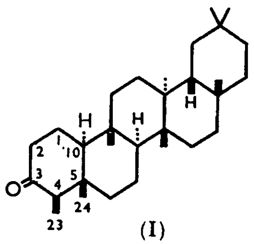
38. *Triterpenoids. Part LVII.*[1] *The Oxidation of Norfriedelanone with Selenium Dioxide.*

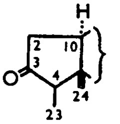
By George Brownlie, F. S. Spring, and Robert Stevenson.

Oxidation of A(1)-norfriedelan-3-one * (II) with selenium dioxide gives A(1)-norfriedel-4(23)-en-3-one (IV). Further oxidation of this αβ-unsaturated ketone with selenium dioxide gives A(1)-norfriedela-2(10) : 4(23)-dien-3-one (V) and A(4)-nor-23-norfriedel-1(10)-ene-2 : 3-dione (VI).

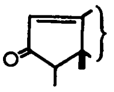
Oxidation of friedelin (I) [2–5] with chromic acid gives friedelindicarboxylic acid, the anhydride of which gives norfriedelanone (II) on pyrolysis.[6] Ruzicka, Jeger, and Ringnes [6] studied the oxidation of norfriedelanone with selenium dioxide and, using acetic acid as solvent, obtained a norfriedelenone of m. p. 260—261°, $[\alpha]_D$ −108°, $\lambda_{max.}$ 2530 Å (log ε 4·2), which was considered to be an αβ-unsaturated ketone. If this diagnosis is correct, possible structures for this compound are (III) and (IV). However, the position of the ultraviolet absorption maximum (2530 Å) is different from that predicted, by using the the usual empirical rules, for either (III) (*ca.* 2340 Å) or (IV) (*ca.* 2300 Å). We have again examined the oxidation of norfriedelanone with selenium dioxide and, using the method described by Ruzicka, Jeger, and Ringnes,[6] we obtained a norfriedelenone having their recorded m. p. and $[\alpha]_D$ but $\lambda_{max.}$ 2290 Å (ε 5500). Its infrared absorption spectrum includes bands at 1642 and 932 cm.$^{-1}$, attributable to a vinylidene group, and the relatively low intensity of its ultraviolet absorption bands is consistent with the presence of a *cisoid* αβ-unsaturated ketone chromophore, so we represent this oxidation product as A(1)-norfriedel-4(23)-en-3-one * (IV). The infrared spectrum of norfriedelanone includes a band at 1738 cm.$^{-1}$, a typical carbonyl stretching frequency for a *cyclo*pentanone. The carbonyl band of A(1)-norfriedel-4(23)-en-3-one (IV) is at 1733 cm.$^{-1}$; the relatively small shift in the carbonyl frequency associated with the conversion of the saturated ketone (II) into the αβ-unsaturated ketone (IV) is apparently characteristic of conjugation between a carbonyl group in a five-membered ring and an exocyclic double bond.[7]

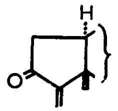


(I)

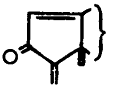


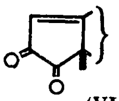
(II)


(III)



(IV)


(V)


(VI)

Oxidation of norfriedelanone with selenium dioxide in dioxan at 200° gives a product which was originally described as a norfriedelenedione [6] but was subsequently identified [2] as A(4)-nor-23-norfriedel-1(10)-ene-2 : 3-dione (VI). Ruzicka *et al.*[6] also obtained this compound by similar oxidation of their norfriedelenone. We find that A(1)-norfriedel-4(23)-en-3-one (IV) with selenium dioxide in dioxan at 200° gives a mixture

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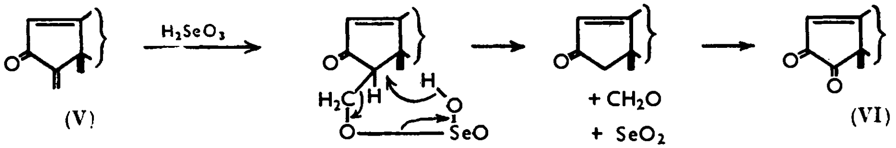
* The friedelin derivatives containing a contracted ring A are named in this paper according to the rules suggested by Allard and Ourisson (*Tetrahedron*, 1957, **1**, 277).

