Tetrahedron. Vol. 28, pp. 3819 to 3826. Pergamon Press 1972. Printed in Great Britain

PHOTOCHEMICAL TRANSFORMATIONS OF GIBBERELLIN A_3 DERIVATIVES

THE ADDITION OF HYDROGEN-DONATING SOLVENTS TO A STRAINED CYCLOHEXENONE

E. P. SEREBRYAKOV, N. S. KOBRINA and V. F. KUCHEROV

Zelinsky Institute for Organic Chemistry, the USSR Academy of Sciencies, Moscow-117913, USSR

and

G. ADAM and K. SCHREIBER

Institute for Plant Biochemistry of the Research Centre for Molecular Biology and Medicine,
German Academy of Sciences at Berlin, Halle/Saale, GDR

(*Received* 22 *February* 1972; *Accepted for publication* 7 *April* 1972)

Abstract—The photochemistry of enone (I) in ethanol, isopropanol and dioxan have been investigated. In all three cases the following reaction types have been found: (a) photoreduction of the Δ^1-double bond leading to the saturated ketone (IV); (b) C-addition of a solvent molecule to this bond leading to the corresponding 1-substituted ketones (VI, XI or XII); (c) photoaromatization of ring A; (d) extensive cyclodimerization leading to the products of type XIII. Only the latter process is observed when I is photolyzed in carbon tetrachloride. In EtOH and iso-PrOH the formation of the O-adducts (V and X) also takes place. Some mechanistical aspects are discussed on the basis of qualitative quenching experiments in ethanol and dioxan.

IN our preliminary communications we described the photolysis of the 3-keto derivative of gibberellin A_3 methyl ester (I) in hydrogen-donating solvents such as ethanol[1] and dioxan.[2] Now we present a more detailed account of these experiments together with additional results obtained upon UV-irradiation of I in isopropanol and carbon tetrachloride.

When I is photolyzed in EtOH (in quartz or pyrex) it gives rise to a complex mixture of products which after chromatography on silica gel afforded the following compounds: (a) the previously described[3] 3-keto-derivative of gibberellin A_1 methyl ester (IV), yields 5–9%; (b) a mixture of previously described[1] phenols II and III, yields 6·5–16%; (c) an alkoxy ketone $C_{22}H_{28}O_7$ (V), yields 3–9%; (d) a keto alcohol $C_{22}H_{28}O_7$ (VI), yields 11–15% and (e) a mixture of lactone-containing dimers.* The transformation of I must be fairly rapid since the composition of the photolysate is nearly the same after 2 or 8 hr irradiation.

The reduced ketone IV was identified by its IR, UV, NMR and mass spectra as well as by TLC. The mixture of phenols II and III was identified in a similar way and shown to be nearly equimolecular by combined gas chromatography-mass spectrometry.

---

* In contrast to these results, the photolysis of I in methanol gives only intractable tars from which no individual products could be isolated.

The structure of the O-adduct V (m.p. 115–118°) is based on the following evidence. Its IR spectrum shows the presence of a γ-lactone (1780 cm^{-1}), a keto group in the saturated 6-membered ring (1720 cm^{-1}), an OH (3475 cm^{-1}), and an exocyclic methylene (1665 and 905 cm^{-1}). The mass spectrum of V displays the same fragmentation pattern which was found earlier[4] to be typical for C-19 gibberellins, but in addition contains a noticeable peak at 305 mu. The corresponding ion must originate from the molecular ion as it follows from the occurrence of a metastable peak at 230·6 mu.; this probably corresponds to the loss of the C_3—C_2—C_1—OEt fragment. The presence of the OEt group is confirmed by the NMR spectrum of V with resonance at δ 1·20 (3H, t, $J = 7$ c/s) and 4·00 ppm (2H, q, $J = 7$ c/s). The signal of the $-\overset{|}{\mathrm{C}}\mathrm{H}-\mathrm{O}-$ grouping at C_1 appears at δ 3·64 as an X-part of an ABX-system ($J_{AX} + J_{BX} = 7$ c/s) which is to some extent masked by the signal of the COOMe group at δ 3·58 ppm. In other respects the NMR spectrum of V is similar to that of the starting enone I (AB-system of protons at C_5 and C_6, an exocyclic methylene). Since enone I slowly adds one molecule of MeOH under mild conditions,[5] it was necessary to check whether the O-adduct could arise from the thermal dark reaction. The light-induced formation of this adduct was proved by the fact that I gives no traces of V on standing in ethanol (28–30°, 40 hr).

