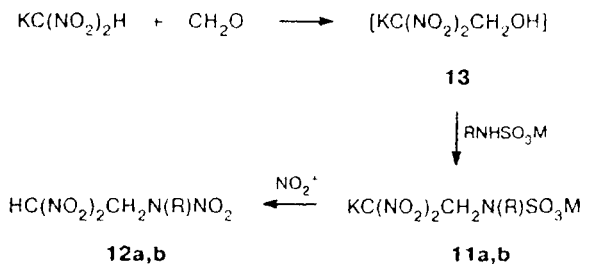
and formaldehyde yields products **11**, whose nitration gives compounds **12**.



Apparently, potassium dinitromethane first reacts with formaldehyde to give an intermediate (**13**), which is further condensed with *N*-alkylsulfamates. This mechanism was confirmed by direct reaction of *N*-alkylsulfamates with salt **13** (Table 1).

The results cited above suggest that the Mannich reaction of *gem*-dinitroalkanes with derivatives of sulfamic acid mainly proceeds *via* products of hydroxymethylation of *gem*-dinitroalkanes rather than sulfamates, as takes place in the classic case.

Experimental

^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer (250 MHz) in $(CD_3)_2CO$ with HMDS as the internal standard. IR spectra were recorded on a UR-20 instrument (KBr).

Condensation of potassium *N*-methylsulfamate with 2,2-dinitropropan-1-ol (4). Potassium *N*-methylsulfamate (1.49 g, 10 mmol) was added to a solution of 2,2-dinitropropan-1-ol (1.58 g, 10.5 mmol) in 5 mL of 40% ethanol, and pH was adjusted to ~4.7. The reaction mixture was concentrated on a rotary evaporator until a crystalline precipitate formed. The precipitate was washed with ether from the unreacted starting compound **4** to give potassium *N*-(2,2-dinitroprop-1-yl)-*N*-methylsulfamate **2a** (~2.77 g, 97%), m.p. 160—162 °C. IR (ν/cm^{-1}): 1330 s, 1558 s, 584 s; ~1200—1210 s.

Nitration of condensation product 2a. Compound **2a** (2.77 g) was added with stirring to a mixture of 98% HNO_3 (6 mL) and 95% H_2SO_4 (4.6 mL) at −10 to −15 °C. The reaction mixture was stirred at −10 to −15 °C for an extra 30 min and poured into a mixture of water and ice (40 g). The crystalline product that formed was filtered off, washed with water, and dried in a desiccator over P_2O_5 *in vacuo* to give *N*-methyl-1-nitramino-2,2-dinitropropane (**3a**) (1.73 g, ~84%), m.p. 67—68 °C (*cf.* Ref. 1: m.p. 67—68 °C).

Compounds **3b**, **3c**, **3d**, **3e**, **7a**, **7b**, **8a**, **8b**, **10a**, **12a**, and **12b** were obtained in a similar way.

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Triterpenoids from *Abies* species
24.* Photochemical fragmentation of trinor-mariesiane hydroxy ketone

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Norrish (type II) photochemical fragmentation of 25,26,27-trinor-17,14-*frido*-9β-lanostane 23-ketone was performed to give the 17α-vinyl derivative, a promising intermediate for the synthesis of 4,4-dimethyl-9β-steroid derivatives.

Key words: triterpenoids, methyl ketones, Norrish photochemical fragmentation of ketones, two-dimensional NMR spectroscopy.

Acids **1** ((24*E*)- and (24*Z*-isomers) with the mariesiane[2] carbon skeleton are the main components of the natural pool of triterpenoid acids from the needles of the Siberian fir (*Abies sibirica* Ledb.). This fact was established by chromatography of the pool of their methyl esters[3] and from the GLC data for neutral methyl

*For Part 23, see Ref. 1.

