PHOTOLYSES AND PYROLYSES OF TRITERPENOID NITRITES*

Jan SEJBAL[a], Jiří KLINOT[a] and Miloš BUDĚŠÍNSKÝ[b]

[a] *Department of Organic Chemistry, Charles University, 128 40 Prague 2*
[b] *Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6*

Received September 13, 1990
Accepted October 10, 1990

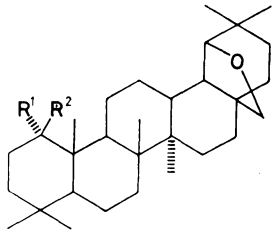
Derivatives of 19β,28-epoxy-18α-oleanane and lupane with nitrosyloxy group in positions 1α, 2β, 3α, 3β and 28 (*II*, *V*, *VIII*, *X* and *XXVII*, respectively) were subjected to photolysis in solution and in the crystalline state, as well as to pyrolysis. In most cases the products identified were alcohols, ketones, olefins and seco derivatives. Photolysis of 2β-nitrite *V* in benzene afforded the known 24- and 25-oximino derivatives *XV* and *XVII*, photolysis of 1α-nitrite *II* in the crystalline state led to the little stable form *XIX* of N-hydroxylactam *XXI* which in solution was easily converted into the derivative of O-acyl-N-alkylhydroxylamine *XXII*. Photolysis of crystalline 3β,28-lupanediyl 3-acetate, 28-nitrite *XXVII* gave 28-norolefins *XXX* and *XXXI* and 13β,28--epoxy derivative *XXXII*.

In connection with our investigations[1-3] on functionalization of non-activated positions in triterpenoids by nitrite photolysis (Barton reaction) we report a study on photolysis and pyrolysis of some 19β,28-epoxy-18α-oleanane and lupane derivatives with nitrosyloxy group in position 1α,2β,3α,3β or 28. In addition to photolysis in solution we also studied the photolysis and pyrolysis in the solid state in order to find out whether intermolecular radical functionalization may take place in solids. Such intermolecular functionalizations have been observed in photolyses or pyrolyses of crystalline clathrates of bile acids[4,5].

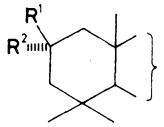
The respective 1α,3α and 3β nitrites *II*, *VIII* and *X* were prepared from the corresponding 19β,28-epoxy-18α-oleananols *I*, *VII* and *IX* by treatment with nitrosyl chloride in pyridine; preparation of the 2β-nitrite[3] *V* and 3β,28-lupanediyl 3-acetate, 28-nitrite[2] (*XXVII*) has already been described. All the derivatives with the nitrite group on the ring A (*II*, *V*, *VIII* and *X*) were irradiated with UV light in a dichloromethane solution in a quartz flask (method *A*), in a benzene solution in a SIAL glass flask (method *B*, the usual conditions of the Barton reaction[6,7]), and as a thin layer of ground crystals of the nitrite (method *C*). Method *D* consisted in pyrolysis of crystalline nitrites at 150°C. The products were separated by column chromatography

* Part XCV in the series Triterpenes; Part XCIV: Collect. Czech. Chem. Commun. *56*, 966 (1991).

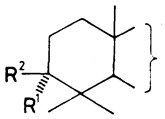
or thin-layer chromatography and in most cases they were directly identified by comparison with authentic samples. The product and yields (rounded to 5%) are summarized in Table I. Oximes *XV* and *XVII*, which were separated only with difficulty, were converted into the hydroxy nitriles *XVI* and *XVIII* by reaction with acetic anhydride followed by alkaline hydrolysis of the acetate according to ref.[3].



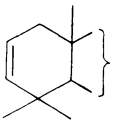
I, R^1 = OH ; R^2 = H
II, R^1 = ONO ; R^2 = H
III, R^1 + R^2 = O



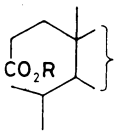
IV, R^1 = OH ; R^2 = H
V, R^1 = ONO ; R^2 = H
VI, R^1 + R^2 = O



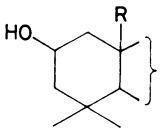
VII, R^1 = OH ; R^2 = H
VIII, R^1 = ONO ; R^2 = H
IX, R^1 = H ; R^2 = OH
X, R^1 = H ; R^2 = ONO
XI, R^1 + R^2 = O



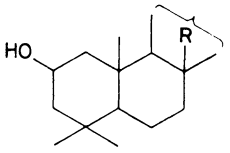
XII



XIII, R = H
XIV, R = CH_3



XV, R = CHNOH
XVI, R = CN



XVII, R = CHNOH
XVIII, R = CN

The photolysis in dichloromethane solution (method *A*) in all cases led only to the parent alcohol; the same result was observed in photolysis of the 1α,3α and 3β nitrites in benzene (method *B*). Photolysis of the 2β-nitrite *V* in benzene afforded, along with small amounts of alcohol *IV* and ketone *VI*, a mixture of 25- and 26--oximino derivatives *XV* and *XVII* as the principal products whose structure had already been determined[3]. The functionalization of the 8β-methyl group (oxime *XVII*), rather distant from the original alkoxy radical in position 2β, was explained[3] by two successive hydrogen radical 1,5-shifts, the first being from the 10β-methyl group to the 2β-O• and the second from the 8β-methyl to the 10β-$CH_2^•$ group.