The C-adduct VI (m.p. 217–221°) displays in the IR spectrum strong bands at 3500–3100 (OH), 1780 (γ-lactone) and 1735–1725 cm^{-1}, the latter being caused by two CO groups (COOMe and 3-ketone). The NMR spectrum of VI reveals the presence of the fragment $\mathrm{CH_3CH(OH)}-\overset{|}{\mathrm{C}}\mathrm{H}-\mathrm{CH_2}-\overset{|}{\mathrm{C}}\mathrm{O}$, since it contains a Me doublet at δ 1·07 ($J = 6$ c/s) which correlates with a one-proton signal at 3·98 ppm ($J = 6$ c/s, $J' = 2$ c/s); saturation at 3·98 ppm transforms that Me doublet into a singlet. The mass spectrum of VI is similar to those of other C-19 gibberellins, but the base peak appears at 304 mu. and seems to correspond to the direct elimination of the fragment C_3—C_2—C_1—CH(OH)CH_3 from the molecular ion. On prolonged acetylation VI affords an amorphous diacetate (VIa), characterized by IR, NMR and mass spectra.

The configuration at C_1 in the O-adduct V and in the C-adduct VI was deduced by the following empirical approach. Two methoxy ketones obtained earlier[5] from I and epimeric at C_1 were used as reference compounds. In the NMR spectra of both methoxy ketones the signals of the methine proton at C_1 appear as well resolved X-parts of the ABX-system. In the low-melting epimer, where $J_{AX} = J_{BX} = 3{\cdot}5$ c/s (three lines) the hydrogen at C_1 must be equatorial and hence this methoxy ketone can be formulated as VII. The high-melting epimer ($J_{AX} + J_{BX} = 12$ c/s, four lines) in which C_1-proton is axial, can be formulated as VIII. This assignment of configurations is opposite to one made earlier[6] on the basis of mass-spectrometric evidence. The comparison of the CD of these two compounds with that of the unsubstituted parent ketone IV shows that the 1β-epimer VII displays nearly the same amplitude as IV while in the 1α-epimer VIII the positive Cotton effect is considerably greater. A similar situation was observed in the case of the previously described 1β-hydroxy ketone (IX) whose stereochemistry at C_1 had been firmly established by chemical studies and NMR spectra;[7] here the amplitude is even smaller than in the parent ketone IV. Since in the case of the O-adduct V the amplitude of the positive

Cotton effect is also very close to that of IV, the OEt group in V appears to possess axial 1β-orientation; this conclusion is in agreement with that derived from the NMR spectrum of V. In the case of the C-adduct VI the amplitude of the positive Cotton effect is about the same as in the case of 1α-methoxy ketone VIII. Therefore, the orientation of the 1-substituent in VI is supposed to be equatorial, that is, 1α. The amplitudes of ketones IV–IX are given in Table 1; a detailed description will be published elsewhere.[8]

TABLE 1. CONFIGURATIONS OF 1-SUBSTITUTED 3-KETO DERIVATIVES OF GIBBERELLIN A_3 METHYL ESTER AS DEDUCED FROM THE NMR SPECTRA AND FROM CD CURVES

Compound	$J_{AX} + J_{BX}$ (in c/s)	Configuration at C_1 (NMR-data)	Amplitude a	Configuration at C_1 (CD-data)
IV	—	—	+144°	—
VII	7	a (1β)	+146·8°	a (1β)
VIII	12	e (1α)	+180°	e (1α)
IX	7	a (1β)	+132°	a (1β)
V	~7 cs	a (1β)	+148°	a (1β)
VI	—	—	+175·8°	e (1α)

The photolysis of I in isopropanol (in quartz) gives qualitatively similar results as the photolysis in ethanol. Both the O-adduct $C_{23}H_{30}O_7$ (X) and the isomeric C-adduct (XI) were obtained in nearly equal yields (5–8%) together with a phenolic fraction containing II and III (6–9%). Again, the dimerization of I was the most prominent process (55–65% yield). The structures of X and XI are based on their IR, NMR and mass spectra (Experimental); no attempt was made to determine the stereochemistry at C_1. The non-equivalence of the Me groups in the side chain of XI as revealed by its NMR spectrum (δ 1·17 ppm, 3H, s and 1·25 ppm, 3H, s instead of a 6-proton singlet) points to the great steric crowding in the C-adduct.

