# Friedelin and Related Compounds. X. Products from Ultraviolet Irradiation of Friedelin

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Ultraviolet irradiation of friedelin (1) in ether solution yields a complex mixture of products from which 5-ethyl-10β-vinyldes-A-friedelane (2) and norfriedelane (4) have been separated and identified. In contrast, irradiation of 1 in reagent grade chloroform solution gives, in high yield, ethyl 3,4-secofriedelan-3-oate (7, R = $C_2H_5$), characterized by hydrolysis to the corresponding acid (7, R = H) and reduction to the corresponding alcohol (8, R = H).

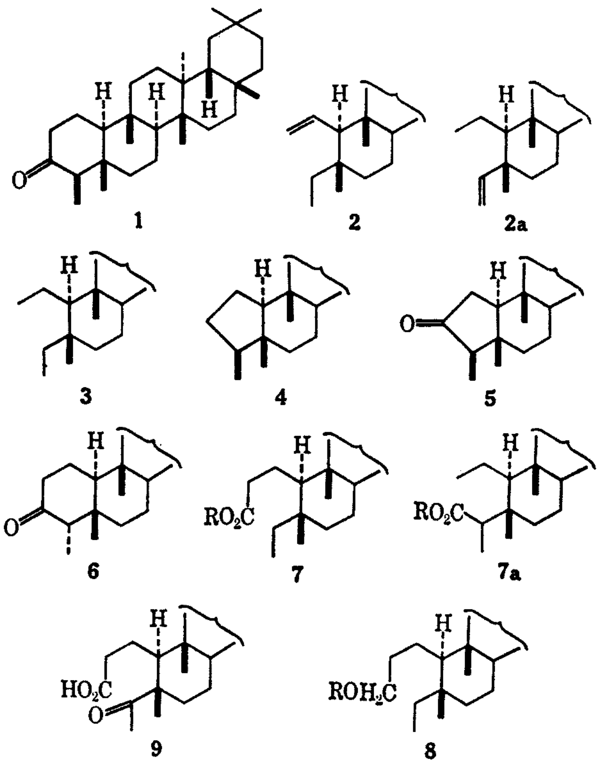
In extension of our studies[1] of general aspects of the chemistry of the pentacyclic triterpene ketone, friedelin (1), a well-known constituent of cork, we have examined the nature of some products obtained by solution ultraviolet (uv) photolysis. Regarded from the viewpoint of irradiation of a naturally occurring cyclohexanone system, friedelin, an α-methylcyclohexanone, affords a structurally interesting variant between the extensively studied steroid 3-ketones (lacking α-alkyl group) and triterpenoid 3-ketones (usually with α,α-dimethyl substitution). The general behavior of the latter types have been well treated in the more comprehensive reviews of nonconjugated cyclic ketone photochemistry.[2-8] Some preliminary work describing the photodecarbonylation of friedelin has been reported[9] and a note which has a bearing on the results reported here has recently appeared.[10]

With regard to the solvents commonly used in the photoirradiation of organic compounds, friedelin is very sparingly soluble in methanol, ethanol, 2-methyl-2-propanol, and acetic acid at room temperature. It is, however, slightly soluble in dioxane (*ca.* 0.6 g/l.) and ether (*ca.* 1 g/l.) and this consideration governed our initial choice of the latter for our study. The progress of the irradiation could be conveniently monitored by thin layer chromatography (tlc) on silica gel G. In this way, four product classes, designated as hydrocarbon, aldehyde, ketone, and hydroxycarbonyl fractions, were readily detected and subsequently separated by column chromatography on alumina.

The hydrocarbon fraction was readily obtained crystalline, but the broad melting point range indicated that it was a mixture. This was fully confirmed by thin layer chromatographic examination, and a partial separation could be effected by the use of silver nitrate impregnated silica gel G and carbon tetrachloride–cyclohexane as the developing medium. In this way, three products of $R_f$ 0.09, 0.42, and 0.66 were obtained. The most strongly absorbed (and minor) product was difficult to crystallize and the nuclear magnetic resonance (nmr) spectrum indicated that it was still a mixture. It was not further examined.

