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PHOTOCHEMISTRY OF ENOLIC SYSTEMS—III[1]

IRRADIATION OF ENOL BENZOATES[2]

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Abstract—Irradiation of enol benzoates with a low pressure mercury lamp was studied. Irradiation of isopropenyl benzoate (I) and the steroidal enol benzoate, XV and XVI, gave the rearranged products, benzoylacetone (II) and α-benzoylketones XVII and XXI respectively. However, irradiation of cyclohexen-1-yl benzoate (III) and its 6-methyl derivative VIII resulted in ring cleavage, as well as benzoyl migration, to give V and XIII respectively.

IN THE irradiation of enol acetates in cyclohexane with a low pressure mercury lamp, the acetyl group migrates from oxygen to the vinylic carbon atom.[1,3] In the thermal rearrangement of enol acetates similar acyl migration as well as other processes occur.[4a,b] Both the thermal and photochemical acyl migrations take place intramolecularly,[3,4a] although in the thermal reaction they probably occur in a concerted manner,[4] whereas the action of the light results in a cleavage of the oxygen–carbonyl bond, to give a radical pair.[3] This radical pair, may be enclosed in a solvent cage,[3] though other mechanisms of their recombination cannot be excluded.

At high temperatures (400–500°)[4], enol benzoates undergo a similar Fries rearrangement in addition to other fragmentation processes, the most significant yielding benzoic acid and acetylene derivatives. A concerted mechanism was also proposed for the latter processes.[4d]

The irradiation of related phenol esters of aromatic and aliphatic acids, thoroughly investigated by several groups,[5] results in an intramolecular migration, to give *ortho* and *para* substituted acyl or aryl phenols. In addition the irradiation of phenyl and substituted phenyl benzoates yields, in some instances, benzoic acid derivatives. The isolation of benzoic acid presumably indicated a cleavage of the phenyl–oxygen bond, although the fate of the other component of this cleavage, the phenyl radical, remained undetermined.[5a,b]

The irradiation of enol benzoates was also performed in cyclohexane, like the

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[1] Part II, M. Gorodetsky and Y. Mazur, *J. Amer. Chem. Soc.* **86**, 5213 (1964).

[2] Published as preliminary communication, M. Gorodetsky and Y. Mazur, *Tetrahedron Letters*, 369 (1963).

[3] A. Yogev, M. Gorodetsky and Y. Mazur, *J. Am. Chem. Soc.* **86**, 5208 (1964).

[4] [a] F. G. Young, F. C. Frostick, J. J. Sanderson and C. H. Hauser, *J. Am. Chem. Soc.* **72**, 3635 (1950); [b] R. J. P. Allan, R. L. Forman and P. D. Ritchie, *J. Chem. Soc.* 2717 (1955); [c] W. M. Muir and P. D. Ritchie, *Ibid.* 2692 (1963); [d] P. E. Reininger and P. D. Ritchie, *Ibid.* 2678 (1963).

[5] [a] J. C. Anderson and C. B. Reese, *Proceedings Chem. Soc.* 217 (1960); [b] J. C. Anderson and C. B. Reese, *J. Chem. Soc.* 1781 (1963); [c] R. A. Finnegan and A. W. Hagen, *Tetrahedron Letters*, 365 (1963); [d] R. A. Finnegan and J. J. Mattice, *Tetrahedron* **21**, 1015 (1965); [e] H. Kobsa, *J. Org. Chem.* **27**, 2293 (1962); [f] W. M. Horspool and P. L. Pauson, *J. Chem. Soc.* 5162 (1965).

irradiation of enol acetates,[3] with a low pressure mercury lamp emitting at 253·7 mμ, and the progress of the reaction was followed by the measurement of the UV absorptions. Enol benzoates have a maximum absorption at *ca.* 230 mμ (ε *ca.* 15,000), and α-benzoylketones produced exist partly in their enolic form, absorbing at longer wavelength at *ca.* 310 mμ.[6,7] The irradiation was therefore followed by UV measurements, and was stopped when the absorption band at *ca.* 310 mμ reached the maximum intensity. The conversion was usually faster than in the corresponding enol acetates[3] which may be due to much higher UV absorption of the enol benzoate system. The latter has a higher extinction coefficient (ε *ca.* 3500), compared with that of enol acetates (ε *ca.* 30–50) at 253·7 mμ mercury line.