The photolysis of I in dioxan (through pyrex) gave a similar product composition. Chromatography on silica gel afforded the following compounds: (a) the reduced ketone IV (4·5%), (b) an adduct of I with dioxan (XII), isolated in 11% yield; (c) the tetracyclic phenol II (4·5%), (d) a mixture of isomeric cyclobutane-type dimers (XIII) obtained in more than 60% yield. In the mass spectrum of XII the peak of the molecular ion appears at 446 mu. which implies the addition of one molecule of dioxan (88 mu.). The UV spectrum of XII contains only the band of a saturated ketone at 282 nm (ε 212); accordingly, XII exhibits a positive Cotton effect at 295 nm (a = +106·5°). The NMR spectrum of XII displays a broad signal centred at 3·76 ppm which accounts for seven protons in the dioxan ring and a $COOCH_3$ group. Since the addition to the β-face of enone I must be sterically less hindered and hence more probable, the configuration of XII at C_1 is assumed to be 1β. The tetracyclic phenol II obtained in dioxan was practically free from admixture of III as could be seen from the GLC analysis, mass spectrum and specific rotation ($[\alpha]_D$ +39·2°).

Also in dioxan the main photochemical reaction of I is the formation of a large dimer fraction which in this case was investigated in a more detailed way. After repeated crystallization a product with m.p. 215–221° (dec) and $[\alpha]_D$ +39·8° was obtained in 32% yield. The mass spectrum (M^+ 716) shows that this product results from the dimerization of I. The IR spectrum contains the bands corresponding to γ-lactone (1780 cm^{-1}), saturated 6-membered ketone and ester carbonyl (1728 cm^{-1}). The presence of saturated keto groups (confirmed by UV absorption at 286 nm and by a positive Cotton effect at 300 nm) indicates a cyclobutane dimer structure (XIII *a*, *b*); for both structural types a mixture of stereoisomers can be supposed. The same product has been obtained upon photolysis of I in carbon tetrachloride in 90% yield.

Since all photochemical transformations of I can be initiated by UV irradiation in pyrex ($\lambda \leq 310$ nm) they must be due to the primary n,π*-excitation of the enone chromophor. When photolysis of I in EtOH was carried out in the presence of 2,3-dimethylbuta-1,3-diene, a triplet quencher with $E_T \leq 60$ kcal/mole,[9] small amounts of the quencher reduced and larger amounts nearly suppressed the dimerization of I