Elemental analysis and the mass spectrum of the product of $R_f$ 0.42 indicated that it was a hydrocarbon, $C_{29}H_{50}$. The presence of a double bond was indicated by a positive tetranitromethane test and the likelihood of its being a vinyl group suggested by strong infrared (ir) bands at 6.11, 9.98, and 10.92 μ. On this evidence, it was considered that the hydrocarbon should have structure 2 or 2a (Chart I). A decision in favor of 2 was made on a detailed examination of the nmr spectrum,[11] reproduced and analyzed in Figures 1–3. This hydrocarbon is consequently formulated as 5-ethyl-10β-vinyldesA-friedelane (2). As expected, the double bond was readily reduced on catalytic hydrogenation to yield 5,10β-diethyldesA-friedelane (3), the $C_{29}H_{52}$ empirical formula being confirmed by the mass spectrum.

CHART I



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[1] Part IX: A. S. Samson and R. Stevenson, *J. Chem. Soc., C,* 2342 (1968).

[2] G. Quinkert, *Angew. Chem. Intern. Ed. Engl.,* **4,** 211 (1965).

[3] R. Srinivasan in "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, New York, N. Y., 1963, p 83.

[4] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p. 224.

[5] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 377.

[6] R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 71.

[7] D. O. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967, p 53.

[8] J. N. Pitts, Jr., and J. K. S. Wan in "The Chemistry of the Carbonyl Group," S. Patai, Ed., John Wiley & Sons, London, 1966, p 823.

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

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

[11] We are indebted to Dr. C. F. Hammer, Georgetown University, for a spectrum of this compound, determined on a Varian HA-100 spectrometer.

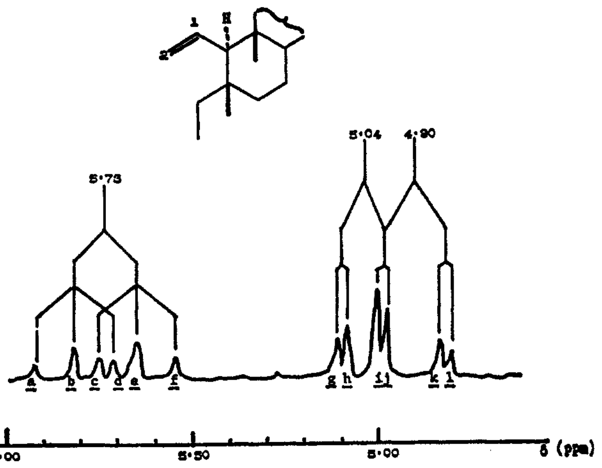

Figure 1.—Nmr spectrum (olefinic region) of hydrocarbon 2, determined using Varian HA-100 spectrometer.

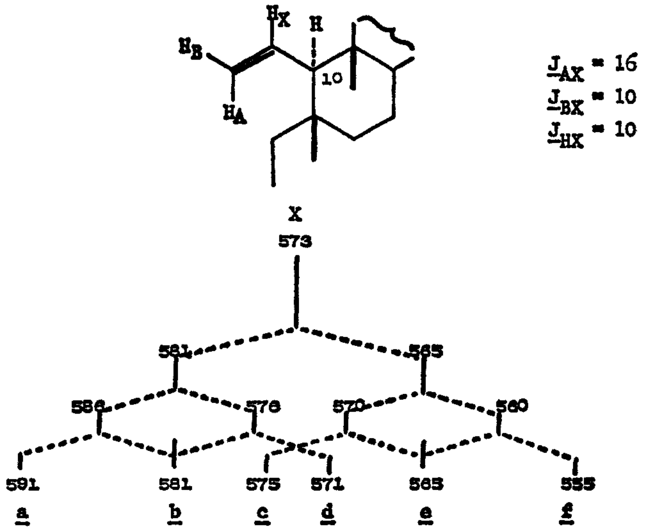

Figure 2.—Pattern ascribed to vinyl proton at C-1 (the X proton).