In the solid state photolyses (method *C*) the reaction mixtures contained ketones along with alcohols. In the case of the 3α- and 3β-nitrites *VIII* and *X* we obtained also small amounts of the 3,4-seco-acid *XIII* which was identified as its known[8] methyl ester *XIV*. The seco-acid *XIII* is undoubtedly a product of subsequent

photolysis of ketone *XI* because this acid was formed on irradiation of crystalline *XI* with unfiltered UV light. When the light of the UV lamp was glass-filtered (method *C*) the photolysis of ketone *XI* did not take place and photolysis of the 3β-nitrite *X* furnished only a mixture of alcohol *IX* and ketone *XI*. Apparently, the irradiated crystals contained the 3,4-seco-triterpenoid ketene: their dissolution in methanol led directly to methyl ester *XIV*. Since in all cases ketones predominated over alcohols, their formation cannot be explained by disproportionation of the

TABLE I
Products of photolysis and pyrolysis of nitrites *II*, *V*, *VIII* and *X*

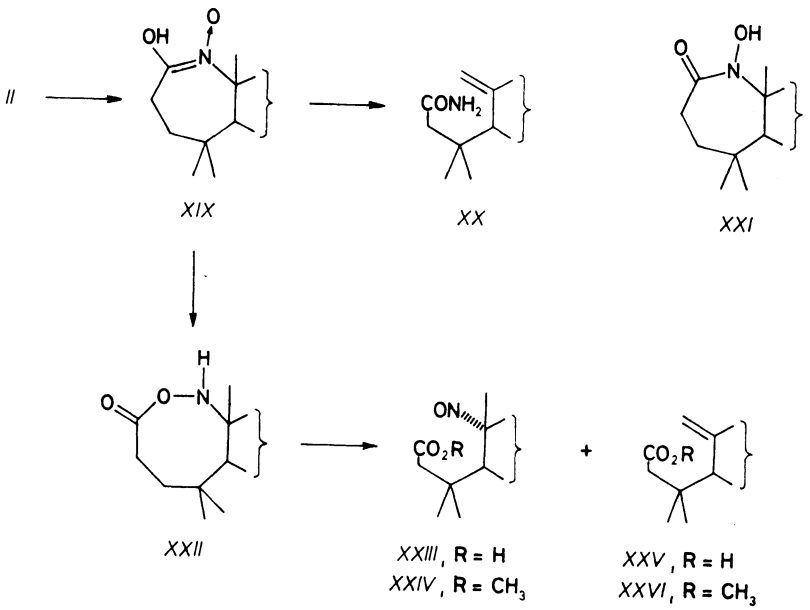
Nitrite	Method[a]	Yield, %				
		alcohol	ketone		other products	
II		*I*	*III*		*XIX*	
	A	90	—		—	
	B	90	—		—	
	C	—	30		60	
	D	70	15		—	
V		*IV*	*VI*	*XII*	*XV*	*XVII*
	A	95	—	—	—	—
	B	10	5	—	40	40
	C	40	45	—	—	—
	D	20	35	40	—	—
VIII		*VII*	*XI*		*XIII*	
	A	80	—		—	
	B	90	—		—	
	C	10	65		10	
	D	60	20		—	
X		*IX*	*XI*	*XII*	*XIII*	
	A	90	—	—	—	
	B	95	—	—	—	
	C	—	80	—	15	
	D	50	35	10	—	

[a] *A* photolysis in dichloromethane, *B* photolysis in benzene, *C* photolysis of crystals, *D* pyrolysis; for conditions see Experimental.

alkoxy radical but rather by its reaction with nitric oxide leading to elimination of hyponitrous acid (for a discussion see ref.[9]).

Pyrolysis (method *D*) of nitrites *II*, *V*, *VIII* and *X* afforded mixtures of alcohols and ketones, similarly as in the case of steroid nitrites[10,11]; the 2β- and 3β-nitrites *V* and *X* gave also olefin *XII* with the double bond in position 2(3).

Photolysis of crystalline 1α-nitrite *II* gave as the principle product the unstable polar compound *XIX* which was separated from the second product, ketone *III*, by very careful crystallization. Compound *XIX* was reduced with zinc in acetic acid to give the 1,10-seco-amide *XX*. The structure of this product followed from comparison of its ^{1}H NMR spectrum with those of other derivatives of 19β,28--epoxy-1,10-seco-18α-olean-10(25)-en-1-oic acid (*XXV*; see ref. 8) and also from IR bands characteristic of primary amides.