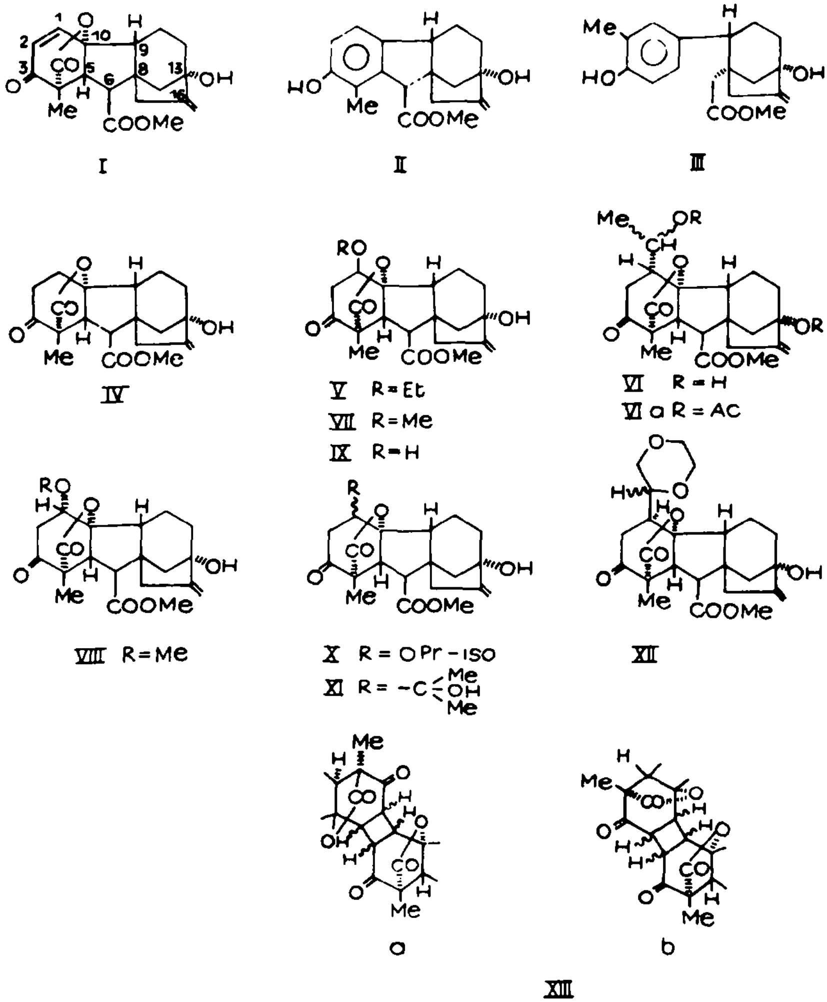

FIG 1

so that the latter reappeared in the photolysate (~26% yield); also the dimer of dimethylbutadiene was obtained and identified by its mass spectrum (M^+ 164). At the same time the formation of the reduced ketone IV and the C-adduct VI fell to ~2 and 6·6%, respectively, while the yields of the O-adduct V (6·2%) and phenols II and III (17·7%) remained unaffected or even slightly increased. Therefore, the dimerization of I, like that of many other conjugated cyclenones[10] proceeds via the lowest triplet state, while the formation of II, III and V seems to take place through states different from T_1 (n,π^*). The experiments with the same quencher in dioxan also showed a strong decrease in the formation of cyclodimers of I (from 62 to 10%) and thus confirmed the role of the lowest triplet state in dimerization of I. At the same time the yield of phenol II increased from 4·5 to 15%. On the other hand, neither the C-adduct XII nor the reduced ketone IV could be detected in the photolysate. Therefore, the formation of these products upon irradiation of I in dioxan takes place via the lowest triplet state. Thus, the formation of IV and also of the C-adducts (VI or XII, respectively) in ethanol or in dioxan appears to proceed through a common pathway (see scheme below).

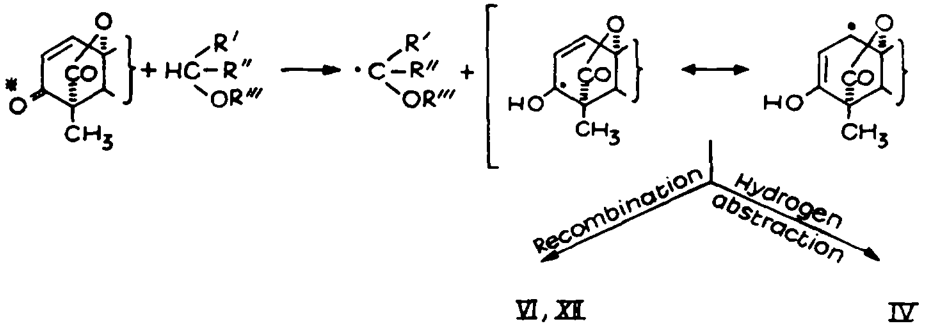

FIG 2

The simultaneous O- and C-addition of EtOH or iso-PrOH to the conformationally rigid cyclohexenone system deserves special attention. The photo-induced addition of aliphatic alcohols to the conjugated cyclenones proceeds differently for 5- and 6-membered systems. The latter are known to form O-adducts,[11–14] while the former react to give C-adducts.[15,16] The polar O-addition to cyclohexenones may be conceived[12] as a combination of photochemical *cis* → *trans* isomerization with thermal Michael addition. 5-Membered enones, uncapable of such isomerization because of the angle strain, undergo C-addition of free-radical type. The case of enone I, where the C-addition of alcohols to a cyclohexenone is observed for the first time, seems to reflect the importance of the ring flexibility for the reactivity of photoexcited cyclenones in hydrogen-donating solvents.

EXPERIMENTAL

M.ps are corrected. IR spectra: UR-10 instrument (Zeiss, Jena). UV spectra: (a) Unicam SP-700 (EtOH) or (b) Ultrascan (Hilger & Watts) (MeOH). NMR spectra: (a) Varian DA-60-IL and Jeol-100 or (b) Varian HA-100. Mass spectra: (a) MX 1303 instrument or (b) electron-attachment mass spectrograph of the Research Institute Manfred von Ardenne. ORD measurements: JASCO-ORD/UV-5 instrument. CD measurements: Spectropol-1 instrument (in dioxan). All irradiations were carried out under dry argon. Column chromatography: (a) KSK silica gel, 60–90 mesh or (b) silica gel Woëlm for partition chromatography.

