Tetrahedron. Vol. 29, pp. 4331 to 4340. Pergamon Press 1973. Printed in Great Britain

MECHANISM OF FORMATION OF UNUSUAL PHOTODEGRADATION PRODUCTS FROM FRIEDELIN

R. AOYAGI, T. TSUYUKI, M. TAKAI and T. TAKAHASHI*
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo Bunkyo-ku, Tokyo, Japan

and

F. KOHEN and R. STEVENSON
Department of Chemistry, Brandeis University, Waltham, Massachusetts, 02154, U.S.A.

(*Received in Japan* 8 *May* 1973; *Received in the UK for publication* 28 *June* 1973)

Abstract—From the photolysate of friedelin **1**, 3,4-seco-3-nor-friedelan-2-al **2** and 3,4-seco-3-nor-friedelan-2-oic acid **3** were obtained in addition to the expected photoproducts. Evidence is provided that **2** and **3** are autoxidation products of the ketene **13** produced by α-cleavage of **1** followed by hydrogen transfer.

Upon irradiation of friedelin **1**, α-cleavage[1] would be expected to occur between C-3 and C-4 because of the 3-oxo-4-methyl structure in the A-ring of friedelin. The consequent acyl–alkyl diradical then would react by three principal pathways, (a) elimination of carbon monoxide to give a hydrocarbon mixture,[2-4] (b) recyclization in two different configurations to give friedelin **1** and 4-epifriedelin **1'**,[5,6] and (c) hydrogen transfer from C-2 to the alkyl radical *via* six-membered ring transition state to a ketene **13**, which further reacts with solvent to afford 3,4-seco-products **5**, **6** or **7**.[3,4] In previous papers[2-6] we reported the photoirradiation of friedelin in various solvents and the isolation and identification of these photochemical products.

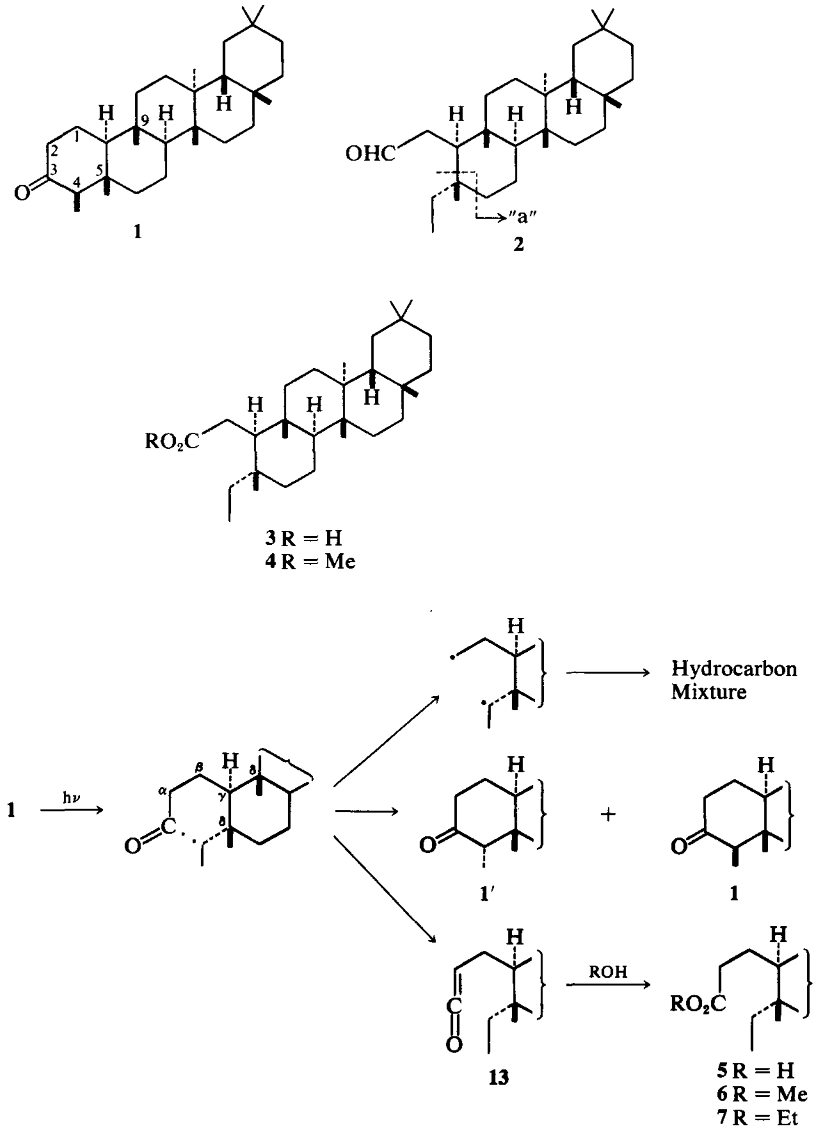
Since the acyl–alkyl diradical bears no hydrogen atom on the δ-carbon atom (C-5) hydrogen transfer to give a δ-unsaturated aldehyde is not observed. From the photolysates of friedelin in n-hexane or in diethyl ether, however, we isolated an aldehyde and an acid as unexpected products and showed them to be the degradation products 3,4 - seco - 3 - nor - friedelan - 2 al **2** and 3,4 - seco - 3 - nor - friedelan - 2 - oic acid **3**, respectively.[7-9] In this paper we wish to describe in detail the structure elucidation and the mechanism of formation of these two products.

Friedelin **1** was irradiated in n-hexane or ether with a high pressure mercury lamp under a N_2 atmosphere at room temperature to give a complex mixture, from which an aldehyde was isolated in about 1% yield after purification by chromatography and crystallization. From the photolysate of friedelin in n-hexane, an acidic fraction was isolated by silica gel column chromatography, and after esterification with diazomethane yielded two methyl esters.