No significant difference was observed between the UV spectrum of the enol benzoates and the saturated benzoates (alkyl esters of benzoic acids). The latter absorb also at *ca.* 230 mμ (ε *ca.* 15,000).[8] The absorption maximum in both the enol benzoates and the benzoate esters shifts by *ca.* 0·5—1 mμ to longer wavelength in methanol, as compared with cyclohexane.[8] The similarity of the UV spectra of enol benzoates and the alkyl esters of benzoic acids suggests a small contribution of the

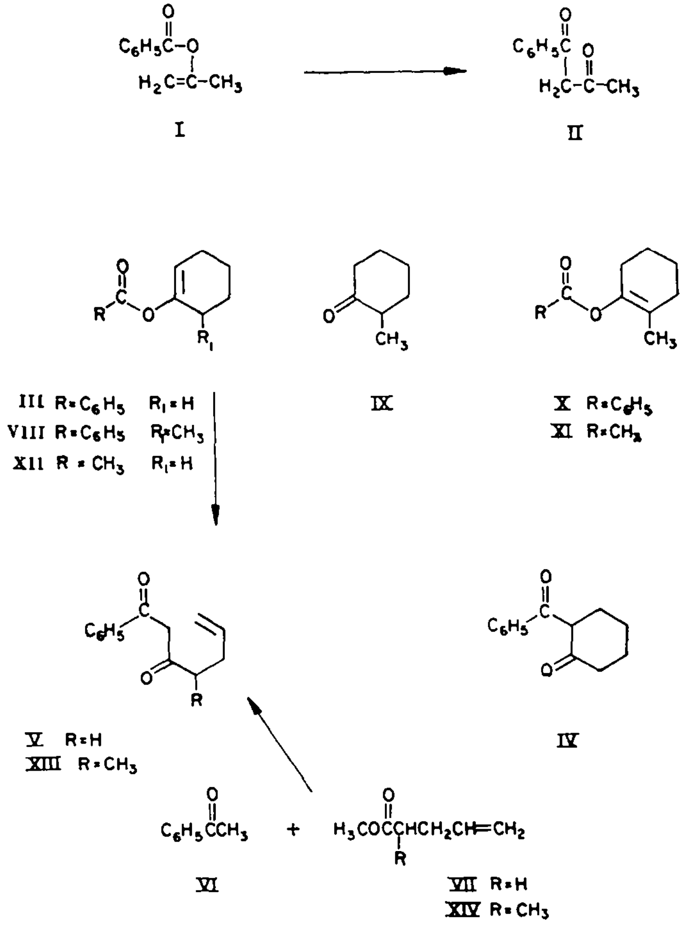

Chart I

double bond to the electronic transition of the benzoate chromophore responsible for the 230 mμ absorption maximum. It is reasonable to assume that the plane containing the $C_6H_5CO—O—$ group is perpendicular to the plane of the double bond, and an overlap between the π orbitals of the double bond and those of the benzoate chromophore is minimal.[9]

Isopropenyl benzoate (I) gave the expected benzoylacetone (II) in a maximum yield after 1·5 hr irradiation, as found by absorption measurements (11%). The pure material was isolated through its copper chelate (6%). The benzoylacetone (II) exists mainly in its enolic form, as seen from its NMR (Table 2). The integration of the appropriate signals in the NMR established the amount of the ketonic form as being less than 10%.[10]

TABLE 1. UV SPECTRA OF α-BENZOYL KETONES

Compound		in cyclohexane				in methanol			
		λ	ε	λ	ε	λ	ε	λ	ε
Benzoyl acetone	II	247	5700	306	13900	247	5700	309	13800
1-Benzoylhex-5-en-2-one	V	247	7200	308	13400	246	5700	313	13800
1-Benzoyl-3-methyl-hex-5-en-2-one	XIII	247	6100	308	15300	247	6000	309	16500
2-Benzoylcholestan-3-one	XVII	244	4100	312	10000	245	5200	313·5	11000
16-Benzoyl-5α-androstan-3β-ol-17-one acetate	XXI	230	6800	313	15900	246	8400	314·5	11500