Photolysis of enone I *in* EtOH

(i) A soln of enone I (990 mg) in abs EtOH (300 ml) was divided in two portions and each was irradiated in a flat-bottomed quartz flask by two lamps PRK-4 (2 × 220 w). The distance between the light source and the flask bottom was 10 cm (28–30°, external air cooling). The evolving CO_2 was trapped by $Ba(OH)_2$. After 2 hr of photolysis both portions were recombined and evaporated to dryness. The residue (∼1 g) was chromatographed on 50 g of silica gel (a).

Elution with benzene–chloroform (3:7 and 2:8) afforded ketone IV (95 mg) as chromatographically pure amorphous solid, identified with the previously described specimen[3] by its IR and mass spectra and by TLC analysis. UV spectrum (a): 294 nm (ε 77). NMR spectrum (a, in $CDCl_3$): δ 1·08 (3H, s); 2·12 (2H, m); 2·70 and 2·98 (2H, AB-system, J_{AB} – 9·5 cs); 3·62 (3H, s); 4·89 (1H) and 5·17 (1H) ppm.

Elution with benzene–chloroform (1:9) and pure chloroform gave a gum (143 mg) which after purification by plate chromatography on alumina (benzene–MeOH 93:7) afforded a mixture of phenols II and III as chromatographically homogeneous amorphous solid. The analysis by combined gas chromatography—mass spectrometry (LKB instrument) showed that phenol II (M^+ 314) and phenol III (M^+ 316) were in nearly equal (∼55:45) amounts. UV-spectrum (α): 228 (ε 5800) and 287 nm (ε 1750).

Elution with pure chloroform gave the crystalline O-adduct V (93 mg), m.p. 115–118° (needles, from ether–hexane). IR spectrum (in KBr pellets): 3475, 1780, 1740, 1720, 1665, 1390, 1210, 1175 and 905 cm^{-1}. NMR spectrum (a, in $CDCl_3$): δ 1·12 (3H, s); 1·20 (3H, t, $J = 7$ cs); 2·18 (2H, m); 2·70 and 3·00 (2H, AB-system, $J_{AB} = 8$ cs); 3·58 (3H, s), 3·64 (1H, X-part of the ABX-system, $J_{AX} + J_{BX} \approx 7$ cs); 4·05 (2H, q, $J = 7$ cs); 4·88 (1H) and 5·18 (1H) ppm. Mass spectrum (a): M^+ 404 (0·35), *m/e* 386 (0·65); 372 (1·0); 358 (0·60); 354 (0·30); 345 and 344 (0·50); 330 (0·40); 305 (0·65); 272 (0·20); 256 (0·45); 145 (0·55) and 135 (0·50) m.u.

Elution with chloroform–EtOAc (9:1 and 8:2) gave a solid, which after crystallization from EtOAc–hexane afforded C-adduct VI (110 mg) as prisms with m.p. 217–221°. IR spectrum (in KBr pellets): 3390, 1780, 1735, 1665, 1390, 1260, 1180, 1100 and 905 cm^{-1}. NMR spectrum (a, in d_6-acetone): δ 0·94 (3H, s); 1·07 (3H, d, $J = 6$ cs); 2·38 (2H, m); 2·68 and 3·12 (2H, AB-system, $J = 11$ cs); 3·62 (3H, s); 3·98 (1H, m, $J = 6$ cs, $J' = 2·5$ cs); 4·78 (1H) and 5·12 (1H) ppm. Mass spectrum (a): M^+ 404 (0·50), *m/e* 386 (0·15); 372 (0·35); 360 (0·15); 358 (0·26); 345 and 344 (0·15); 342 (0·10); 328 (0·25); 314 (0·10); 304 (1·0); 303 (0·30); 300 (0·15); 286 (0·10); 255 (0·25); 245 (0·28); 163 (0·40) and 135 (0·55) mu.

Acetylation with Ac_2O-pyridine (20°, 14 days) followed by plate chromatography on alumina (benzene-EtOAc 9:1) afforded the diacetate VIa as chromatographically pure amorphous solid. IR spectrum (in KBr pellets): 1780, 1735, 1240, 1230, 905 cm^{-1}. NMR spectrum (a, in $CDCl_3$): δ 1·05 (3H, d, $J = 6$ cs); 1·17 (3H, s); 1·93 (3H, s); 2·05 (3H, s); 2·70 and 3·12 (2H, AB-system, $J_{AB} = 9$ cs); 3·60 (3H, s), 4·90 (1H); 5·05 (1H, m) and 5·20 (1H) ppm. Mass spectrum: M^+ 488, *m/e* 446, 428, 404, 386, 384, 346, 342 and 280 (base peak) mu.