The remaining hydrocarbon of $R_f$ 0.66, which represented 30–40% of the total hydrocarbon mixture, readily crystallized but melted over a rather wide range and required further chromatographic treatment for purification. The mass spectrum and empirical analysis indicated that it was isomeric with 2, but no unsaturation could be detected from the nmr and ir spectra and it gave a negative tetranitromethane test. It was therefore considered to be pentacyclic and a direct comparison with norfriedelane (4), prepared by Huang-Minlon reduction of norfriedelanone (5), established its identity. This provides an interesting example of a photodecarbonylation of an unstrained saturated cyclic ketone, which although common in the gas phase is considered of more rare occurrence in the condensed phase,[3] unless facilitated by certain structural features, notably homoconjugation or cyclopropylcarbinyl substitution.[12]

The aldehyde fraction was one of the minor products (5–10% yield) and was, from tlc examination, still a mixture of at least two compounds. There appeared to be considerable instability attendant upon isolation and attempted recrystallization, and no reproducible homogeneous product was obtained. The hydroxycarbonyl fraction likewise was a mixture of at least three constituents which we were unable to obtain crystalline.

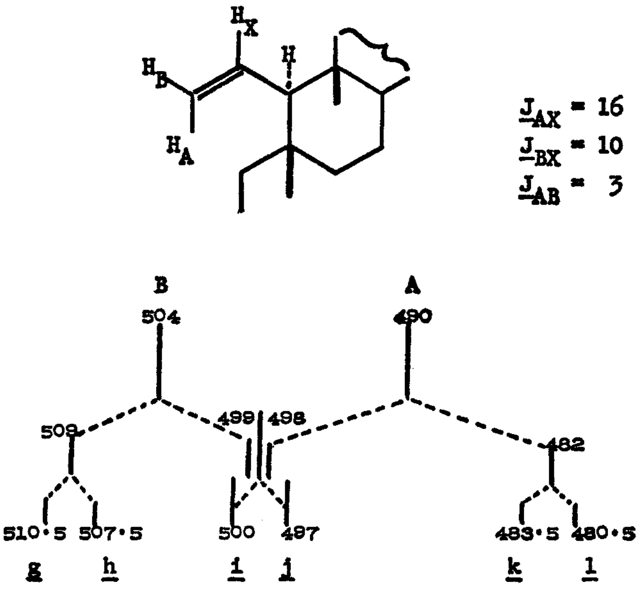

Figure 3.—Pattern ascribed to vinyl protons at C-2 (A, B protons).

The ketone fraction could be reproducibly isolated and after crystallization had mp 249–253°. Since, on base treatment, it readily yielded friedelin, mp 263–265°, we considered the likelihood that it had the structure of 4-epifriedelin (6). An attempt to substantiate this by comparing the nmr spectrum in both deuteriochloroform and benzene solution with that of friedelin, a method for determining whether the methyl group of an α-methylcyclohexanone has an equatorial or axial conformation,[13] showed that the "photo ketone" and friedelin were indistinguishable. On passing from $CDCl_3$ to $C_6H_6$, the signal due to the methyl group at C-4 undergoes a downfield shift ($\Delta\delta$ – 0.08) as expected for friedelin. Similarly, a comparison of the ir and mass spectra and optical rotatory dispersions confirmed the close similarity. In the recent report of the irradiation of friedelin suspended in refluxing ethanol,[10] there was obtained in about 5% yield a ketone, mp 257.5°, which also was epimerized by base to friedelin and accordingly formulated as 6. Although no spectrometric data are therein reported, we have been informed[14] that this product and friedelin are distinct by nmr and ir spectra, but that 6 is converted into 1 on exposure to alumina, *i.e.*, under our conditions of isolation. We conclude that the "photo ketone" which we isolated is predominantly the more stable ketone 1. As expected, the alcohol obtained by lithium aluminum hydride reduction was identified as friedelan-3β-ol.