The aldehyde[4,8,9] had m.p. 182° and molecular formula $C_{29}H_{50}O$, (elemental analysis and mass spectrometry). This corresponds to a loss of one carbon atom from friedelin ($C_{30}H_{50}O$). The IR spectrum showed bands at 2740 and 1727 cm^{-1} characteristic of an aldehyde group, but bands due to olefinic bending (ν_{C-H}) and double bond stretching ($\nu_{C=C}$) vibrations were not observed. This was supported by a negative tetranitromethane test and no high intensity UV absorption above 200 mμ. In the NMR spectrum an aldehydic proton (δ 9·78 ppm, t, $J = 2·5$ Hz) and an α-methylene group (δ 2·32 ppm, m, 2H) were detected. These observations suggest that the aldehyde must be tetracyclic. The C-4 secondary methyl function, δ 0·88 ppm (d, $J = 7$ Hz) in friedelin, was absent. This is most reasonably explained by the presence of 3,4-seco-A-ring, and is substantiated by a peak at *m/e* 358 (relative intensity 8%, $[M-56]^+$) due to fragmentation "a" in the mass spectrum (Scheme 1). From these observations, the aldehyde was formulated as 3,4-seco-3-nor-friedelan-2-al **2**[10] and this was confirmed by comparison with a specimen prepared by the following unequivocal procedure.

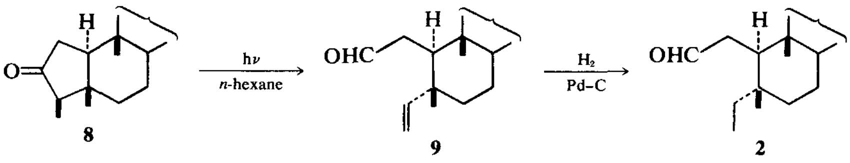
Norfriedelin **8**[11] in n-hexane was irradiated using a high pressure mercury lamp to give 3,4 - seco - 3 - nor - feiedel - 4(23) - en - 2 - al **9**.[12] This unsaturated aldehyde was then hydrogenated in the presence of palladium-carbon to yield a product, m.p. 181–181·5° identical with the seco-nor-aldehyde isolated from the photolysate of friedelin. Thus, the aldehyde was 3,4 - seco - 3 - nor - friedelan - 2 - al **2**.

The two methyl esters (R_f 0·67 and 0·56) derived from the acid fraction were separated by silica gel column chromatography and that with lower R_f identified as methyl 3,4-seco-friedelan-3-oate **6** by direct comparison with an authentic sample. The



SCHEME 1

methyl ester with higher R_f had m.p. 173° and a carbonyl absorption band at 1735 cm^{-1} in the IR spectrum. The NMR methyl signal patterns due to seven angular methyl groups were almost identical in these two esters. The mass spectrum of the latter showed the molecular ion peak at *m/e* 444, which was 14 mass units (corresponding to CH_2) lower than that of the former (M^+ 458). Moreover, the peaks of $(M\text{-}56)^+$ characteristic for the 3,4-seco-structure were observed in both esters. A



SCHEME 2

loss of 56 mass units could be interpreted by the above-mentioned fragmentation "a".

From these facts, the methyl ester (R_f 0·67, m.p. 173°) was inferred to be the lower homologue, methyl 3,4-seco-3-nor-friedelan-2-oate **4**, and this was established by comparison with an authentic sample[7] obtained by the Barbier–Wieland degradation of ethyl 3,4-seco-friedelan-3-oate **7**.

The well-known photocleavage of cyclohexanones to yield δ-unsaturated aldehyde by α-cleavage followed by transfer of a hydrogen atom from a δ-carbon atom through a six membered transition state is unavailable for friedelin because of the quaternary C-5 atom. Since the formation of the saturated nor-aldehyde from UV irradiation of friedelin is unusual, a mechanistic investigation was carried out.

A solution of $2\alpha,2\beta,4\alpha$-trideuteriofriedelin **1**-d_3 in n-hexane was irradiated under the same conditions, the reaction products separated by silica gel chromatography, and the aldehyde and the acidic fraction were isolated as before.

The aldehyde **2**-d_3, after crystallization from diethyl ether, was shown to contain three deuterium atoms by the mass spectrometric determination. The locations of the deuterium atoms were determined by NMR spectral measurement. The signal at δ 9·78 ppm (t, $J = 2·5$ Hz) attributable to an aldehydic proton of **2** was absent in **2**-d_3 and the multiplet centered at δ 2·32 ppm (C-1 methylene) of **2** appeared as a doublet at δ 2·32 ppm ($J = 5·3$ Hz, 2H) in the deuteriated aldehyde. Thus, one of the three deuterium atoms of **2**-d_3 is a deuterioformyl function (C-2) and two hydrogen atoms are located at C-1.

Reduction of the deuteriated aldehyde (**2**-d_3) with lithium aluminum hydride afforded an alcohol (**12**-d_3), which gave the molecular ion peak at *m/e* 419. The NMR spectra of 3,4 - seco - 3 - nor-friedelan - 2 - ol **12** and the deuteriated alcohol **12**-d_3 in deuteriochloroform are shown in Figs 1a and 1b, respectively. On addition of Eu(dpm)$_3$ as shift reagent, the C-23 methyl group was readily assignable, and a triplet signal (Fig 1c) due to the C-23 methyl group of non-labelled alcohol **12** appeared as a singlet (Fig 1d) in the case of **12**-d_3. This indicates that the methylene group at C-4 of **12**-d_3 was labelled with two deuterium atoms. It may be, therefore, concluded that the C-2 and C-4 atoms have been retained, that the C-3 atom has been extruded, and that the deuteriated aldehyde should be formulated as 2,4,4 - trideuterio - 3,4 - seco - 3 - nor - friedelan - 2 - al **2**-d_3.

The acidic fraction was methylated with diazomethane and separated into labelled methyl 3,4-seco-3-nor-friedelan-2-oate **4**-d_2 and methyl 3,4-seco-friedelan-3-oate **6**-d_3. Mass spectrometric examination showed that the former contained two and the latter contained three deuterium atoms, and from the foregoing, these deuterium atoms may be placed at the 4,4- and 2,4,4-positions, respectively (Scheme 4).

These findings are rationalized by the mechanistic pathway involving autoxidation of the ketene **13**-d_3. Although Staudinger *et al*[13] have proposed that a ketene may decompose *via* an oxygen-adduct such as **14** to give an aldehyde and carbon dioxide, mechanistic proof is lacking. Evidence of the formation from friedelin **1** of the intermediate ketene **13** as a precursor of the aldehyde **2** from friedelin **1** was demonstrated as follows. On completion of irration of **1**, oxygen-free methanol was immediately added to the reaction mixture under a nitrogen atmosphere, solvents were removed under reduced pressure and the residue examined by TLC and mass spectrometry. The presence of the aldehyde **2** was scarcely detectable and the main reaction product was methyl 3,4-seco-friedelan-3-oate **6**.