On standing for several days in solution, attempted chromatography, or refluxing a chloroform solution for 20 min, compound *XIX* turned into two compounds. The less abundant product was not obtained in a pure state; according to the ^{1}H NMR spectrum of the mixture it was a 1,10-seco-olean-10(25)-ene derivative (characteristic broad singlets of double bond protons at δ 4·66 and 5·02). The principal product *XXII* was separated by chromatography. Its reaction with sodium hydroxide in methanol gave a mixture of the known[8] 1,10-seco-acid *XXV* with 10(25)-double bond and another seco-acid *XXIII* whose structure was determined after conversion

into the methyl ester *XXIV*. The IR spectrum of *XXIV* displayed a dominant band at 1 534 cm^{-1}, characteristic of monomeric C-nitroso compounds, and in its ^1H NMR spectrum the C(10) methyl signal was shifted downfield to δ 1·61: this corresponds to the expected shift due to the neighbouring nitroso group[12]. The seco--acid *XXIII* represents a higher oxidation state than the starting compound *XXII*: thus the alkaline hydrolysis is accompanied either by oxidation with air oxygen or by disproportionation of an intermediate (possibly a hydroxylamine derivative) leading to the seco-acid *XXIII*.

The structure of the primary (*XIX*) as well as the secondary (*XXII*) product of photolysis of nitrite *II* follows from the above-mentioned reactions and from their IR, UV, NMR and mass spectra (for the ^{13}C NMR shifts see Table II; the assignment of signals is based on ref.[13]). According to elemental analyses and mass spectra, both compounds are isomeric with the starting nitrite *II*. As known from the literature[7,14–19], in cases when in nitrite photolyses the C—C bond adjacent to the nitrite group is broken, the reaction gives rise to N-hydroxy lactams (cyclic hydroxamic acids) of the type *XXI*. For this and other possible structures containing a –CO—N– grouping we may expect a carbonyl band at about 1 630–1 660 cm^{-1} in the IR spectrum. However, the spectrum of compound *XXII* exhibits a strong band at 1 722 cm^{-1}, corresponding rather to a lactone carbonyl. An IR band at

TABLE II

Carbon-13 chemical shifts in compounds *XIX* and *XXII*

Carbon	*XIX*	*XXII*	Carbon	*XIX*	*XXII*
1	168·73	179·30	16	36·64	36·70
2	39·18	38·97	17	36·22	36·24
3	30·00	36·61	18	46·53	46·63
4	36·96	32·85	19	87·77	87·90
5	52·36	46·56	20	41·39	41·46
6	21·21	20·32	21	32·74	32·65
7	32·67	32·94	22	26·25	26·16
8	41·47[a]	40·90[a]	23	33·44[c]	29·41[c]
9	47·97	41·22	24	23·93[c]	26·33[c]
10	71·95	65·77	25	19·44[c]	14·95[c]
11	26·00[b]	21·25	26	16·65	15·57
12	25·86[b]	25·90	27	13·27	13·61
13	34·33	34·19	28	71·26	71·23
14	41·98[a]	41·01[a]	29	24·50	24·49
15	26·51	26·66	30	28·75	28·76

[a–c] Values denoted by the same letters may be interchanged.

3 310 cm^{-1} and a broad singlet at δ 6·16 in the ^1H NMR spectrum indicate the presence of an N—H bond. All these facts are consistent with the O-acyl-N-alkyl--hydroxylamine structure *XXII*. The mentioned structure is also supported by the fact that the substance gives no colour reaction with ferric chloride[20] and reacts with sodium hydroxide to give nitroso acid *XXIII* in which the nitrogen atom is bonded to C(10). Consistent with the structure *XXII* is also the chemical shift of the carbon atoms C(1) (δ 179·3) and C(10) (δ 65·8).

Compound *XIX* gives a violet colouration with ferric chloride, typical for hydroxamic and N-alkylhydroxamic acids[20], and its mass spectrum exhibits an ion of m/z 455 ($M^+ - 16$) corresponding to the loss of oxygen atom, typical for N-oxides. A broad band at 3 170 cm^{-1} in the IR spectrum and a broad singlet at δ 9·30 in the ^1H NMR spectrum indicate the presence of a strongly bonded hydroxyl. Compound *XIX* does not absorb in the region 1 600 – 1 800 cm^{-1}, however, it displays a strong band at 1 590 cm^{-1}. This value seems to be too low for an N-hydroxy lactam of the type *XXI*, and corresponds best to the values found for nitrones[2,21]. Therefore we describe the structure by formula *XIX*, i.e. as a tautomeric form of the N-hydroxy lactam *XXI*. The marked downfield shift of the C(10) methyl group protons (δ 1·52) and of the C(10) carbon atom (δ 71·95) may be explained by cumulation of highly polar groups in the close vicinity of these atoms. The intramolecular N-acyl → → O-acyl rearrangement of compound *XIX* (in the form of *XXI*) may lead to the derivative *XXII*.