In contrast to this complex mixture of products obtained by irradiation of friedelin in ether solution, there was readily isolated a homogeneous product in 80% yield when the irradiation was conducted in untreated reagent grade chloroform, in which 1 is much more soluble. This was accompanied only by a small

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(12) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

(13) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 165–170.

(14) Professor T. Takahashi, Department of Chemistry, University of Tokyo, Japan, personal communication, 1968.

hydrocarbon fraction from which norfriedelane (**4**) was isolated. The principal product showed carbonyl absorption (λ 5.75 μ) in the ir but was unlikely to be a ketone since it failed to yield an oxime; the Beilstein and tetranitromethane tests indicated that it was halogen free and saturated. The parent peak of the mass spectrum (*m/e* 472) indicated an increase in molecular weight over friedelin (426 mass units) corresponding to addition of the elements of ethanol. The presence of an ethyl ester function was suggested by the nmr spectrum from the two proton quartet at δ 4.14 ($J$ = 6 cps) characteristic of the methylene protons of the carbethoxyl group, and this was confirmed by the mass spectrum which gave strong fragment signals appropriate for $(M - C_2H_5)^+$ and $(M - OC_2H_5)^+$. This information established the empirical formula for the irradiation product as $C_{32}H_{56}O_2$ and its nature as a tetracyclic carboxylic acid ethyl ester. The formulation, ethyl 3,4-secofriedelan-3-oate (**7**, R = $C_2H_5$) and also the less likely alternative (**7a**, R = $C_2H_5$) satisfied those requirements. The ethyl seco ester (**7**, R = $C_2H_5$) would be regarded as an unexceptional product of irradiation in *ethanol* solution as a consequence of α cleavage on the side of the more highly substituted carbon atom, followed by an intramolecular disproportionation (by migration of a hydrogen atom from C-2 to C-4) and reaction of the consequent ketene with solvent. The fact that it is produced by irradiation in the normal chloroform of commerce shows that **1** is an extremely efficient scavenger of the ethanol which is present as a preservative.

The ethyl ester structure (**7**, R = $C_2H_5$) was confirmed by base hydrolysis to yield the corresponding carboxylic acid (**7**, R = H) with correct molecular weight. Reduction of the ethyl ester with lithium aluminum hydride gave the alcohol (**8**, R = H) which was characterized by acetylation to yield 3,4-secofriedelan-3-yl acetate (**8**, R = Ac). The nmr spectra of both alcohol and acetate show that the carbinol protons are adjacent to a carbon atom bearing two hydrogen atoms and consequently excludes the alternative structure (**7a**) of the ethyl ester. The same conclusion has been reached by chemical interconversion[10] involving Huang-Minlon reduction of friedonic acid (**9**) to give **7** (R = H).

## Experimental Section

All melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Specific rotations were determined in chloroform solution. Nmr spectra were determined in $CDCl_3$ solution with tetramethylsilane as internal reference using a Varian A-60 spectrometer, unless otherwise stated. For analytical tlc, silica gel G in 0.25-mm layers was used, and detection was effected by exposure to an iodine atmosphere.

**Friedelin (1).**—The material used in this work was isolated from cork[15] or cork "smoker wash solids,"[16] as previously described. Crude friedelin, so obtained, had mp 253–257°. Tlc using benzene–chloroform (1:1) indicated an impurity ($R_f$ 0.58), in addition to friedelin ($R_f$ 0.39). A solution of crude friedelin (900 mg) in benzene (15 ml) was chromatographed on alumina (Merck acid, 30 g). Elution with petroleum ether (bp 30–60°, 150 ml) yielded a fraction (152 mg) containing both friedelin and the impurity. Elution with benzene–petroleum ether (1:4) gave pure friedelin as needles (685 mg), $R_f$ 0.39, mp 266–269°. This is the highest melting point yet reported for friedelin. The nmr spectrum (methyl group region) in $CDCl_3$ showed signals at 44 (1), 50 (1/2), 54 (1), 57 (1/2), 58 (1), 61 (2), 64 (1), and 72 (1) cps. The nmr spectrum (methyl group region) in $C_6H_6$ showed signals at 40 (1), 46 (1), 55 (1/2), 59 (1), 62 (1/2), 64 (1), 65 (1), 66 (1), and 75 (1) cps.