Cyclohexen-1-yl benzoate (III)[4a,11] (λ_{max}^{MeOH} 229 mμ; ε 14,800) on irradiation gave a new absorption maximum at 308 mμ which after 1 hr attained its maximum value. This UV maximum and a positive reaction with ferric chloride solution indicated the presence of a α-benzoylketone which was not the expected 2-benzoylcyclohexanone (IV) but a α-benzoyl derivative of an aliphatic ketone, 1-benzoylhex-5-en-2-one (V). Both the IR and NMR spectra (Table 2) indicated the presence of a terminal methylene group. The identity of this irradiation product was proved by direct comparison with an authentic sample prepared by condensation of acetophenone (VI) with the methyl ester of pent-4-enoic acid (VII). The photochemical conversion of enol benzoate III to the benzoyl ketone V as found by the UV measurements was *ca.* 12%, and the yield of pure material *ca.* 10%. In addition, 44% of starting material could be isolated.

Mixtures of 6-methylcyclohexen-1-yl benzoate (VIII) and 2-methylcyclohexen-1-yl benzoate (X)[12] of similar composition were obtained from 2-methylcyclohexanone

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[6] R. D. Campbell and H. M. Gilow, *J. Amer. Chem. Soc.* **82**, 5426 (1960).

[7] B. Eistert, W. Reiss and H. Wurzler, *Liebigs Ann.* **650**, 133 (1961).

[8] E.g. 5α-androstan-3β,17β-diol 3-acetate,17-benzoate absorbs in the UV at: $\lambda_{max}^{cyclohexane}$ 229 mμ (ε 14,600); λ_{max}^{MeOH} 229·5 mμ (ε 14,700), according to our determination. Cf. L. Dorfman, *Chem. Rev.* **53**, 47 (1953).

[9] A similar conformation of vinyl acetates was postulated by us previously: A. Yogev and Y. Mazur, *Tetrahedron* **22**, 1317 (1966).

[10] The ratio of the enolic to the ketonic forms cannot be determined with certainty by the UV spectrum (Table 1), since the peaks at 247 and at 309 mμ may be due to the enolic forms. Cf. Refs. 6 and 7.

[11] A. N. Nesmeyanov, I. F. Lutsenko and Z. M. Tumanova *Chem. Abstr.* **44**, 7223e (1950).

[12] An enol benzoate of 2-methylcyclohexanone was previously reported: A. N. Nesmeyanov, I. F. Lutsenko and N. S. Ananchenko, *Chem. Abstr.* **49**, 3836h (1955). This mixture was previously regarded by us as a pure 6-methylcyclohexen-1-yl benzoate (VIII), Ref. 2.

Table 2.* NMR spectra of α-benzoyl ketones

Compound		aliphatic protons		vinylic protons		aromatic protons	
			a	b	c	e	f
Benzoyl acetone	II	2·07 s (CH_3)	3·99 s	6·08 s		7·33	8·00
1-Benzoylhex-5-en-2-one	V	2·46 s 2·47 s	4·05 s	6·17 s	5·00 5·08	7·41	7·91
1-Benzoyl-3-methyl-hex-5-en-2-one	XIII	1·19 d (CH_3) J, 7 c/s 2·41	4·12 s	6·19 s	5·01 5·12	7·47	7·97
2-Benzoylcholestan-3-one	XVII	0·59 s (CH_3) 1·03 (CH_3)				7·50	
16-Benzoyl-5α-androstan-3β-ol-17-one acetate	XXI	0·62 s (CH_3) 0·93 s (CH_3)				7·50	7·60

* These data were obtained with an A/60 Varian Spectrometer, and are given in ppm downfield from tetramethylsilane serving as internal reference. The previously reported chemical shifts (Ref. 2) were obtained from measurements done on a HR/60 Varian spectrometer.

a, —CH_2— of the ketonic form; b, =CH— of the enolic form;
c, terminal methylene; f, *ortho*-hydrogens;
e, *meta*- and *para*-hydrogens; s, singlets; d, doublet.