More polar eluents (chloroform-EtOAc and pure EtOAc) afforded amorphous material (495 mg) identical with the previously described[1b] mixture of lactone-containing dimers of I by its IR spectrum and TLC behaviour.

(ii) A soln of enone I (1·00 g) in abs EtOH (300 ml) was photolyzed (in two portions) for 8 hr and the products were chromatographed on 50 g of silica gel (a). Elution with benzene–chloroform (2:8) afforded 60 mg of pure IV and then a gum (104 gm) which after plate chromatography on alumina gave the mixture of phenols II and III (67 mg) in about 1:1 ratio as judged by IR and mass spectra. Elution with chloroform afforded the O-adduct V (40 mg) with m.p. 113–117°, while the elution with chloroform–EtOAc (8:2) gave the C-adduct VI (160 mg) with m.p. 213–218°. More polar eluents afforded 570 mg of amorphous dimerization products.

(iii) A soln of enone I (1350 mg) in abs EtOH (405 ml) was irradiated in a cylindrical water-cooled (18–20°) pyrex reactor for 8 hr (lamp PPK-2M, 375 w) and the photolysate was chromatographed on 50 g silica gel (a) as described above. Ketone IV (70 mg) and the mixture of phenols II and III (45 mg) were obtained as white solid foams. Further elution afforded the O-adduct V (m.p. 115–117°, 50 mg), then the C-adduct VI (m.p. 213–219°, 124 mg) and the dimerization products (650 mg).

(iv) To a soln of enone I (500 mg) in abs EtOH (150 ml) freshly distilled 2,3-dimethylbuta-1,3-diene (4·6 g) was added and the resulting mixture (substrate-to-quencher ratio ∼1:40) was irradiated through pyrex for 8 hr. The products were chromatographed on 30 g of silica gel (a). Elution with benzene–chloroform (2:8) afforded first a gum (197 mg) containing IV and I (IR and UV data) from which the starting enone I (m.p. 179–182°, 110 mg) could be isolated by fractional crystallization from EtOAc. The mother liquor was re-cromatographed on 5 g of alumina to give pure IV (10 mg) and more I (21 mg). Elution with benzene–chloroform (1:9) gave pure phenolic fraction (79 mg) containing only II and III (ε_{285} = 1710, M^+ 314 and 316). Fractions eluted with pure chloroform contained the O-adduct V (35 mg). Elution with chloroform–EtOAc (9:1 and 8:2) afforded the crystalline C-adduct VI (m.p. 205–216°, 37 mg). Further elution with more polar solvents gave only 16 mg of dimers.

Attempted thermal addition of EtOH *to* I

A soln of enone I (200 mg) in 60 ml of abs EtOH was left for 40 hr in the dark at room temp (20–23°). Column chromatography afforded 195 mg of pure starting material, m.p. 179–183°, and no other products.

Photolysis of enone I *in* iso-PrOH

Enone I (500 mg) was dissolved in 150 ml of pure dry iso-PrOH and irradiated in quartz for 8 hr ($Ba(OH)_2$-test positive). The photolysis products were chromatographed on 25 g of silica gel (a).

Elution with benzene–chloroform (2:8) afforded ketone IV (17 mg) as yellowish solid foam. Elution with benzene–chloroform (1:9) gave a gum (51 mg) which was re-chromatographed on 2 g of silica gel to give the O-adduct X as chromatographically pure white solid foam (41 mg). IR spectrum (KBr pellets): 3450, 1775, 1730, 1660, 1170, 905 cm^{-1}. UV spectrum (a): 279 nm (ε 63). NMR spectrum (a, in $CDCl_3$): δ 1·17 (3H, s): 1·22 (6H, d, J = 6 cs): 2·53 (2H, m): 2·73 and 3·00 (2H, AB-system, J_{AB} = 9 cs); 3·67 (3H, s + 1H, m): 3·90 (1H, diffuse septiplet with J = 6 cs); 4·91 (1H) and 5·20 (1H) ppm. Mass spectrum (a): M^+ 418 (0·15), *m/e* 400 (0·10): 386 (1·00): 372 (0·40): 358 (0·60): 356 (0·35): 342 (0·25): 286 (0·20): 136 (0·45) mu.