**Irradiation of Friedelin in Ether Solution.**—A solution of friedelin (250 mg, mp 266–269°) in ether (250 ml) was irradiated in a quartz vessel at room temperature for 1.75 hr using a high pressure quartz mercury vapor lamp (Hanovia, 8A-36). This was repeated twice, and the combined residue [$R_f$ 0.06, 0.13, 0.22, 0.38, 0.58, and 0.88 using benzene–chloroform (1:1)] obtained after solvent removal, was dissolved in petroleum ether–benzene (5 ml) and chromatographed on alumina (Moore, 30 g). Elution with petroleum ether (100 ml) yielded the **hydrocarbon fraction** (200 mg, $R_f$ 0.88). Elution with petroleum ether–benzene (4:1) yielded the **aldehyde fraction** (88 mg). Elution with petroleum ether–benzene (1:1, 375 ml) yielded the **ketone fraction** (332 mg) and with chloroform (250 ml) there was obtained the **hydroxycarbonyl fraction** (240 mg, $R_f$ 0.06, 0.13, 0.22).

Some experiments to determine the variation in product composition with time of irradiation indicated that the hydrocarbon and hydroxycarbonyl fractions increased at the expense of the aldehyde and ketone fractions (Table I).

TABLE I

FRACTIONS ISOLATED FROM FRIEDELIN[a]

| | Mg | | | | |
|---|---|---|---|---|---|
| | 1 hr | 1.75 hr | 4.5 hr | 6 hr | 17 hr |
| Hydrocarbon | 19 | 40 | 61 | 80 | 83 |
| Aldehyde | 11 | 16 | 24 | | |
| Ketone | 107 | 65 | 48 | 12 | |
| Hydroxycarbonyl | 32 | 48 | 52 | 92 | 97 |

[a] 200 mg.

**Examination of the Hydrocarbon Fraction.**—Crystallization from methylene chloride–methanol gave prisms: mp 155–162°; $[\alpha]_D$ +35° (*c*, 1.7); $\lambda^{KBr}$ 6.10, 9.92, 10.90 μ. Examination by tlc on silver nitrate impregnated silica gel G, using carbon tetrachloride–cyclohexane as developing solvent and detecting with 2% perchloric acid, indicated three spots of $R_f$ 0.09, 0.42, and 0.66. A separation of this mixture (105 mg) was effected by preparative tlc and the fractions were eluted with petroleum ether.

The product ($R_f$ 0.09, 15 mg) resisted crystallization and the nmr spectrum (unsharp absorption signals in methyl group region) indicated that it was still a mixture.

The product ($R_f$ 0.42, 32 mg) crystallized from methylene chloride–methanol to give **5-ethyl-10β-vinylde-A-friedelane** (**2**) as small needles: mp 191–192°; $[\alpha]_D$ +36° (*c*, 1.87); $\lambda^{KBr}$ 6.11, 9.98, 10.92 μ.

*Anal.* Calcd for $C_{29}H_{50}$: C, 87.36; H, 12.64. Found: C, 87.26; H, 12.48.