The formation of the seco-nor-aldehyde **2** is, therefore, explained by the autoxidation of the ketene **13**. After the photoirradiation of **1** under the same conditions, dry air was introduced for 8·5 h in the dark and then methanol was added. The yield of the seco-nor-aldehyde **2** increased. On the contrary the yield of the seco methyl ester **6** was exceedingly reduced.

If the above ketene autoxidation mechanism actually pertains, the C-3 atom should be extruded as carbon dioxide. This was supported by a study of the irradiation of ^{18}O-friedelin. A solution of 3-nitriminofriedelane **15**[14] in water containing 20% $H_2{}^{18}O$ and dioxane was heated under reflux for 34 h. Column chromatographic separation and recrystallization gave ^{18}O-labelled friedelin (**1**-^{18}O); isotopic abundance was determined by mass spectrometry by comparison with the relative intensities of peaks at *m/e* 428, 427, and 426 of **1**. In the mass spectrum of **1**-^{18}O, the percentage increase (30·7%) in relative intensity of the peak at *m/e* 428 corresponded to the isotopic content of ^{18}O-atom in the labelled friedelin (**1**-^{18}O) (Table 1).

Photoirradiation of **1**-^{18}O in n-hexane under the same conditions and column chromatographic separation yielded the aldehyde and the acids. The latter was treated with diazomethane to afford **4** and **6**-^{18}O. Mass spectrometric examination showed that

Table 1. ^{18}O-Isotopic abundance*

Compounds	M	M+1	M+2	ΔM+1	ΔM+2
1	100	34·6	6·4		
1-^{18}O	100	36·7	37·1	2·1	30·7
6 (from **1**)	100	35·5	6·6		
6 (from **1**-^{18}O)	100	38·8	33·2	3·3	26·6
4 (from **1**)	100	33·9	6·8		
4 (from **1**-^{18}O)	100	36·3	11·0	2·4	4·2
2 (from **1**)	100	34·0	6·1		
2 (from **1**-^{18}O)	100	37·6	9·0	3·6	2·9

*Relative intensity.

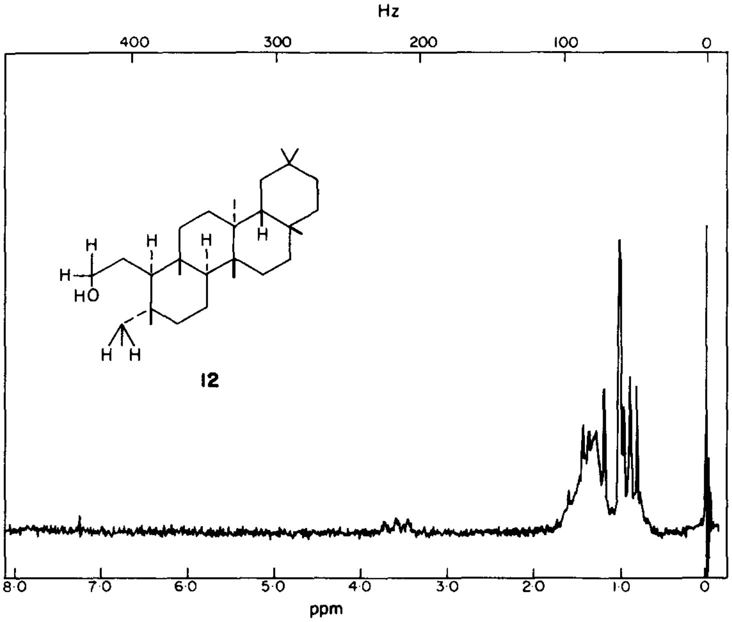


Fig 1a

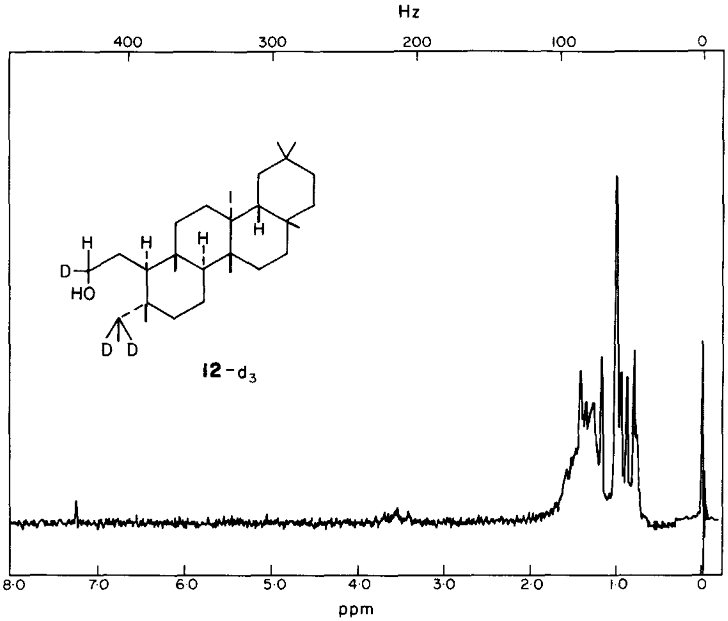


Fig 1b

whereas the aldehyde **2** and the seco-nor-methyl ester **4** contained essentially no ^{18}O, this was not so for the seco-methyl ester (**6**-^{18}O) (Table 1).

The intermediacy of the ketene **13** was further demonstrated. 3,4-Seco-friedelan-3-oyl chloride **16** was treated with triethylamine in n-hexane to afford the ketene **13**, whose formation was confirmed by reaction with deuteriomethanol to afford methyl 3,4-seco-2-deuteriofriedelan-3-oate **6**-d$_1$. After removal of triethylamine hydrochloride, a slow stream of dry oxygen was passed through the solution overnight at room temperature. The reaction