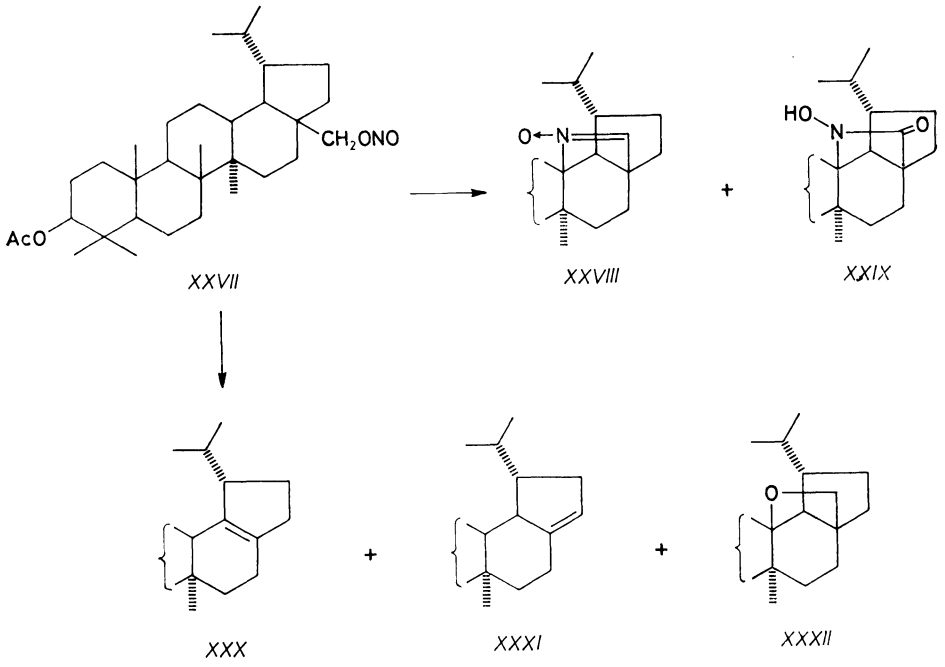
Thus, the photolysis of nitrite *II* leads to the ketone *III* and to the N-oxide *XIX*. The formation of the latter may be described by the many times published scheme[7,14–19]: cleavage of the C—C bond affords the nitrosoaldehyde which is cyclized to the N-hydroxylactam: this, surprisingly, in this case is more stable in the tautomeric form *XIX*, probably for steric reasons (proximity of 11α-H). Another surprising fact is that the most stable link in the reaction pathway is the O-acyl-N--alkylhydroxylamine derivative *XXII* with eight-membered ring A.

The assumed structure of the intermediate nitrosoaldehyde is indicated by the IR spectra of the irradiated crystalline 1α-nitrite *II*, measured in Nujol (bands at 1 720, 2 725 and 2 820 cm^{-1}) as, well as by a signal at δ 9·78 in the ^1H NMR spectrum measured immediately after dissolution of the crystals in deuteriochloroform; however, these facts do not represent any unequivocal structural proof.

The configuration at C(10) in compounds *XIX* and *XXII–XXIV* is not certain since the recombination of the radical at C(10) and the NO$^\bullet$ radical may be accompanied by isomerization; a similar isomerization has been observed with steroid compounds[14,17] at C(13). However, models show that such an isomerization is not probable because an attack by the NO$^\bullet$ radical from the β-side of the skeleton is hindered by the 8β-methyl group.

We also studied solid state photolysis of another nitrite type, the 28-nitrite *XXVII*. It is known[2] that in benzene solution this compound affords products of attack in the

position 13, i.e. N-oxide *XXVIII* and N-hydroxylactam *XXIX*. The photolysis of crystalline nitrite *XXVII* led, however, to norolefins *XXX* and *XXXI* and to 13β,28-ether *XXXII*. Compounds *XXXI* and *XXXII* are known[22], the structure of *XXX* is suggested on the basis of its mass spectrum (M^+, m/z 454) and absence of an olefinic proton signal in its ^1H NMR spectrum.



13β,28-Epoxy derivatives are characteristic products of reaction of lupane 28--hydroxy derivatives with lead tetraacetate[22], the formation of various 28-norolefins was observed with several types of functionalization with a steering group in position 28 (see e.g. refs[2,22]). However, both these types of compounds are not common products of nitrite photolysis in solution[6,7,9]. Thus, in the photolysis of crystalline 28-nitrite *XXVII* the radical NO$^\bullet$ does not take part in the further reactions.

In conclusion we may say that in solid state photolyses neither of the studied nitrites gave products of intermolecular functionalization, however, as exemplified by nitrites *II* and *XXVII*, interesting products may be formed that are different from those arising in solution photolyses.

EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. Optical rotations were measured in chloroform on an ETL-NPL (Bendix–Ericsson) polarimeter; accuracy ±2° (concentration 0·4—0·8). The IR spectra in chloroform were taken on a PE 684 (Perkin–Elmer)