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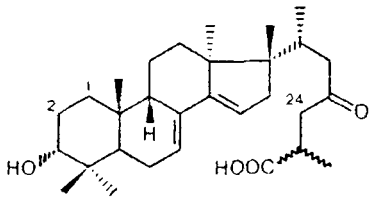
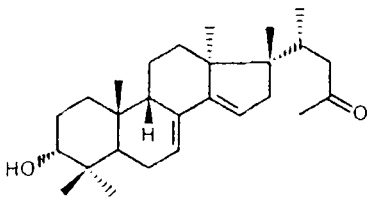
ketones generated by fragmentation of these acids under the action of an ethanolic alkali solution.[4] Both acids **1** give the same methyl ketone **2** during this fragmentation. The easy generation of compound **2** and the availability of the initial pool of triterpenoid acids makes methyl ketone **2** a promising starting compound for the preparation of various 4,4-dimethyl-9β-steroid derivatives with a stereochemically modified tetracyclic moiety.



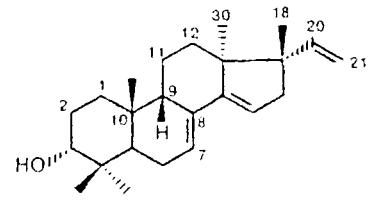
1



2

This work deals with the possibility of the further shortening of the side chain in the molecule of the derivative **2** using the known Norrish (type II) photochemical fragmentation of ketones.[5–6]

The molecule of ketol **2** contains two chromophore groups, *viz.*, the keto group and the cisoid diene system, which is responsible for the UV spectrum with the maximum at 228 nm (log ε 3.76).[7] The former group is able to cause the Norrish fragmentation of the molecule **2** under UV irradiation, while the photochemical participation of the latter moiety is not quite predictable. However, the hexanortriterpenoid derivative **3** was found to be the only isolable product of the photochemical reaction of ketone **2** in MeOH. As the derivative **3** is less polar than the starting compound, it could be isolated quantitatively from the mixture of products by single chromatography on SiO_2. The yield of alkene **3** was *ca.* 50% with respect to reacted hydroxy ketone **2**, the other products being the complex mixture of the highly polar compounds without a distinct major component (TLC data).



3

Table 1. ^{13}C and ^{1}H NMR data for compound **3** ($CDCl_3$, TMS)

C atom	^{13}C NMR, δ*	^{1}H NMR, δ (*J*/Hz)**
1	28.74 t	0.94; 2.03 (α-HC(1))
2	25.22 t	1.59; 1.96
3	76.53 d	3.44 narr.m
4	37.08 s	—
5	38.03 d	1.53 dd (11.5; 5.0)
6	23.10 t	1.84–2.10 (2 H)
7	120.97 d	5.58 br.d (7.0)
8	136.52 s	—
9	53.39 d	1.41 m
10	34.77 s	—
11	24.86 t	1.36; 1.82
12	31.13 t	1.36 (α-HC(12)); 1.69 (β-HC(12))
13	51.22 s	—
14	151.83 s	—
15	114.73 d	5.23 narr.m
16	42.31 t	1.88 dd (16; 3) (α-HC(16)); 2.56 br.d (16) (β-HC(12))
17	50.90 s	—
18	21.03 q	1.02 s
19	22.27 q	0.96 s
20	144.99 d	5.94 dd (17.0; 11.0)
21	111.39 t	4.90–5.00 m (2 H)
28	28.11 q	0.97 s
29	22.92 q	0.91 s
30	24.02 q	0.76 s

* The signals were assigned using the data published for the related compound.[7]

** The signals of the protons of the angular methyl groups were assigned taking into account the following cross peaks observed in the COSYLR spectrum: $H_3C(18)$/α-HC(16); $H_3C(19)$/α-HC(1); $H_3C(29)$/HC(3); and $H_3C(30)$/β-HC(12).

The molecular structure of compound **3** resulting from the Norrish (type II) photochemical fragmentation of molecule **2** was confirmed by ^{13}C and ^{1}H NMR (Table 1, two-dimensional $^{1}H-^{1}H$ COSY and COSYLR NMR spectra were used), mass spectrometry, and IR spectroscopy data (see Experimental). The remarkable downfield shift of the signals of C(18) and C(30) is worthy of note. This can be explained by the appearance of the vinyl group at C(17) likely causing this shift.