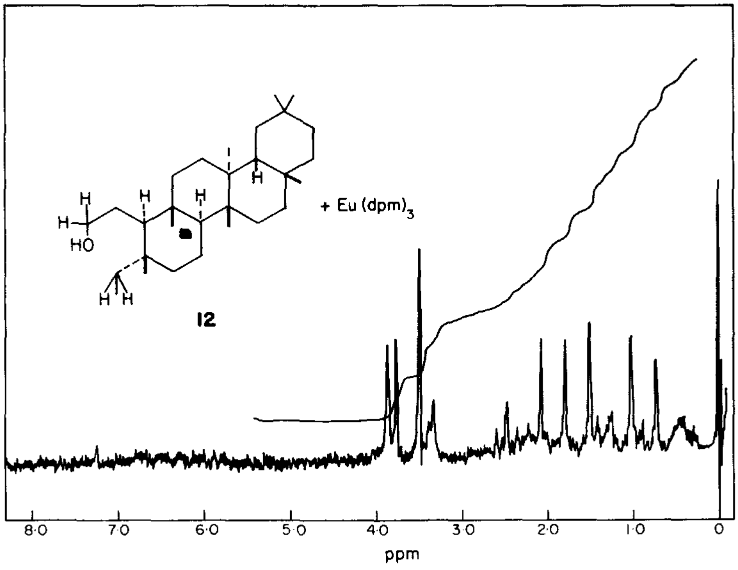


Fig 1c

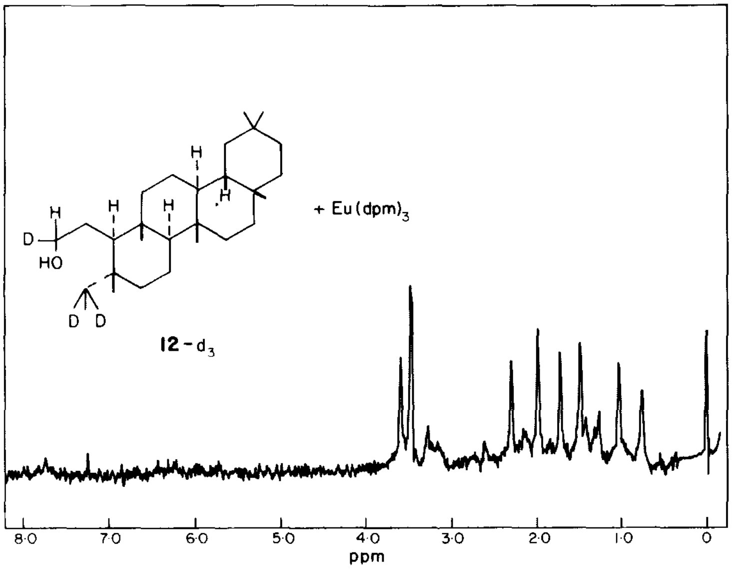
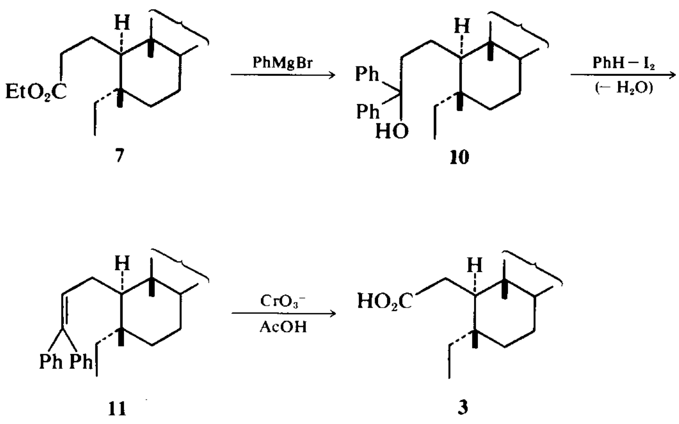


Fig 1d

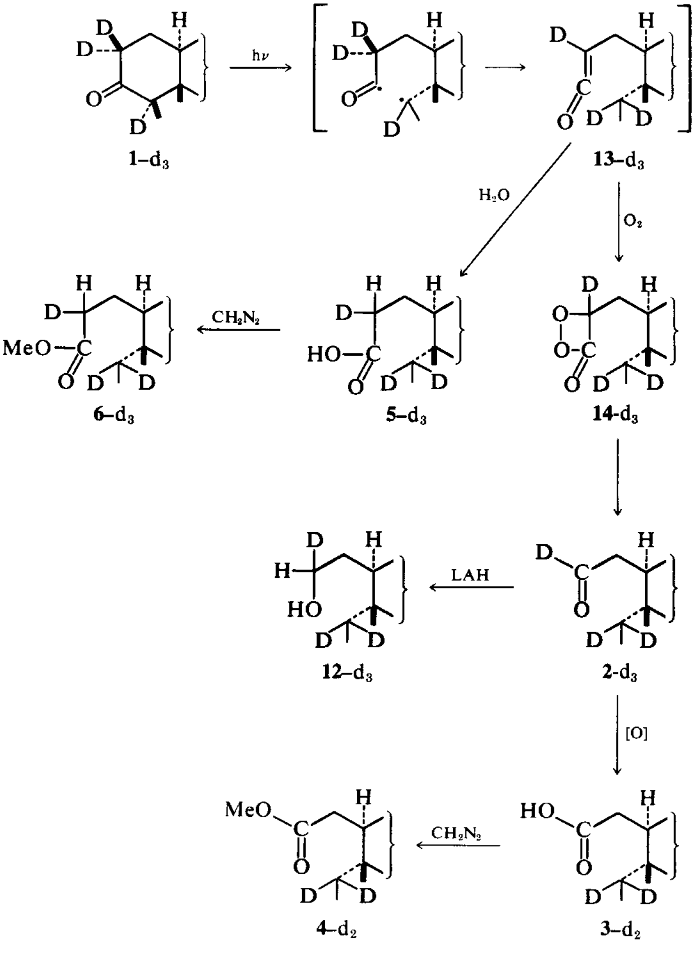
product was chromatographed on silica gel and an oxygen-adduct and the aldehyde **2** were isolated. The oxygen-adduct, tentatively formulated as **14** showed IR absorption bands at 1740 and 1168 cm^{-1}, NMR δ 4·1–4·5 ppm (m, 1H, $-O-\underset{|}{C}\underline{H}-CH_2-$) and M$^+$ 458.

Thus these observations support the conclusion that the seco-nor-aldehyde **2** is an autoxidation product formed from the ketene **13** during work-up.