spectrophotometer; wavenumbers in cm^{-1}. ^1H NMR spectra of compounds *XIX*, *XX* and *XXII* were measured on a Varian XL-200 (200 MHz, FT-mode) instrument in deuteriochloroform with tetramethylsilane as internal standard, ^{13}C NMR spectra were obtained with the same instrument (50·31 MHz, "attached proton test" technique) in deuteriochloroform, chemical shifts being referenced to the solvent signal and calculated according to the relationship $\delta(CDCl_3) = 77{\cdot}00$. ^1H NMR spectra of the other compounds were taken on a Tesla BS 487A (80 MHz, CW-mode) instrument in deuteriochloroform using hexamethyldisiloxane as internal standard (chemical shifts were calculated for tetramethylsilane according to the relation $\delta(HMDS) = 0{\cdot}063$ and rounded to two decimal places). The coupling constants (in Hz) were obtained by first order analysis. Mass spectra of compounds *XIX* and *XXII* were measured on ZAB-EQ (Vacuum Generators) spectrometer, ionizing electron energy 60 eV, the other spectra were measured on a Varian MAT 311 instrument, ionizing electron energy 70 eV. The direct inlet temperature was 150—180°C. UV spectra were taken on a Varian SP-700 instrument in cyclohexane. The identity of substances prepared by different procedures was checked by thin-layer chromatography and IR and ^1H NMR spectra. Thin-layer chromatography (TLC) was performed on plates of silica gel G (Merck; detection by spraying with 10% sulfuric acid and heating) or on Silufol foils (Kavalier; detection with 5% ethanolic phosphomolybdic acid and heating). Preparative TLC was carried out on Kieselgel 60 G (Merck), column chromatography on silica gel Silpearl (Kavalier). Photolyses were performed by irradiation with a 125 W low-pressure mercury lamp RKW (Tesla). Analytical samples were dried in vacuo over phosphorus pentoxide at room temperature.

The starting compounds were prepared according to the following references: *I* (ref.[23]), *V* (ref.[3]), *VII* (ref.[24]), *IX* (ref.[25]), *XXVII* (ref.[2]). The preparation of authentic samples used for comparison is described in refs[2,3,8,22–29].

General Procedure for Preparation of Nitrites *II*, *VIII* and *X*

Nitrosyl chloride was distilled into a solution of the hydroxy derivative (2 g) in pyridine (100 ml) with cooling to −20°C, until the mixture had permanent orange colour. Water (40 ml) was added during 10 min with stirring. The separated crystalline nitrite was filtered, dried in a desiccator over sulfuric acid and used in the subsequent reaction without further purification. An analytical sample was prepared by crystallization from benzene–ethanol (cooling the saturated solution from 30°C to −20°C).

19β,28-*Epoxy*-18α-*oleanan*-1α-*yl nitrite* (II); yield 1·93 g (93%). M.p. 229—231°C, $[\alpha]_D$ +119°. IR spectrum: 1 633 (NO); 1 031 (COC). For $C_{30}H_{49}NO_3$ (471·7) calculated: 76·39% C, 10·47% H, 2·97% N; found: 76·21% C, 10·43% H, 2·83% N.

19β,28-*Epoxy*-18α-*oleanan*-3α-*yl nitrite* (VIII); yield 75%. M.p. 230—233°C (slow decomposition from 180°C), $[\alpha]_D$ +17°. IR spectrum: 1 634 (NO); 1 030 (COC). For $C_{30}H_{49}NO_3$ (471·7) calculated: 76·39% C, 10·47% H, 2·97% N; found: 76·32% C, 10·59% H, 3·12% N.

19β,28-*Epoxy*-18α-*oleanan*-3β-*yl nitrite* (X); yield 86%. M.p. 276—280°C (at 235°C rapid decomposition), $[\alpha]_D$ +42°. IR spectrum: 1 632 (NO); 1 030 (COC). For $C_{30}H_{49}NO_3$ (471·7) calculated: 76·39% C, 10·47% H, 2·97% N; found: 76·35% C, 10·58% H, 2·76% N.

Photolyses and Pyrolyses of Nitrites *II*, *V*, *VIII* and *X*

The reactions were performed with 100 mg of the starting nitrite; the yields of the individual products are given in Table I. In case of a single product, the yield given is after crystallization from methanol, otherwise the products were separated by TLC (silica gel 10 g) in ether–light

petroleum (1 : 2) and the yields are given for uncrystallized chromatographically pure fractions. For nitrite *V* and method *B* the yields of oximes *XV* and *XVII* were determined only after conversion[3] into the hydroxy nitriles *XVI* and *XVIII* (by heating with acetic anhydride and alkaline hydrolysis of the formed acetate).

Method A: The nitrite was dissolved in dichloromethane (10 ml) and nitrogen was bubbled through the solution, which was then irradiated in a quartz flask with an external mercury lamp for 30 min.

Method B: After bubbling nitrogen, a solution of the nitrite in benzene (3 ml) was irradiated in a SIAL flask with an external mercury lamp for 2 h. The benzene was distilled off under diminished pressure.

Method C: A thin layer of the ground nitrite on a glass plate was irradiated with a mercury lamp from a distance of 20 cm for 30 min. The crystals were then dissolved in benzene.

Method D: The nitrite was heated on a Koffer block to 150°C for 30 min and the melt was dissolved in chloroform.

