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FRIEDELIN AND RELATED COMPOUNDS—V[1]

THE ACTION OF N-BROMOSUCCINIMIDE ON FRIEDELIN AND DERIVATIVES

VINAYAK V. KANE and ROBERT STEVENSON
Department of Chemistry, Brandeis University, Waltham 54, Massachusetts

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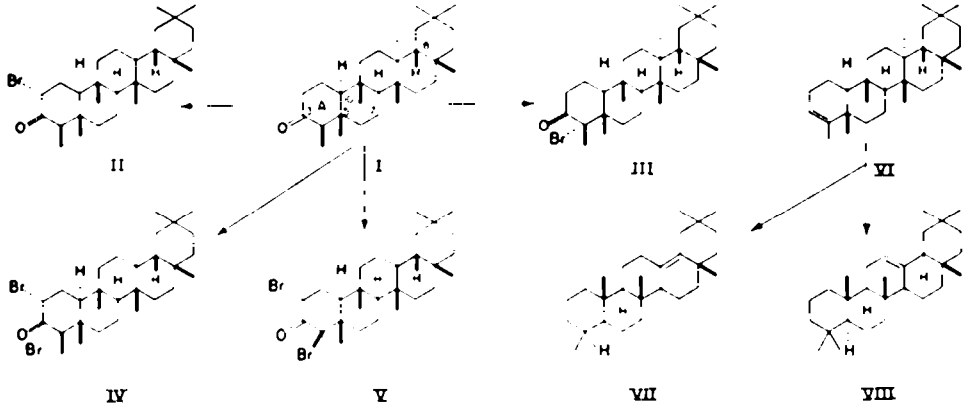
Abstract—Friedelin gives 4α-bromofriedelin on treatment with N-bromosuccinimide. 2α-Bromofriedelin, 4α-bromofriedelin and friedelane are preferentially oxidized to the corresponding Δ^{18}-olefins.

A STUDY of the bromination products of the pentacyclic triterpenoid ketone, friedelin (I), proved extremely valuable not only in revealing the structural detail of the terminal ring A but also in establishing the absolute configuration. Corey and Ursprung[2] showed that direct monobromination of friedelin gave 2α (axial)-bromofriedelin (II) and that the isomeric 4α (axial)-bromofriedelin (III) could be obtained by bromination of the appropriate enol benzoate. A more complex situation exists with regard to the preparation of the dibromoketones. A dibromofriedelin prepared in chloroform solution in the presence of hydrogen bromide showed an ultraviolet absorption maximum at 332 mμ, indicative of both bromine atoms having axial conformations, and has accordingly been regarded[2] as 2α:4α-dibromofriedelin (IV). A second dibromofriedelin, described by Djerassi and coworkers[3], and prepared by bromination of 2α-bromofriedelin in acetic acid, showed an ultraviolet absorption (310·5 mμ) indicative of one axial α-bromine atom and has been formulated as 2α:4β-dibromofriedelin (V), in agreement with rotatory dispersion data. A third isomer prepared by Takahashi and Ourisson[4] by dibromination of friedelin in chloroform–acetic acid shows an absorption inflection at 320 mμ. No structure has been assigned to this dibromoketone or an unstable tribromoketone also described by these workers. On experiencing difficulties in obtaining reproducible results by direct bromination of friedelin, we sought alternative methods and have examined the action of N-bromosuccinimide on friedelin and derivatives.

Treatment of friedelin (I) in carbon tetrachloride solution with a molar equivalent of N-bromosuccinimide gave, in excellent yield, 4α-bromofriedelin (III). Since 2α-bromofriedelin is isolated on direct bromination of friedelin this forms a marked contrast with the behavior of the 3-ketosteroids where, in both the cholestane and coprostane series, the same monobromination products are isolated by either procedure.[5] By treatment of 4α-bromofriedelin (III) with bromine in acetic acid solution, isomerization rather than further substitution occurred, and 2α-bromofriedelin (II) was isolated. As anticipated from this result, the 4α-bromoketone

[1] Part IV: R. Stevenson, *J. Org. Chem.* **26**, 2142 (1961).
[2] E. J. Corey and J. J. Ursprung, *J. Amer. Chem. Soc.* **78**, 5041 (1956).
[3] C. Djerassi, J. Osiecki, R. Riniker and B. Riniker, *J. Amer. Chem. Soc.* **80**, 1216 (1958).
[4] T. Takahashi and G. Ourisson, *Bull. Soc. Chim. Fr.* 353 (1956).
[5] C. Djerassi and C. R. Scholz, *Experientia* **3**, 107 (1947).