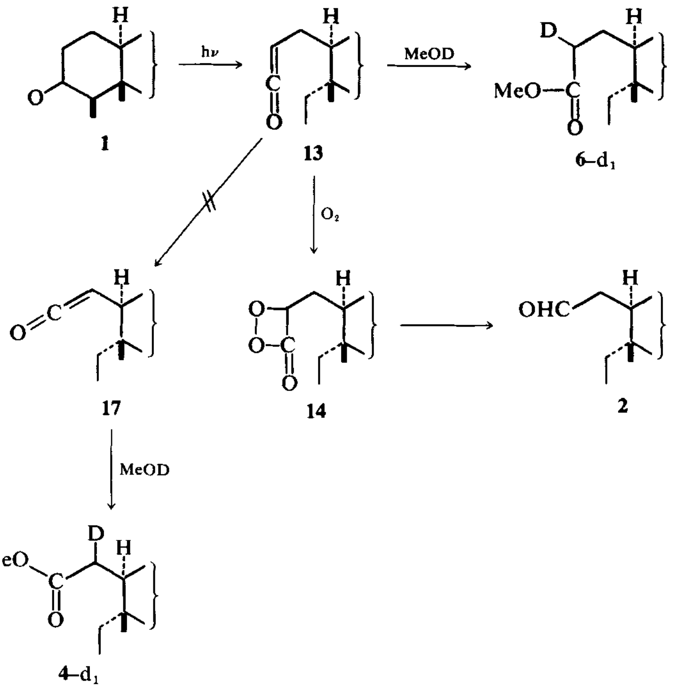
The formation of 3,4-seco-3-nor-friedelan-2-oic acid **3** is rationalized by the oxidation of the seco-nor-aldehyde **2**. Although **2** is rather stable in air at room temperature, it can be oxidized to the seco-nor-acid **3** on heating a benzene [illegible] small quantity of water. This pathway was substantiated by the above mentioned experiments using appropriate D and ^{18}O labels. On methyl esterification of the acid fraction of the photolysate of 2,2,4-



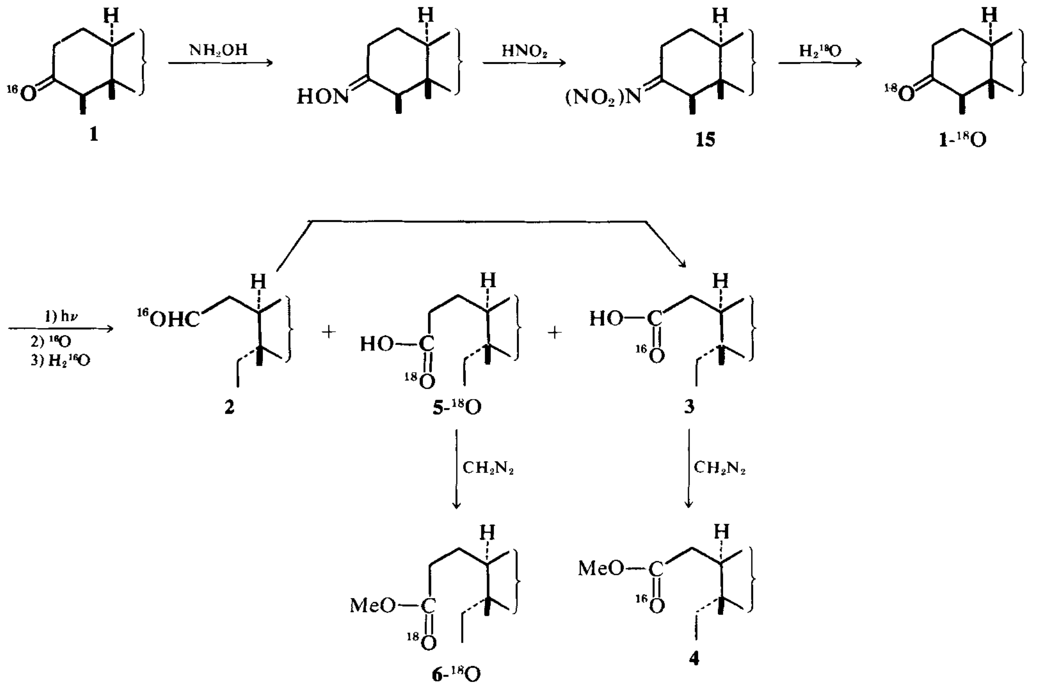
SCHEME 3



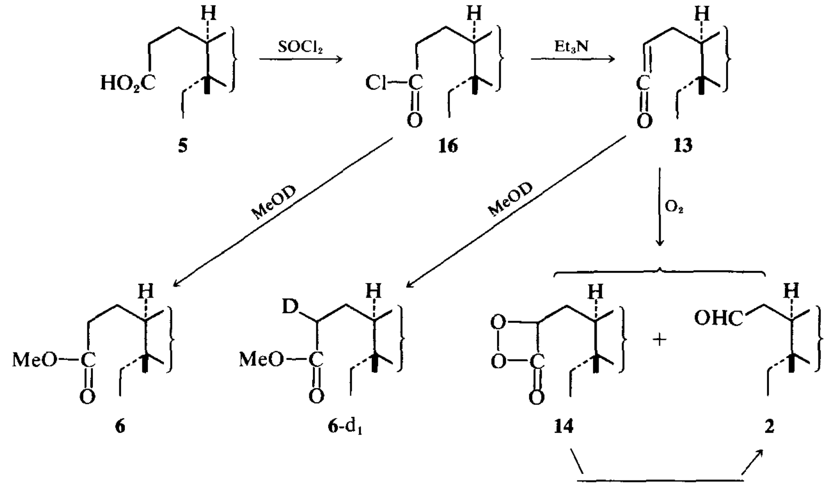
SCHEME 4



SCHEME 5



SCHEME 6



SCHEME 7

trideuteriofriedelin 1-d_3, the dideuterio-seco-nor-ester 4-d_2 considered to be derived from the trideuterio-sec-nor-aldehyde (2-d_3) was obtained (Scheme 4). Furthermore, in the case of friedelin-^{18}O, no ^{18}O-atom was detected in the seco-nor-ester 4 (Scheme 6).

On completion of the irradiation of friedelin 1 in n-hexane, dry oxygen was passed into the solution and then deuteriomethanol was added. The reaction products were separated and examined by TLC and the mass spectrometry. The ester fraction was shown to consist exclusively of methyl 3,4-seco-2-deuteriofriedelan-3-oate 6-d_1, M^+ 459, and that methyl 3,4-seco-3-nor-1-deuteriofriedelan-2-oate 4-d_1, M^+ 445, whose formation would be expected by the reaction of a seco-nor-ketene such as 17 with deuteriomethanol, was absent. The formation of an intermediate such as the seco-nor-ketene 17 in the reaction sequence (Scheme 5) is consequently excluded.