Photolysis of Ketone *XI*

The photolysis of crystalline ketone *XI* (100 mg) (conditions of method *C*, vide supra) for 18 h led to a mixture of products which on column chromatography on silica gel (10 g, elution with ether–light petroleum 1 : 5) afforded 19β,28-epoxy-3,4-seco-18α-oleanan-3-oic acid (*XIII*) as the sole product, yield 60 mg (55%), m.p. 275–276°C (acetone–water), $[\alpha]_D$ +50°. IR spectrum: 2 600–3 500 (COOH); 1 738 (COOH); 1 032 (COC). ^{1}H NMR spectrum (80 MHz): 0·80 s, 0·81 s, 0·83 s, 0·92 s and 0·99 s, 5 × 3 H (5 × CH_3); 2·13 m, 2 H (2-H_2, $\sum J = 8$); 3·50 s, 1 H (H-19α); 3·41 d, 1 H and 3·75 d, 1 H (2 × 28-H, $J = 8$). Mass spectrum *m/z* (%): 458 (M^+, 51), 440 (12), 427 (30), 387 (24), 385 (42), 273 (10), 247 (21), 245 (22), 203 (47) 177 (42), 81 (100). For $C_{30}H_{50}O_3$ (458·7) calculated: 78·55% C, 10·99% H; found: 78·38% C, 10·83% H. Methylation with diazomethane afforded the methyl ester *XIV*, m.p. 170–171°C, $[\alpha]_D$ +50°, identical with an authentic sample[26] (reported[26] m.p. 171–172°C, $[\alpha]_D$ +49°). The ester *XIV* was also obtained in 47% yield by dissolving the crystals after photolysis of the ketone *XI* in methanol and concentrating the solution.

After irradiation of ketone *XI* through the SIAL glass for 28 h, most of the starting material was recovered and no products were detected.

Photolysis of Crystalline 1α-Nitrite *II*

Ground crystalline nitrite *II* (1 g) was irradiated as described by method *C*. After irradiation, the crystals were dissolved in chloroform (10 ml) forming a pale cyanic solution; according to TLC immediately after the dissolution the solution contained only the 1-oxo derivative *III* and compound *XIX* in approximate ratio 1 : 2. On cooling to −10°C, the solution deposited crystals of compound *XIX* which was purified by cooling its acetone solution (saturated at room temperature) to −20°C; yield 0·47 g (47%), m.p. 206–210°C, $[\alpha]_D$ +54°. IR spectrum: 3 170 broad (OH); 1 590 (C=N); 1 031 (COC). ^{1}H NMR spectrum (200 MHz): 0·80 s, 0·93 s, 0·96 s, 3 × 3 H, 1·03 s, 9 H, 1·52 s, 3 H (7 × CH_3); 2·22 dq, 1 H (H-11α, $J = 13·0, 2·5, 2·5, 2·5$); 2·37 dd, 1 H (H-9α or H-5α, $J = 11·8, 2·4$); 2·54–2·81 m, 2 H (H-2α and H-2β); 3·55 s, 1 H (H-19α); 3·45 d, 1 H and 3·77 d, 1 H (2 × 28-H, $J = 8$); 9·30 bs, 1 H (OH, $W_{1/2} = 40$ Hz). Mass spectrum *m/z* (%): 471 (M^+, 5), 455 (30), 440 (12), 356 (10), 256 (10), 199 (10), 185 (15), 166 (95), 153 (100), 138 (50). UV spectrum: λ_{max} 225 nm, ε 3 600. For $C_{30}H_{49}NO_3$ (471·7)

calculated: 76·39% C, 10·47% H, 2·97% N; found: 76·21% C, 10·61% H, 3·22% N. Compound *XIX* gives a violet colouration with ethanolic ferric chloride.

Chromatography of mother liquors on a column of silica gel (45 g, eluent ether–light petroleum 1 : 4) afforded successively the 1-oxo derivative *III* (0·28 g; 30%), identical with an authentic sample[23], and the product *XXII* (0·13 g; 13%). After crystallization from methanol, compound *XXII* had m.p. 190–194°C, $[\alpha]_D$ +112°. IR spectrum: 3 310 (NH); 1 722 (C=O); 1 283, 1 256, 1 027 (COC). ^{1}H NMR spectrum (200 MHz): 0·80 s, 0·92 s, 0·93 s, 0·94 s, 0·97 s, 0·99 s and 1·01 s, 7 × CH_3); 2·20 dd, 1 H (H-9α or H-5α, J = 12·2 and 2·8); 2·54–3·03 bm, 3 H; 3·53 bs, 1 H (H-19α); 3·45 d, 1 H and 3·77 d, 1 H (2 × 28-H, J = 7·8); 6·16 bs, 1 H (NH, $W_{1/2}$ = 8). Compound *XXII* does not react with TAI. Mass spectrum m/z (%): 471 (M^+, 14), 456 (17), 398 (18), 360 (9), 356 (12), 341 (15), 257 (18), 213 (8), 203 (12), 166 (50), 153 (58), 57 (100). UV spectrum transparent above 210 nm. For $C_{30}H_{49}NO_3$ (471·7) calculated: 76·39% C, 10·47% H, 2·97% N; found: 76·23% C, 10·51% H, 3·12% N. No colouration with ethanolic ferric chloride.