(IX) either with benzoyl chloride, or with isopropenyl benzoate and sulphuric acid. In the NMR spectrum (Table 2) both the vinylic proton and the doublet assigned to the secondary methyl group of VIII were present.[13] Irradiation of this enol benzoate mixture (VIII and X) resulted in a benzoyl derivative of an aliphatic ketone (XIII), having a terminal methylene group derived from the enol benzoate VIII. Conversion reached its maximum after 4 hr (absorption maximum at 380 mμ), and the yield of pure XIII was 22%. In the IR, bands due to a terminal methylene group were observed, and the NMR showed signals assigned to a secondary methyl group as well as to the terminal methylene group (Table 2). This compound was identical with 1-benzoyl-3-methylhex-5-en-2-one (XIII), obtained by condensation of acetophenone (VI) and methyl of 2-methylpent-4-enoate (XIV).

Different results were obtained when steroidal enol benzoates were irradiated. The irradiation of cholest-2-en-3-ol benzoate XV[14] ($\lambda_{max}^{cyclohexane}$ 229 mμ; ε 14,600, λ_{max}^{MeOH} 230 mμ; ε (17,400) for 16 hr resulted in 2-benzoylcholestan-3-one (XVII) which was obtained in *ca.* 20% yield. This diketone was isolated in its enolic forms XVIIa and XVIIb, as seen from its NMR spectrum (Table 2), in which no signal for

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[13] A similar mixture of the corresponding enol acetates XI and XII is obtained under kinetically controlled O-acetylation of 2-methylcyclohexanone (IX), using isopropenyl acetate, but if acetic anhydride is used, IX is converted almost entirely to the thermodynamically more stable isomer XI. It seems, therefore that both methods of O-benzoylation result in kinetically controlled products; cf. H. O. House and V. Kramar, *J. Org. Chem.* **28**, 3362 (1963); and Ref. 17.

[14] L. Ruzicka and W. H. Fischer, *Helv. Chim. Acta* **19**, 1371 (1936).

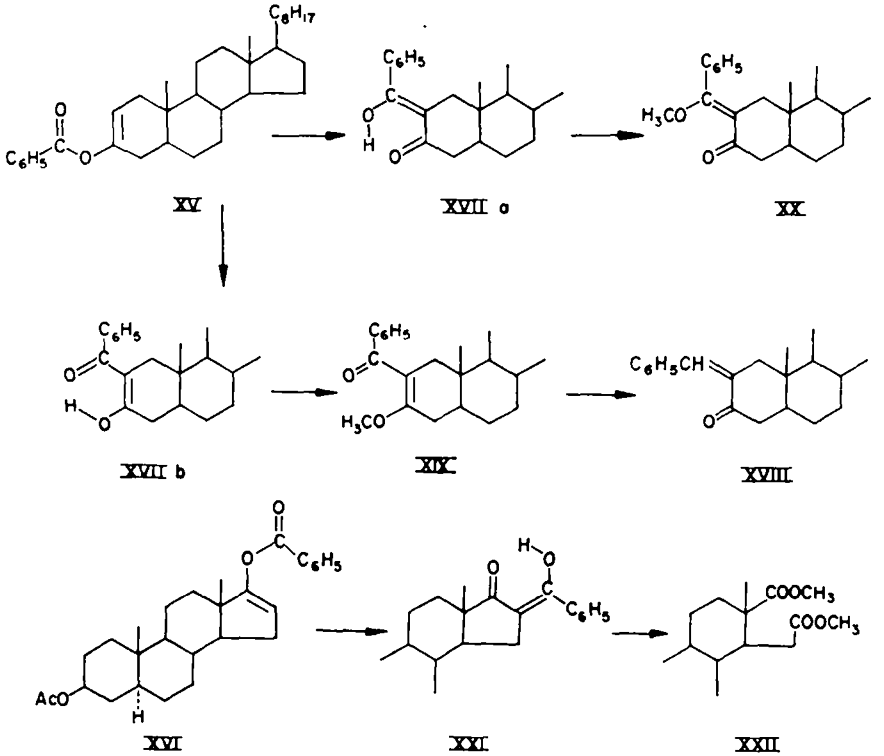

Chart 2

the proton at C2 of the ketonic form could be observed. Both characteristic UV absorption bands of α-benzoyl ketones were present in spectrum of the diketone XVII (Table 1).