EXPERIMENTAL

All m.ps were determined on a hot stage and are uncorrected. IR and mass spectra were measured using Hitachi EPI-G2 and Hitachi RMU-6 spectrometers. NMR spectra were taken on a Hitachi Model R-20, R-24, or a JEOL-JNM-C-60 spectrometer at 60 MHz, using TMS as internal standard. Silica gel column chromatographs and TLC were carried out on Wakogel C-200 (Wako Pure Chemicals) and Kieselgel G nach Stahl (Merck), respectively.

Isolation of 3,4-seco-3-nor-friedelan-2-oic acid **3** *from the photoreaction product of friedelin* **1**. Friedelin **1**, 1·00 g, in n-hexane (500 g) was heated under reflux under argon for 1 h and the resulting soln was irradiated with a high pressure mercury lamp (100 W, Rikosha) under argon for 8 h. After evaporation of solvent, the residue was chromatographed giving hydrocarbon, aldehyde, ketone and acid fractions as reported previously.[2–9] The acidic fraction, eluted with benzene–diethyl ether (10:1), was methylated with diazomethane in diethyl ether. The methylated product, which showed two spots with R_f values 0·67 and 0·56, on TLC developed with petroleum ether–benzene (4:1), was subjected to silic gel chromatography. The methyl ester (R_f 0·56) was identical with authentic methyl 3,4-seco-friedelan-3-oate **6**. The methyl ester (R_f 0·67) was crystallized from acetone to give methyl 3,4-seco-3-nor-friedelan-2-oate **4**, 105 mg, yield 10%, m.p. 173–174°; IR $\nu_{C=O}$ 1735 cm^{-1}; NMR ($CDCl_3$) δ 3·68 ($COOC\underline{H}_3$, s), 2·23 ppm ($—CO—C\underline{H}_2—$, d, $J =$ 4·8 Hz); MS, M^+ at *m/e* 444; Found C, 81·27; H, 11·81. Calc for $C_{30}H_{52}O_2$ C, 81·27; H, 11·79%.

The methyl ester **4** in ethanol was heated with potassium hydroxide under reflux. Crystallization from benzene gave 3,4-seco-3-nor-friedelan-2-oic acid **3**, m.p. 249–250°; IR $\nu_{C=O}$ 1695 cm^{-1}.

Methyl 3,4-seco-3-nor-friedelan-2-oic acid **3** *from friedelin* **1**. Ethyl 3,4-seco-friedelan-3-oate **7**, 450 mg, prepared by the photoreaction of friedelin **1** in ethanol, was dissolved in tetrahydrofuran, and magnesium (500 mg) was added. Bromobenzene (2 ml) in tetrahydrofuran (10 ml) was added and the reaction mixture was heated under reflux for 1 h. After usual work-up, crystallization from petroleum ether gave 3,3-diphenyl-3,4-seco-friedelan-3-ol **10**, m.p. 189–190°; IR $\nu_{O—H}$ 3560 cm^{-1}; Found C, 86·45; H, 11·17. Calc for $C_{42}H_{62}O$ C, 86·53; H, 10·72%.

The diphenylcarbinol **10**, 864 mg in benzene (2 ml) was dehydrated by heating with iodine under reflux for 5 h. The reaction product, after washing with sodium thiosulphate aqueous soln and then evaporation to dryness, was dissolved in petroleum ether and passed through a silica gel column (40 g). 3,3-Diphenyl-3,4-seco-friedel-2-ene **11**, eluted with petroleum ether, was crystallized from light petroleum:benzene, m.p. 202–203°; IR$\nu_{C=C}$ 1595 cm^{-1}; Found C, 89·14; H, 10.72. Calc for $C_{42}H_{60}O$ C, 89·29; H, 10·71%.

The diphenylethylene **11**, 677 mg, was dissolved in a mixture of benzene (20 ml) and acetic acid (30 ml), and oxidized with chromiun trioxide (1·0 g) in acetic acid (20 ml) and water (1 ml) at room temp for 40 h. An excess of the oxidizing reagent was destroyed by addition of methanol and the reaction product was extracted with diethyl ether. On crystallization from benzene, 3,4-seco-3-nor-friedelan-2-oic acid **3** was obtained, m.p. 249–250°; Found C, 80·51; H, 12·47. Calc for $C_{29}H_{50}O_2$ C, 80·49; H, 12·11%. This was methylated with diazomethane in diethyl ether to give methyl 3,4-seco-3-nor-friedelan-2-oate **4**, m.p. 173–174°; Found C, 81·27; H, 11·81%. Calc for $C_{30}H_{52}O_2$ C, 81·02; H, 11·79%. This was identical with the specimen obtained from the photoreaction of friedelin by comparison of IR, NMR, MS, TLC, and GLC (column: Diasolid H-523, temp 240°, retention time 14·5 min).

Isolation of 3,4-*seco*-3-*nor-friedelan*-2-*al* **2** *from the photoreaction product of friedelin* **1**. (i) *In n-hexane*: Irradiation of friedelin **1**, 1·00 g in n-hexane (500 g) gave the same reaction mixture as above. This was separated by silica gel column chromatography and a crude aldehyde fraction was eluted with petroleum ether–benzene (10 : 1). The aldehyde fraction, containing a ketene, was chromatographed on alumina to afford **2** (6·2 mg). (ii) *In ether*: To a soln of friedelin **1** (1·00 g) in diethyl ether (1 l), nitrogen was introduced for 1 h at room temp, and the soln was irradiated at room temp under N_2 for 2·25 h with a high pressure quartz mercury lamp (Hanovia 8A-36). After solvent removal under reduced pressure, the residue from two such experiments was dissolved in a mixture of petroleum ether–benzene (4 : 1) and passed through a column (silica gel, 0·05–0·20 mm, Merck; 300 g). After the hydrocarbon mixture, the crude aldehyde fraction (84 mg) was eluted with the same solvent and was subjected to further rechromatographic purification on alumina (Woelm, neutral, 15 g and then repeated on 20 g). Crystallization from ether gave **2** (18 mg), m.p. 182°; IR ν_{C-H} 2740, $\nu_{C=O}$ 1727 cm^{-1}; NMR δ 2.32 (OHC—C$\underline{H}_2$—C—, m), 9·78 ppm (C$\underline{H}$O, t, J=2·5 Hz); Found C, 84·29; H, 12·00. Calc for $C_{29}H_{50}O$ C, 83·99; H, 12·25%. MS; *m/e* (relative intensity) 414 (65, M$^+$), 399 [29, (M-15)$^+$], 386 [21, (M-28)$^+$; aldehyde], 385 [8, (M-29)$^+$], 371 [10, (M-43)$^+$; loss of —CH_2—CHO], 358 [8, (M-56)$^+$; fission "a"], 273 (69), 261(18), and 205(100).