Reaction of Derivative *XXII* with Sodium Hydroxide

A mixture of *XXII* (0·25 g), sodium hydroxide (0·2 g) and methanol (5 ml) was refluxed for 6 h, diluted with water, acidified with dilute hydrochloric acid and the products were extracted with ether. The ethereal layer was washed with saturated solution of sodium hydrogen carbonate and water, dried over sodium sulfate and the solvent were evaporated. The residue was chromatographed on a column of silica gel (30 g) in ether–light petroleum (1 : 5) to give acid *XXV* (120 mg; 50%), m.p. 192–194°C, $[\alpha]_D$ −25°, identical (as well as its methyl ester *XXVI*, prepared by treatment of *XXV* with diazomethane) with an authentic sample[8]. Further elution afforded 60 mg (23%) of amorphous 19β,28-epoxy-10α-nitroso-1,10-seco-18α-oleanan-1-oic acid (*XXIII*). IR spectrum: 3 550–2 800, 1 755 and 1 737 (COOH); 1 536 (NO); 1 032 (COC). Methylation with diazomethane and crystallization of the product from chloroform–methanol gave methyl ester *XXIV*, m.p. 280–285°C (dec., at 178–180°C change from platelets to needles), $[\alpha]_D$ +29°. IR spectrum: 1 731 (CO); 1 534 (NO); 1 028 and 1 006 (COC). ^{1}H NMR spectrum (80 MHz): 0·78 s, 0·80 s, 0·87 s, 0·92 s, 4 × 3 H, 0·96 s, 2 × 3 H and 1·61 s, 3 H (7 × CH_3); 2·26 m, 2 H; 3·67 s, 3 H (OCH_3); 3·49 s, 1 H (H-19α; 3·44 d, 1 H and 3·75 d, 1 H (2 × 28-H, J = 8). UV spectrum: λ_{max} 280 nm, ε 170. Mass spectrum m/z (%): 471 (M^+ − NO, 6), 445 (4), 399 (3), 341 (19), 323 (8), 129 (100), 97 (92), 95 (81) For $C_{31}H_{51}NO_4$ (501·8) calculated: 74·21% C, 10·25% H, 2·79% N; found: 74·12% C, 10·03% H, 2·99% N.

19β,28-Epoxy-1,10-seco-18α-olean-10(25)-en-1-oic Acid Amide (*XX*)

Zinc dust (0·3 g; pretreated with iodine vapours for 24 h) was added to a solution of *XIX* (180 mg) in acetic acid (5 ml) and the mixture was refluxed until the starting compound disappeared (TLC, about 5 h). The zinc was filtered off, the filtrate was diluted with water and the product was taken up in ether. The ethereal extract was washed successively with water, saturated sodium hydrogen carbonate solution and again with water, dried over sodium sulfate and the solvent was evaporated. The residue was purified by preparative TLC on Silica gel (200 × 200 mm plate) in ether–light petroleum (1 : 1) to remove less polar impurities. Crystallization from chloroform–ethanol gave 135 mg (77%) of amide *XX*, m.p. 203–205°C, $[\alpha]_D$ −23°. IR spectrum: 3 533, 3 499, 3 415 (NH_2); 1 680 and 1 592 ($CONH_2$); 1 641 and 895 ($C=CH_2$); 1 031 (COC). ^{1}H NMR spectrum (200 MHz): 0·79 s, 0·82 s, 0·94 s, 0·97 s, 1·00 s and 1·05 s, 6 × 3 H (6 × CH_3); 1·86 to 2·55 m, 4 H; 3·45 d, 1 H and 3·79 bd, 1 H (2 × 28-H, J = 8); 3·56 s, 1 H (H-19α); 4·66 bs, 1 H and 5·03 bs, 1 H (2 × 25-H); 5·33 bs, 2 H (NH_2, $W_{1/2}$ = 25). For $C_{30}H_{49}NO_2$ (455·7) calculated: 79·07% C, 10·84% H, 3·07% N; found: 79·13% C, 10·67% H, 3·23% N.

Photolysis of 3β,28-Lupanediyl 3-Acetate, 28-Nitrite (*XXVII*)

The ground nitrite *XXVII* (0·35 g) was irradiated with a UV lamp from a distance of 20 cm for 8 h. The product mixture was then dissolved in chloroform and subjected to TLC on silica gel (25 g; impregnated with 5% of silver nitrate) in light petroleum. The most mobile zone after crystallization from chloroform–methanol afforded 43 mg (16%) of 28-nor-17(22)-lupen-3β-yl acetate (*XXXI*), identical with an authentic sample[10]. ^{1}H NMR spectrum (80 MHz): 0·86 s, 6 H (CH_3-4α and CH_3-4β); 0·88 s, 3 H (CH_3-10β); 0·95 s, 3 H (CH_3-14α); 1·01 s, 3 H (CH_3-8β); 0·77 d, 3 H (CH_3-20, J = 7·0); 0·86 d, 3 H (CH_3-20, J = 7·0); 2·03 s, 3 H ($OCOCH_3$); 4·49 m, 1 H (H-3α); 5·09 bs, 1 H (H-22); the spectrum agrees with data in ref.[10] excepting signals of methyl groups in the side chain: ref.[10] gives 0·83 d (J = 6·5) and 0·905 d (J = 6·5).