Further elution with benzene–chloroform (1:9) and with pure chloroform gave 60 mg of gummy material which was re-chromatographed on silica gel (2 g). The mixture of phenols II and III (37 mg) was obtained and characterized by its UV, IR and mass spectra as above. Elution with chloroform–EtOAc (9:1) gave a brownish gum which was re-chromatographed on silica gel (2·5 g) to afford 43 mg of C-adduct XI as a white solid foam. IR spectrum (KBr pellets): 3400–3340, 1770, 1730, 1660, 1130, 905 cm^{-1}. UV spectrum (a): 279 nm (ε 55). NMR spectrum (a): δ 1·13 (3H, s): 1·17 (3H, s): 1·25 (3H, s): 2·17 (2H, m): 2·59 and 2·95 (2H, AB-system. J_{AB} = 8 cs): 3·63 (3H, s): 4·89 (1H) and 5·17 (1H) ppm. Mass spectrum (a): M^+ 418 (0·05); *m/e* 400 (0·15) 386 (0·45): 374 (0·25): 358 (0·30): 342 (0·15): 330 (0·10): 304 (0·30): 244 (0·15): 135 (1·0) mu. Further elution with more polar eluents gave only lactone-containing dimers (305 mg).

Photolysis of enone I *in dioxan*

(i) A soln of enone I (200 mg) in abs dioxan (25 ml) was irradiated in a pyrex vessel (lamp Th U 500, distance 6 cm, external air cooling). After 5·5 hr ($Ba(OH)_2$-test positive) the soln was evaporated and the residue was adsorbed on celite (400 mg) and chromatographed on 24 g of silica gel (b).

Elution with methylene chloride–EtOAc afforded ketone IV (9 mg) as chromatographically pure yellowish solid foam. Elution with methylene chloride–EtOAc 9:1 gave a foam (50 mg) which was re-chromatographed on 5 g of silica gel (b) to give the dioxan-addition product (XII) as chromatographically homogeneous white foam (28 mg), $[\alpha]_D^{20}$ +93·8° (c = 0·482, $CHCl_3$). IR spectrum (in CCl_4): 3610, 3080, 1790, 1736, 1660, 1172, 903 cm^{-1}. UV spectrum (b, in MeOH): 282 nm (ε 212). NMR spectrum (b, in $CDCl_3$): δ 1·23 (3H, s); 3·76 (10H, m): 5·00 (1H) and 5·28 (1H) ppm. Mass spectrum (b): M^+ 446, *m/e* 418, 414, 402, 387, 372, 360, 342, 328, 314, 304, 301, 254, 231, 199, 171, 163, 135, 121 mu. ORD (in MeOH): $[M]_{319}$ +5400°, $[M]_{296}$ =0°, $[M]_{269}$ −5250°, $[M]_{261}$ −5100°, $[M]_{254}$ −5000°, $[M]_{225}$ −0°, a = +106·5°.* Further elution with CH_2Cl_2–EtOAc 85:15 afforded amorphous phenol II (8 mg) with $[\alpha]_D^{19}$ +39·2° (c = 0·620, in EtOH), M^+ 314.

Elution of the former column with CH_2Cl_2–EtOAc 6:4 and gradually with pure EtOAc gave amorphous mixture of lactone-containing dimers (124 mg). Repeated crystallization from CH_2Cl_2–hexane afforded a crystalline fraction of dimers (62 mg) with m.p. 215–221° (dec) and $[\alpha]_D^{17}$ +39·8° (c = 0·500 in $CHCl_3$). IR spectrum (Nujol): 3595, 3073, 1780, 1728, 1643, 1173, 903 cm^{-1}, UV spectrum (b): 286 nm (shoulder, ε = 790). Mass spectrum (b): M^+ 716, *m/e* 698, 684, 672, 654, 628, 612, 552, 400, 356, 341, 321, 314, 254 (base peak) mu. ORD (in MeOH): $[M]_{320}$ +4200°, $[M]_{300}$ =0°, $[M]_{278}$ −5760°, $[M]_{269}$ −6280°, $[M]_{248}$ −10,060°, $[M]_{234}$ =0°, a = +142°.

---

* Note added in proof: On CD-measurements in dioxan XII showed amplitude a = +191°.