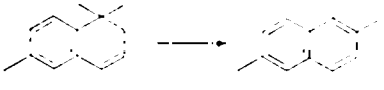
([α]$_D$ + 92°) is unstable in chloroform containing hydrogen bromide at room temperature, the presumed equilibrium mixture ([α]$_D$ ca. − 75°) being formed after 24 hr. Similar equilibration of 2α-bromofriedelin gave the same result.



Since this route for obtaining a dibromofriedelin was unsuccessful, the alternative method of treating 2α-bromofriedelin (II) with N-bromosuccinimide was examined. The isolated product was an unsaturated monobromo ketone, $C_{30}H_{47}OBr$, the presence of an ethylenic function being indicated by a positive tetranitromethane test. Examination of the ultraviolet and infrared spectra of this ketone showed the double bond was *not* conjugated to the carbonyl group and that the α-bromine atom retained an axial conformation. In view of the marked propensity of certain friedelin derivatives to undergo molecular rearrangement - the most notable example of which is probably the acid isomerization of friedel-3-ene (VI) to the mixture of olean-13:18-ene (VII) and 18α-olean-12-ene (VIII)[6,7] - it was considered that this non-conjugated bromoketone had probably arisen by a molecular rearrangement of a 2α:4-dibromoketone intermediate (or derived radical or cation) with elimination of hydrogen bromide. A precedent for such a postulated rearrangement is provided by the action of silver acetate on 4α-bromofriedelin (III) to yield a product[2] which was shown[8] to be a mixture of the non-conjugated ketones, alnus-5-enone (IX, R = H) and alnus-5(10)-enone (X, R = H). An interesting molecular rearrangement involving an 1:2-alkyl group shift under normal N-bromosuccinimide reaction conditions has been described.[9]

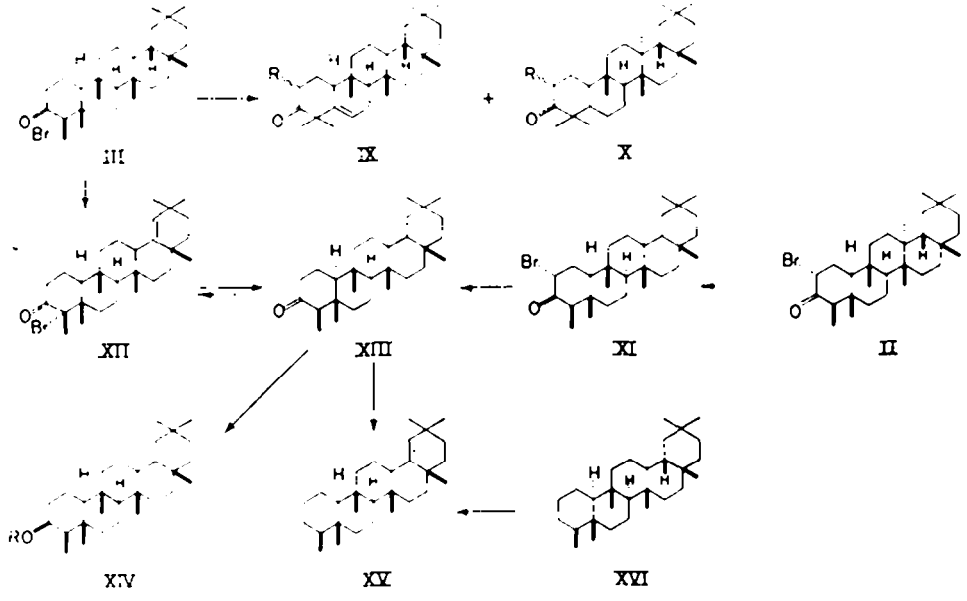
The possibility that the unsaturated bromoketone, $C_{30}H_{47}OBr$ derived from II could be represented as a 2-bromoalnusenone (IX, R = Br or X, R = Br) was