Experimental

The melting point was determined on a Kofler stage. The IR spectrum was recorded on a UR-20 instrument. The NMR spectra of $CDCl_3$ solutions were registered on a Bruker AM-400 spectrometer with working frequencies of 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C. The high resolution mass spectrum was obtained on a Finnigan MAT-8200 mass spectrometer (EI, 70 eV). The optical rotation was determined on a Polamat A polarimeter at 580 nm in $CHCl_3$.

Column chromatography was performed on KSK Silica gel with a compound–sorbent ratio of 1:20 (w/w) (elution with

hexane containing 10—25% of Et_2O). TLC was carried out on Silufol plates. The spots were visualized by spraying with concentrated H_2SO_4 and subsequent heating.

22,23,24,25,26,27-Hexanor-3α-hydroxy-17,14-*frido*-9β-lanosta-7,14,20-triene (3). A solution of 140 mg of hydroxy ketone **2** (m.p. 84—85 °C, prepared by the previously described method[8]) in MeOH (20 mL) was placed in a quartz cylindrical 30-cm cell (with an inner diameter of 20 mm and wall thickness of 2 mm) and heated to reflux in a water bath in order to remove dissolved oxygen from methanol. The cell was then cooled quickly to ~20 °C, sealed with a polyethylene stopper, and irradiated (using no filter) with the full light of a DRSh-1000 high-pressure mercury vapor lamp, the cell being cooled with an air stream from a ventilator. After 10 h of irradiation methanol was removed, and the residue was chromatographed on SiO_2 (5 g). Elution with a 9 : 1 hexane—ether mixture yielded 30 mg of product **3** with m.p. 118—120 °C (from pentane) and $[\alpha]^{22}_{580}$ +133.8° (*c* 0.89; $CHCl_3$). UV (C_2H_5OH), λ_{max}/nm: 232 (ε 8800). IR (CCl_4), ν/cm^{-1}: 905, 1640, 3090 (—CH=CH_2), 3620 (OH). MS, *m/z* (I_{rel} (%)): 340 [M]$^+$ (100), 307 (26), 187 (26), 145 (28), 55 (90). High resolution MS, *m/z*: 340.27565; calculated for $C_{24}H_{36}O$: 340.27660. ^{13}C and ^1H NMR spectra are given in Table 1.

Elution with a 4 : 1 hexane—Et_2O mixture resulted in 80 mg of starting compound **2**, and the mixture of highly polar substances (30 mg) was eluted with Et_2O.

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Influence of *E*/*Z* isomerism of aldoximes on the direction of their alkylation with oxirane

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The reaction of *Z*-2-furaldoxime with oxirane afforded the *N*-alkylation product, *viz.*, α-2-furyl-*N*-(2-hydroxyethyl)nitron, in good yield. *E*-Benzaldoxime gave predominantly the *O*-alkylation product, while its *Z* isomer was converted into a mixture with the *N*-alkylation product slightly predominating.

Key words: oxirane, aldoximes, α-aryl-*N*-(2-hydroxyethyl)nitrons.

Oximes and oxiranes are attractive, simple, and readily available initial compounds for preparing α-aryl-*N*-(2-hydroxyethyl)nitrons. However, attempts to alkylate benzaldoxime[1,2] (m.p. 31—33 °C, which corresponds to the *E* isomer[3]) resulted in nitron in a yield of only 3—6%. In all cases, a product of *O*-alkylation of oxime or products of its subsequent oxidation were obtained as the major reaction products.[1] At the same time, in the case of alkylation of oximes with alkyl halides, the orientation of alkylation (*O*- or *N*-) depends directly on the *E* or *Z* configuration of the oxime used.[4] It was also reported[5] that the reaction of *Z*-benzaldoxime with 1,2-epoxybutane afforded *trans*-5-ethyl-2-phenyl-3-hydroxyoxazolidine in 70% yield. It is known[6] that 3-hydroxyoxazolidines can exist in tautomeric equilibrium with the open form of α-arylnitron. Based on the aforesaid, we suggested that the use of oximes with the *Z* configuration should shift the direction of the reaction

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