[1] Part LVI, Smith, Smith, and Spring, *Tetrahedron*, 1958, **2**, in the press.
[2] Brownlie, Spring, Stevenson, and Strachan, *J.*, 1956, 2419.
[3] Corey and Ursprung, *J. Amer. Chem. Soc.*, 1956, **78**, 5041.
[4] Takahashi and Ourisson, *Bull. Soc. chim. France*, 1956, 353.
[5] Dutler, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1955, **38**, 1268.
[6] Ruzicka, Jeger, and Ringnes, *ibid.*, 1944, **27**, 972.
[7] Wiesner, Armstrong, Bartlett, and Edwards, *J. Amer. Chem. Soc.*, 1954, **76**, 6068.

separated by chromatography into bisnorfriedelenedione (VI) and a compound, $C_{29}H_{44}O$, m. p. 253—255°, $[\alpha]_D$ +190°, $\lambda_{max.}$ 2520 Å (ε 13,500), which we consider to be A(1)-norfriedela-2(10) : 4(23)-dien-3-one (V). In agreement the infrared spectrum of this diene includes bands at 1706 (>CO of a *cyclo*pentenone), 1650 and 940 (vinylidene), and 1585 and 879 cm.$^{-1}$ (conjugated C:C in the ring). The course of the oxidation of norfriedelanone (II) to bisnorfriedelenedione (VI) with selenium dioxide is now represented as (II) $\longrightarrow$ (IV) $\longrightarrow$ (V) $\longrightarrow$ (VI). This extrusion of a methyl (or methylene) group is, in our experience, unique and a possible mechanism is as annexed.



The difference in the ultraviolet absorption spectrum of our norfriedelenone from that described by Ruzicka *et al.*,[6] coupled with the similar melting points and specific rotations, is curious. It is also remarkable that, although the melting point and ultraviolet absorption spectrum of Ruzicka's norfriedelenone are in fair agreement with those of A(1)-norfriedela-2(10) : 4(23)-dien-3-one (V), the specific rotations of the two compounds are distinct. Although Corey and Ursprung [3] have also described the oxidation of norfriedelanone with selenium dioxide in acetic acid, the ultraviolet absorption spectrum and the specific rotation reported by these authors are apparently quotations of those observed by Ruzicka *et al.*[6] The principal infrared absorption bands observed by them for their preparation of norfriedelenone appear to identify it as A(1)-norfriedela-2(10) : 4(23)-dien-3-one (V).

EXPERIMENTAL

Rotations were measured for $CHCl_3$ and ultraviolet absorption spectra for EtOH solutions. Grade II alumina and light petroleum, b. p. 60—80°, were used for chromatography.

Friedelindicarboxylic Acid.—Friedelin was oxidised with chromium trioxide as described by Ruzicka *et al.*[6] and the acidic oxidation product isolated in the usual way. The acid was esterified by diazomethane, and the neutral ester was chromatographed in light petroleum–benzene (10 : 1). Elution with light petroleum–benzene (1 : 2) gave a fraction which crystallised from chloroform–methanol, yielding dimethyl friedelindicarboxylate as plates, m. p. 175—177°, $[\alpha]_D$ +2·5° (*c* 1·4). Ruzicka *et al.*[6] give m. p. 174—176°, $[\alpha]_D$ +10°. Saponification of the ester with 5% methanolic potassium hydroxide for 3 hr. gave friedelindicarboxylic acid as prisms (from methanol), m. p. 287—288°. Ruzicka *et al.*[6] give m. p. 288°, $[\alpha]_D$ +21°.

Friedelindicarboxylic anhydride was prepared from the dicarboxylic acid as described by Ruzicka *et al.*[6] It separates from acetic anhydride as needles, m. p. 264—266°, $[\alpha]_D$ +75·5° (*c* 0·9). Ruzicka *et al.*[6] give m. p. 264—265°, $[\alpha]_D$ +74°.