[6] G. Brownlie, F. S. Spring, R. Stevenson and W. S. Strachan, *J. Chem. Soc.* 2419 (1956).
[7] G. Brownlie, M. B. E. Fayez, F. S. Spring, R. Stevenson and W. S. Strachan, *J. Chem. Soc.* 1377 (1956).
[8] J. M. Beaton, F. S. Spring, R. Stevenson and J. L. Stewart, *Tetrahedron* **2**, 246 (1958).
[9] R. A. Barnes and G. R. Buckwalter, *J. Amer. Chem. Soc.* 73, 3858 (1951) have shown that treatment of 1,1,6-trimethyl-1,2-dihydronaphthalene (A) with N-bromosuccinimide gave an allylic bromide which was aromatized to 1,2,6-trimethylnaphthalene (B) either by silver ion or heat (temperature of refluxing carbon tetrachloride).



excluded, however, when it was established that the product $C_{30}H_{48}O$ obtained by zinc debromination in neutral solution differed from either alnusenone (IX, R = H and X, R = H).

When 4α-bromofriedelin (III) was treated with N-bromosuccinimide under conditions identical to those which the 2α-bromoketone (II) had been subjected, there was obtained a second isomeric non-conjugated axial bromosubstituted ketone, $C_{30}H_{47}OBr$ which yielded, however, the same debromination product, $C_{30}H_{48}O$. Since we regard this ketone, from the evidence described later, as having the constitution, friedel-18-en-3-one (XIII), the isomeric bromoketones obtained from II and III by the action of N-bromosuccinimide are assigned the structures, 2α-bromofriedel-18-en-3-one (XI) and 4α-bromofriedel-18-en-3-one (XII) respectively. It was established, furthermore, that the debromination of XI and XII to XIII had proceeded in the expected manner since ketone (XIII) regenerated the 4α-bromoketone (XII) on treatment with N-bromosuccinimide.



Reduction of the ketone (XIII) with lithium aluminum hydride gave in high yield an alcohol (XIV, R H), further characterized as its acetate (XIV, R = Ac) and reduction by the Huang-Minlon method gave the unsaturated hydrocarbon (XV). Comparison of the specific rotation values (see Table 1) of the unsaturated ketones, produced by N-bromosuccinimide oxidation (and their derivatives) and the friedelin analogues shows such close correspondence as to suggest strongly that the former in fact possess a friedelane skeleton and not that of a rearranged skeleton. This conclusion is further supported by a comparison of the previously reported optical rotatory dispersion curves[3] of I, II and III (in dioxane solution) with their respective analogues XIII, XI and XII which agree well in the sign of the Cotton effect and the wavelength locations of peaks and troughs (see experimental).

Whereas the action of N-bromosuccinimide on the ketones (II) and (III) would be expected *a priori* to yield products which are dibromofriedelins, αβ-unsaturated

ketones or rearranged non-conjugated ketones, the circumstantial evidence provided by the rotation data indicate that the products are ethylenic non-conjugated friedelins and hence that attack has proceeded at a site not activated by the carbonyl group. In seeking chemical support for this conclusion, the action of N-bromosuccinimide on the saturated hydrocarbon, friedelane (XVI), was examined and from the reaction mixture the unsaturated hydrocarbon (XV), identical in all respects with that prepared by Huang-Minlon reduction of the ketone (XIII), was isolated. It remained, consequently to locate the site of the double bond introduced by the N-bromosuccinimide oxidation.

TABLE 1

	$[\alpha]_D$		
2α-Bromoketone (XI)	139 [a]	140 [a]	2α-Bromofriedelin (II)
4α-Bromoketone (XII)	87 [a]	92 [a]	4α-Bromofriedelin (III)
Ketone (XIII)	28 [a]	22 [b]	Friedelin (I)
Alcohol (XIV, R = H)	25 [a]	22 [b]	Friedelan-3β-ol
Acetate (XIV, R = Ac)	30 [a]	34 [b]	Friedelan-3β-ol acetate
Hydrocarbon (XV)	17 [a]	22 [b]	Friedelane (XVI)

[a] Values reported in experimental. [b] Values reported in ref. 6.