Since the attempt to synthesize the benzoylcholestanone XVII failed, its structure was proved by conversion to the known 2-benzylidencholestan-3-one (XVIII).[15] The benzoylketone XVII was etherefied with diazomethane to a crystalline compound, which showed in its UV spectrum two absorption maxima at λ 250 and 287 mμ (ε 9700 and 4400). This indicated a mixture of the two enol ethers XIX and XX with the former in preponderence.[7] Reduction of this mixture with sodium borohydride and subsequent dehydration with acid,[16] gave a mixture from which the desired benzylidene derivative XVIII[15] was obtained in *ca.* 38% yield. It was identified by comparison with an authentic sample prepared by condensation of cholestan-3-one with benzaldehyde.

Chromatographic separation of the irradiation products of cholest-2-en-3-ol benzoate (XV) gave, in addition to the diketone XVII, the starting enol benzoate, and a new compound. The latter was isomeric with the benzoyl ketone XVII, and its spectral data indicated that it is a hydroxy ketone. However, its structure has not been determined yet.

[15] M. W. Goldberg and H. Kirchensteiner, *Helv. Chim. Acta* **26**, 288 (1943); D. H. R. Barton, A. J. Head and P. J. May, *J. Chem. Soc.* 935 (1957).

[16] For the method see: R. D. Campbell and H. M. Gilow, *J. Amer. Chem. Soc.* **82**, 2389 (1960), and Ref. 7.

Irradiation of 5α-androst-16-en-3β,17-diol 3-acetate 17-benzoate (XVI) (λ_{max}^{MeOH} 231 mμ; ε 13,000) prepared from 5α-androstan-3β-ol-17-one acetate and isopropenyl benzoate in the presence of acid resulted in 22% of the 16-benzoyl-5α-androstan-3β-ol-17-one acetate (XXI). This compound showed in its UV spectrum both absorption bands characteristic of α-benzoyl ketone chromophore (Table 1). The benzoyl androstanone XXI was isolated in its enolic form, as evident from its NMR spectrum (Table 2) in which the signals due to the proton at C16 of the ketonic form are missing. It is assumed that the enolic form of the benzoyl androstanone XXI has the exocyclic double bond, as in the corresponding acetyl ketone.[17]

The structure of the benzoyl androstanone XXI was proved by chromic acid oxidation, and subsequent esterification to the known dimethyl ester of the etiobilianic acid (XXII),[18] prepared by chromic acid oxidation of the 16-benzyliden-androstan-3β-ol-17-one acetate.

The α-benzoylketones obtained by irradiation of the enol benzoates mentioned, were generally accompanied by benzoic acid which may have been formed during isolation by hydrolysis of the unreacted enol benzoates. On the other hand, the possibility of a cleavage of the phenyl-oxygen bond on the irradiation of the enol benzoates is not excluded.

Recently, photolysis of vinyl benzoate using light of a different wavelength was described, leading to the rearranged product, benzoylacetaldehyde, and also to acetophenone.[4c]

The unusual hydrogen shift and ring cleavage observed in cyclohexenyl benzoates III and VIII may have occurred after the photochemical rearrangement to the corresponding benzoylcyclohexanones. The oxygen atom of the excited benzoyl chromophore could abstract a γ-hydrogen atom, leaving a radical on the corresponding carbon atom, and subsequently lead to a C—C bond cleavage. Since direct irradiation of benzoylcyclohexanone (IV) did not yield the aliphatic diketone V, this possibility seems less likely although it cannot be excluded.

Alternatively, the ring cleavage may precede the benzoyl migration. The irradiation of enol benzoates may thus lead to excitation of a double bond electron (a $\pi \rightarrow \pi^*$-transition) which is delocalized throughout the benzoate chromophore, leaving a localized electron charge on the C-2 vinylic carbon atom. The 1:3 hydrogen shift and subsequent ring cleavage then follow. Dissociation into the radical pair and their recombination gives the α-benzoylketone. On the other hand, the primary excited species may derive from a $n \rightarrow \pi^*$ transition of one of the lone pair electrons on the oxygen. Such an excited state may also involve a partial localization of an electron charge on the same vinylic carbon atom, C2. The phenyl group may facilitate this excitation process by its electron donating effect. In the steroidal enol benzoates as in the enol acetates,[3] the primary excited species may be decomposed directly to the corresponding radical pair. Additional work is in progress to elucidate the mechanism of the ring cleavage of cyclohexenyl benzoates.

EXPERIMENTAL

All m.ps were taken in capillaries and were uncorrected. UV spectra were determined on a Cary 14 spectrophotometer, and the IR spectra on a Perkin–Elmer Infracord. The rotations were

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[17] M. Gorodetsky, E. Levy, R. D. Youssefyeh and Y. Mazur, *Tetrahedron* **22**, 2039 (1966).