3,4-*Seco*-3-*nor-friedelan*-2-*al* **2** *from* 3,4-*seco*-3-*nor-friedel*-4(23)-*en*-2-*al* **9**. 3,4-Seco-3-nor-friedel-4(23)-en-2-al **9** (60 mg)[12] prepared from norfriedelin **8** was hydrogenated over Pd-C (14 mg) in ethanol (50 ml). Usual treatment gave a residue which was recrystallized from ether to afford **2** (41 mg), m.p. 181–181·5°, identical with the specimen obtained from the photoreaction of **1** (IR, NMR, MS, and TLC).

Photochemical reaction of $2\alpha,2\beta,4\alpha$-*trideuterio-friedelin* (**1**-d_3) *in n-hexane*. (i) *Preparation of* $2\alpha,2\beta,4\alpha$-*trideuterio-friedelin* **1**-d_3: Friedelin **1** (1·00 g) in dioxane (40 ml) was heated under reflux with 2 ml of 30% sodium deuterioxide (isotopic purity: 99 atom % D) in D_2O for two days. After the solvent had been removed, the residue was extracted with chloroform and then with diethyl ether. The extracts were combined, dried and evaporated to dryness. The residue was subjected to this treatment four times and finally crystallized from ethyl acetate to give 0·53 g **1**-d_3. Mass spectrometry showed that the deuteriated friedelin consisted of $-d_3$ (80%), $-d_2$ (20%), $-d_1$ (0%), and $-d_0$ (0%). (ii) *Photochemical reaction of* **1**-d_3 *in n-hexane*: **1**-d_3 (330 mg) in n-hexane (500 g) was heated under reflux under N_2 for 30 min and the resulting soln, after cooling, was irradiated with a high pressure mercury lamp for 27 h under N_2 at room temp, then evaporated under reduced pressure. The residue was dissolved in petroleum ether–benzene (10 : 1), passed through a column (silica gel, 33 g) and aldehyde and acid fractions were collected. The aldehyde fraction was crystallized from diethyl ether to give 19·1 mg 2,4,4-trideuterioaldehyde **2**-d_3, IR $\nu_{C=O}$ 1730 cm^{-1}; NMR ($CDCl_3$) δ 2·32 (d, $J = 5{\cdot}3$ Hz, C-1 methylene), no signal at δ 9·78 ppm; *m/e* 417.

The acidic fraction was treated with diazomethane in diethyl ether and chromatographed on silica gel (4 g, dry column) to afford deuterated seco-nor-ester **4**-d_2 (15·1 mg) and seco-ester **6**-d_3 (14·2 mg). By mass spectrometric determination, the empirical formulae, $C_{30}H_{50}D_2O_2$ for **4**-d_2 (M$^+$ 446) and $C_{31}H_{51}D_3O_2$ for **6**-d_3 (M$^+$ 461) respectively, were confirmed.

Reduction of 2,4,4-*trideuterio*-3,4-*seco*-3-*norfriedelan*-2-*al* **2**-d_3. 2,4,4-Trideuterio-aldehyde **2**-d_3, 18 mg in ether (6 ml) was heated with $LiAlH_4$ under reflux for 4 h. After usual work-up and crystallization from petroleum ether, 17 mg of 2,4,4-trideuterio-3,4-seco-3-nor-friedelan-2-ol **12**-d_3 was obtained, M$^+$ 419; NMR ($CDCl_3$) in Fig 1b.

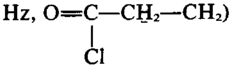
Photochemical reaction of friedelin **1** *in n-hexane followed by addition of oxygen-free methanol*. Irradiation of friedelin **1** (1·00 g) in n-hexane (500 g) was carried out during 9 h under N_2 as before, then methanol (30 ml, dried over Mg and de-oxygenated by N_2) was added. The flask was tightly stoppered and allowed to stand overnight. On removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (100 g). Elution with petroleum ether–benzene (3 : 1) gave methyl 3,4-seco-friedelan-3-oate **6** (460·3 mg after crystallization from methanol–water) M$^+$ 458, friedelin **1** (239 mg) and 3,4-seco-friedelan-3-oic acid **5** (6·1 mg). Neither methyl 3,4-seco-3-nor-friedelan-2-oate **4**, nor 3,4-seco-3-nor-friedelan-2-al **2** was detectable.

Photochemical reaction of friedelin **1** *in n-hexane followed by oxygenation*. Friedelin **1** (500 mg) in n-hexane (500 g) was irradiated in a usual manner for 13 h and then a slow stream of dry oxygen was passed through the soln for 8·5 h in the dark. After dry methanol (30 ml) was added, the solvents were removed under reduced pressure and the residue was chromatographed on silica gel (85 g). Elution with petroleum ether–benzene (3 : 1) gave 3,4-seco-3,4-seco-3-nor-friedelan-2-al **2** (35 mg) and methyl 3,4-seco-friedelan-3-oate **6** (42 mg).

Preparation and photochemical reaction of friedelin **1**-^{18}*O*. A soln of 3-nitriminofriedelane **15** (412 mg) in water containing 20% of $H_2{}^{18}O$ (1 ml) and dioxane (40 ml) was heated under reflux for 34 h. The soln was concentrated and addition of methanol gave a precipitate. This product (319 mg) was separated by silica gel (20 g) chromatography into the starting material **15** (89 mg) and labelled friedelin (273 mg). On crystallization from chloroform–methanol, friedelin containing friedelin-^{18}O was obtained (213 mg), m.p. 257–258° and the IR spectrum showed carbonyl stretching bands at 1710 cm^{-1} ($\nu_{C={}^{16}O}$) and 1670 cm^{-1} ($\nu_{C={}^{18}O}$) in a ratio of 4 : 1. The isotopic abundance in **1**-^{18}O was determined by mass spectrometry.