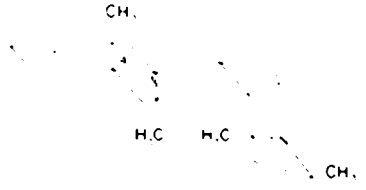
The unsaturated hydrocarbon (XV) resisted catalytic hydrogenation but yielded an oxide, $C_{30}H_{50}O$, on treatment with perbenzoic acid, indicating that the double bond has a degree of steric hindrance comparable to the Δ^{12}-trisubstituted ethylenic linkage in the β-amyrin series.[10] The terminal ultraviolet absorption of compounds (XIII), (XIV, R = H) and (XV) indicate that the double bond is tri-substituted,[11] although no bands in the infrared spectra were sufficiently distinct to be unequivocally assigned to this system.[12] The resistance to hydrogenation of XV further suggests that the ethylenic system is not disubstituted, and the friedelane skeleton does not permit the existence of a tetrasubstituted double bond. In addition, the nuclear magnetic resonance spectrum[13] of the ketone (XIII) run in deuterochloroform solution with tetramethylsilane as an internal reference at 60 mc frequency showed a singlet signal at 300 cps attributable to an olefinic proton not conjugated with the carbonyl group.

The location of the double bond introduced by the action of N-bromosuccinimide on bromoketones (II) and (III) and hydrocarbon (XVI) is consequently restricted to position 1(10), 7 or 18. The exclusion of positions 1(10) and 7 was effected by examining the dehydrobromination of XII with silver acetate in the manner previously employed for the transformation III → IX → X. Under these conditions, there was isolated a dehydrobrominated product, $C_{30}H_{46}O$, which showed no high intensity ultraviolet absorption above 220 mμ. Since there is no conjugation of carbonyl or ethylenic functions in this dienone product, the original double bond could not have been located in ring A or B.

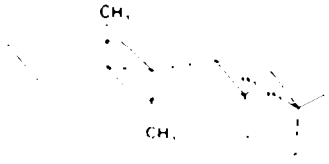
Although there has been much work on synthetic applications of allylic bromination

[10a] L. Ruzicka, H. W. Huyser, M. Pfeiffer and C. F. Seidel, *Liebigs Ann.* **471**, 21 (1929).
[b] L. Ruzicka, H. Silbermann and M. Furter, *Helv. Chim. Acta* **15**, 482 (1932).
[11a] T. G. Halsall, *Chem. & Ind.* 867 (1951).
[b] P. Bladon, H. B. Henbest and G. W. Wood, *J. Chem. Soc.* 2737 (1952).
[12] A. R. H. Cole and D. W. Thornton, *J. Chem. Soc.* 1332 (1957) have noted very low C=C stretching intensity in Δ^{18}-unsaturated pentacyclic triterpenoids.
[13] We are indebted to Dr. Leroy Johnson (Varian Associates) for this determination.

and detailed mechanisms have been forwarded,[14] comparatively little is known with regard to the action of N-bromosuccinimide on saturated systems. It has been established that cyclohexane[15,16] and cycloheptane[16] yield the cycloalkyl bromide with N-bromosuccinimide under certain conditions and that decalin gives a tetrabromo-octahydronaphthalene[17] which can also be obtained from the probable intermediate 9,10-octalin. Cason and coworkers[18] have also drawn attention to the fact that N-bromosuccinimide is not a reagent of general utility for the α-bromination of saturated esters due to selective attack on tertiary hydrogen atoms at other sites in the molecule.



XVII



XVIII

The experiments described in this work establish that in friedelin, the tertiary axial α-hydrogen atom at position 4 is more reactive towards N-bromosuccinimide than the secondary hydrogen atoms at position 2, but that the presence of a 2α-bromine atom effectively prevents abstraction of the 4α-hydrogen atom by its 1:3-diaxial blocking effect to the approach of a succinimide radical. In absence of the activating C-3 carbonyl group or where there is deactivation due to the steric influence of the neighboring axial halogen, the most reactive hydrogen is the tertiary C-18 atom. An examination of an all-chair form (XVII) of friedelane shows that, as a consequence of the *cis*-junction of rings D and E, a severe steric interaction must exist between the 13α- and 20α-methyl groups. Whereas this interference is removed if the terminal ring E adopts a boat conformation (XVIII),[19] an unfavorable 1:4-diaxial "boat prow-and-stern" methyl interaction is a consequence. The steric strain inherent in both conformations of this *cis* D/E system is relieved by dissociation of the 18β-hydrogen atom and formation of the ethylenic trigonal system. The driving force for the backbone rearrangement[20] of friedelene (VI) to the oleanenes (VII) and (VIII) can be attributed also to the same steric interactions.