It gave a pale yellow color with tetranitromethane in chloroform solution. The nmr spectrum included signals at 43, 48, 52, 54, 59, and 71 cps (methyl groups) and at δ 4.90, a pair of doublets (*trans* "A" proton at C-2, $J_{AX}$ = 16 cps, $J_{AB}$ = 3 cps), at 5.04, a pair of doublets (*cis* "B" proton at C-2, $J_{BX}$ = 10 cps, $J_{AB}$ = 3 cps), and at 5.73, a pair of triplets (octet with two coincident signals, $J_{AX}$ = 16 cps, $J_{BX}$ = 10 cps, $J_{10\alpha\text{-}HX}$ = 10 cps). The product ($R_f$ 0.66, 34 mg) crystallized from methylene chloride–methanol as prisms, mp 163–170°, and showed no high intensity uv absorption above 200 mμ. This was dissolved in petroleum ether and chromatographed on neutral alumina (Woelm), eluted with the same solvent, and crystallized from methylene chloride–methanol as prisms (mp 203–205°, 17 mg). This was again chromatographed in the same way and crystallized to give norfriedelane (**4**) as platelets (8 mg), mp 215–217°, $[\alpha]_D$ +43° (*c*, 1.7) with ir spectrum (KBr) identical with that of a specimen obtained by Huang-Minlon reduction of norfriedelanone (see below).

*Anal.* Calcd for $C_{29}H_{50}$: C, 87.36; H, 12.64. Found: C, 87.14; H, 12.67.

**Examination of the Aldehyde Fraction.**—Crystallization of this product from methylene chloride–methanol gave small needles: mp 166–168°; $[\alpha]_D$ +15.5° (*c*, 1.93); $\lambda^{KBr}$ 3.65, 5.79 μ. It gave no high intensity uv absorption above 200 mμ and a negative tetranitromethane test.

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(15) N. L. Drake and R. P. Jacobsen, *J. Amer. Chem. Soc.*, **57**, 1570 (1935).

(16) R. Stevenson, *J. Org. Chem.*, **26**, 2142 (1961).

*Anal.* Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Calcd for $C_{29}H_{50}O$: C, 83.99; H, 12.15. Found: C, 84.29; H, 12.00.

The nmr spectrum (methyl group region) in $CDCl_3$ showed signals at 48 (1), 53 (1), 57 (1), 59 (2), 62 (1), and 71 (1) cps. There were also signals at $\delta$ 2.32, multiplet (two protons adjacent to carbonyl), and at 9.78, triplet (aldehyde proton, $J$ = 2–3 cps).

Tlc examination of this product [benzene–chloroform (1:1)] indicated the presence of two constituents, $R_f$ 0.58 (major) and 0.47 (minor). Recrystallization from acetone gave the aldehyde as small needles with the same mp 166–168°, from which the minor impurity was absent, but with considerable attendant loss.

**Examination of the Ketone Fraction.**—Crystallization from methylene chloride–methanol gave the "photo ketone" as needles: mp 249–253°; $[\alpha]_D$ −15° ($c$, 1.9); $\lambda^{KBr}$ 5.82 $\mu$.

*Anal.* Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.40; H, 11.68.

The nmr spectrum (methyl group region) in $CDCl_3$ showed signals at 44 (1), 50 ($^1/_2$), 53.5 (1), 56 ($^1/_2$), 57 (1), 60 (2), 63.5 (1), and 71 (1) cps. The nmr spectrum (methyl group region) in $C_6H_6$ showed signals at 38 (1), 43.5 (1), 54 ($^1/_2$), 58 (1), 60.5 ($^1/_2$), 63 (2), 65 (1), and 74 (1) cps.

**Examination of Hydroxycarbonyl Fraction.**—Tlc inspection indicated that this was a mixture of at least three constituents ($R_f$ 0.06, 0.13, and 0.22): $\lambda^{CHCl_3}$ 2.90, 5.85 $\mu$. No homogeneous crystalline products could be isolated.