A(1)-*Norfriedelan*-3-*one*.—Friedelindicarboxylic anhydride (1 g.) was heated at 280° for 1 min. The pressure was then reduced to 14 mm. and heating continued. The combined residue and sublimate were dissolved in light petroleum and chromatographed on alumina. Elution with benzene and crystallisation of the product from chloroform–methanol gave norfriedelanone (600 mg.) as plates, m. p. 232—235°, $[\alpha]_D$ −84° (*c* 1·2), $\nu_{max.}$ (in Nujol) 1730 cm.$^{-1}$ (Found: C, 84·1; H, 11·85. Calc. for $C_{29}H_{48}O$: C, 84·4; H, 11·7%). Ruzicka *et al.*[6] give m. p. 231—232°, $[\alpha]_D$ −84°.

A(1)-*Norfriedel*-4(23)-*en*-3-*one*.—A solution of norfriedelanone (100 mg.) in acetic acid (10 c.c.) was refluxed with selenium dioxide (220 mg.) for 30 min. The solution was filtered and the yellow filtrate worked up in the usual way. Crystallisation of the product (70 mg.) from chloroform–methanol gave blades, m. p. 259—261°, $[\alpha]_D$ −97° (*c* 1·2). Purification of this product by chromatography to remove a slight yellow colour, and crystallisation from chloroform–methanol, gave A(1)-*norfriedel*-4(23)-*en*-3-*one* as blades, m. p. 261—263°, $[\alpha]_D$ −104° (*c* 1·1), $\lambda_{max.}$ 2290 Å (ε 5500), $\nu_{max.}$ (in CS_2) 1733 s, 1642 w, 932 m cm.$^{-1}$ (Found: C, 84·85;

H, 11·6. $C_{29}H_{46}O$ requires C, 84·8; H, 11·3%). It does not give a colour with tetranitromethane. Repetition of the experiment under the exact conditions described by Ruzicka *et al.*[6] gave the same product.

A(1)-*Norfriedel*-4(23)-*en*-3-*ol*.—Lithium aluminium hydride (50 mg.) was added to a solution of A(1)-norfriedel-4(23)-en-3-one (50 mg.) in ether (20 c.c.), and the mixture kept overnight. The product was isolated without the use of mineral acid and crystallised from chloroform–methanol to give A(1)-*norfriedel*-4(23)-*en*-3-*ol* as small plates, m. p. 250—253°, $[\alpha]_D$ +41° (*c* 0·5), ε_{2040} 1150 (Found: C, 84·0; H, 11·4. $C_{29}H_{48}O$ requires C, 84·4; H, 11·7%). The alcohol does not give a colour with tetranitromethane.

Oxidation of A(1)-*Norfriedel*-4(23)-*en*-3-*one with Selenium Dioxide at* 200°.—Solutions of A(1)-norfriedel-4(23)-en-3-one (280 mg.) in dioxan (12 c.c.) and selenium dioxide (1·0 g.) in dioxan (3 c.c.) were mixed and heated at 200° for 16 hr. in a sealed tube. The product, isolated in the usual way, was chromatographed in light petroleum–benzene (2 : 1) on alumina. Elution with benzene gave a fraction (50 mg.) which on crystallisation from chloroform–methanol gave A(1)-*norfriedela*-2(10) : 4(23)-*dien*-3-*one* as blades, m. p. 253—255°, $[\alpha]_D$ +190° (*c* 0·8), $\lambda_{max.}$ 2520 Å (ε 13,500), $\nu_{max.}$ (in CCl_4) 1704 s, 1650 w, 1585 m, 940 m, 879 m cm.$^{-1}$ (Found: C, 85·5; H, 11·2. $C_{29}H_{44}O$ requires C, 85·2; H, 10·9%). A mixture with A(1)-norfriedel-4(23)-en-3-one had m. p. 241—244°. Continued elution of the column with benzene–ether (1 : 1) gave a fraction (30 mg.) which on crystallisation from methanol gave A(4)-nor-23-norfriedel-1(10)-ene-2 : 3-dione as orange needles, m. p. 266—268°, $[\alpha]_D$ +235° (*c* 2·0), $\lambda_{max.}$ 2800 Å (ε 7500), $\nu_{max.}$ (in $CHCl_3$) 1764 m, 1712 s, 1575 m, 874 w cm.$^{-1}$. Ruzicka *et al.*[6] give m. p. 269—270° $[\alpha]_D$ +241°, $\lambda_{max.}$ 2800 Å (ε 10,000).

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