[18] H. Hirschmann, *J. Biol. Chem.* **150**, 363 (1943).

done in $CHCl_3$. The irradiations were performed with an immersion Hanau low pressure NT 6/20 UV Hg lamp in an externally cooled tube of 40-mm dia. and *ca.* 150 ml volume.

Irradiation of isopropenyl benzoate (I)

A solution of I (0·92 g) in cyclohexane (100 ml) was irradiated for 1·5 hr. Aliquots were taken out during the irradiation and their absorbance established. A new absorption peak at 309 mμ appeared during the irradiation, whose molecular extinction coefficient reached the value of 1860 after 1·5 hr irradiation. The solvent was evaporated *in vacuo*, the residue was then dissolved in MeOH (100 ml), treated with a saturated solution of cupric acetate (5 ml), and heated for 5 min on a water bath. Extraction with ether gave crystals of the copper chelate of II (0·075 g, 6%, m.p. 186–189°).

The chelate (1 g) obtained from several irradiation experiments, was dissolved in ether (100 ml), and was shaken with a cold HClaq. solution (10%). Evaporation of the ether gave crystals which were sublimed to give II (0·6 g), m.p. 53–54°; λ_{max}^{KBr} 6·28, 6·44, 6·66 and 6·74 μ, identical with an authentic sample (lit. m.p. 59–60°).[19]

Cyclohexen-1-yl benzoate (III)

A solution of cyclohexanone (24·5 g) in light petroleum (b.p. 100–120°; 300 ml) was treated with benzoyl chloride (58 ml). After heating under reflux for 48 hr, the solution was distilled *in vacuo*. The first fractions consisted of the starting materials, and the following fraction of III, b.p. 136–138°/1 mm; n_D^{20} 1·5468; λ_{max}^{neat} 5·75, 5·90, 6·22 μ. Lit.[4a,11]: b.p. 138–142°/2 mm, n_D^{20} 1·547.

Irradiation of cyclohexen-1-yl benzoate (III)

A solution of III (0·539 g) in cyclohexane (80 ml) was irradiated for 1 hr. The molecular extinction coefficient at 313 mμ increased during the irradiation, its values being after 0·5, 1 and 2 hr: 1630, 1920 and 2000 respectively. The solvent was evaporated and the residue was chromatographed on 15 g alumina. Elution with a mixture of pentane–benzene 9:1 gave 0·239 g of starting material. The second fraction eluted with benzene gave V (0·054 g, 10%) which gave a strong red coloration with $FeCl_3$ solution, b.p. 123–124°/1 mm; n_D^{20} 1·5845; $\lambda_{max}^{CHCl_3}$ 6·21, 6·33, 10·9, 10·08 μ. (Found: C, 77·14; H, 6·90. $C_{13}H_{14}O_2$ requires: C, 77·20; H, 6·98%.)

The chelate of V was prepared by treating the methanolic solution of V with a saturated solution of cupric acetate: m.p. 134–135°; λ_{max}^{KBr} 6·07, 6·28, 6·43, 6·60 and 6·73 μ.

1-*Benzoylhex-5-en-2-one* (V).

A solution of VI (3 g) in dry ether (10 ml) was added to a stirred suspension of $NaNH_2$ (3·9 g) in dry ether (20 ml) dropwise during 15 min. The reaction mixture was stirred for another 15 min, and was then treated dropwise with a solution of methyl ester of pent-4-enoic acid (5·9 g) prepared by methylation of the corresponding acid,[20] in dry ether (20 ml). After heating under reflux for 2 hr, with stirring, and further stirring for 24 hr at room temp, the reaction mixture was poured into water, acidified and the material isolated from ether. It was then dissolved in MeOH (10 ml), treated with saturated solution of cupric acetate (5 ml), and the precipitate filtered off. Decomposition of the copper chelate (in ether) with a cold solution of 10% HCl, and distillation *in vacuo*, gave V (3·7 g), b.p. 124–125°/1 mm; n_D^{20} 1·5845, identical with the compound obtained by irradiation of III. Its copper chelate, m.p. 133–135°, proved to be also identical with that of the irradiation product.