EXPERIMENTAL[21]

4α-*Bromofriedelin* (III). N-Bromosuccinimide (150 mg) was added to a solution of friedelin (250 mg) in carbon tetrachloride (70 cm³) and the mixture heated under reflux by means of infrared lamp. After about 12 min an orange color appeared, followed by decolorization over 30 sec. After a

[14] H. J. Dauben, Jr. and L. L. McCoy, *J. Amer. Chem. Soc.* **81**, 4863 (1959) survey reaction variables in terms of mechanism and give leading references to previous work.
[15] M. C. Ford and W. A. Waters, *J. Chem. Soc.* 2240 (1952).
[16] Ng. Ph. Buu-Hoi and P. Demerseman, *J. Org. Chem.* **18**, 649 (1953).
[17] R. A. Barnes, *J. Amer. Chem. Soc.* **70**, 145 (1948).
[18] J. Cason, N. L. Allinger and D. E. Williams, *J. Org. Chem.* **18**, 842 (1953).
[19] C. Djerassi, J. Osiecki and W. Closson, *J. Amer. Chem. Soc.* **81**, 4587 (1959).
[20] W. Laird, F. S. Spring and R. Stevenson, *J. Amer. Chem. Soc.* **82**, 4108 (1960).
[21] All melting points were determined on a Gallenkamp melting point apparatus. Unless otherwise noted, rotations were measured in chloroform solution. The microanalyses were determined by Schwarzkopf Microanalytical Laboratory (Woodside, N.Y.).

reaction time of 30 min, the mixture was cooled, filtered and the solvent removed. The residue was recrystallized twice from chloroform–methanol to give 4α-bromofriedelin as needles (110 mg), m.p. 198–199°, $[\alpha]_D$ + 92° (*c*, 1·3), ν^{CHCl_3} 1710 cm^{-1}, λ^{CHCl_3} 308·5 mμ. Lit.[2] m.p. 196–197°, $[\alpha]_D$ + 90·5°.

2α-Bromofriedelin (II). (a) A saturated solution (2 drops) of hydrogen bromide in chloroform was added to a solution of friedelin (1·53 g) in chloroform (50 cm^3), followed by a solution of bromine (0·658 g) in chloroform (15 cm^3). The bromine color faded almost immediately to pale yellow which persisted after stirring for 15 min, when the solvents were removed under reduced pressure. Crystallization of the residue from chloroform–methanol gave needles, m.p. 206–207°, $[\alpha]_D$ 117° which after two further recrystallizations gave 2α-bromofriedelin (751 mg), as colorless needles, m.p. 214° (dec.), $[\alpha]_D$ +140° (*c*, 1·1), ν^{CHCl_3} 1710 cm^{-1}, λ^{CHCl_3} 310 mμ. Lit.[2] m.p. 210°, $[\alpha]_D$ 140°.

(b) A solution of bromine (34 mg) in acetic acid (10 cm^3) was added dropwise over 20 min to a solution of 4α-bromofriedelin (100 mg) in ether (30 cm^3) and acetic acid (50 cm^3). The residue, after removal of solvents under reduced pressure, was crystallized twice from chloroform–methanol to give the 2α-bromoketone (25 mg), m.p. and mixed m.p. 216–216·5°, $[\alpha]_D$ 140°, λ^{CHCl_3} 310 mμ.

Attempted bromination of the 4α-bromoketone in carbon tetrachloride solution in the absence or presence of calcium carbonate yielded only unchanged starting material. The specific rotation of the 4α-bromoketone in chloroform solution containing hydrogen bromide changed on standing from +90° to +8° (5 min), +0° (1 hr), 11° (2 hr), 71° (14 hr) and 78° (24 hr). The specific rotation of 2α-bromoketone in chloroform saturated with hydrogen chloride changed to 74° after 24 hr.