(ii) To a soln of enone I (100 mg) in abs dioxan (12 ml) freshly distilled 2,3-dimethylbuta-1,3-diene (0·727 g) was added and the resulting mixture (substrate-to-quencher ratio $\sim$1:32) was irradiated through pyrex for 5·5 hr. The photolysis product was chromatographed on 12 g of silica gel (b) as described before. Elution with CH_2Cl_2 gave 59 mg of a gum containing the starting enone I but no saturated ketone IV (IR, UV, and mass spectral data) from which pure starting enone I (m.p. 180–185°, 24 mg) could be isolated by fractional crystallization from acetone–hexane. Elution with CH_2Cl_2–EtOAc 7:3 gave pure amorphous phenol II (13 mg), $[\alpha]_D^{20}$ +38·2° (c = 0·631). Further elution with CH_2Cl_2–EtOAc 6:4 up to pure EtOAc afforded only 10 mg amorphous dimers (IR, UV and TLC behaviour) after crystallization from CH_2Cl_2, m.p. 216–223° (dec).

Photolysis of enone I *in carbon tetrachloride*

A saturated soln of enone I (90 mg) in CCl_4 (150 ml) was irradiated in a pyrex vessel for 2·5 hr. Already after 10 min precipitation of the dimers XIII began. The collected product was crystallized from CH_2Cl_2–hexane yielding 81·3 mg XIII, m.p. 216–223° (dec) and $[\alpha]_D^{18}$ +43·2° (c = 0·530), mass spectrum (b): M^+ 716; ORD (in MeOH): a + 120°, which shows identical behaviour in the IR and UV spectra as well as TLC with the dimers XIII obtained in dioxane.

Addendum. In this communication, as in an earlier,[7b] the nomenclature names of compounds used or obtained were ommitted. The representative nomenclature names are 20-nor-1β-ethoxy-10α,13α-dihydroxy-3-oxo-ent-gibberell-16-ene-7,19-dioic acid, 19 → 10 lactone methyl ester for V and 20-nor-1α-(1′-hydroxyethyl)-10α,13α-dihydroxy-3-oxo-ent-gibberell-16-ene-7,19-dioic acid, 19 → 10 lactone, methyl ester for VI.

Acknowledgement—We are indebted to Dr. B. V. Rosynov and Mr. A. I. Kalinovsky (Moscow) and Dr. Habil. R. Tümmler (Dresden) for mass spectra; we are also indebted to Mrs. U. Hof (Halle) and to Ms. S. I. Poludnitzyna (Moscow) for technical assistance.

REFERENCES

[1] I. A. Gurvich, N. S. Kobrina, E. P. Serebryakov and V. F. Kucherov, *Izvest. Akad Nauk SSSR, Ser. Khim.* 2342 (1969)

[2] G. Adam, *Z. Chem.* **10**, 140 (1970)

[3] I. A. Gurvich, N. S. Kobrina and V. F. Kucherov, *Izvest. Akad. Nauk SSSR, Ser. Khim.* 2626 (1968)

[4] N. Takahashi, N. Murofushi, S. Tamura, N. Wasada, H. Hoshina, T. Tsuchiya, S. Sasaki, T. Aoyama and E. Watanabe, *Org. Mass Spectrom.* **2**, 711 (1969) and refs therein

[5] I. A. Gurvich, I. M. Milštein, V. F. Kucherov, *Izvest. Akdd. Nauk SSSR, Ser. Khim.* 184 (1966)

[6] I. A. Gurvich, S. S. Yufit, I. M. Milštein and V. F. Kucherov, *Ibid.* 2233 (1966)

[7] [a] I. A. Gurvich, N. S. Kobrina and V. F. Kucherov, *Ibid.* 184 (1970);
[b] I. A. Gurvich, N. S. Kobrina, E. P. Serebryakov and V. F. Kucherov, *Tetrahedron* **27**, 5901 (1971)

[8] E. P. Serebryakov, N. S. Kobrina and V. F. Kucherov, *Izvest. Akad. Nauk SSSR, Ser. Khim.* in press

[9] G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.* **85**, 477 (1963)

[10] P. E. Eaton, *Accounts Chem. Res.* **1**, 50 (1968)

[11] B. J. Ramey and P. G. Gardner, *J. Am. Chem. Soc.* **89**, 3949 (1967)

[12] M. Rubin, *Israel. J. Chem.* **7**, 49 (1969)

[13] P. J. Kropp and H. J. Krauss, *J. Org. Chem.* **32**, 3222 (1967)

[14] T. Matsuura and K. Ogura, *J. Am. Chem. Soc.* **88**, 2602 (1966)

[15] M. Pfau, R. Dulou and M. Vilkas, *C.R. Acad. Sci., Paris* **254**, 1817 (1962)

[16] [a] J. A. Williams and P. Bladon, *Tetrahedron Letters* 257 (1964);
[b] P. Bladon and J. A. Williams, *J. Chem. Soc.* (C), 2032 (1967)