Further zone after crystallization from methanol gave 85 mg (28%) of 28-nor-17-lupen-3β-yl acetate (*XXX*), m.p 168–171°C, $[\alpha]_D$ −4°. IR spectrum: 1 732 ($OCOCH_3$). ^{1}H NMR spectrum (80 MHz): 0·84 s, 6 H (CH_3-4α and CH_3-4β); 0·86 s, 3 H (CH_3-10β); 0·95 s, 6 H (CH_3-8β and CH_3-14α); 2·03 s, 3 H ($OCOCH_3$); 4·48 m, 1 H (3α-H, $\sum J$ = 16). Mass spectrum m/z (%): 454 (M^+, 14), 439 (2), 411 (13), 394 (11), 379 (5), 351 (15), 289 (33), 249 (16), 229 (27), 189 (100). For $C_{31}H_{50}O_2$ (454·7) calculated: 81·88% C, 11·08% H; found: 82·03% C, 10·89% H.

The most polar part was crystallized from acetone to give 126 mg (38%) of 13β,28-epoxylupan-3β-yl acetate (*XXXII*) identical with an authentic sample[22].

The authors are indebted to Dr S. Hilgard for measurement of the IR *and* UV *spectra and to Dr J. Protiva and Dr J. Malát for the mass spectral measurements.*

REFERENCES

1. Vystrčil A., Pouzar V.: Collect. Czech. Chem. Commun. *39*, 3304 (1974).
2. Protiva J., Budějínský M., Vystrčil A.: Collect. Czech. Chem. Commun. *42*, 1220 (1977).
3. Sejbal J., Klinot J., Vystrčil A.: Collect. Czech. Chem. Commun. *52*, 118 (1988).
4. Friedman N., Lahav M., Leiserowitz L., Popovitz R., Tang C. P., Zaretzkii Z.: J. Chem. Soc., Chem. Commun. *1975*, 846.
5. Lahav M., Leiserowitz L., Popovitz R., Tang C. P.: J. Am. Chem. Soc. *100*, 2542 (1978).
6. Heusler K., Kalvoda J. in: *Organic Reactions in Steroid Chemistry* (J. Fried and J. A. Edwards, Eds), Vol. II, p. 237. Van Nostrand, New York 1972.
7. Nussbaum A. L., Robinson C. H.: Tetrahedron *17*, 35 (1962).
8. Sejbal J., Klinot J., Hrnčířová D., Vystrčil A.: Collect. Czech. Chem. Commun. *50*, 2753 (1985).
9. Barton D. H. R., Hesse R. H., Pechet M. M., Smith L. C.: J. Chem. Soc., Perkin Trans. 1 *1979*, 1159.
10. Barton D. H. R., Ramsay G. C., Wege D.: J. Chem. Soc., C *1967*, 1915.
11. Barton D. H. R., Beaton J. M., Geller L. E., Pechet M. M.: J. Am. Chem. Soc. *83*, 4076 (1961).
12. Freeman J. P.: J. Org. Chem. *28*, 2508 (1963).
13. Budějínský M., Klinot J.: Collect. Czech. Chem. Commun. *54*, 1928 (1989).
14. Robinson C. H., Gnoj D., Mitchell A., Oliveto E. P., Barton D. H. R.: Tetrahedron *21*, 743 (1965).
15. Suginome H., Osada A.: J. Chem. Soc., Perkin Trans. 1 *1982*, 1963.
16. Suginome H., Maeda N., Kaji M.: J. Chem. Soc., Perkin Trans. 1 *1982*, 111.
17. Suginome H., Yonekura N., Mizuguchi T., Misamune T.: Bull. Chem. Soc. Jpn. *50*, 3010 (1977).

18. Kabasakalian R., Townley A.: J. Org. Chem. *27*, 3562 (1962).
19. Robinson C. H.: J. Am. Chem. Soc. *83*, 1771 (1961).
20. Yale L.: Chem. Rev. *33*, 209 (1944).
21. Hamer J., Macaluso A.: Chem. Rev. *64*, 473 (1964).
22. Vystrčil A., Protiva J.: Collect. Czech. Chem. Commun. *39*, 1382 (1974).
23. Huneck S.: Chem. Ber. *98*, 2291 (1965).
24. Klinot J., Vystrčil A.: Collect. Czech. Chem. Commun. *31*, 1079 (1966).
25. Schulze H., Pieroh K.: Ber. Dtsch. Chem. Ges. *55*, 2332 (1922).
26. Klinot J., Vystrčil A.: Collect. Czech. Chem. Commun. *27*, 377 (1962).
27. Nair M. R., Hilgard S., Klinot J., Waisser K., Vystrčil A.: Collect. Czech. Chem. Commun. *41*, 770 (1976).
28. Klinot J., Waisser K., Streinz L., Vystrčil A.: Collect. Czech. Chem. Commun. *35*, 3610 (1970).
29. Ruzicka L., Brünger H., Gustus E. L.: Helv. Chim. Acta *15*, 634 (1932).

Translated by M. Tichý.