**Norfriedelane (4) from Norfriedelanone (5).**—A mixture of norfriedelanone[17] (118 mg), hydrazine hydrate (99%, 1.8 ml), and diethylene glycol (13 ml) was heated at 150° for 10 min, potassium hydroxide (1.2 g) was then added, and heating was continued at 150° for 45 min. Solvent was then removed by distillation, until a solution temperature of 210° was attained; the mixture heated for a further 6 hr, cooled, poured into water, and extracted with chloroform. The washed and dried extract was evaporated, and the residue was dissolved in petroleum ether and chromatographed on alumina (Moore). Elution with the same solvent (50 ml) yielded norfriedelane (76 mg), which crystallized from methylene chloride–methanol as platelets: mp 219–221°; $[\alpha]_D$ +46° ($c$, 1.59) (lit.[18] mp 220–221° for norfriedelane prepared by catalytic hydrogenation of norfriedelene).

**5,10β-Diethylde-A-friedelane (3).**—A solution of 5-ethyl-10β-vinylde-A-friedelane (50 mg) in acetic acid (20 ml) and cyclohexane (20 ml) was stirred under a hydrogen atmosphere at atmospheric pressure and temperature using prereduced platinum oxide (31 mg) as catalyst. When hydrogen uptake had ceased (2 hr), catalyst and solvent were removed, and a solution of the residue in petroleum ether was chromatographed on alumina (Moore). Elution with the same solvent gave **5,10β-diethylde-A-friedelane** (38 mg) which crystallized from methylene chloride–methanol as small needles: mp 208–209°; $[\alpha]_D$ +25° ($c$, 1.4). It gave a negative tetranitromethane test.

*Anal.* Calcd for $C_{29}H_{52}$: C, 86.92; H, 13.08. Found: C, 87.12; H, 13.11.

**Action of Base on the "Photo Ketone."**—A solution of the "photo ketone" (mp 243–246°, 36 mg) in ethanolic potassium hydroxide solution (1%, 25 ml) was heated under reflux for 2 hr. On cooling, crystals separated, were collected, and recrystallized from methylene chloride–methanol to give friedelin, mp and mmp 263–265°.

**Action of Lithium Aluminum Hydride on the "Photo Ketone."**—Lithium aluminum hydride (65 mg) in ether (25 ml) was added to a solution of the "photo ketone" (100 mg) in the same solvent (25 ml); the mixture was heated under reflux for 6 hr, then worked up in the usual way. Crystallization of the product gave friedelan-3β-ol, mp 273–277°, $[\alpha]_D$ +19° ($c$, 1.2), identified by tlc and ir comparison with an authentic specimen (mp 279–281°, $[\alpha]_D$ +21°) obtained in a similar manner from friedelin.

**Irradiation of Friedelin in Chloroform Solution.**—A solution of friedelin (101 mg, mp 253–258°) in chloroform (150 ml, Fisher Certified ACS, containing 0.75% ethyl alcohol as preservative) was irradiated in a Pyrex vessel under a nitrogen atmosphere for 12 hr, after which no starting material remained by tlc analysis. Evaporation of the solvent yielded a residue (127 mg) which was chromatographed on alumina (40 g, Thomas, neutral). Elution with petroleum ether (30 ml) gave a product (6 mg) and with petroleum ether–benzene (1:1, 60 ml ) gave a solid (84 mg) which was further purified by preparative tlc ($R_f$ 0.45 with benzene–chloroform (1:1)) and crystallized from methylene chloride-methanol to give **ethyl 3,4-secofriedelan-3-oate** (7, R = $C_2H_5$) as fine needles (72 mg): mp 110–111°, raised to 114.5–115° on recrystallization; $\lambda^{KBr}$ 5.75 $\mu$; $[\alpha]_D$ −6° ($c$, 1.0). It gave negative tetranitromethane and Beilstein tests.

*Anal.* Calcd for $C_{32}H_{56}O_2$: C, 81.29; H, 11.94. Found: C, 81.30; H, 12.01.