2α-Bromofriedel-18-en-3-one (XI). N-Bromosuccinimide (43 mg) was added to a solution of 2α-bromofriedelin (100 mg) in carbon tetrachloride (70 cm^3), the mixture refluxed for 30 min with an infrared lamp and worked up in the usual way. Crystallization of the product from chloroform–methanol gave *2α-bromofriedel-18-en-3-one* as small needles (32 mg), m.p. 207–208° (dec.), $[\alpha]_D$ 139° (*c*, 2·0), ν^{CHCl_3} 1710 cm^{-1}, λ^{CHCl_3} 311 mμ. Ultraviolet end absorption, ε 750 (220 mμ), 1990 (215 mμ), 4350 (210 mμ), λ^{CS_2} 3·45, 3·50, 5·84, 7·22, 7·40, 8·25, 8·45, 8·49, 8·93, 9·83, 10·00, 10·20, 10·92, 11·64 μ. It gives a yellow color with tetranitromethane in chloroform solution.

(Found: C, 71·42; H, 9·48; Br, 16·35. Calc. for $C_{30}H_{47}OBr$: C, 71·55; H, 9·41; Br, 15·87%). R.D. in dioxane (*c*, 0·053): $[\alpha]_{700}$ 34°, $[\alpha]_{589}$ 117°, $[\alpha]_{335}$ −3370°, $[\alpha]_{300}$ −3717°, $[\alpha]_{240}$ +2620°.

Friedel-18-en-3-one (XIII). Zinc dust (13 g) was added portionwise over 1 hr to a refluxing solution of 2α-bromofriedel-18-en-3-one (365 mg) in benzene–ethanol (1:1, 150 cm^3). After a further reflux period of 2 hr, the hot solution was filtered and the solvents removed under reduced pressure. The residue was extracted with chloroform, the extract washed with water, dried (Na_2SO_4) and evaporated to give the product which was crystallized from chloroform–methanol to give *friedel-18-en-3-one* as needles, m.p. 266–269°, vac. m.p. 280–282°, $[\alpha]_D$ 28° (*c*, 2·05) ν^{CHCl_3} 1706 cm^{-1}, λ^{CHCl_3} 290 mμ (inflexion), λ^{CS_2} 3·45, 3·50, 5·85, 7·22, 7·27, 7·40, 8·22, 8·37, 9·05, 9·33, 9·83, 10·93, 11·65 μ. It gives a yellow color with tetranitromethane in chloroform solution.

(Found: C, 84·58; H, 11·19. Calc. for $C_{30}H_{48}O$: C, 84·84; H, 11·39%).
R.D. in dioxane (*c*, 0·052): $[\alpha]_{700}$ −46°, $[\alpha]_{589}$ 0°, $[\alpha]_{314}$ 1610°, $[\alpha]_{278}$ −1490°, $[\alpha]_{240}$ −954°.

Friedel-18-en-3β-ol (XIV, R = H). A solution of friedel-18-en-3-one (300 mg) in anhydrous ether (150 cm^3) was refluxed with lithium aluminum hydride (250 mg), the product isolated in the usual way and crystallized from chloroform–methanol to give needles, m.p. 273–275°. Recrystallization from chloroform–ethyl acetate yielded *friedel-18-en-3β-ol* as needles, m.p. 277–279°, $[\alpha]_D$ −25° (*c*, 1·2). Ultraviolet end absorption, ε 590 (220 mμ), 1420 (215 mμ), 3520 (210 mμ). λ^{CHCl_3} 3·45, 3·50, 6·86, 7·26, 7·36, 9·85, 10·10, 10·34, 10·90, 11·64 μ. It gives a yellow color with tetranitromethane in chloroform.

(Found: C, 83·88; H, 11·72. Calc. for $C_{30}H_{50}O$: C, 84·44; H, 11·81%).