6-Methyl-cyclohexen-1-yl-benzoate (VIII)

(a) A solution of IX (44 g) and benzoyl chloride (88 g) in light petroleum (b.p. 100–120°, 500 ml) was heated under reflux for 40 hr. Distillation *in vacuo* gave first fractions consisting of the starting materials, and then an additional fraction of VIII and X (37 g; 43%), b.p. 116–118°/1 mm; n_D^{20} 1·5380; $\lambda_{max}^{CHCl_3}$ 5·86 and 6·24 μ. (Found: C, 77·70; H, 7·58. $C_{14}H_{16}O_2$ requires: C, 77·75; H, 7·46%.)

(b) A solution of IX (5 g) and I (15 g) was treated with 2 drops of conc. H_2SO_4, and then heated

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[19] J. M. Sprague, L. J. Beckham and H. Adkins, *J. Amer. Chem. Soc.* **56**, 2665 (1934).

[20] R. P. Linstead and H. N. Rydon, *J. Chem. Soc.* 580 (1933).

under reflux for 4 hr. The reaction mixture was poured into ice and water, extracted with ether, and washed with $NaHCO_3$aq. The material thus obtained was distilled *in vacuo*, to give VIII and X (12 g), b.p. 116–118°/1 mm, identical with the enol benzoate prepared under (a).

Irradiation of methylcyclohexen-1-benzoates (VIII *and* X)

A solution of VIII and X (0·537 g) in cyclohexane (80 ml) was irradiated for 4 hr. The molecular extinction coefficient at 309 mμ, after 1 and 4 hr had the values of 770 and 2500 respectively. The solvent was evaporated, and the residue chromatographed on 15 g silica. Elution with pentane–benzene 4:1 gave an oil (positive reaction with $FeCl_3$ solution) which was distilled *in vacuo*, to yield XIII (0·064 g, 12%), b.p. 103–104°/0·6 mm; n_D^{20} 1·5700; $\lambda_{max}^{CHCl_3}$ 5·81, 5·97 6·26, 6·39, 10·07 and 10·88 μ. (Found: C, 77·76; H, 7·55. $C_{14}H_{16}O_2$ requires: C, 77·75; H, 7·46%.)

1-*Benzoyl-3-methylhex-5-en-2-one* (XIII)

A solution of VI (1·05 g) in dry ether (10 ml) was added to a stirred suspension of $NaNH_2$ (1·4 g) in dry ether (20 ml) dropwise during 15 min. The reaction mixture was stirred for another 15 min, and was then treated dropwise with a solution of XIV (2·34 g) in 10 ml ether, prepared by methylation of the corresponding acid.[21] After heating under reflux for 2 hr while stirring, and further stirring at room temp for 24 hr, the reaction mixture was poured into water, acidified and the material isolated from ether. Distillation *in vacuo* gave XIII (1·7 g, 43%), b.p. 103–104°/0·6 mm; n_D^{20} 1·5700, identical with the compound obtained by irradiation of VIII.

Cholest-2-en-3-ol benzoate (XV)

Prepared according to the literature,[15] m.p. 123–125°, $[\alpha]_D$ +48, $\lambda_{max}^{CHCl_3}$ 5·97 and 6·24 μ. Lit.[15] m.p. 127–128°.

Irradiation of cholest-2-en-3-ol-benzoate (XV)

A solution of XV (2·2 g) in cyclohexane (80 ml) was irradiated for 16 hr, after which the UV absorption maximum at 309 mμ had an ε of 4200. The solvent was then evaporated, and the residue was chromatographed on 60 g of silica. Elution with pentane–benzene 9:1 gave 0·26 g (10%) of the starting material. Elution with pentane–benzene 3:1 gave XVII (0·45 g, 20%), m.p. 120–122° (from ether–MeOH) $[\alpha]_D$ −53·5°; λ_{max}^{KBr} 5·81, 6·3 and 6·43 μ. (Found: C, 82·88; H, 10·46; $C_{34}H_{50}O_2$ requires: C, 83·21, H, 10·27%.)

The next fraction, eluted with benzene–ether 3:1 gave 0·35 g of a crystalline material which after recrystallization from ether–MeOH melted at 187–188° (0·15 g, 7%); $[\alpha]_D$ +45°; mol. wt. 490 (from the mass spectrum). (Found: C, 82·88; H, 10·46%; $C_{34}H_{50}O_2$ requires: C, 83·21; H, 10·27%.)