The nmr spectrum (methyl group region) showed signals at 48, 53, 57.5, 59.5, 61, 68.5, and 71 cps and also at $\delta$ 4.14, quartet ($J$ = 6 cps) ($OCH_2CH_3$), and 2.42, multiplet (C-2 protons). The mass spectrum had prominent peaks at $m/e$ 472 ($M^+$), 457 $(M - CH_3)^+$, 443 $(M - C_2H_5)^+$, and 427 $(M - OC_2H_5)^+$.

The petroleum ether eluted product from several experiments were combined (43 mg) and recrystallized from methylene chloride–methanol to give a solid (28 mg) shown by tlc to be a mixture. Purification by preparative tlc on silver nitrate impregnated silica gel G using carbon tetrachloride gave the major constituent ($R_f$ 0.71, 11 mg) which on crystallization from methylene chloride–methanol gave norfriedelane (4), mp 217–219°, with ir spectrum identical with that of authentic specimen.

Performing the same experiment in $CHCl_3$ from which the preservative $C_2H_5OH$ had been removed (either by appropriate treatment with alumina or concentrated sulfuric acid) yielded only a noncrystalline intractable mixture.

**3,4-Secofriedelan-3-oic Acid (7, R = H).**—Ethyl 3,4-secofriedelan-3-oate (50 mg) was added to 5% ethanolic potassium hydroxide solution (45 ml); the mixture was heated under reflux for 1 hr, then worked up in the usual way. Crystallization from ethyl acetate–methanol, then acetone–methanol, gave **3,4-secofriedelan-3-oic acid** as fine needles: mp 208.5–210°; $[\alpha]_D$ −5° ($c$, 1.2).

*Anal.* Calcd for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79. Found: C, 80.70; H, 11.41.

The nmr spectrum (methyl group region) showed signals at 48.5, 53.5, 58, 60, 61, and 71.5 cps. The mass spectrum had prominent peaks at $m/e$ 444 ($M^+$), 429 $(M - CH_3)^+$, and 415 $(M - C_2H_5)^+$.

**3,4-Secofriedelan-3-ol (8, R = H).**—Lithium aluminum hydride (21 mg) was added to a solution of ethyl 3,4-secofriedelan-3-oate (25 mg) in ether (10 ml), the mixture was heated under reflux for 1 hr and worked up in the usual way, and the product was crystallized from chloroform–methanol to give **3,4-secofriedelan-3-ol** as needles: mp 182.5–184°; $[\alpha]_D$ −14° ($c$, 0.4).

*Anal.* Calcd for $C_{30}H_{54}O$: C, 83.56; H, 12.64. Found: C, 83.90; H, 12.62.

The nmr spectrum (methyl group region) showed signals at 47, 53, 53.5, 59.5, 61, and 71 cps and also at $\delta$ 2.23, triplet (C-3 protons). The mass spectrum shows peaks at $m/e$ 430 ($M^+$), 415 $(M - CH_3)^+$, and 401 $(M - C_2H_5)^+$.

**3,4-Secofriedelan-3-yl Acetate (8, R = Ac).**—The alcohol (52 mg) was dissolved in pyridine (2.5 ml) and acetic anhydride (2.5 ml) was added. The mixture was heated at 100° for 1.5 hr and worked up in the usual way and the product was crystallized from chloroform–methanol as fine needles (38 mg): mp 121.5–122.5°; $[\alpha]_D$ −8° ($c$, 0.9).

*Anal.* Calcd for $C_{32}H_{56}O_2$: C, 81.29; H, 11.94. Found: C, 80.99; H, 11.87.

The nmr spectrum (methyl group region) showed signals at 48, 54, 59, 61, 62, and 72 cps and also at $\delta$ 3.98 t ($J$ = 6 cps, C-3 protons) and 1.95 (acetate).

**Registry No.**—1, 559-74-0; 2, 14356-57-1; 3, 14363-60-1; 4, 7506-14-1; 7 (R = $C_2H_5$), 19553-16-3; 7 (R = H), 19553-17-4; 8 (R = H), 19553-18-5; 8 (R = Ac), 19553-19-6.

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