 MHz): 0.81+0.93+1.23/3*s*, CH_3-4′, -4″, and -18; ca. 2.04/finely split signal, CH_3-19; 2.08/*s*, 17-OCOCH_3; ca. 3.76/*m*, CH-5; ca. 4.7/*bt*, CH-17; 6.30/*m* (8 lines), CH-2; 7.62/*m* (5 lines), CH-1; (C_6D_6, 100 MHz): 0.74+0.82+1.44/3*s*, CH-4′, -4″, and -18; 1.21+1.24/2*s* (ca. 1.5H each), CH_3-19; 1.72/*s*, 17-OCOCH_3; 3.49+3.59/2*t* (ca. 0.5H each), CH-5; ca. 4.7/*bt*, CH-17; 6.11/*m* (6 lines), CH-2; ca. 7.1/*m* (C_6D_6 signal partly superimposed), CH-1. Decoupling experiments of the samples in $CDCl_3$ and C_6D_6 solutions gave $J_{1,2} = 5.5$ and $J_{1,5} \sim J_{2,5}$ = ca. 2. Mass spectrum: $M^+ = 370$ ($C_{23}H_{30}O_4$).

The UV. spectrum of a 0.01N CH_3ONa/CH_3OH solution of **25** showed absorption maxima at 242 (9300) and 305 (4660) [constant values after 2 h standing at room temperature, unchanged on acidification with CH_3COOH], indicative of a *mixture of* **25**+**27**.

The elemental analyses were carried out by Mr. *W. Manser* of the Microanalytical Laboratory of the ETH Zürich. NMR. spectra were measured in our Instrumental Division (Prof. *W. Simon*), and mass spectra by PD Dr. *J. Seibl*.

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