Friedel-18-en-3β-yl acetate (XIV, R = Ac). Treatment of the alcohol (50 mg) with acetic anhydride (2 cm^3) in pyridine (1 cm^3) at 100° for 1 hr and working up in the usual way gave a solid, which was crystallized from chloroform–methanol to give *friedel-18-en-3β-yl acetate* as needles (32 mg), m.p. 281–282°, $[\alpha]_D$ +30° (*c*, 1·34). λ^{CS_2} 3·44, 3·50, 5·77, 7·22, 7·30, 7·38, 8·07, 8·22, 8·60, 9·85, 10·26, 11·66 μ. It gives a yellow color with tetranitromethane in chloroform.

(Found: C, 81·99; H, 11·18. Calc. for $C_{32}H_{52}O_2$: C, 82·63; H, 11·38%).

Friedel-18-ene (XV). Potassium hydroxide (1·7 g) and hydrazine hydrate (99–100%, 2 cm^3) were added to a suspension of friedel-18-en-3-one (170 mg) in diethylene glycol (17 cm^3), the mixture refluxed for 1 hr, the temperature raised to 210° by concentration of the solution, and refluxing continued for a further 5 hr. After cooling the mixture was poured into water (50 cm^3), extracted with

chloroform (3 × 50 cm³), and the extract washed with water and dried (Na_2SO_4). Removal of the solvent gave a solid (80 mg) which after several recrystallizations from chloroform–methanol or chloroform–ethyl acetate gave *friedel*-18-*ene* as needles, m.p. 242–244°, $[\alpha]_D$ + 17° (*c*, 1·6), $\lambda_{max}^{CS_2}$ 3·45, 3·50, 7·22, 7·27, 7·43, 8·35, 9·19, 9·32, 9·52, 9·82, 10·05, 10·22, 10·90, 11·63, 14·20 μ. Ultraviolet end absorption, ε 670 (220 mμ), 2140 (215 mμ), 4080 (210 mμ). It gives a yellow color with tetranitromethane in chloroform.

(Found: C, 87·97; H, 11·99. Calc. for $C_{30}H_{50}$: C, 87·73; H, 12·27%).

The hydrocarbon was recovered unchanged from attempted hydrogenation with platinum oxide in cyclohexane–acetic acid at atmospheric and 39 lbs/in² pressure and from treatment with osmium tetroxide in ether–pyridine solution.

18ξ:19ξ-*Epoxyfriedelane*. A chloroform solution (5 cm³) of perbenzoic acid (62 mg/cm³) was added to friedel-18-ene (96 mg) in chloroform (20 cm³) and allowed to stand at 5° for 24 hr. (Estimated uptake was 0·93 mole.) After washing with potassium bicarbonate solution and water, the dried (Na_2SO_4) solution was evaporated to give a solid, m.p. 238–239°, $[\alpha]_D$ + 35° (*c*, 1·6). Five more recrystallizations from chloroform–ethyl acetate gave 18ξ:19ξ-*epoxyfriedelane* as needles, m.p. 260–261°, $[\alpha]_D$ + 34 (*c*, 1·2). It gives no color with tetranitromethane and shows no carbonyl absorption in the infrared. $\lambda_{max}^{CHCl_3}$ 3·46, 6·84, 7·24, 7·35, 9·00, 10·05, 10·65, 10·95, 11·93 μ.

(Found: C, 84·28; H, 11·93. Calc. for $C_{30}H_{50}O$: C, 84·44; H, 11·81%).

4α-*Bromofriedel*-18-*en*-3-*one* (XII). (a) N-Bromosuccinimide (32 mg) was added to a solution of friedel-18-en-3-one (70 mg) in carbon tetrachloride (20 cm³), the mixture refluxed with irradiation from an infrared lamp for 30 min, cooled and filtered. The residue, obtained on evaporation of the filtrate was crystallized from chloroform–ethyl acetate to give the product (35 mg, m.p. 180–181°) which on two further recrystallizations from the same solvents yielded 4α-*bromofriedel*-18-*en*-3-*one* as very fine needles, m.p. 185–186°, $[\alpha]_D$ + 87° (*c*, 1·62), $\lambda_{max}^{CHCl_3}$ 307 mμ, $\lambda_{max}^{CHCl_3}$ 3·45, 3·50, 5·86, 6·24 (*w*), 6·88, 7·21, 7·26 (*sh*), 7·36, 7·60, 9·06, 9·17, 9·31, 9·83, 10·19, 10·45, 10·95, 11·62 μ. It gives a yellow color with tetranitromethane in chloroform solution.