Irradiation of friedelin-^{18}O (**1**-^{18}O, 213 mg) in n-hexane (500 g) soln under a nitrogen atmosphere for 9 h, using a high pressure mercury lamp, followed by solvent removal under reduced pressure yielded a residue which was chromatographed on silica gel (100 g) to give **2** (21·3 mg) and an acidic fraction. The latter was esterified with diazomethane and crystallized from acetone to give **4** (8·3 mg) and **6**-^{18}O (17·8 mg). The ^{18}O-isotopic abundance in these products was examined by the the mass spectrometry.

Preparation of 3,4-*seco-friedel*-2-*en*-3-*one* **13**. A soln of 3,4-seco-friedelan-3-oic acid **5** (100 mg) in thionyl chloride (1 ml) was heated under reflux for 2·5 h. Removal of the solvent and crystallization from dry petroleum ether gave 3,4-seco-friedelan-3-oyl chloride **16** (60·2 mg), m.p. 173–174°; IR $\nu_{C=O}$ 1800 cm^{-1}; NMR ($CDCl_3$) δ 2·93 ppm (t,

$J = 8{\cdot}5$ Hz,  $O{=}\underset{\displaystyle |\atop Cl}{C}{-}CH_2{-}CH_2$); MS (*m*/*e*) M^+ (464, 462), $[M{-}CH_3]^+$ (449, 447), $[M{-}HCl]^+$ (426), and $[M{-}HCl{-}CH_3]^+$ (411). 3,4-Seco-friedelan-3-oyl chloride **16** (37 mg) was dissolved in n-hexane (50 ml) and kept at 0° under N_2. Triethylamine (1 ml) in n-hexane (10 ml) was added and the reaction mixture was allowed to stand for three days in a refrigerator. The precipitated triethylamine hydrochloride was removed and the filtrate evaporated under reduced pressure. The residue was dissolved in 50 ml of n-hexane. A portion was added to deuteriomethanol and the formation of methyl 3,4-seco-2-deuterio-friedelan-3-oate **6**-d_1 (M^+ 459) and **6** (M^+ 458) due to the reaction of **16** with deuteriomethanol was confirmed by mass spectrometry.

Reaction of 3,4-*seco-friedel*-2-*en*-3-*one* **13** *with oxygen.* To the n-hexane soln of **13**, dry oxygen was introduced overnight at room temp and the reaction mixture was passed through a silica gel column (50 g). Elution with petroleum ether–benzene (4:1) gave 3,4-seco-3-nor-friedelan-2-al **2** (0·5 mg) and the oxygen-adduct **14** (0·2 mg). The latter showed IR 1740 and 1168 cm^{-1} and NMR ($CDCl_3$) δ 4·1–4·5 ppm (m, 1H); MS M^+ 458.

Photochemical reaction of friedelin **1** *in n-hexane followed by oxygenation and addition of deuteriomethanol.* Friedelin **1** (1·00 g) in n-hexane (500 g) was irradiated under N_2 for 10 h as before then dry oxygen was passed through the soln in the dark for 3·5 h and then deuteriomethanol (2 ml) was added. On chromatographic separation on silica gel (100 g), 3,4-seco-3-nor-friedelan-2-al **2** (109·2 mg), methyl 3,4-seco-friedelan-3-oate **6** (11·5 mg), 3,4-seco-3-nor-friedelan-2-oic acid **3** (13·9 mg), and 3,4-seco-friedelan-3-oic acid **5** (14·6 mg) were obtained. Mass spectrometric examination did not detect methyl 3,4-seco-nor-1-deuteriofriedelan-2-oate **4**-d_1 (M^+ 445) in the ester fraction.

Oxidation of 3,4-*seco*-3-*nor-friedelan*-2-*al* **2**. 3,4-Seco-3-nor-friedelan-2-al **2** containing the ketene **13** and the oxygen-adduct **14** was dissolved in benzene containing a small quantity of water and heated gently. The acid fraction was separated by silica gel chromatography and methylated with diazomethane. The reaction mixture was examined by GLC and shown to be a mixture of methyl 3,4-seco-3-nor-friedelan-2-oate **4** (Diasolid H-523, 250°, R_t 30·0 min; OV-17, 250°, R_t 16·3 min), and methyl 3,4-seco-friedelan-3-oate **6** (Diasolid H-523, 250°, R_t 42·8 min; OV-17, 250°, R_t 23·6 min).

REFERENCES

[1] Cf. R. O. Kan, *Organic Photochemistry*, McGraw-Hill, New York (1966)

[2] F. Kohen and R. Stevenson, *Chem. and Ind.* 1844 (1966)

[3] T. Tsuyuki, S. Yamada and T. Takahashi, *Bull. Chem. Soc. Japan* **41**, 511 (1968)

[4] F. Kohen, A. Samson and R. Stevenson, *J. Org. Chem.* **34**, 1355 (1969)

[5] T. Tsuyuki, R. Aoyagi, S. Yamada and T. Takahashi, *Tetrahedron Letters* 5263 (1968)

[6] R. Aoyagi, S. Yamada, T. Tsuyuki and T. Takahashi, *Bull. Chem. Soc. Japan* **46**, 959 (1973)

[7] M. Takai, R. Aoyagi, S. Yamada, T. Tsuyuki and T. Takahashi, *Bull. Chem. Soc. Japan* **43**, 972 (1970)

[8] R. Stevenson, T. Tsuyuki, R. Aoyagi and T. Takahashi, *Ibid.* **44**, 2567 (1971)

[9] R. Aoyagi, T. Tsuyuki, T. Takahashi and R. Stevenson, *Tetrahedron Letters* 3397 (1972)

[10a] G. R. Chopra, A. C. Jain and T. R. Seshadri, *Indian J. Chem.* **8**, 401 (1970), *Chem. Abstr.*, **73**, 45626g (1970); [b] R. Aoyagi, Y. Moriyama, T. Tsuyuki and T. Takahashi, *Bull. Chem. Soc. Japan* **46**, 569 (1973)

[11] L. Ruzicka, O. Jeger and P. Ringnes, *Helv. Chim. Acta* **27**, 972 (1944)

[12] R. Aoyagi, T. Tsuyuki and T. Takahashi, *Bull. Chem. Soc. Japan* **43**, 3967 (1970)

[13] H. Staudinger, K. Dyckerhoff, H. W. Klever and K. Luzicka, *Ber.* **58**, 1079 (1925)

[14] R. Stevenson, *J. Org. Chem.* **26**, 2142 (1961)