Methylation of 2-*benzoylcholestan*-3-*one* (XVII)

A solution of XVII (0·45 g) in MeOH (10 ml) was treated with excess diazomethane in ether. After being left at room temp for 2 days, the solution was evaporated to dryness *in vacuo*, and the residue chromatographed on 15 g silica. Elution with benzene gave 0·1 g of XIX and XX, m.p. 122–125°; $[\alpha]_D$ +25°; λ_{max}^{EtOH} 250 and 287 mμ (ε 9700 and 4400). (Found: C, 83·27; H, 10·50; $C_{35}H_{52}O_2$ requires: C, 83·28; H, 10·38%.)

2-*Benzylidencholestan*-3-*one* (XVIII)

A solution of XIX and XX (0·027 g) in MeOH (8 ml) was treated with a solution of $NaBH_4$ (0·025 g) in MeOH (2 ml). After being left for 2 hr at room temp, it was acidified with 10% HClaq (5 ml) and heated under reflux for 0·5 hr. The resulting solution was made basic with 10% NaOHaq, and the material isolated from ether. The residue was chromatographed on 5 g silica. Elution with pentane–benzene 4:1 gave XVIII (0·01 g), m.p. 120–122°; $[\alpha]_D$ −103°; $\lambda_{max}^{CHCl_3}$ 5·96 and 6·28 μ; identical with an authentic sample prepared from cholestan-3-one and benzaldehyde (lit.[16] m.p. 126–128°).

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[21] S. Stallberg-Stenhagen, *Arch. Kemi* 23A No. 15 (1947).

5α-Androst-16-en-3β,17-diol 3-acetate 17-benzoate (XVI)

A solution of 5α-androstan-3β-ol-17-one acetate (1·57 g) in I (8 ml) was treated with 2 drops of conc. H_2SO_4, and heated at 170–180° for 2 hr. The solution was then poured into a cold $NaHCO_3$aq and the material isolated from ether, and chromatographed on 50 g alumina. Elution with pentane-benzene 4:1 gave XVI (0·83 g), m.p. 152–154°; $[\alpha]_D$ +40°; $\lambda_{max}^{CHCl_3}$ 5·77, 6·16 and 6·23 μ. (Found: C, 77·42; H, 8·63. $C_{28}H_{36}O_4$ requires: C, 77·03; H, 8·31%.)

Irradiation of 5α-androst-16-en-3β,17-diol 3-acetate,17-benzoate (XVI)

A solution of XVI (1·29 g) in cyclohexane (80 ml) was irradiated for 6 hr. The maximum absorption at 311 mμ had the ε value after 2, 3 and 6 hr: 3200, 4150 and 4500 respectively. The solvent was evaporated to dryness, and the residue chromatographed on 40 g silica. Elution with benzene and recrystallization from ether gave XXI (22%, 0·293 g), m.p. 160–162° $[\alpha]_D$ −64·5°; λ_{max}^{KBr} 5·80, 6·09, 6·23, 6·36 and 6·71 μ. (Found: C, 77·09; H, 8·28. $C_{28}H_{36}O_4$ requires: C, 77·03; H, 8·31%.)

Dimethyl ester of 3β-hydroxy-etiobilianic acid (XXII)

A solution of XXI (0·05 g) in AcOH (5 ml) was treated with a solution of chromic acid (0·04 g) in 80% AcOH (2 ml). The solution was heated at 60° for 2 hr, MeOH was then added and the solvent evaporated to dryness. The material was isolated from ether, extracted with 10% NaOH, and the NaOH solution heated on water bath for 2 hr, acidified with 10% HClaq, and the material isolated from ether. The residue was dissolved in MeOH (5 ml), treated with excess diazomethane in ether, and left for 1 hr at room temp. The methylated material was crystallized from hexane–benzene to give XXII (0·037 g), m.p. 109–110°; $[\alpha]_D$ −25°; $\lambda_{max}^{CHCl_3}$ 5·82 μ; identical with an authentic sample prepared by oxidation of 16-benzyliden-5α-androstan-3β-ol-17-one acetate (Lit.[18] XXII: m.p. 111–112°; $[\alpha]_D$ −24°).