(Found: C, 71·80; H, 9·83. Calc. for $C_{30}H_{47}OBr$: C, 71·55; H, 9·41%).

R.D. in dioxane (*c*, 0·050): $[\alpha]_{700}$ + 104°, $[\alpha]_{589}$ + 80°, $[\alpha]_{334}$ + 1450°, $[\alpha]_{285}$ − 1904°, $[\alpha]_{265}$ − 1564°.

(b) N-Bromosuccinimide (75 mg) was added to a solution of 4α-bromofriedelin (200 mg) in carbon tetrachloride (53 cm³). Treatment as in (a) above gave the crude unsaturated bromoketone (115 mg, m.p. 178–181°) which on two further crystallizations yielded 50 mg, m.p. 186–187°, $[\alpha]_D$ + 86° (*c*, 2·56) with identical infrared spectrum. In another experiment, 1·2 g of 4α-bromofriedelin gave 0·6 g of pure 4α-bromofriedel-18-en-3-one.

Debromination of 4α-bromofriedel-18-en-3-one (300 mg) by zinc in benzene–alcohol as described for the 2α-bromo isomer gave friedel-18-en-3-one (148 mg) as needles, m.p. and mixed m.p. 266–269°, $[\alpha]_D$ + 26° (*c*, 1·85).

The action of silver acetate on 4α-*bromofriedel*-18-*en*-3-*one*. A solution of 4α-bromofriedel-18-en-3-one (115 mg) in ether (50 cm³) was added to a solution of silver acetate (112 mg) in water (2 cm³) and acetic acid (60 c m³). The mixture was distilled until the boiling vapor temperature was 110°, refluxed for 20 min, filtered and evaporated. The residue was extracted with chloroform (150 cm³), the extract washed with water, dried (sodium sulfate) and the product, obtained on evaporation, was crystallized from chloroform–methanol to give a product (48 mg) regarded as a mixed crystal (needles) of *alnusa*-5:18-*dien*-3-*one* and *alnusa*-5(10):18-*dien*-3-*one*, m.p. 233–235°, $[\alpha]_D$ − 42·5° (*c*, 1·46). It gives a yellow color with tetranitromethane in chloroform solution and shows no high-intensity ultraviolet absorption. Ultraviolet end absorption: ε 1055 (220 mμ), 2020 (215 mμ), 4960 (210 mμ).

(Found: C, 85·01; H, 10·98. Calc. for $C_{30}H_{48}O$: C, 85·24; H, 10·97%).

2α-Bromofriedel-18-en-3-one was recovered unchanged after identical treatment.

Action of N-*bromosuccinimide on friedelane*. N-Bromosuccinimide (98 mg) was added to a solution of friedelane (200 mg, m.p. 252–254°, $[\alpha]_D$ + 21°, prepared by Huang-Minlon reduction of friedelin) in carbon tetrachloride (100 cm³), and the mixture heated by an infrared lamp. A yellow color appeared after refluxing for 12 min, then disappeared after a further 30 sec. After a total reflux time of 30 min, the mixture was cooled, filtered and the solvent removed under reduced pressure. Crystallization of the solid residue from chloroform–ethyl acetate gave a product, m.p. 220–221°, unchanged on two further crystallizations. Two further crystallizations from a larger volume of these solvents gave friedel-18-ene as blades, m.p. and mixed m.p. 242–245°, $[\alpha]_D$ + 17° (*c*, 1·6). The infrared spectrum (in KBr pellet) was superimposable on that of the sample obtained by Huang-Minlon reduction of

friedel-18-en-3-one and had bands at 1650 (weak), 1465, 1440, 1385, 1360, 1318, 1265, 1160, 1123, 1092, 1079, 1054, 1020, 1000, 981, 964, 948, 920, 821, 680 cm $^{-1}$.

In another similar experiment, friedelane (300 mg) yielded friedel-18-ene (75 mg, m.p. 241–242°), raised to m.p. 242–244°, $[\alpha]_D$ −18·5° (*c*, 1·52) after a further crystallization.

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